ATHABASCA UNIVERSITY CHEMISTRY 350 ORGANIC CHEMISTRY I



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Athabasca University Chemistry 350 Organic Chemistry I

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CHAPTER OVERVIEW

1: STRUCTURE AND BONDING

This chapter provides a review of material covered in a standard freshman general-chemistry course (such as Athabasca University's *Chemistry 217/ 218*) through a discussion of the following topics:

- the differences between organic and inorganic chemistry.
- the shapes and significance of atomic orbitals.
- electron configurations.
- ionic and covalent bonding.
- molecular orbital theory.
- hybridization.
- the structure and geometry of the compounds methane, ethane, ethylene and acetylene.

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1.0: INTRODUCTION

OBJECTIVES

After completing this section, you should be able to

1. Define organic chemistry as the study of carbon-containing compounds.
2. Explain why the results of the experiments carried out by Chevreul and Wöhler contributed to the demise of the “vital force” theory.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- organic chemistry

All living things on earth are formed mostly of carbon compounds. The prevalence of carbon compounds in living things has led to the epithet “carbon-based” life. The truth is we know of no other kind of life. Early chemists regarded substances isolated from *organisms* (plants and animals) as a different type of matter that could not be synthesized artificially, and these substances were thus known as *organic compounds*. The widespread belief called vitalism held that organic compounds were formed by a vital force present only in living organisms. The German chemist Friedrich Wohler was one of the early chemists to refute this aspect of vitalism, when, in 1828, he reported the synthesis of urea, a component of many body fluids, from nonliving materials. Since then, it has been recognized that organic molecules obey the same natural laws as inorganic substances, and the category of organic compounds has evolved to include both natural and synthetic compounds that contain carbon. Some carbon-containing compounds are *not* classified as organic, for example, carbonates and cyanides, and simple oxides, such as CO and CO_2. Although a single, precise definition has yet to be identified by the chemistry community, most agree that a defining trait of organic molecules is the presence of carbon as the principal element, bonded to hydrogen and other carbon atoms.



Figure 1.0.1: *All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by “annszyp”/Wikimedia Commons; credit right: modification of work by George Shuklin)*

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

CONTRIBUTORS AND ATTRIBUTIONS

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1.1: ATOMIC STRUCTURE- THE NUCLEUS

Objective

After completing this section, you should be able to describe the basic structure of the atom.

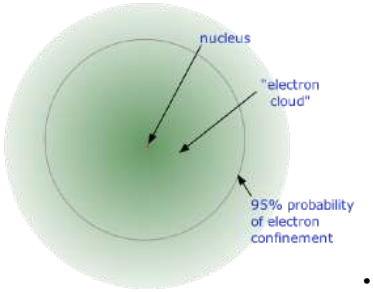
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- atomic number
- atomic weight
- electron
- mass number
- neutron
- proton

THE NUCLEAR ATOM EDIT SECTION

The precise physical nature of atoms finally emerged from a series of elegant experiments carried out between 1895 and 1915. The most notable of these achievements was Ernest Rutherford's famous 1911 alpha-ray scattering experiment, which established that



- Almost all of the *mass* of an atom is contained within a tiny (and therefore extremely dense)*nucleus* which carries a positive electric charge whose value identifies each element and is known as the *atomic number* of the element.
- Almost all of the *volume* of an atom consists of empty space in which electrons, the fundamental carriers of negative electric charge, reside. The extremely small mass of the electron (1/1840 the mass of the hydrogen nucleus) causes it to behave as a quantum particle, which means that its location at any moment cannot be specified; the best we can do is describe its behavior in terms of the probability of its manifesting itself at any point in space. It is common (but somewhat misleading) to describe the volume of space in which the electrons of an atom have a significant probability of being found as the *electron cloud*. The latter has no definite outer boundary, so neither does the atom. The radius of an atom must be defined arbitrarily, such as the boundary in which the electron can be found with 95% probability. Atomic radii are typically 30-300 pm.

PROTONS AND NEUTRONS EDIT SECTION

The nucleus is itself composed of two kinds of particles. *Protons* are the carriers of positive electric charge in the nucleus; the proton charge is exactly the same as the electron charge, but of opposite sign. This means that in any [electrically neutral] atom, the number of protons in the nucleus (often referred to as the *nuclear charge*) is balanced by the same number of electrons outside the nucleus.

> *Because the electrons of an atom are in contact with the outside world, it is possible for one or more electrons to be lost, or some new ones to be added. The resulting electrically-charged atom is called an ion.*

The other nuclear particle is the *neutron*. As its name implies, this particle carries no electrical charge. Its mass is almost the same as that of the proton. Most nuclei contain roughly equal numbers of neutrons and protons, so we can say that these two particles together account for almost all the mass of the atom.

ATOMIC NUMBER (Z)

What single parameter uniquely characterizes the atom of a given element? It is not the atom's relative mass, as we will see in the section on isotopes below. It is, rather, the number of protons in the nucleus, which we call the *atomic number* and denote by the symbol *Z*. Each proton carries an electric charge of +1, so the atomic number also specifies the electric charge of the nucleus. In the neutral atom, the *Z protons* within the nucleus are balanced by *Z electrons* outside it.



Atomic numbers were first worked out in 1913 by Henry Moseley, a young member of Rutherford's research group in Manchester.

Moseley searched for a measurable property of each element that increases linearly with atomic number. He found this in a class of X-rays emitted by an element when it is bombarded with electrons. The frequencies of these X-rays are unique to each element, and they increase uniformly in successive elements. Moseley found that the square roots of these frequencies give a straight line when plotted against Z; this enabled him to sort the elements in order of increasing atomic number.

You can think of the atomic number as a kind of serial number of an element, commencing at 1 for hydrogen and increasing by one for each successive element. The chemical name of the element and its symbol are uniquely tied to the atomic number; thus the symbol "Sr" stands for strontium, whose atoms all have $Z = 38$.

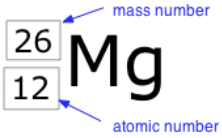
MASS NUMBER (A)

This is just the sum of the numbers of protons and neutrons in the nucleus. It is sometimes represented by the symbol *A*, so

in which *Z* is the atomic number and *N* is the *neutron number*.

NUCLIDES AND THEIR SYMBOLS

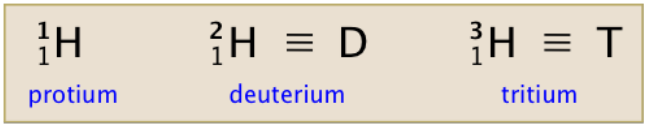
The term *nuclide* simply refers to any particular kind of nucleus. For example, a nucleus of atomic number 7 is a nuclide of nitrogen. Any nuclide is characterized by the pair of numbers (*Z* ,*A*). The element symbol depends on *Z* alone, so the symbol ^{26}Mg is used to specify the mass-26 nuclide of manganese, whose name implies *Z*=12. A more explicit way of denoting a particular kind of nucleus is to add the atomic number as a subscript. Of course, this is somewhat redundant, since the symbol Mg **always** implies *Z*=12, but it is sometimes a convenience when discussing several nuclides.



Two nuclides having the **same** atomic number but different mass numbers are known as *isotopes*. Most elements occur in nature as mixtures of isotopes, but twenty-three of them (including beryllium and fluorine, shown in the table) are monoisotopic. For example, there are three *natural isotopes* of magnesium: ^{24}Mg (79% of all Mg atoms), ^{25}Mg (10%), and ^{26}Mg (11%); all three are present in all compounds of magnesium in about these same proportions.

	Z	mass numbers
H	1	1 2 3
He	2	3 4
Li	3	6 7
Be	4	9
B	5	10 11
C	6	12 13 14
N	7	14 15
O	8	16 17 18
F	9	19
Ne	10	20 21 22

Approximately 290 isotopes occur in nature. The two heavy isotopes of hydrogen are especially important— so much so that they have names and symbols of their own:



Deuterium accounts for only about 15 out of every one million atoms of hydrogen. Tritium, which is radioactive, is even less abundant. All the tritium on the earth is a by-product of the decay of other radioactive elements.

ATOMIC WEIGHTS EDIT SECTION

Atoms are of course far too small to be weighed directly; weight measurements can only be made on the massive (but unknown) numbers of atoms that are observed in chemical reactions. The early combining-weight experiments of Dalton and others established that hydrogen is the lightest of the atoms, but the crude nature of the measurements and uncertainties about the formulas of many compounds made it difficult to develop a reliable scale of the relative weights of atoms. Even the most exacting weight measurements we can make today are subject to experimental uncertainties that limit the precision to four significant figures at best.

THE PERIODIC TABLE

The elements are arranged in a periodic table, which is probably the single most important learning aid in chemistry. It summarizes huge amounts of information about the elements in a way that facilitates the prediction of many of their properties and chemical reactions. The elements are arranged in seven horizontal rows, in order of increasing atomic number from left to right and top to bottom. The rows are called periods, and they are numbered from 1 to 7. The elements are stacked in such a way that elements with similar chemical properties form vertical columns, called groups, numbered from 1 to 18 (older periodic tables use a system based on roman numerals). Groups 1, 2, and 13–18 are the main group elements, listed as A in older tables. Groups 3–12 are in the middle of the periodic table and are the transition elements, listed as B in older tables. The two rows of 14 elements at the bottom of the periodic table are the lanthanides and the actinides, whose positions in the periodic table are indicated in group 3.

✔ EXAMPLE 1.1.1

An element with three stable isotopes has 82 protons. The separate isotopes contain 124, 125, and 126 neutrons. Identify the element and write symbols for the isotopes.

Given: number of protons and neutrons

Asked for: element and atomic symbol

Strategy:

A. Refer to the periodic table and use the number of protons to identify the element.
B. Calculate the mass number of each isotope by adding together the numbers of protons and neutrons.
C. Give the symbol of each isotope with the mass number as the superscript and the number of protons as the subscript, both written to the left of the symbol of the element.

Solution:

A The element with 82 protons (atomic number of 82) is lead: Pb.

B For the first isotope, A = 82 protons + 124 neutrons = 206. Similarly, A = 82 + 125 = 207 and A = 82 + 126 = 208 for the second and third isotopes, respectively. The symbols for these isotopes are $^{206}_{82}Pb$, $^{207}_{82}Pb$, and $^{208}_{82}Pb$, which are usually abbreviated as ^{206}Pb, ^{207}Pb, and ^{208}Pb.

? EXERCISE 1.1.1

Identify the element with 35 protons and write the symbols for its isotopes with 44 and 46 neutrons.

Answer

$^{79}_{35}Br$ and $^{81}_{35}Br$ or, more commonly, ^{79}Br and ^{81}Br.

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- Prof. Steven Farmer (Sonoma State University)

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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1.2: ATOMIC STRUCTURE- ORBITALS

After completing this section, you should be able to

1. describe the physical significance of an orbital.
2. list the atomic orbitals from 1*s* to 3*d* in order of increasing energy.
3. sketch the shapes of *s* and *p* orbitals.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- nodal plane
- node
- orbital
- quantum mechanics
- wave function

ATOMIC ORBITALS

An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

One way of representing electron probability distributions was illustrated in Figure 6.5.2 for the 1*s* orbital of hydrogen. Because Ψ^2 gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of Ψ^2 versus distance from the nucleus (r) is a plot of the *probability density*. The 1*s* orbital is spherically symmetrical, so the probability of finding a 1*s* electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of r, the electron probability density is very small but *not* zero.

In contrast, we can calculate the *radial probability* (the probability of finding a 1*s* electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of x spherical shells of radius r_1, r_2, r_3,…, r_{x-1}, r_x. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (part (a) in Figure 1.2.1), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (part (b) in Figure 1.2.1), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 1.2.1. In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing r (part (c) in Figure 1.2.1). Because the surface area of the spherical shells increases more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (part (d) in Figure 1.2.1). Most important, when r is very small, the surface area of a spherical shell is so small that the *total* probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (part (d) in Figure 1.2.1).

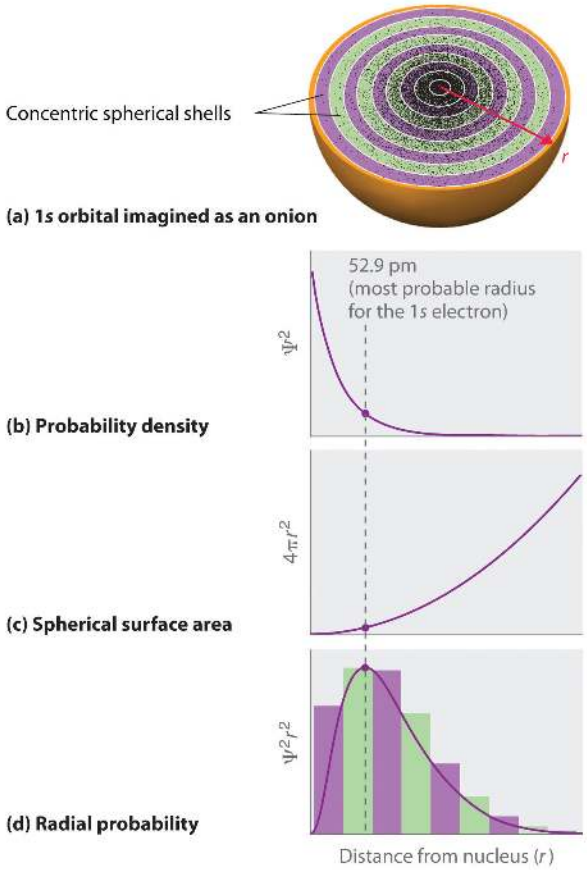


Figure 1.2.1 *Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at r = 0 and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the radial probability) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.*

For the hydrogen atom, the peak in the radial probability plot occurs at r = 0.529 Å (52.9 pm), which is exactly the radius calculated by Bohr for the n = 1 orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 1.2.2 compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in Figure 1.2.2). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.

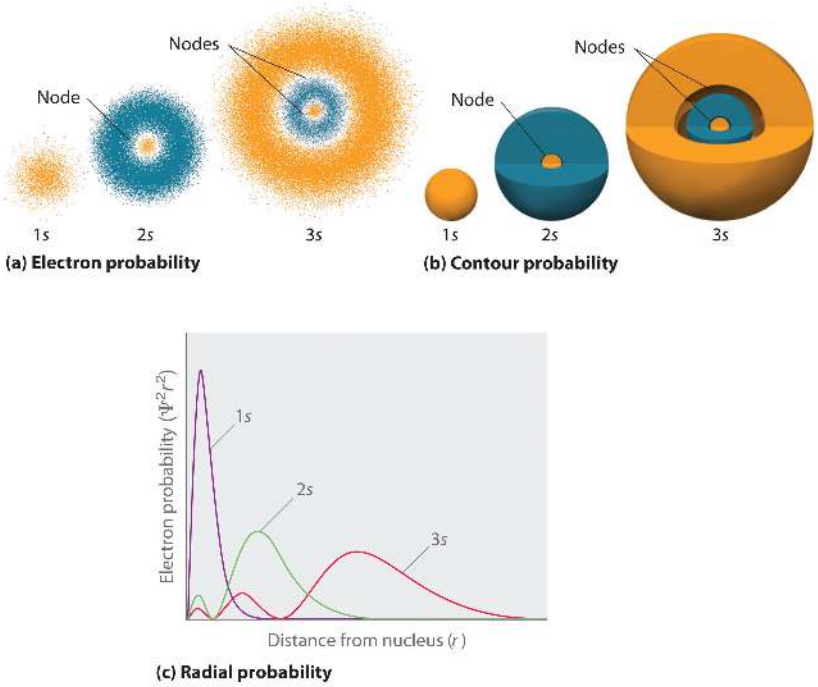


***Figure 1.2.2**: Probability Densities for the 1s, 2s, and 3s Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (r) in all directions (radial probability), the most probable radius increases as n increases, but the 2s and 3s orbitals have regions of significant electron probability at small values of r.*

S ORBITALS

Three things happen to *s* orbitals as *n* increases (Figure 1.2.2):Edit section

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the *s* orbitals also become higher in energy as *n* increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1*s*, 2*s*, and 3*s* orbitals in part (b) in Figure 1.2.2. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

P ORBITALSEDIT SECTION

Only *s* orbitals are spherically symmetrical. As the value of l increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2*p* subshell has $l = 1$, with three values of m_l (−1, 0, and +1), there are three 2*p* orbitals.

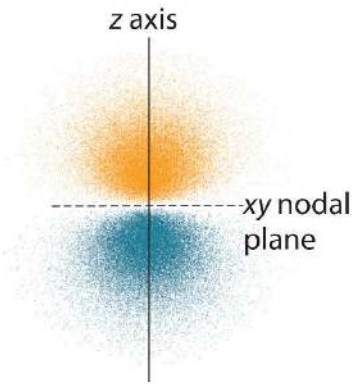


Figure 1.2.3: *Electron Probability Distribution for a Hydrogen 2p Orbital. The nodal plane of zero electron density separates the two lobes of the 2p orbital. As in Figure 1.2.2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).*

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 1.2.3. Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 1.2.4, the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and *y* axis ($2p_y$), respectively. Note that each *p* orbital has just one nodal plane. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

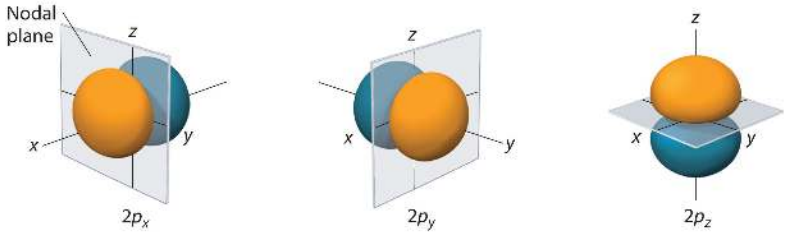


Figure 1.2.4 The Three Equivalent 2*p* Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2*p* orbital. The phase of the wave function is positive (orange) in the region of space where *x*, *y*, or *z* is positive and negative (blue) where *x*, *y*, or *z* is negative.

Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in Figure 1.2.4.

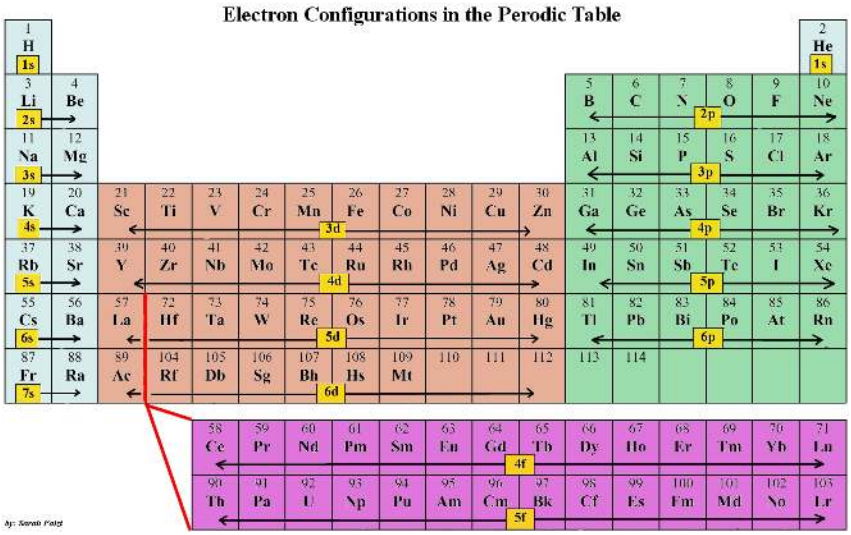
he electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells. Commonly, the electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss of or gain of electrons in their subsequent orbitals. Many of the physical and chemical properties of elements can be correlated to their unique electron configurations. The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the element.

ELECTRON CONFIGURATIONS EDIT SECTION

Before assigning the electrons of an atom into orbitals, one must become familiar with the basic concepts of electron configurations. Every element on the periodic table consists of atoms, which are composed of protons, neutrons, and electrons. Electrons exhibit a negative charge and are found around the nucleus of the atom in electron orbitals, defined as the volume of space in which the electron can be found within 95% probability. The four different types of orbitals (s,p,d, and f) have different shapes, and one orbital can hold a maximum of two electrons. The p, d, and f orbitals have different sublevels, thus can hold more electrons.

As stated, the electron configuration of each element is unique to its position on the periodic table. The energy level is determined by the period and the number of electrons is given by the atomic number of the element. Orbitals on different energy levels are similar to each other, but they occupy different areas in space. The 1s orbital and 2s orbital both have the characteristics of an s orbital (radial nodes, spherical volume probabilities, can only hold two electrons, etc.) but, as they are found in different energy levels, they occupy different

spaces around the nucleus. Each orbital can be represented by specific blocks on the periodic table. The s-block is the region of the alkali metals including helium (Groups 1 & 2), the d-block are the transition metals (Groups 3 to 12), the p-block are the main group elements from Groups 13 to 18, and the f-block are the lanthanides and actinides series.



Using the periodic table to determine the electron configurations of atoms is key, but also keep in mind that there are certain rules to follow when assigning electrons to different orbitals. The periodic table is an incredibly helpful tool in writing electron configurations. For more information on how electron configurations and the periodic table are linked, visit the Connecting Electrons to the Periodic Table module.

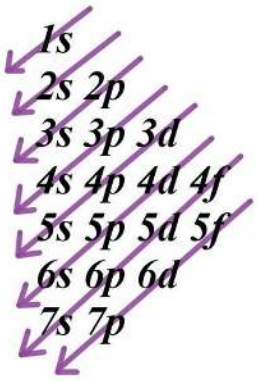
RULES FOR ASSIGNING ELECTRON ORBITALS EDIT SECTION

OCCUPATION OF ORBITALS EDIT SECTION

Electrons fill orbitals in a way to minimize the energy of the atom. Therefore, the electrons in an atom fill the principal energy levels in order of increasing energy (the electrons are getting farther from the nucleus). The order of levels filled looks like this:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, and 7p

One way to remember this pattern, probably the easiest, is to refer to the periodic table and remember where each orbital block falls to logically deduce this pattern. Another way is to make a table like the one below and use vertical lines to determine which subshells correspond with each other.



THE NUMBER OF VALENCE ELECTRONS

The number of valence electrons of an element can be determined by the periodic table group (vertical column) in which the element is categorized. With the exception of groups 3–12 (the transition metals), the units digit of the group number identifies how many valence electrons are associated with a neutral atom of an element listed under that particular column.

The periodic table of the chemical elements

Periodic table group	Valence electrons
Group 1: alkali metals	1
Group 2: alkaline earth metals	2
Groups 3-12: transition metals	2* (The 4s shell is complete and cannot hold any more electrons)
Group 13: boron group	3
Group 14: carbon group	4
Group 15: pnictogens	5
Group 16: chalcogens	6
Group 17: halogens	7
Group 18: noble gases	8**

** The general method for counting valence electrons is generally not useful for transition metals. Instead the modified **d electron count method** is used.*

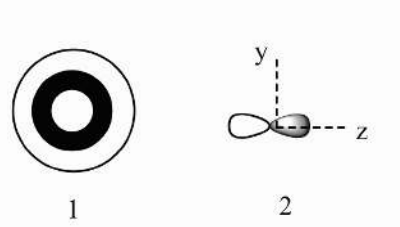
*** Except for helium, which has only two valence electrons.*

EXERCISES

QUESTIONS

Q1.2.1

Label the following orbitals:



SOLUTIONS

S1.2.1

1 = 3*s* ; 2 = $2p_z$

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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1.3: ATOMIC STRUCTURE- ELECTRON CONFIGURATIONS

Objective

After completing this section, you should be able to write the ground-state electron configuration for each of the elements up to and including atomic number 36.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- ground-state electronic configuration
- Hund's rule
- Pauli exclusion principle
- aufbau principle

The electron configuration of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

THE AUFBAU PRINCIPLE

We construct the periodic table by following the aufbau principle (from German, meaning "building up"). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 6.29, recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to m_s = +½, which is arbitrarily written first, and one with spin down ↓, corresponding to m_s = −½. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

H: 2*p* ___ ___ ___
2*s* ___
1*s* ↑___

From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number *n* and their value of *l* (*s*, *p*, *d*, or *f*), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1*s* orbital, which is the orbital lowest in energy (Figure 6.29"), and the electron configuration is written as $1s^1$ and read as "one-s-one."

A neutral helium atom, with an atomic number of 2 (Z = 2), has two electrons. We place one electron in the orbital that is lowest in energy, the 1*s* orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore

He: 2*p* ___ ___ ___
2*s* ___
1*s* ↑↓___

written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

The next element is lithium, with Z = 3 and three electrons in the neutral atom. We know that the 1*s* orbital can hold two of the electrons with their spins paired. Figure 6.29 tells us that the next lowest energy orbital is 2*s*, so the orbital diagram for lithium is

Li: 2*p* ___ ___ ___
2*s* ↑___
1*s* ↑↓___

This electron configuration is written as $1s^22s^1$.

The next element is beryllium, with Z = 4 and four electrons. We fill both the 1*s* and 2*s* orbitals to achieve a $1s^22s^2$ electron configuration:

Be: 2*p* ___ ___ ___
2*s* ↑↓
1*s* ↑↓

When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Because all three 2*p* orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2 2s^2 2p^1$:

B: 2*p* ↑ ___ ___
2*s* ↑↓
1*s* ↑↓

At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2*p* orbital that already has an electron, or should it go in one of the empty 2*p* orbitals? If it goes in an empty 2*p* orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the 2*p* orbitals are degenerate?

(a) 2*p* ↑↓ ___ ___
2*s* ↑↓
1*s* ↑↓

(b) 2*p* ↑ ↓ ___
2*s* ↑↓
1*s* ↑↓

(c) 2*p* ↑ ↑ ___
2*s* ↑↓
1*s* ↑↓

Because of electron-electron repulsions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates Hund's rule (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

When we get to nitrogen ($Z = 7$, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

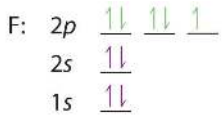
N: 2*p* ↑ ↑ ↑
2*s* ↑↓
1*s* ↑↓

with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

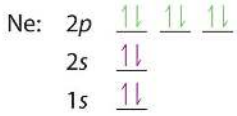
At oxygen, with $Z = 8$ and eight electrons, we have no choice. One electron must be paired with another in one of the 2*p* orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration. Because all the 2*p* orbitals are degenerate, it doesn't matter which one has the pair of electrons.

O: 2*p* ↑↓ ↑ ↑
2*s* ↑↓
1*s* ↑↓

Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:



When we reach neon, with $Z = 10$, we have filled the $2p$ subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:



Notice that for neon, as for helium, all the orbitals through the $2p$ level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

VALENCE ELECTRONS

As we continue through the periodic table in this way, writing the electron configurations of larger and larger atoms, it becomes tedious to keep copying the configurations of the filled inner subshells. In practice, chemists simplify the notation by using a bracketed noble gas symbol to represent the configuration of the noble gas from the preceding row because all the orbitals in a noble gas are filled. For example, [Ne] represents the $1s^2 2s^2 2p^6$ electron configuration of neon ($Z = 10$), so the electron configuration of sodium, with $Z = 11$, which is $1s^2 2s^2 2p^6 3s^1$, is written as $[Ne]3s^1$:

Neon	Z = 10	$1s^2 2s^2 2p^6$
Sodium	Z = 11	$1s^2 2s^2 2p^6 \mathbf{3}s^1 = [Ne]\mathbf{3}s^1$

Because electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, they are rarely involved in chemical reactions. This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, which are called the valence electrons. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium and lithium, we have:

Sodium	$1s^2 2s^2 2p^6 3s^1 = [Ne]3s^1$
Lithium	$1s^2 2s^1 = [He]2s^1$

It is readily apparent that both sodium and lithium have one s electron in their valence shell. We would therefore predict that sodium and lithium have very similar chemistry, which is indeed the case.

As we continue to build the eight elements of period 3, the $3s$ and $3p$ orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration $[Ne]3s^2 3p^6$, corresponding to a filled valence shell.

✔ EXAMPLE 1.3.1

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, $Z = 15$. What is its valence electron configuration?

Given: atomic number

Asked for: orbital diagram and valence electron configuration for phosphorus

Strategy:

A. Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.

B. Referring to Figure 6.29, draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.

C. Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

Solution:

A Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

B The additional five electrons are placed in the next available orbitals, which Figure 6.29 tells us are the 3*s* and 3*p* orbitals:

P: [Ne] 3*p* ___ ___ ___
3*s* ___

Because the 3*s* orbital is lower in energy than the 3*p* orbitals, we fill it first:

P: [Ne] 3*p* ___ ___ ___
3*s* ⇅

Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:

P: [Ne] 3*p* ↑ ↑ ↑
3*s* ⇅

The electron configuration is [Ne]$3s^2 3p^3$.

C We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^2 3p^3$.

? EXERCISE 1.3.1

Draw an orbital diagram and use it to derive the electron configuration of chlorine, $Z = 17$. What is its valence electron configuration?

Answer

[Ne]$3s^2 3p^5$; $3s^2 3p^5$

The general order in which orbitals are filled is depicted in Figure 1.3.1. Subshells corresponding to each value of *n* are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4*s* orbital is filled prior to the 3*d* orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is [Ar]$4s^1$, and the configuration of calcium is [Ar]$4s^2$. Five 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* orbitals. Notice that the last member of this row is the noble gas krypton ($Z = 36$), [Ar]$4s^2 3d^{10} 4p^6$ = [Kr], which has filled 4*s*, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5*s*, 4*d*, and 5*p* orbitals are filled sequentially.

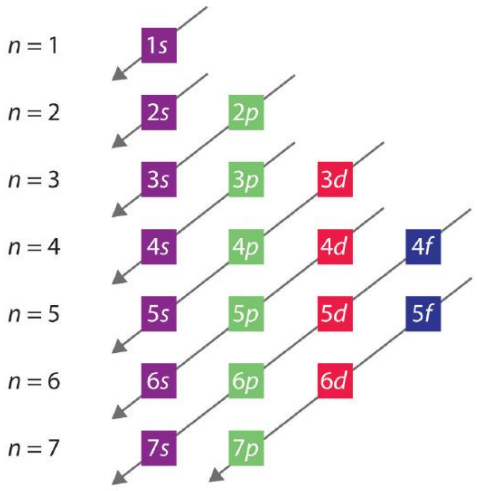


Figure 1.3.1: *Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.*

The sixth row of the periodic table will be different from the preceding two because the 4*f* orbitals, which can hold 14 electrons, are filled between the 6*s* and the 5*d* orbitals. The elements that contain 4*f* orbitals in their valence shell are the lanthanides. When the 6*p* orbitals are

finally filled, we have reached the next (and last known) noble gas, radon (Z = 86), [Xe]$6s^2 4f^{14} 5d^{10} 6p^6$ = [Rn]. In the last row, the 5*f* orbitals are filled between the 7*s* and the 6*d* orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

EXAMPLE 1.3.2

Write the electron configuration of mercury (Z = 80), showing all the inner orbitals.

Given: atomic number

Asked for: complete electron configuration

Strategy:

Using the orbital diagram in Figure 1.3.1 and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

Solution:

By placing the electrons in orbitals following the order shown in Figure 1.3.1 and using the periodic table as a guide, we obtain

$1s^2$	row 1	2 electrons
$2s^2 2p^6$	row 2	8 electrons
$3s^2 3p^6$	row 3	8 electrons
$4s^2 3d^{10} 4p^6$	row 4	18 electrons
$5s^2 4d^{10} 5p^6$	row 5	18 electrons
	row 1–5	54 electrons

After filling the first five rows, we still have 80 − 54 = 26 more electrons to accommodate. According to Figure 1.3.2, we need to fill the 6*s* (2 electrons), 4*f* (14 electrons), and 5*d* (10 electrons) orbitals. The result is mercury's electron configuration:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} = \text{Hg} = [\text{Xe}]6s^2 4f^{14} 5d^{10}$$

with a filled 5*d* subshell, a $6s^2 4f^{14} 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

EXERCISE 1.3.2

Give the electron configurations for Al, Br, and Fe.

Answer

Al = $1s^2 2s^2 2p^6 3s^2 3p^1$ Br = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$ Fe = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

SUMMARY

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**.

EXERCISES

QUESTIONS

Q1.3.1

Give the electron configurations for Al, Br, Fe.

SOLUTIONS

S1.3.1

Al = $1s^2 2s^2 2p^6 3s^2 3p^1$

Br = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

Fe = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

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- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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1.4: DEVELOPMENT OF CHEMICAL BONDING THEORY

Objectives

After completing this section, you should be able to

1. draw Lewis Dot Symbols for main group elements and ions.
2. describe the three-dimensional nature of molecules.
3. sketch a tetrahedral molecule, CX_4, using the "wedge-and-broken-line" method of representation.
4. make a ball-and-stick model of a simple tetrahedral molecule such as methane, CH_4.
5. draw Lewis Dot Structures for 2 electron group molecules.
6. draw Lewis Dot Structures for 3 electron group molecules.
7. draw Lewis Dot Structures for 4 electron group molecules.

STUDY NOTES

To draw Lewis structures successfully, you need to know the number of valence electrons present in each of the atoms involved. Memorize the number of valence electrons possessed by each of the elements commonly encountered in organic chemistry: C, H, O, N, S, P and the halogens.

When drawing any organic structure, you must remember that a neutral carbon atom will almost always have four bonds. Similarly, hydrogen always has one bond; neutral oxygen atoms have two bonds; and neutral nitrogen atoms have three bonds. By committing these simple rules to memory, you can avoid making unnecessary mistakes later in the course.

The "wedge-and-broken-line" type of representation, which helps to convey the three-dimensional nature of organic compounds, will be used throughout the course.

BONDING OVERVIEW

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond wil be discussed and the general properties found in typical substances in which the bond type occurs

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involves a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involves one nonmetallic element with another
3. Metallic bonds These bonds are found in solid metals (copper, iron, aluminum) with each metal bonded to several neighboring groups and bonding electrons free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

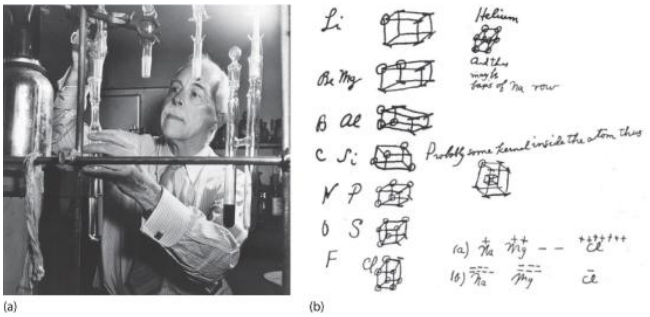


Figure 1.4.1*: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.*

LEWIS SYMBOLS

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called Lewis electron dot symbols, often shortened to *Lewis dot symbols*—that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

NOTE

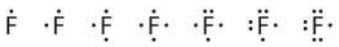
Lewis Dot symbols:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is $[Ne]3s^2 3p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration $[He]2s^2 2p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



The number of dots in the Lewis dot symbol is the same as the number of valence electrons, which is the same as the last digit of the element's group number in the periodic table. Lewis dot symbols for the elements in period 2 are given in Figure 1.4.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 1.4.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Element	Electron config.	Electron dot symbol
Li	$[He]2s^1$	Li
Be	$[He]2s^2$	Be
B	$[He]2s^2 2p^1$	B
C	$[He]2s^2 2p^2$	C
N	$[He]2s^2 2p^3$	N
O	$[He]2s^2 2p^4$	O
F	$[He]2s^2 2p^5$	F
Ne	$[He]2s^2 2p^6$	Ne

Figure 1.4.2: *Lewis Dot Symbols for the Elements in Period 2*

THE OCTET RULE

Lewis's major contribution to bonding theory was to recognize that atoms tend to lose, gain, or share electrons to reach a total of eight valence electrons, called an *octet*. This so-called octet rule explains the stoichiometry of most compounds in the *s* and *p* blocks of the

periodic table. We now know from quantum mechanics that the number eight corresponds to one *ns* and three *np* valence orbitals, which together can accommodate a total of eight electrons. Remarkably, though, Lewis's insight was made nearly a decade before Rutherford proposed the nuclear model of the atom. An exception to the octet rule is helium, whose $1s^2$ electron configuration gives it a full $n = 1$ shell, and hydrogen, which tends to gain or share its one electron to achieve the electron configuration of helium.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



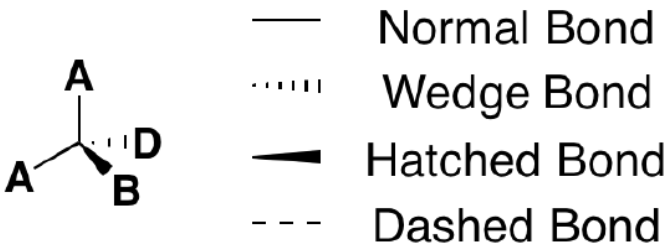
No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

NOTE

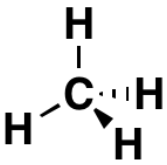
Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

MOLECULAR SHAPE

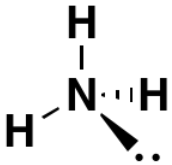
A stick and wedge drawing of methane shows the tetrahedral angles...(The wedge is coming out of the paper and the dashed line is going behind the paper. The solid lines are in the plane of the paper.)



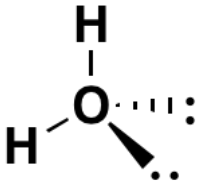
The following examples make use of this notation, and also illustrate the importance of including non-bonding valence shell electron pairs (colored blue) when viewing such configurations.



Methane

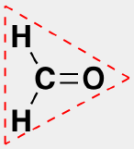


Ammonia



Water

Bonding configurations are readily predicted by valence-shell electron-pair repulsion theory, commonly referred to as **VSEPR** in most introductory chemistry texts. This simple model is based on the fact that electrons repel each other, and that it is reasonable to expect that the bonds and non-bonding valence electron pairs associated with a given atom will prefer to be as far apart as possible. The bonding configurations of carbon are easy to remember, since there are only three categories.

Configuration	Bonding Partners	Bond Angles	Example
Tetrahedral	4	109.5º	
Trigonal	3	120º	
Linear	2	180º	

In the three examples shown above, the central atom (carbon) does not have any non-bonding valence electrons; consequently the configuration may be estimated from the number of bonding partners alone. For molecules of water and ammonia, however, the non-bonding electrons must be included in the calculation. In each case there are four regions of electron density associated with the valence shell so that a tetrahedral bond angle is expected. The measured bond angles of these compounds (H_2O 104.5º & NH_3 107.3º) show that they are closer to being tetrahedral than trigonal or linear. Of course, it is the configuration of atoms (not electrons) that defines the the shape of a molecule, and in this sense ammonia is said to be pyramidal (not tetrahedral). The compound boron trifluoride, BF3, does not have non-bonding valence electrons and the configuration of its atoms is trigonal. Nice treatments of VSEPR theory have been provided by Oxford and Purdue. The best way to study the three-dimensional shapes of molecules is by using molecular models. Many kinds of model kits are available to students and professional chemists.

TWO ELECTRON GROUPS

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, .

AX_2: BEH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is



Figure 1.4.3: *Lewis Structure for BeH_2*

2. There are two electron groups around the central atom. We see from Figure 1.4.2 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 1.4.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

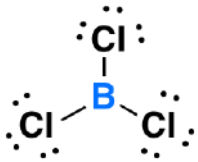
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 1.4.3). The structure of CO_2 is shown in Figure 1.4.2.1.

THREE ELECTRON GROUPS

AX_3: BCL_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



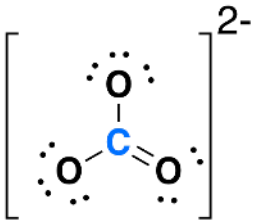
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 1.4.2).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 1.4.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 1.4.2.1.

AX_3: CO_3^{2-}

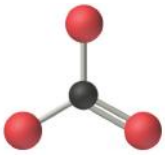
1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as



2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of . We minimize repulsions by placing the three groups 120° apart (Figure 1.4.2).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure 1.4.3 that the molecular geometry of CO_3^{2-} is trigonal planar.

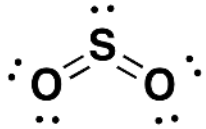


Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 1.4.2).

3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 1.4.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures 1.4.2.1 and 1.4.3).

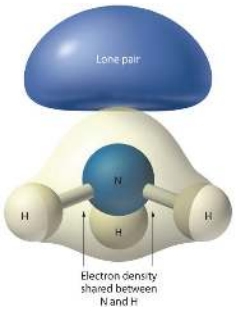
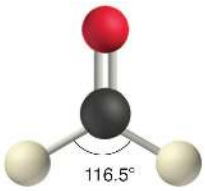


Figure 1.4.4: *The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair*

As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

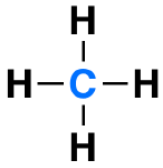


FOUR ELECTRON GROUPS

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4: CH_4

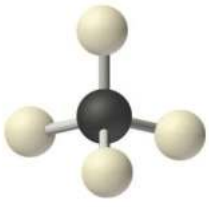
1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is



2. There are four electron groups around the central atom. As shown in Figure 1.4.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

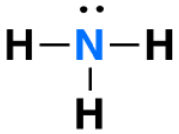
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 1.4.3).



Molecular geometry
(tetrahedral)

AX_3E: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 1.4.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 1.4.3 and Figure 1.4.4).

AX_2E_2: H_2O

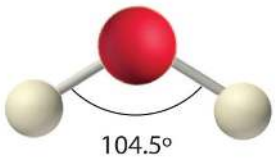
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 1.4.2.

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.. This molecular shape is essentially a tetrahedron with two missing vertices.



QUESTIONS

Q1.4.1

List the bond angles for each of the following compounds: BH_3, CF_4, H_2O.

Q1.4.2

Why is sulfur dioxide a bent molecule (bond angle less than 180°)?

SOLUTIONS

S1.4.1

HBH = 120°

FCF = 109.5°

OHO = 104°

S1.4.2

This deviation is due to the lone pairs on the sulfur. These force the molecule to exhibit a “bent” geometry and therefore a deviation from the 180°.

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1.5: THE NATURE OF CHEMICAL BONDS- VALENCE BOND THEORY

Objectives

After completing this section, you should be able to

1. explain how covalent bonds are formed as a result of the ability of atoms to share electrons.
2. describe the formation of covalent bonds in terms of the overlapping of atomic orbitals.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- bond strength
- covalent bond
- ionic bond
- Lewis structure
- lone-pair electron
- nonbonding electron
- sigma (σ) bond
- valence bond theory

VALENCE BOND THEORY

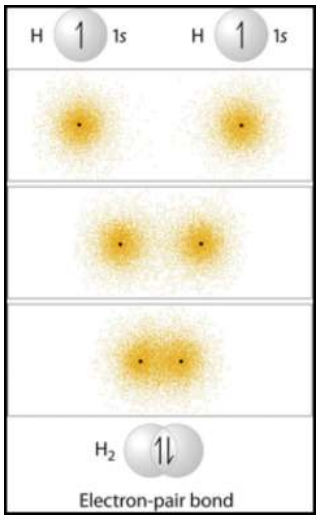
As we have been discussing how to use Lewis structures to depict the bonding in organic compounds, we have been very vague so far in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms – but how does this happen, and how does it lead to the formation of a bond holding the two atoms together? Two main models have been developed to described how covalent bonds are formed: valence bond theory and molecularly orbital theory.

Valence bond theory is most often used to describe bonding in organic molecules. In this model, covalent bonds are considered to form from the overlap of two atomic orbitals on different atoms, each orbital containing a single electron. The electrons become paired in the orbital overlap bonding the atoms together.

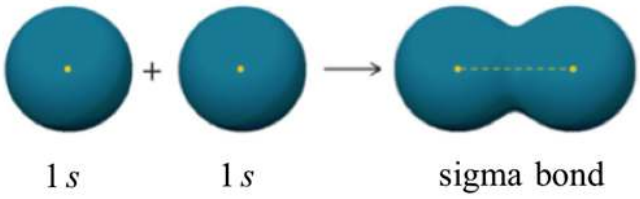
The simplest example valence bond theory can be demonstrated by the H_2 molecule. We can see from the periodic table that each hydrogen atom has a single valence electron. If 2 hydrogen atoms come together to form a bond, then each hydrogen atom effectively has a share in both electrons and thus each resembles the noble gas helium and is more stable. The 2 electrons shared in the orbital overlap are represented by a single dash between the atoms.



Valence bond theory describes a chemical bond as the overlap of atomic orbitals. In the case of the hydrogen molecule, the 1s orbital of one hydrogen atom overlaps with the 1s orbital of the second hydrogen atom to form a molecular orbital called a sigma bond which contains two electrons of opposite spin. The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.



ne more characteristic of the covalent bond in H_2 is important to consider at this point. The two overlapping 1*s* orbitals can be visualized as two spherical balloons being pressed together. This means that the bond has **cylindrical symmetry**: if we were to take a cross-sectional plane of the bond at any point, it would form a circle. This type of bond is referred to as a **σ(sigma) bond**.



The energy of the system depends on how much the orbitals overlap. The energy diagram below illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is called the the bond lengths between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration.

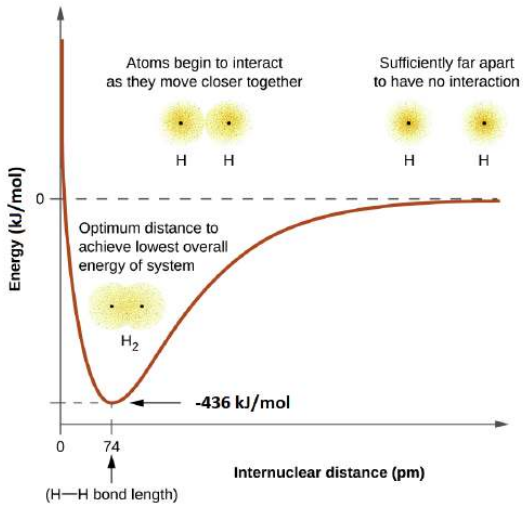


Figure **1.5.2** A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen **Atoms**

This optimal internuclear distance is the **bond length**. For the H_2 molecule, the distance is 74 pm (picometers, 10^{-12} meters). Likewise, the difference in potential energy between the lowest energy state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond dissociation energy,** or, more simply**, bond strength**. For the hydrogen molecule, the H-H bond strength is equal to about 435 kJ/mol. This means it would take 435 kJ to break one mole of H-H bonds.

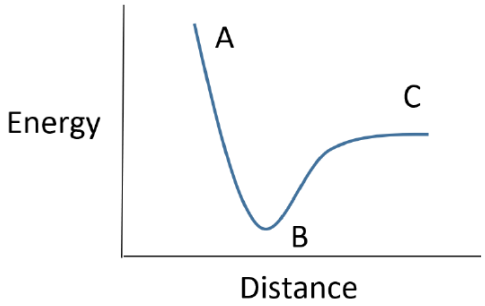
Every covalent bond in a given molecule has a characteristic length and strength. In general, the length of a typical carbon-carbon single bond in an organic molecule is about 150 pm, while carbon-carbon double bonds are about 130 pm, carbon-oxygen double bonds are about 120 pm, and carbon-hydrogen bonds are in the range of 100 to 110 pm. The strength of covalent bonds in organic molecules ranges from about 234 kJ/mol for a carbon-iodine bond (in thyroid hormone, for example), about 410 kJ/mole for a typical carbon-hydrogen bond, and up to over 800 kJ/mole for a carbon-carbon triple bond.

REPRESENTATIVE BOND ENERGIES AND LENGTHS

Bond	Length (pm)	Energy (kJ/mol)	Bond	Length (pm)	Energy (kJ/mol)
H-H	74	436	C-O	140.1	358
H-C	106.8	413	C=O	119.7	745
H-N	101.5	391	C≡O	113.7	1072
H-O	97.5	467	H-Cl	127.5	431
C-C	150.6	347	H-Br	141.4	366
C=C	133.5	614	H-I	160.9	298
C≡C	120.8	839	O-O	148	146
C-N	142.1	305	O=O	120.8	498
C=N	130.0	615	F-F	141.2	159
C≡N	116.1	891	Cl-Cl	198.8	243

EXERCISE

For the following energy diagram for energy vs. intermolecular distance is for a fluorine molecule (F_2). Please describe the importance for points A, B, & C on the graph.



SOLUTION

A - Repulsive Forces are present, nuclei are too close to one another.

B - Optimal distance between the two orbitals to have a bond (the bond length)

C - Cannot form a bond, the orbitals are too far apart.

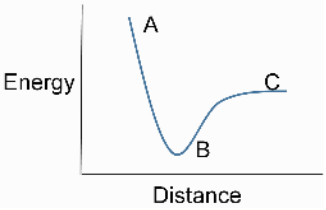
QUESTIONS

Q1.5.1

Draw an energy diagram for energy vs. intermolecular distance for a fluorine molecule (F_2) and describe the regions of the graph.

SOLUTIONS

S1.5.1



A - Repulsive Forces are present, p-orbitals are too close together

B - Optimal distance between the two p-orbitals to have a bond (the bond length)

C - Cannot form a bond, orbitals are too far away

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Richard Banks (Boise State University)

  Prof. Steven Farmer (Sonoma State University)

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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1.6: SP³ HYBRID ORBITALS AND THE STRUCTURE OF METHANE

Objective

After completing this section, you should be able to describe the structure of methane in terms of the sp^3 hybridization of the central carbon atom.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

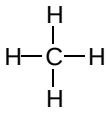
- bond angle
- hybridization
- sp^3 hybrid

STUDY NOTES

The tetrahedral shape is a very important one in organic chemistry, as it is the basic shape of all compounds in which a carbon atom is bonded to four other atoms. Note that the tetrahedral bond angle of $\mathrm{H-C-H}$ is 109.5°.

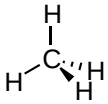
VALENCE BOND THEORY

Valence bond theory's use of overlapping atomic orbitals to explain how chemical bonds form works well in simple diatomic molecules such as H_2. However, when molecules with more than two atoms form stable bonds, we require a more detailed model. A good example is methane (CH_4). According to valence bond theory, the structure of a covalent species can be depicted using a Lewis structure.



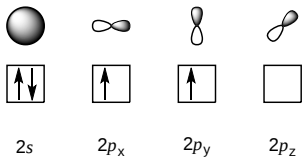
1

Experimentally, it has been shown that the four carbon-hydrogen bonds in the methane molecule are identical, meaning they have the same bond energy and the same bond length. Also, VSEPR theory suggests that the geometry at the carbon atom in the methane molecule is tetrahedral **(2)**, and there exists a large body of both theoretical and experimental evidence supporting this prediction.



2

According to valence bond theory, to form a covalent bond forms when an unpaired electron in one atom overlaps with an unpaired electron in a different atom. Now, consider the the electron configuration of the four valence electrons in carbon.



There is a serious mismatch between the electron configuration of carbon ($1s^2 2s^2 2p^2$) and the predicted structure of methane. The modern structure shows that there are only 2 unpaired electrons to share with hydrogens, instead of the 4 needed to create methane. Also, the p_x and p_y orbitals are at 90° to each other. They would form perpendicular bonds instead of the tetrahedral 109.5° bond angle predicted by VSEPR and experimental data. Lastly, there are two different orbitals, 2*s* and 2*p*, which would create different types of C-H bonds. As noted earlier, experimentally, the four carbon-hydrogen bonds in the methane molecule are identical.

HYBRID ORBITALS

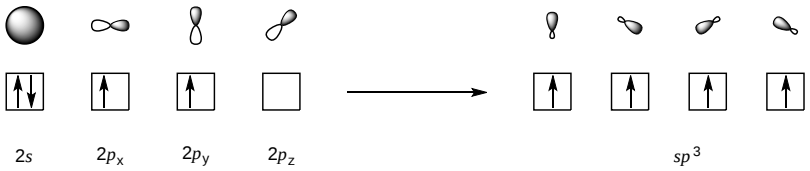
An answer to the problems posed above was offered in 1931 by Linus Pauling. He showed mathematically that an *s* orbital and three *p* orbitals on an atom can combine to form four equivalent hybrid atomic orbitals.

IMPORTANT IDEALS IN UNDERSTANDING HYBRIDIZATION

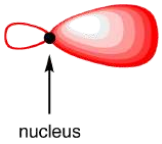
1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom create the molecular geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds.
7. Lone pair electrons are often contained in hybrid orbitals

SP^3 HYBRIDIZATION IN METHANE

In order to explain this observation, valence bond theory relies on a concept called **orbital hybridization**. In this picture, the four valence orbitals of the carbon (one 2*s* and three 2*p* orbitals) combine mathematically (remember: orbitals are described by equations) to form four equivalent **hybrid orbitals**, which are named ***sp*^{3} orbitals** because they are formed from mixing one *s* and three *p* orbitals. In the new electron configuration, each of the four valence electrons on the carbon occupies a single sp^3 orbital creating four unpaired electrons.



The shape of an sp^3 hybridized orbital is a combination of *s* and *p* atomic orbitals.



Each sp^3-hybridized orbital bears an electron, and electrons repel each other. To minimize the repulsion between electrons, the four sp^3-hybridized orbitals arrange themselves around the carbon nucleus so that they are as far away as possible from each other, resulting in the tetrahedral arrangement predicted by VSPER. The carbon atom in methane is called an "sp^3-hybridized carbon atom." The larger lobes of the sp^3 hybrids are directed towards the four corners of a tetrahedron, meaning that the angle between any two orbitals is 109.5^o.

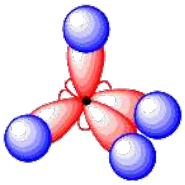


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BONDING IN METHANE

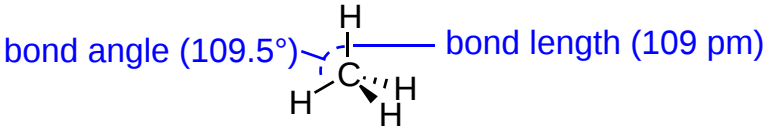
Each C-H bond in methane, then, can be described as an overlap between a half-filled 1*s* orbital in four hydrogen atoms and the larger lobe of one of the four half-filled sp^3 hybrid orbitals form a four equivalent sigma (σ) bond. This orbital overlap is often described using the notation: sp^3(C)-1*s*(H). The formation of sp^3 hybrid orbitals successfully explains the tetrahedral structure of methane and the equivalency of the the four C-H bonds.

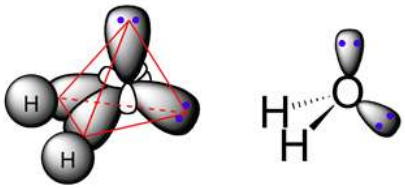
What remains is an explanation of why the sp^3 hybrid orbitals form. When the *s* and 3 *p* orbitals in carbon hybridize the resulting sp^3 hybrid orbital is unsymmetrical with one lobe larger than the other. This means the larger lobe can overlap more effectively with orbitals from other bonds making them stronger. Hybridizing allows for the carbon to form stronger bonds than it would with unhybridized *s* or *p* orbitals.



6

The four carbon-hydrogen bonds in methane are equivalent and all have a bond length of 109 pm (1.09 x 10-10 m), bond strength of of 429 kJ/mol. All of the H-C-H bond angles are 109.5°.



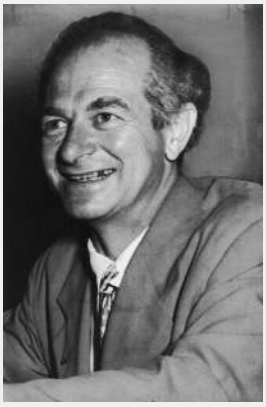


LOOKING CLOSER: LINUS PAULING

Arguably the most influential chemist of the 20th century, Linus Pauling (1901–1994) is the only person to have won two individual (that is, unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book *The Nature of the Chemical Bond* is one of the most significant books ever published in chemistry.

Pauling's big contribution to chemistry was valence bond theory, which combined his knowledge of quantum mechanical theory with his knowledge of basic chemical facts, like bond lengths and and bond strengths and shapes of molecules. Valence bond theory, like Lewis's bonding theory, provides a simple model that is useful for predicting and understanding the structures of molecules, especially for organic chemistry. .

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.



Linus Pauling was one of the most influential chemists of the 20th century.

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
  - Gamini Gunawardena from the OChemPal site (Utah Valley University)
- Dr. Krista Cunningham

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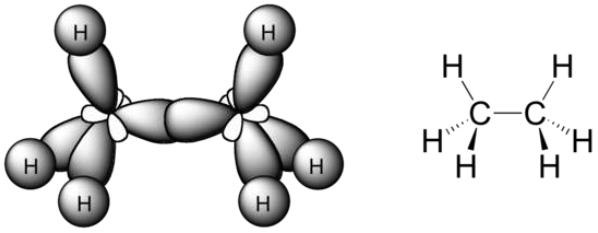
1.7: SP³ HYBRID ORBITALS AND THE STRUCTURE OF ETHANE

Objective

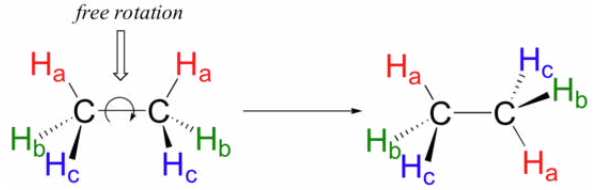
After completing this section, you should be able to describe the structure of ethane in terms of the *sp*^{3} hybridization of the two carbon atoms present in the molecule.

BONDING IN ETHANE

In the ethane molecule, the bonding picture according to valence orbital theory is very similar to that of methane. Both carbons are sp^3-hybridized, meaning that both have four bonds arranged with tetrahedral geometry. The carbon-carbon bond, with a bond length of 1.54 Å, is formed by overlap of one sp^3 orbital from each of the carbons, while the six carbon-hydrogen bonds are formed from overlaps between the remaining sp^3 orbitals on the two carbons and the 1*s* orbitals of hydrogen atoms. All of these are sigma bonds.



Because they are formed from the end-on-end overlap of two orbitals, *sigma bonds are free to rotate*. This means, in the case of ethane molecule, that the two methyl (CH_3) groups can be pictured as two wheels on a hub, each one able to rotate freely with respect to the other.



In chapter 3 we will learn more about the implications of rotational freedom in sigma bonds, when we discuss the 'conformation' of organic molecules.

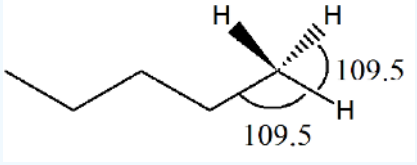
The sp^3 bonding picture is also used to described the bonding in amines, including ammonia, the simplest amine. Just like the carbon atom in methane, the central nitrogen in ammonia is sp^3-hybridized. With nitrogen, however, there are five rather than four valence electrons to account for, meaning that three of the four hybrid orbitals are half-filled and available for bonding, while the fourth is fully occupied by a (non-bonding) pair of electrons.

C_2H_4, also known as ethylene or ethene, is a gaseous material created synthetically through steam cracking. In nature, it is released in trace amounts by plants to signal their fruits to ripen. Ethene consists of two sp^2-hybridized carbon atoms, which are sigma bonded to each other and to two hydrogen atoms each. The remaining unhybridized p orbitals on the carbon form a pi bond, which gives ethene its reactivity.

? EXERCISE 1.7.1

Draw hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) and predict the bond angles within this molecule.

Answer



All the bond angles will be the same.

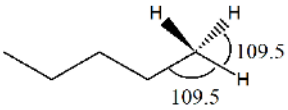
QUESTIONS

Q1.7.1

Draw pentane, $CH_3CH_2CH_2CH_2CH_3$, predict the bond angles within this molecule.

SOLUTIONS

S1.7.1



All the bond angles will be the same size.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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1.8: SP² HYBRID ORBITALS AND THE STRUCTURE OF ETHYLENE

Objectives

After completing this section, you should be able to

1. account for the formation of carbon-carbon double bonds using the concept of sp^2 hybridization.
2. describe a carbon-carbon double bond as consisting of one σ bond and one π bond.
3. explain the difference between a σ bond and a π bond in terms of the way in which *p* orbitals overlap.

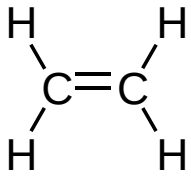
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

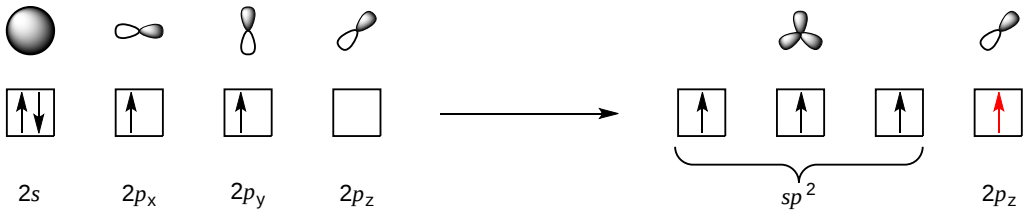
- pi (π) bond
- sp^2 hybrid

BONDING IN ETHYLENE

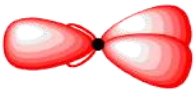
Thus far valence bond theory has been able to describe the bonding in molecules containing only single bonds. However, when molecules contain double or triple bonds the model requires more details. Ethylene (commonly knows as ethene), CH_2CH_2, is the simplest molecule which contains a carbon carbon double bond. The Lewis structure of ethylene indicates that there are one carbon-carbon double bond and four carbon-hydrogen single bonds. Experimentally, the four carbon-hydrogen bonds in the ethylene molecule have been shown to be identical. Because each carbon is surrounded by three electron groups, VSEPR theory says the molecule should have a trigonal planar geometry. Although each carbon has fulfilled its tetravalent requirement, one bond appears different. Clearly, a different type of orbital overlap is involved.



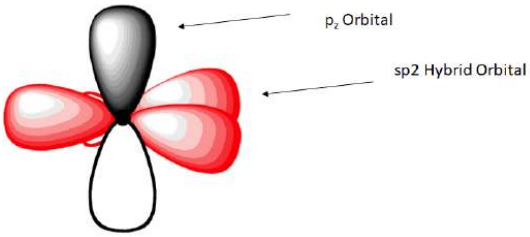
The sigma bonds formed in ethene is by the participation of a different kind of hybrid orbital. Three atomic orbitals on each carbon – the 2*s*, $2p_x$ and $2p_y$ – combine to form three sp^2 hybrids, leaving the $2p_z$ orbital unhybridized. Three of the four valence electrons on each carbon are distributed to the three sp^2 hybrid orbitals, while the remaining electron goes into the unhybridized p_z orbital. Each carbon in ethene is said to be a "sp^2-hybridized carbon." The electron configuration of the sp^2 hybridized carbon shows that there are four unpaired electrons to form bonds. However, the unpaired electrons are contained in two different types of orbitals so it is to be expected that two different types of bonds will form.



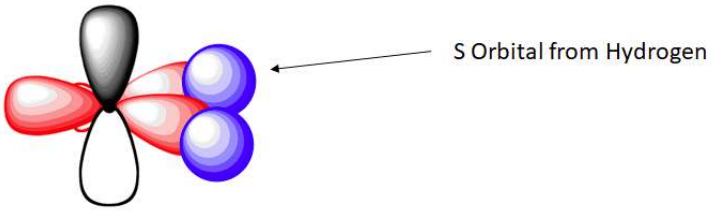
The shape of the sp^2-hybridized orbital has be mathematically shown to to be roughly the same as that of the sp^3-hybridized orbital. To minimize the repulsion between electrons, the three sp^2-hybridized orbitals are arranged with a trigonal planar geometry. Each orbital lobe is pointing to the three corners of an equilateral triangle, with angles of 120° between them. Again, geometry and hybrization can be tied together. Atoms surrounded by three electron groups can be said to have a trigonal planar geometry and sp^2 hybridization.



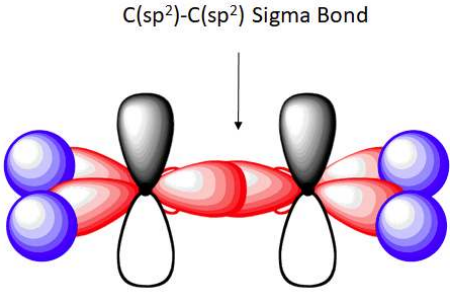
The unhybridized $2p_z$ orbital is *perpendicular* to the plane of the trigonal planar sp^2 hybrid orbtals.



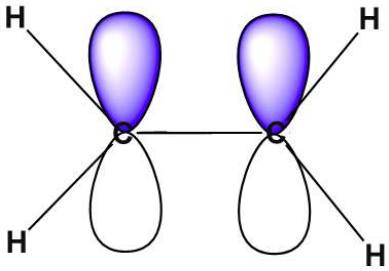
In the ethylene molecule, each carbon atom is bonded to two hydrogen atoms. Thus, overlap two sp^2-hybridized orbitals with the 1s orbitals of two hydrogen atoms for the C-H sigma bonds in ethylene (sp^2(C)-1s(H). Consequently, consistent with the observations, the four carbon-hydrogen bonds in ethylene are identical.



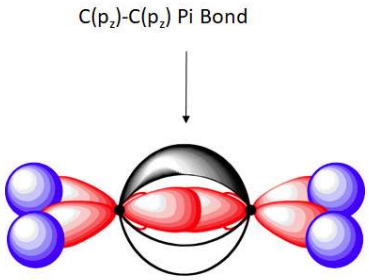
The C-C sigma bond in ethylene is formed by the overlap of an sp^2 hybrid orbital from each carbon.



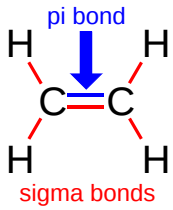
The overlap of hybrid orbitals or a hybrid orbital and a 1s orbtial from hydrogen creates the sigma bond framework of the ethylene molecule. However the unhybridized p_z orbital on each carbon remains.



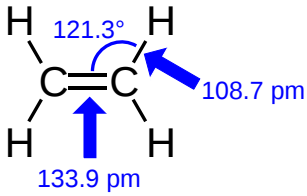
The unhybridized pz orbitals on each carbon overlap to a π bond (pi). The orbital overlap is commonly written as p_z(C)-1p_z(C). In general multiple bonds in molecular compound are formed by the overlap of unhybridized p orbitals. It should be noted that the carbon-carbon double bond in ethlene is made up of two different types of bond, a sigma and a pi.



Overall, ethylene is said to contain five sigma bonds and one pi bond. Pi bonds tend to be weaker than sigma bonds because the side-by-side overlap the p orbitals give a less effective orbital overlap when compared to the end-to-end orbital overlap of a sigma bond. This makes the pi much easier to break which is one of the most important ideas in organic chemistry reactions as we will see in Chapter 7 and subsequent chapters.

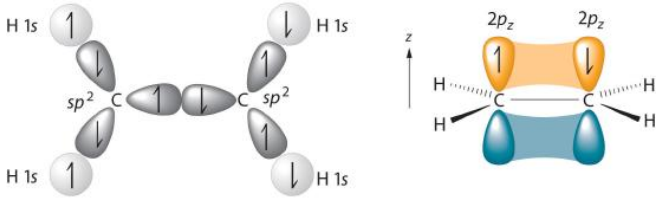


An ethylene molecule is said to be made up of five sigma bonds and one pi bond. The three sp^2 hybrid orbitals on each carbon orient to create the basic trigonal planer geometry. The H-C-C bond angle in ethylene is 121.3º which is very close to the 120º predicted by VSEPR. The four C-H sigma bonds in ethylene . The carbon-carbon double bond in ethylene is both shorter (133.9 pm) and almost twice as strong (728 kJ/mol) than the carbon- carbon single bond in ethylene (154 pm & 377 kJ/mol). Each of the four carbon-hydrogen bond in ethylene are equivalent has have a length of 108.7 pm



RIGIDITY IN ETHENE

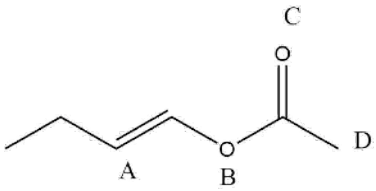
Because they are the result of side-by-side overlap (rather then end-to-end overlap like a sigma bond), *pi bonds are not free to rotate.* If rotation about this bond were to occur, it would involve disrupting the side-by-side overlap between the two $2p_z$ orbitals that make up the pi bond. If free rotation were to occur the p-orbitals would have to go through a phase where they are 90° from each other, which would break the pi bond because there would be no overlap. Since the pi bond is essential to the structure of ethene it must not break, so there can be not free rotation about the carbon-carbon sigma bond. The presence of the pi bond thus 'locks' the six atoms of ethene into the same plane.



(a) C_2H_4 σ-bonded framework (b) C_2H_4 π bonding

EXERCISE

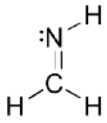
1) Consider the following molecule:



At each atom, what is the hybridization and the bond angle and the bond angle predicted by VSPER?

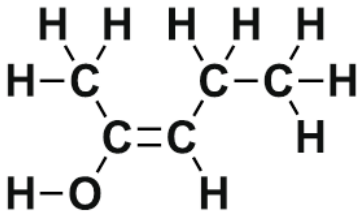
2)

a: Describe the orbitals which overlap to the carbon-nitrogen sigma bond and pie bond in the molecule below:



b: What kind of orbital holds the nitrogen lone pair?

3) For the following molecule please indicate with atoms are being held in the same plane by the carbon-carbon double bond:



SOLUTIONS

1)

A - sp^2, 120°

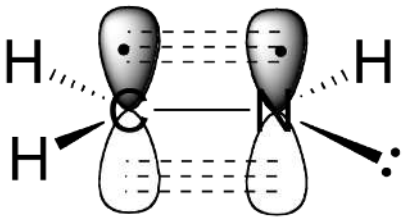
B - sp^3, 109°

C - sp^2, 120° (with the lone pairs present)

D - sp^3, 109°

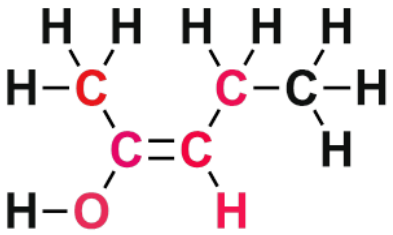
2)

a) The carbon and nitrogen atoms are both sp^2 hybridized. The carbon-nitrogen double bond is composed of a sigma bond formed from two sp^2 orbitals, and a pi bond formed from the side-by-side overlap of two unhybridized *2p* orbitals.



b) As shown in the figure above, the nitrogen lone pair electrons occupy one of the three sp^2 hybrid orbitals.

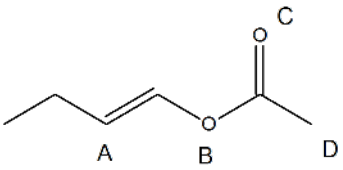
3)



QUESTIONS

Q1.8.1

Consider the following molecule:



At each atom, what is the hybridization and the bond angle? At atom A draw the molecular orbital.

SOLUTIONS

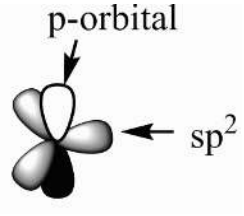
S1.8.1

A - sp^2, 120°

B - sp^3, 109°

C - sp^2, 120° (with the lone pairs present)

D - sp^3, 109°



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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1.9: SP HYBRID ORBITALS AND THE STRUCTURE OF ACETYLENE

Objectives

After completing this section, you should be able to

1. use the concept of *sp* hybridization to account for the formation of carbon-carbon triple bonds, and describe a carbon-carbon triple bond as consisting of one σ bond and two π bonds.
2. list the approximate bond lengths associated with typical carbon-carbon single bonds, double bonds and triple bonds. [You may need to review Sections 1.7 and 1.8.]
3. list the approximate bond angles associated with sp^3-, sp^2- and sp-hybridized carbon atoms, and hence, predict the bond angles to be expected in given organic compounds. [If necessary, review Sections 1.6, 1.7 and 1.8.]
4. account for the differences in bond length, bond strength and bond angles found in compounds containing sp^3-, sp^2- and sp-hybridized carbon atoms, such as ethane, ethylene and acetylene.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- *sp* hybrid

STUDY NOTES

The bond angles associated with sp^3-, sp^2- and sp-hybridized carbon atoms are approximately 109.5, 120 and 180°, respectively.

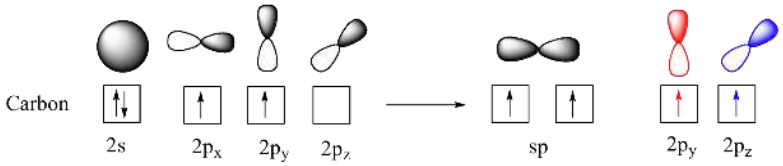
BONDING IN ACETYLENE

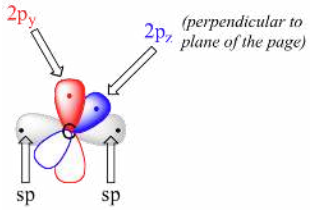
Finally, the hybrid orbital concept applies well to triple-bonded groups, such as alkynes and nitriles. Consider, for example, the structure of ethyne (common name acetylene), the simplest alkyne.



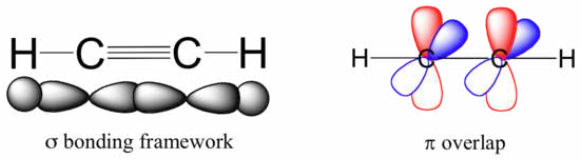
ethyne
(acetylene)

This molecule is linear: all four atoms lie in a straight line. The carbon-carbon triple bond is only 1.20Å long. In the hybrid orbital picture of acetylene, both carbons are **sp-hybridized**. In an sp-hybridized carbon, the 2*s* orbital combines with the $2p_x$ orbital to form two sp hybrid orbitals that are oriented at an angle of 180°with respect to each other (eg. along the x axis). The $2p_y$ and $2p_z$ orbitals remain unhybridized, and are oriented perpendicularly along the y and z axes, respectively.

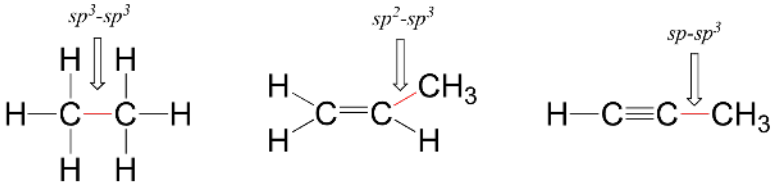




The C-C sigma bond, then, is formed by the overlap of one sp orbital from each of the carbons, while the two C-H sigma bonds are formed by the overlap of the second sp orbital on each carbon with a 1*s* orbital on a hydrogen. Each carbon atom still has two half-filled $2p_y$ and $2p_z$ orbitals, which are perpendicular both to each other and to the line formed by the sigma bonds. These two perpendicular pairs of *p* orbitals form two pi bonds between the carbons, resulting in a triple bond overall (one sigma bond plus two pi bonds).



The hybrid orbital concept nicely explains another experimental observation: single bonds adjacent to double and triple bonds are progressively shorter and stronger than 'normal' single bonds, such as the one in a simple alkane. The carbon-carbon bond in ethane (structure A below) results from the overlap of two sp^3 orbitals.



A B C

In alkene B, however, the carbon-carbon single bond is the result of overlap between an sp^2 orbital and an sp^3 orbital, while in alkyne C the carbon-carbon single bond is the result of overlap between an sp orbital and an sp^3 orbital. These are all single bonds, but the bond in molecule C is shorter and stronger than the one in B, which is in turn shorter and stronger than the one in A.

The explanation here is relatively straightforward. An sp orbital is composed of one *s* orbital and one *p* orbital, and thus it has 50% *s* character and 50% *p* character. sp^2 orbitals, by comparison, have 33% *s* character and 67% *p* character, while sp^3 orbitals have 25% *s* character and 75% *p* character. Because of their spherical shape, 2*s* orbitals are smaller, and hold electrons closer and 'tighter' to the nucleus, compared to 2*p* orbitals. Consequently, bonds involving sp + sp^3 overlap (as in alkyne C) are shorter and stronger than bonds involving sp^2 + sp^3 overlap (as in alkene B). Bonds involving sp^3-sp^3overlap (as in alkane A) are the longest and weakest of the group, because of the 75% '*p*' character of the hybrids.

HYBRIDIZATION SUMMARY

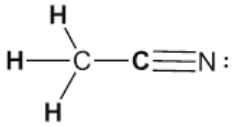
- A single bond is a sigma bond.
- A double bond is made up of a sigma bond and a pi bond.
- A triple bond is made up of a sigma bond and two pi bonds.
- Sigma bonds are made by the overlap of two hybrid orbitals or the overlap of a hybrid orbital and a s orbital from hydrogen.
- Pi bonds are made by the overlap of two unhybridized p orbitals.
- Lone pair electrons are usually contained in hybrid orbitals.

The hybrid orbitals used (and hence the hybridization) depends on how many electron groups are around the atom in question. An electron group can mean either a bonded atom or a lone pair. Molecular geometry is also decided by the number of electron groups so it is directly linked to hybridization.

# of Electron Groups	Hybrid Orbital Used	Example	Basic Geometry	Basic Bond Angle
2	sp	—C≡	Linear	180°
3	sp^2	C=	Trigonal Planar	120°
4	sp^3	C	Tetrahedral	109.5°

EXERCISES

1) For the molecule acetonitrile:



Acetonitrile

a) How many sigma and pi bonds does it have?

b) What orbitals overlap to form the C-H sigma bonds?

c) What orbitals overlap to form the C-C sigma bond?

d) What orbitals overlap to form the C-N sigma bond?

e) What orbitals overlap to the form the C-N pi bonds?

f) What orbital contains the lone pair electrons on nitrogen?

SOLUTIONS

1)

a) 5 sigma and 2 pi

b) An sp^3 hybrid orbital from carbon and an a s orbital from hydrogen.

c) An sp^3 hybrid orbital from one carbon and an a sp orbital from the other carbon.

d) An sp hybrid orbital from carbon and an a sp orbital from nitrogen.

e) An p_y and p_z orbital from carbon and an p_y and p_z orbital from nitrogen.

f) An sp hybrid orbital.

QUESTIONS

Q1.9.1

1-Cyclohexyne is a very strained molecule. By looking at the molecule explain why there is such a intermolecular strain using the knowledge of hybridization and bond angles.



SOLUTIONS

S1.9.1

The alkyne is a sp hybridized orbital. By looking at a sp orbital, we can see that the bond angle is 180°, but in cyclohexane the regular angles would be 109.5°. Therefore the molecule would be strained to force the 180° to be a 109°.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
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1.10: HYBRIDIZATION OF NITROGEN, OXYGEN, PHOSPHORUS AND SULFUR

Objective

After completing this section, you should be able to apply the concept of hybridization to atoms such as N, O, P and S explain the structures of simple species containing these atoms.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- lone pair electrons

STUDY NOTES

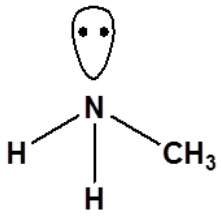
Nitrogen is frequently found in organic compounds. As with carbon atoms, nitrogen atoms can be sp^3-, sp^2- or sp-hybridized.

Note that, in this course, the term “lone pair” is used to describe an unshared pair of electrons.

The valence-bond concept of orbital hybridization can be extrapolated to other atoms including nitrogen, oxygen, phosphorus, and sulfur. In other compounds, covalent bonds that are formed can be described using hybrid orbitals.

METHYL AMINE

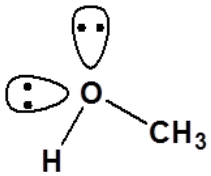
The nitrogen is sp^3 hybridized which means that it has four sp^3 hybrid orbitals. Two of the sp^3 hybridized orbitals overlap with s orbitals from hydrogens to form the two N-H sigma bonds. One of the *sp3* hybridized orbitals overlap with an sp^3 hybridized orbital from carbon to form the C-N sigma bond. The lone pair electrons on the nitrogen are contained in the last sp^3 hybridized orbital. Due to the *sp3* hybridization the nitrogen has a tetrahedral geometry. However, the H-N-H and H-N-C bonds angles are less than the typical 109.5^o due to compression by the lone pair electrons.



Methylamine

METHANOL

The oxygen is sp^3 hybridized which means that it has four sp^3 hybrid orbitals. One of the sp^3 hybridized orbitals overlap with s orbitals from a hydrogen to form the O-H signma bonds. One of the *sp3* hybridized orbitals overlap with an sp^3 hybridized orbital from carbon to form the C-O sigma bond. Both the sets of lone pair electrons on the oxygen are contained in the remaining sp^3 hybridized orbital. Due to the *sp3* hybridization the oxygen has a tetrahedral geometry. However, the H-O-C bond angles are less than the typical 109.5^o due to compression by the lone pair electrons.

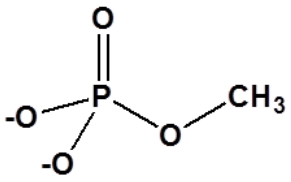


Methanol

METHYL PHOSPHATE

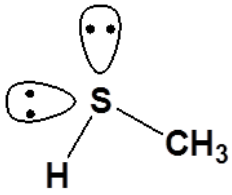
Phosphorus can have have expanded octets because it is in the n = 3 row. Typically, phosphorus forms five covalent bonds. In biological molecules, phosphorus is usually found in organophosphates. Organophosphates are made up of a phosphorus atoms bonded to four

oxygens, with one of the oxygens also bonded to a carbon. In methyl phosphate, the phosphorus is sp^3 hybridized and the O-P-O bond angle varying from 110 to 112°.

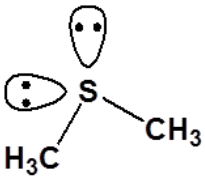


METHANETHIOL & DIMETHYL SULFIDE

In biological system, sulfur is typically found in molecules called thiols or sulfides. In a thiol, the sulfur atim is conded to one hydrogens and one carbon and is analogous to an alcohol. In a sulfide, the sulfur is bonded to two carbons. In both cases the sulfur is sp^3 hybridized and the bond angles are much less than the typicall 109.5°.



Methanethiol

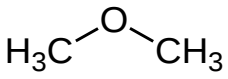


Dimethyl sulfide

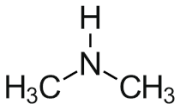
EXERCISE

1) Insert the missing lone pairs of electrons in the following molecules, and tell what hybridization you expect for each of the indicated atoms.

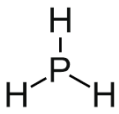
a) The oxygen is dimethyl ether:



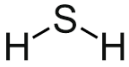
b) The nitrogen in dimethyl amine:



c) The phosphorus in phosphine:



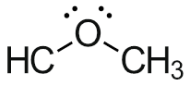
d) The sulfur in hydrogen sulfide:



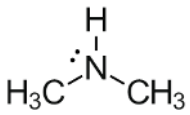
SOLUTION

1)

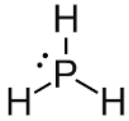
a) sp^3 hybridization



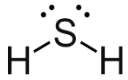
b) sp^3 hybridization



c) sp^3 hybridization



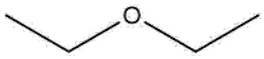
d) sp^3 hybridization



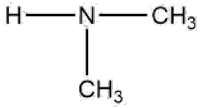
QUESTIONS

Q1.10.1

Identify geometry and lone pairs on each heteroatom of the molecules given.



Diethyl Ether



Dimethylamine

SOLUTIONS

S1.10.1

Diethyl ether would have two lone pairs of electrons and would have a bent geometry around the oxygen.

Dimethyl amine would have one lone pair and would show a pyramidal geometry around the nitrogen.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

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1.11: THE NATURE OF CHEMICAL BONDS- MOLECULAR ORBITAL THEORY

Objectives

After completing this section, you should be able to

1. describe the formation of covalent bonds in terms of molecular orbitals.
2. account for differences in bond length and strength in terms of the efficiency with which atomic orbitals overlap.
3. draw simple molecular orbital diagrams (e.g., for the H_2 molecule) showing the formation of bonding and antibonding orbitals.

KEY TERMS

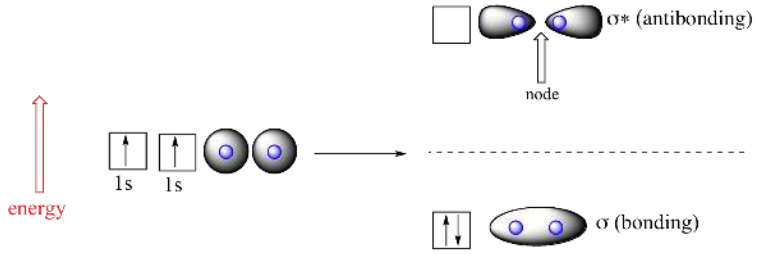
Make certain that you can define, and use in context, the key terms below.

- antibonding MO
- bonding MO
- molecular orbital (MO) theory

As we have seen, valence bond theory does a remarkably good job at explaining the bonding geometry of many of the functional groups in organic compounds. There are some areas, however, where the valence bond theory falls short. It fails to adequately account, for example, for some interesting properties of compounds that contain alternating double and single bonds. In order to understand these properties, we need to think about chemical bonding in a new way, using the ideas of molecular orbital (MO) theory.

ANOTHER LOOK AT THE H_2 MOLECULE: BONDING AND ANTIBONDING SIGMA MOLECULAR ORBITALS

Let's go back and consider again the simplest possible covalent bond: the one in molecular hydrogen (H_2). When we described the hydrogen molecule using valence bond theory, we said that the two 1*s* orbitals from each atom overlap, allowing the two electrons to be shared and thus forming a covalent bond. In molecular orbital theory, we make a further statement: we say that the two atomic 1*s* orbitals don't just overlap, they actually *combine to form two completely new orbitals*. These two new orbitals, instead of describing the likely location of an electron around a single nucleus, describe the location of an electron pair around two or more nuclei. The bonding in H_2, then, is due to the formation of a new **molecular orbital** (MO), in which a pair of electrons is delocalized around two hydrogen nuclei. An important principle of quantum mechanical theory is that when orbitals combine, the number of orbitals before the combination takes place must equal the number of new orbitals that result – orbitals don't just disappear! (we saw this previously when we discussed hybrid orbitals: one *s* and three *p* orbitals make four sp^3 hybrids). When two atomic 1*s* orbitals combine in the formation of H_2, the result is two molecular orbitals called **sigma (σ) orbitals**. According to MO theory, the first sigma orbital is lower in energy than either of the two isolated atomic 1*s* orbitals – thus this sigma orbital is referred to as a **bonding molecular orbital**. The second, **sigma-star (σ*) orbital** is higher in energy than the two atomic 1*s* orbitals, and is referred to as an **antibonding molecular orbital** (in MO theory, a star (*) sign always indicates an antibonding orbital).



Following the *aufbau* ('building up') principle, we place the two electrons in the H_2 molecule in the lowest energy orbital, which is the (bonding) sigma orbital.

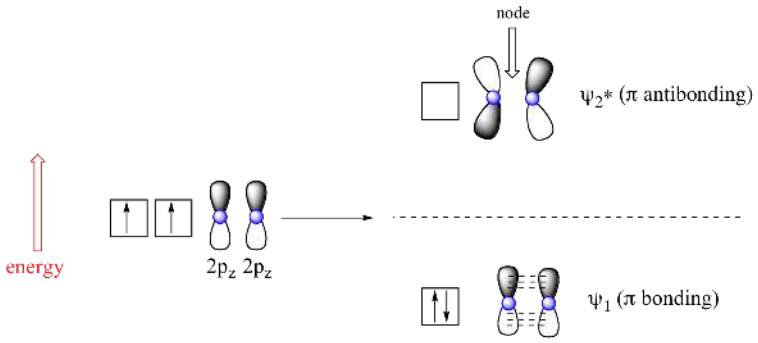
The bonding sigma orbital, which holds both electrons in the ground state of the molecule, is egg-shaped, encompassing the two nuclei, and with the highest likelihood of electrons being in the area between the two nuclei. The high-energy, antibonding sigma-star orbital can be visualized as a pair of droplets, with areas of higher electron density near each nucleus and a 'node', (area of zero electron density) midway between the two nuclei.

Remember that we are thinking here about electron behavior as *wave behavior*. When two separate waves combine, they can do so with what is called constructive interference, where the two amplitudes reinforce one another, or destructive interference, where the two

amplitudes cancel one another out. Bonding MO's are the consequence of constructive interference between two atomic orbitals which results in an attractive interaction and an increase in electron density between the nuclei. Antibonding MO's are the consequence of destructive interference which results in a repulsive interaction and a 'canceling out' of electron density between the nuclei (in other words, a node),

MO THEORY AND PI BONDS - CONJUGATION

The advantage of MO theory becomes more apparent when we think about pi bonds, especially in those situations where two or more pi bonds are able to interact with one another. Let's first consider the pi bond in ethene from an MO theory standpoint (in this example we will be disregarding the various sigma bonds, and thinking *only* about the pi bond). According to MO theory, the two atomic $2p_z$ orbitals combine to form two **pi (π) molecular orbitals**, one a low-energy π bonding orbital and one a high-energy **π-star (π*) antibonding molecular orbital**. These are sometimes denoted, in MO diagrams like the one below, with the Greek letter psi (Ψ) instead of π.



In the bonding Ψ_1 orbital, the two shaded lobes of the $2p_z$ orbitals interact constructively with each other, as do the two unshaded lobes (remember, the shading choice represents mathematical (+) and (-) signs for the wavefunction). Therefore, there is increased electron density between the nuclei in the molecular orbital – this is why it is a bonding orbital.

In the higher-energy antibonding Ψ_2* orbital, the shaded lobe of one $2p_z$ orbital interacts destructively with the unshaded lobe of the second $2p_z$ orbital, leading to a node between the two nuclei and overall repulsion.

By the *aufbau* principle, the two electrons from the two atomic orbitals will be paired in the lower-energy $\Psi_1$orbital when the molecule is in the ground state.

EXERCISES

1. Draw a simple molecular orbital diagram for each of the following molecules
    a. nitrogen, N_2.
    b. oxygen, O_2.

ANSWERS:

Answers

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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1.12: DRAWING CHEMICAL STRUCTURES

Objectives

After completing this section, you should be able to

1. propose one or more acceptable Kekulé structures (structural formulas) for any given molecular formula
2. write the molecular formula of a compound, given its Kekulé structure.
3. draw the shorthand structure of a compound, given its Kekulé structure.
4. interpret shorthand structures and convert them to Kekulé structures.
5. write the molecular formula of a compound, given its shorthand structure.

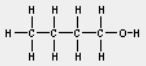
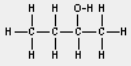
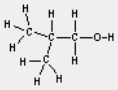
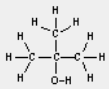
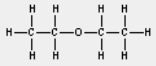
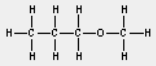
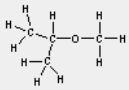
STUDY NOTES

When drawing the structure of a neutral organic compound, you will find it helpful to remember that

- each carbon atom has four bonds.
- each nitrogen atom has three bonds.
- each oxygen atom has two bonds.
- each hydrogen atom has one bond.

It is necessary to draw structural formulas for organic compounds because in most cases a molecular formula does not uniquely represent a single compound. Different compounds having the same molecular formula are called **isomers**, and the prevalence of organic isomers reflects the extraordinary versatility of carbon in forming strong bonds to itself and to other elements. When the group of atoms that make up the molecules of different isomers are bonded together in fundamentally different ways, we refer to such compounds as **constitutional isomers**. There are seven constitutional isomers of $C_4H_{10}O$, and structural formulas for these are drawn in the following table. These formulas represent all known and possible $C_4H_{10}O$ compounds, and display a common structural feature. There are no double or triple bonds and no rings in any of these structures.

Structural Formulas for C_4H_{10O} isomers

Kekulé Formula	Condensed Formula	Shorthand Formula
	$CH_3(CH_2)_3OH$	
	$C_2H_5CH(OH)CH_3$	
	$(CH_3)_2CHCH_2OH$	
	$(CH_3)_3COH$	
	$(C_2H_5)_2O$	
	$CH_3(CH_2)_2OCH_3$	
	$(CH_3)_2CHOCH_3$	

Simplification of structural formulas may be achieved without any loss of the information they convey. In **condensed structural formulas** the bonds to each carbon are omitted, but each distinct structural unit (group) is written with subscript numbers designating multiple substituents, including the hydrogens. **Shorthand (line) formulas** omit the symbols for carbon and hydrogen entirely. Each straight line

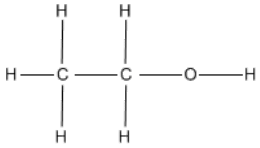
segment represents a bond, the ends and intersections of the lines are carbon atoms, and the correct number of hydrogens is calculated from the tetravalency of carbon. Non-bonding valence shell electrons are omitted in these formulas.

Developing the ability to visualize a three-dimensional structure from two-dimensional formulas requires practice, and in most cases the aid of molecular models. As noted earlier, many kinds of model kits are available to students and professional chemists, and the beginning student is encouraged to obtain one.

KEKULÉ FORMULA

A structural formula displays the atoms of the molecule in the order they are bonded. It also depicts how the atoms are bonded to one another, for example single, double, and triple covalent bond. Covalent bonds are shown using lines. The number of dashes indicate whether the bond is a single, double, or triple covalent bond. Structural formulas are helpful because they explain the properties and structure of the compound which empirical and molecular formulas cannot always represent.

Ex. Kekulé Formula for Ethanol:



CONDENSED FORMULA

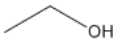
Condensed structural formulas show the order of atoms like a structural formula but are written in a single line to save space and make it more convenient and faster to write out. Condensed structural formulas are also helpful when showing that a group of atoms is connected to a single atom in a compound. When this happens, parenthesis are used around the group of atoms to show they are together.

Ex. Condensed Structural Formula for Ethanol: CH_3CH_2OH (Molecular Formula for Ethanol C_2H_6O).

SHORTHAND FORMULA

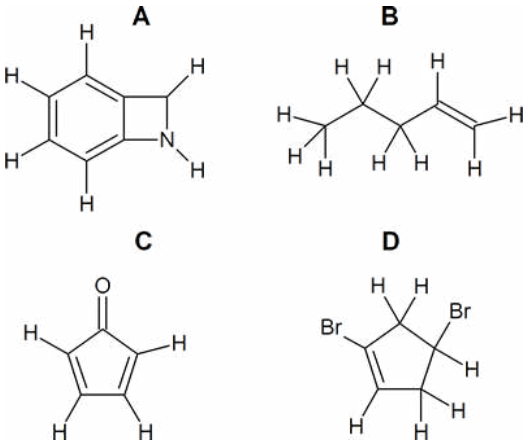
Because organic compounds can be complex at times, line-angle formulas are used to write carbon and hydrogen atoms more efficiently by replacing the letters with lines. A carbon atom is present wherever a line intersects another line. Hydrogen atoms are then assumed to complete each of carbon's four bonds. All other atoms that are connected to carbon atoms are written out. Line angle formulas help show structure and order of the atoms in a compound making the advantages and disadvantages similar to structural formulas.

Ex.Shorthand Formula for Ethanol:



EXERCISES

Write down the molecular formula for each of the compounds shown here.



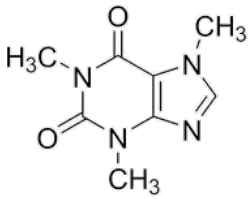
ANSWERS:

A. C_7H_7N
B. C_5H_{10}
C. C_5H_4O
D. $C_5H_6Br_2$

QUESTIONS

Q1.12.1

Below is the molecule for caffeine. Give the molecular formula for it.



SOLUTIONS

S1.12.1

$C_8H_{10}O_2N_4$

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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1.S: STRUCTURE AND BONDING (SUMMARY)

CONCEPTS & VOCABULARY

1.0: Prelude to Structure and Bonding

- Organic compounds contain carbon atoms bonded hydrogen and other carbon atoms.
- Organic chemistry studies the properties and reactions of organic compounds.

1.1: Atomic Structure: The Nucleus

- Atoms are comprised of **protons**, **neutrons** and **electrons**. Protons and neutrons are found in the nucleus of the atom, while electrons are found in the electron cloud around the nucleus. The relative electrical charge of a proton is +1, a neutron has no charge, and an electron's relative charge is -1.
- The number of protons in an atom's nucleus is called the **atomic number, *Z***.
- The **mass number, *A***, is the sum of the number of protons and the number of neutrons in a nucleus.
- The type of element an atom represents is defined by the atomic number, *Z* in the atom. All atoms of one specific element have the same number of protons (Z).
- Atoms that have the same atomic number (Z), but different mass numbers (A) are called **isotopes**.

1.2: Atomic Structure: Orbitals

- An **atomic orbital** is the probability description of where an electron can be found. The four basic types of orbitals are designated as ***s***, ***p***, ***d***, and ***f***.

1.3: Atomic Structure: Electron Configurations

- The order in which electrons are placed in atomic orbitals is called the **electron configuration** and is governed by the ***aufbau* principle**.
- Electrons in the outermost shell of an atom are called **valence electrons**. The number of valence electrons in any atom is related to its position in the periodic table. Elements in the same periodic group have the same number of valence electrons.

1.4: Development of Chemical Bonding Theory

- **Lewis Dot Symbols** are a way of indicating the number of valence electrons in an atom. They are useful for predicting the number and types of covalent bonds within organic molecules.
- The **molecular shape** of molecules is predicted by Valence Shell Electron Pair Repulsion (VSEPR) theory. The shapes of common organic molecules are based on **tetrahedral**, **trigonal planar** or **linear** arrangements of electron groups.

1.5: The Nature of Chemical Bonds: Valence Bond Theory

- **Covalent bonds** form as valence electrons are shared between two atoms.
- **Lewis Structures** and **structural formulas** are common ways of showing the covalent bonding in organic molecules.
- **Formal charge** describes the changes in the number of valence electrons as an atom becomes bonded into a molecule. If the atom has a net loss of valence electrons it will have a positive formal charge. If the atom has a net gain of valence electrons it will have a negative formal charge.
- Atomic orbitals often change as they overlap to form molecular orbitals. This process is known as **orbital hybridization**. The common types of hybrid orbitals in organic molecules are ***sp*^{3}**, ***sp*^{2}**, and ***sp***.

1.6: *sp*^{3} Hybrid Orbitals and the Structure of Methane

- The four identical C-H single bonds in CH_4 form as the result of sigma bond overlap between the sp^3 hybrid orbitals of carbon and the *s* orbital of each hydrogen.

1.7: *sp*^{3} Hybrid Orbitals and the Structure of Ethane

- The C-C bond in C_2H_6 forms as the result of sigma bond overlap between a sp^3 hybrid orbital on each carbon. and the *s* orbital of each hydrogen. The six identical C-H single bonds in form as the result of sigma bond overlap between the sp^3 hybrid orbitals of carbon and the *s* orbital of each hydrogen.

1.8: *sp*^{2} Hybrid Orbitals and the Structure of Ethylene

- The C=C bond in C_2H_4 forms as the result of both a sigma bond overlap between a sp^2 hybrid orbital on each carbon and a pi bond overlap of a *p* orbital on each carbon

1.9 *sp* Hybrid Orbitals and the Structure of Acetylene

- The carbon-carbon triple bond in C_2H_4 forms as the result of one sigma bond overlap between a *sp* hybrid orbital on each carbon and two pi bond overlaps of *p* orbitals on each carbon.

1.10: Hybridization of Nitrogen, Oxygen, Phosphorus and Sulfur

- The atomic orbitals of nitrogen, oxygen, phosphorus and sulfur can hybridize in the same way as those of carbon.

1.11: The Nature of Chemical Bonds: Molecular Orbital Theory

- **Molecular Orbital theory (MO**) is a more advanced bonding model than Valence Bond Theory, in which two atomic orbitals overlap to form *two* molecular orbitals – a bonding MO and an anti-bonding MO.

1.12: Drawing Chemical Structures

- **Kekulé Formulas** or **structural formulas** display the atoms of the molecule in the order they are bonded.
- **Condensed structural formulas** show the order of atoms like a structural formula but are written in a single line to save space.
- **Skeleton formulas** or **Shorthand formulas** or **line-angle formulas** are used to write carbon and hydrogen atoms more efficiently by replacing the letters with lines.
- **Isomers** have the same molecular formula, but different structural formulas

SKILLS TO MASTER

Skill 1.1 Determine the number of protons, neutrons, and electrons in a nuclide.

Skill 1.2 Write the electron configuration and orbital diagram for an atom.

Skill 1.3 Determine the number of valence electrons in an atom.

Skill 1.4 Draw the molecular formula, Lewis Dot Structure, structural formula, condensed structural formula, shorthand formula and wedge-dash structure of simple organic molecules.

Skill 1.5 Use Lewis Dot structures to predict molecular shape, bond angle, hybridization.

Skill 1.6 Calculate formal charge on an atom in a molecule.

Skill 1.7 Determine the number of sigma and pi bonds in organic molecules.

Skill 1.8 Determine relative bond energy and bond length based on atoms involved in the bond and bond type.

Skill 1.9 Describe and draw the orbital overlap and types of bonding in simple organic molecules like methane, ethane, ethylene and acetylene.

Skill 1.10 Describe the bonding in organic molecules using both the Valence Bond Theory and Molecular Orbital Theory.

MEMORIZATION TASKS (MT)

MT 1.1 Memorize the number of valence electrons in the atoms - C, H, N, O, and the halides.

MT 1.2 Memorize the number of bonds and lone pairs to atoms of carbon, hydrogen, oxygen and nitrogen that result in formal charges of zero.

CONTRIBUTORS

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CHAPTER OVERVIEW

2: POLAR COVALENT BONDS; ACIDS AND BASES

This chapter provides a review of the more advanced material covered in a standard introductory chemistry course through a discussion of the following topics:

- the drawing and interpretation of organic chemical structures.
- the use of ball-and-stick molecular models.
- the concept of formal charge.
- the use of electronegativities to determine bond polarity, and the application of this knowledge to determining whether a given molecule possesses a dipole moment.
- the Brønsted-Lowry and Lewis definitions of acids and bases, acidity constants and acid-base reactions.

2.0: Prelude
2.1: Polar Covalent Bonds- Electronegativity
2.2: Polar Covalent Bonds- Dipole Moments
2.3: Formal Charges
2.4: Resonance
2.5: Rules for Resonance Forms
2.6: Drawing Resonance Forms
2.7: Acids and Bases- The Brønsted-Lowry Definition
2.8: Acid and Base Strength
2.9: Predicting Acid-Base Reactions from pKa Values
2.10: Organic Acids and Organic Bases
2.11: Acids and Bases- The Lewis Definition
2.12: Noncovalent Interactions Between Molecules
2.13: Molecular Models
2.S: Polar Covalent Bonds; Acids and Bases (Summary)

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2.0: Prelude

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2.1: POLAR COVALENT BONDS- ELECTRONEGATIVITY

OBJECTIVES

After completing this section, you should be able to

1. describe how differences in electronegativity give rise to bond polarity.
2. arrange a given series of the elements most often encountered in organic chemistry (C, H, O, S, P and the halogens) in order of increasing or decreasing electronegativity, without referring to a table of electronegativities.
3. predict the positive and negative ends of a given bond formed between any two of the elements listed in Objective 2, above, without the use of a table of electronegativities or a periodic table.
4. predict the positive and negative ends of a given bond formed between any two elements not listed in Objective 2, above, using a periodic table.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- electronegativity inductive effect
- polar colvalent bond

STUDY NOTES

Students often wonder why it is important to be able to tell whether a given bond is polar or not, and why they need to know which atoms carry a partial positive charge and which a partial negative charge. Consider the chloromethane (CH_3Cl) molecule. The carbon atom is shown as carrying a partial positive charge. Now, recall that opposite charges attract. Thus, it seems reasonable that the slightly positive carbon atom in chloromethane should be susceptible to attack by a negatively charged species, such as the hydroxide ion, OH^-. This theory is borne out in practice: hydroxide ions react with chloromethane by attacking the slightly positive carbon atom in the latter. It is often possible to rationalize chemical reactions in this manner, and you will find the knowledge of bond polarity indispensible when you start to write reaction mechanisms. **Note:** Because of the small difference in electronegativity between carbon and hydrogen, the $C-H$ bond is normally assumed to be nonpolar.

ELECTRONEGATIVITY

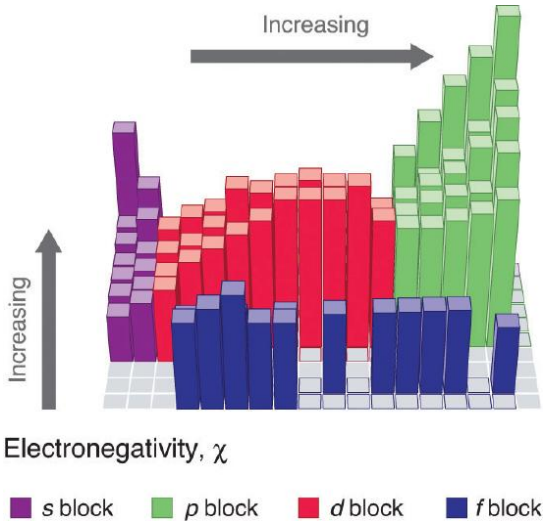
The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called electronegativity (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

NOTE

Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The **greater** the value, the **greater** the attractiveness for electrons.



Unfortunately there is no direct way of measuring electronegativity. Dipole-moment measurements tell us about the electrical behavior of *all* electron pairs in the molecule, not just the bonding pair in which we are interested. Also, the polarity of a bond depends on whether the bond is a single, double, or triple bond and on what the other atoms and electron pairs in a molecule are. Therefore the dipole moment cannot tell us quantitatively the difference between the electronegativities of two bonded atoms. Various attempts have been made over the years to derive a scale of electronegativities for the elements, none of which is entirely satisfactory. Nevertheless most of these attempts agree in large measure in telling us which elements are more electronegative than others. The best-known of these scales was devised by the Nobel prize-winning California chemist Linus Pauling (1901 to 1994) and is shown in the periodic table found below. In this scale a value of 4.0 is arbitrarily given to the most electronegative element, fluorine, and the other electronegativities are scaled relative to this value.

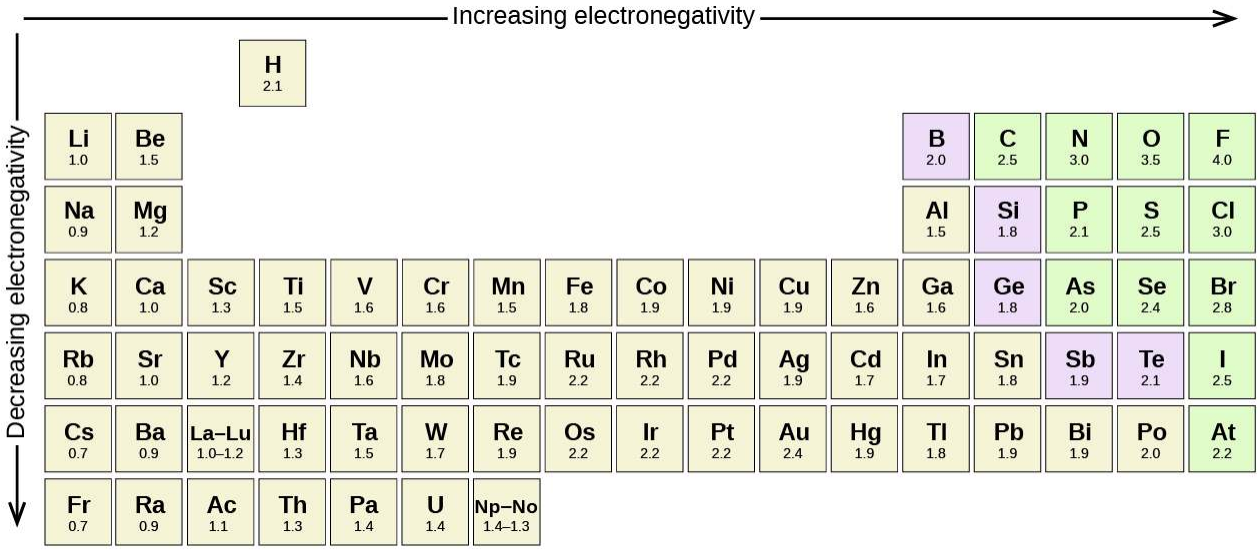


Figure \PageIndex1: Pauling scale electronegativities of elements

WHAT IF TWO ATOMS OF EQUAL ELECTRONEGATIVITY BOND TOGETHER?

Consider a bond between two atoms, A and B. If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found on average half way between the two atoms:

To get a bond like this, A and B would usually have to be the same atom. You will find this sort of bond in, for example, H2 or Cl2 molecules. Note: It's important to realize that this is an average picture. The electrons are actually in a molecular orbital, and are moving

around all the time within that orbital. This sort of bond could be thought of as being a "pure" covalent bond - where the electrons are shared evenly between the two atoms.

WHAT IF B IS SLIGHTLY MORE ELECTRONEGATIVE THAN A?

B will attract the electron pair rather more than A does.



That means that the B end of the bond has more than its fair share of electron density and so becomes slightly negative. At the same time, the A end (rather short of electrons) becomes slightly positive. In the diagram, "δ" (read as "delta") means "slightly" - so $\delta+$ means "slightly positive".

A polar bond is a covalent bond in which there is a separation of charge between one end and the other - in other words in which one end is slightly positive and the other slightly negative. Examples include most covalent bonds. The hydrogen-chlorine bond in HCl or the hydrogen-oxygen bonds in water are typical.



If B is a lot more electronegative than A, then the electron pair is dragged right over to B's end of the bond. To all intents and purposes, A has lost control of its electron, and B has complete control over both electrons. Ions have been formed. The bond is then an ionic bond rather than a covalent bond.

A "SPECTRUM" OF BONDS

The implication of all this is that there is no clear-cut division between covalent and ionic bonds. In a pure covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end. How far does this dragging have to go before the bond counts as ionic? There is no real answer to that. Sodium chloride is typiclly considered an ionic solid, but even here the sodium has not completely lost control of its electron. Because of the properties of sodium chloride, however, we tend to count it as if it were purely ionic. Lithium iodide, on the other hand, would be described as being "ionic with some covalent character". In this case, the pair of electrons has not moved entirely over to the iodine end of the bond. Lithium iodide, for example, dissolves in organic solvents like ethanol - not something which ionic substances normally do.

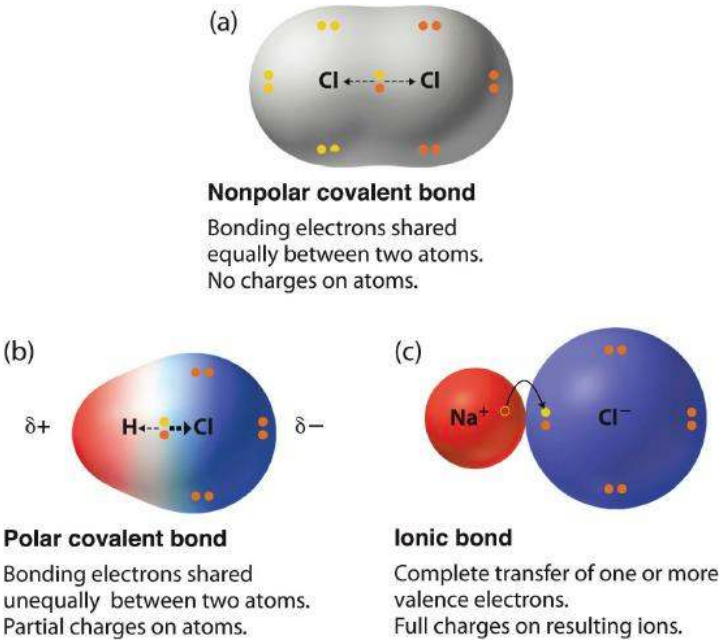


Figure \PageIndex3: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

EXAMPLE 1: POLAR BONDS VS. POLAR MOLECULES

In a simple diatomic molecule like HBr, if the bond is polar, then the whole molecule is polar. What about more complicated molecules?

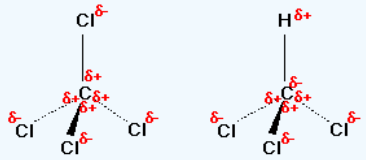


Figure: (left) CCl_4 (right) $CHCl_3$

Consider CCl_4, (left panel in figure above), which as a molecule is not polar - in the sense that it doesn't have an end (or a side) which is slightly negative and one which is slightly positive. The whole of the outside of the molecule is somewhat negative, but there is no overall separation of charge from top to bottom, or from left to right.

In contrast, $CHCl_3$ is a polar molecule (right panel in figure above). The hydrogen at the top of the molecule is less electronegative than carbon and so is slightly positive. This means that the molecule now has a slightly positive "top" and a slightly negative "bottom", and so is overall a polar molecule.

A polar molecule will need to be "lop-sided" in some way.

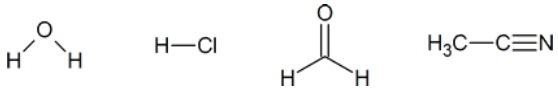
SUMMARY

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

- No electronegativity difference between two atoms leads to a non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond.
- A large electronegativity difference leads to an ionic bond.

EXERCISES

1. Identify the positive and negative ends of each of the bonds shown below.



2. Which of the following elements is the more electronegative?

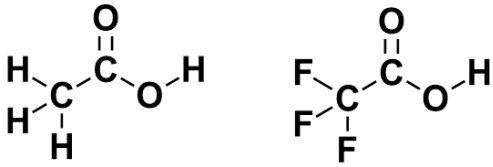
a) Br or C

b) C or H

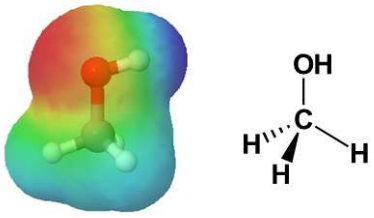
c) Cl or I

d) C or Li

3. Which of the following molecules would you expect to have the more polarized O-H bond?

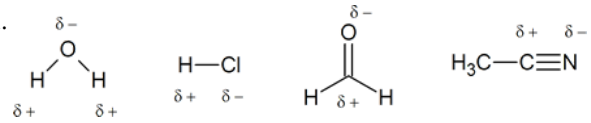


4. Predict the direction of polarizing C-O bond in methanol by looking at its electrostatic potential map.



Methanol

SOLUTIONS

1. 

2.

a) Br

b) C

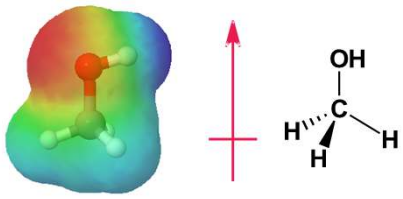
c) Cl

d) C

3.

The molecule on the right would have the more polorized O-H bond. The presence of the highly electronegative fluorines would draw electrons away by the inductive effect.

4.



Methanol

QUESTIONS

Q2.1.1

Rank the following from least polar to most polar using knowledge of electronegativity

CH_3CH_2-Li CH_3CH_2-K CH_3CH_2-F CH_3CH_2-OH

SOLUTIONS

S2.1.1

(least polar) OH < F < Li < K (most polar)

CONTRIBUTORS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.
- Jim Clark (Chemguide.co.uk)

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2.2: POLAR COVALENT BONDS- DIPOLE MOMENTS

Objectives

After completing this section, you should be able to

1. explain how dipole moments depend on both molecular shape and bond polarity.
2. predict whether a molecule will possess a dipole moment, given only its molecular formula or Kekulé structure.
3. use the presence or absence of a dipole moment as an aid to deducing the structure of a given compound.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- dipole moment

STUDY NOTES

You must be able to combine your knowledge of molecular shapes and bond polarities to determine whether or not a given compound will have a dipole moment. Conversely, the presence or absence of a dipole moment may also give an important clue to a compound's structure. BCl_3, for example, has no dipole moment, while NH_3 does. This suggests that in BCl_3 the chlorines around boron are in a trigonal planar arrangement, while the hydrogens around nitrogen in NH_3 would have a less symmetrical arrangement (e.g., trigonal pyramidal, T-shaped). Remember that the C—H bond can usually be assumed to be nonpolar.

MOLECULAR DIPOLE MOMENTS

You previously learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (part (a) in Figure 2.2.8). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (part (b) in Figure 2.2.8); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

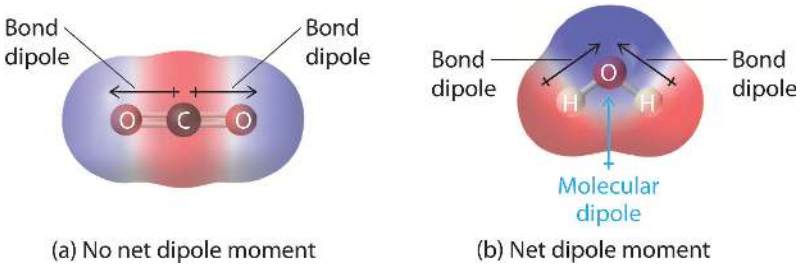


Figure 2.2.8 *How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.*

Other examples of molecules with polar bonds are shown in Figure 2.2.9. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical.

Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment.

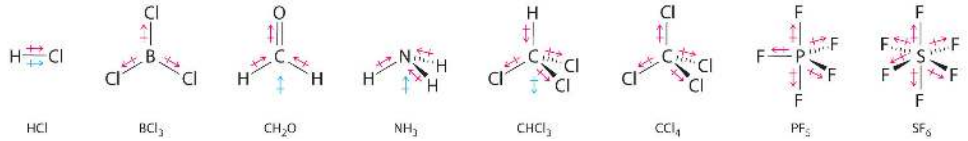


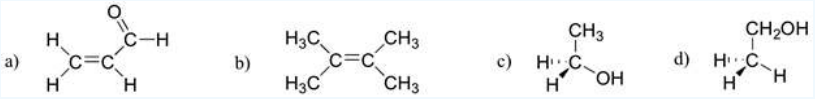
***Figure 2.2.9**: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).*

NOTE

Molecules with asymmetrical charge distributions have a net dipole momentEdit section

EXERCISE \PageIndex1

Which of the molecules below have molecular dipole moments?



Answer

Only molecule (b) does *not* have a molecular dipole, due to its symmetry (bond dipoles are equal and in opposite directions). Add texts here.

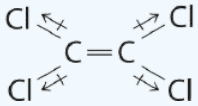
EXERCISE \PageIndex2

Draw out the line structure of the molecule with a molecular formula of C_2Cl_4. Indicate all of the individual bond polarities and predict if the molecule is polar or nonpolar.

Answer

Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and does not have a net dipole

Cl2C=CCl2" id="MathJax-Element-47-Frame" role="presentation" style="position:relative;" tabindex="0">moment.



EXERCISE \PageIndex3

The following molecule has no net dipole moment, explain.

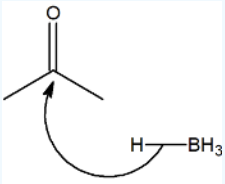


Answer

The hydroxyl groups are oriented opposite of one another and therefore the dipole moments would “cancel” one another out. Therefore having a zero net-dipole.

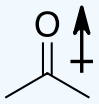
EXERCISE \PageIndex4

Within reactions with carbonyls, such as a hydride reduction reaction, the carbonyl is attacked from the carbon side and not the oxygen side. Using knowledge of electronegativity explain why this happens.



Answer

The oxygen is more electronegative than the carbon and therefore creates a dipole along the bond. This leads to having a partial positive charge on the carbon and the reduction can take place.



EXERCISE \PageIndex1

Which molecule(s) has a net dipole moment?

a. H_2S
b. NHF_2
c. BF_3

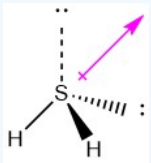
Answer

Strategy:

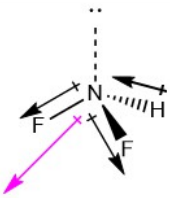
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

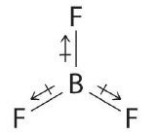
Solution:

The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent. The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.





- The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:

ADDITIONAL EXERCISE

1. Determine whether each of the compounds listed below possesses a dipole moment. For the polar compounds, indicate the direction of the dipole moment.
   a. $O=C=O$
   b. ICl
   c. SO_2
   d. CH_3-O-CH_3
   e. $CH_3C(=O)CH_3$

Answer:

1. a. carbon dioxide is nonpolar
   b. net dipole moment on iodine monochloride
   c. net dipole moment on sulfur dioxide
   d. net dipole moment on dimethyl ether
   e. net dipole moment on 2-propanone

QUESTIONS

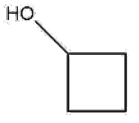
Q2.2.1

The following molecule has no dipole moment in the molecule itself, explain.

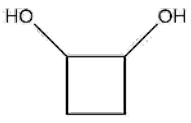


Q2.2.2

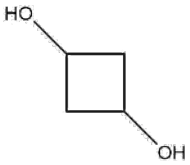
Which of the following molecules has a net dipole?



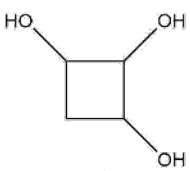
1



3



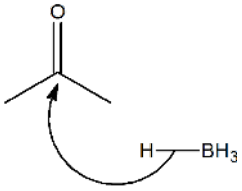
2



4

Q2.2.3

Within reactions with carbonyls, such as a reduction reaction, the carbonyl is attacked from the carbon side and not the oxygen side. Using knowledge of electronegativity explain why this happens.



SOLUTIONS

S2.2.1

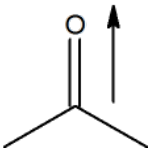
The hydroxyl groups are oriented opposite of one another and therefore the dipole moments would “cancel” one another out. Therefore having a zero net-dipole.

S2.2.2

1, 3, and 4 have a net dipoles.

S2.2.3

The oxygen is more electronegative than the carbon and therefore creates a dipole along the bond. This leads to having a partial positive charge on the carbon and the reduction can take place.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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2.3: FORMAL CHARGES

OBJECTIVES

After completing this section, you should be able to

1. determine which atoms, if any, of a given simple compound (e.g., HNO_3, $CH_2{=}N{=}N$, $CH_3{-}N{=}C$) carry formal charges, and apply the principles used to more complex examples. (The Lewis structure, Kekulé structure or molecular formula would normally be provided.)
2. draw the Lewis structure, the Kekulé structure, or both, of a compound of known molecular formula in which certain atoms possess a formal charge.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- formal charge
- valence electrons
- bonding and non-bonding electrons
- carbocations

STUDY NOTES

Too much emphasis can easily be placed on the concept of formal charge, and the mathematical approach is hard to justify. In this course, you will certainly need to be able to recognize whether a given species carries a charge (i.e., is an ion).

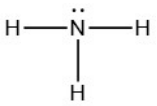
A **formal charge** compares the number of electrons around a "neutral atom" (an atom not in a molecule) versus the number of electrons around an atom in a molecule. Formal charge is assigned to an atom in a molecule by assuming that electrons in all chemical bonds are shared equally between atoms, regardless of relative electronegativity. To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Non-bonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the two bonded atoms, so one electron from each bond goes to each atom.

The formal charge of each atom in a molecule can be calculated using the following equation:

Formal Charge = (# of valence electrons in free atom) - (# of lone-pair electrons) - (1/2 # of bond pair electrons) *Eqn. 2.3.1*

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From the Lewis structure, the nitrogen atom in ammonia has one lone pair and three bonds with hydrogen atoms. Substituting into Equation 2.3.1, we obtain

Formal Charge of N = (5 valence e-) - (2 lone pair e-) - (1/2 x 6 bond pair e-) = 0

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule has no non-bonding electrons and one bond. Using Equation 2.3.1 to calculate the formal charge on hydrogen, we obtain

Formal Charge of H = (1 valence e-) - (0 lone pair e-) - (1/2 x 2 bond pair e-) = 0

The sum of the formal charges of each atom must be equal to the overall charge of the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall neutral charge of the NH_3 molecule.

Typically, the structure with the most formal charges of zero on atoms is the more stable Lewis structure. In cases where there MUST be positive or negative formal charges on various atoms, the most stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges for polyatomic ions.

EXAMPLE 2.3.1

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

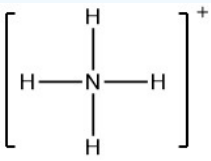
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and non-bonding electrons associated with each atom and then use Equation 2.3.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



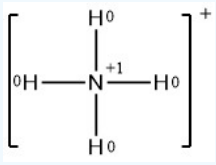
The nitrogen atom in ammonium has zero non-bonding electrons and 4 bonds. Using Equation 2.3.1, the formal charge on the nitrogen atom is therefore

$$\textit{Formal Charge of N} = \textit{(5 valence e-) - (0 lone pair e-) - (1/2 x 8 bond pair e-)} = +1$$

Each hydrogen atom in has one bond and zero non-bonding electrons. The formal charge on each hydrogen atom is therefore

$$\textit{Formal Charge of H} = \textit{(1 valence e-) - (0 lone pair e-) - (1/2 x 2 bond pair e-)} = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus

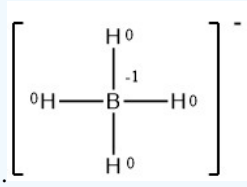


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1, which is the same a s the overall charge of the ammonium polyatomic ion.

EXERCISE \PageIndex1

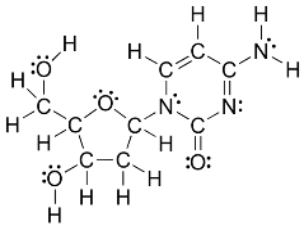
Write the formal charges on all atoms in BH_4^-.

Answer



COMMON BONDING PATTERNS IN ORGANIC STRUCTURES

The calculation method reviewed above for determining formal charges on atoms is an essential starting point for a novice organic chemist, and works well when dealing with small structures. But this method becomes unreasonably time-consuming when dealing with larger structures. It would be exceptionally tedious to determine the formal charges on each atom in 2'-deoxycytidine (one of the four nucleoside building blocks that make up DNA) using equation 2.3.1.

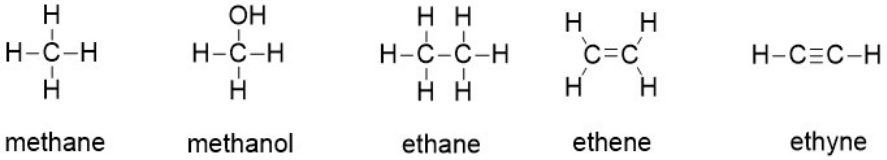


2'-deoxycytidine

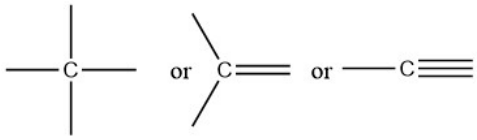
And yet, organic chemists, and especially organic chemists dealing with biological molecules, are expected to draw the structure of large molecules such as this on a regular basis. Clearly, you need to develop the ability to quickly and efficiently draw large structures and determine formal charges. Fortunately, this only requires some practice with recognizing common bonding patterns.

CARBON

Carbon, the most important element for organic chemists. In the structures of methane, methanol, ethane, ethene, and ethyne, there are four bonds to the carbon atom. And each carbon atom has a formal charge of zero. In other words, carbon is ***tetravalent***, meaning that it commonly forms four bonds.



methane methanol ethane ethene ethyne



Carbon usually has 4 bonds

Carbon is tetravalent in most organic molecules, but there are exceptions. Later in this chapter and throughout this book are examples of organic ions called 'carbocations' and carbanions', in which a carbon atom has a positive or negative formal charge, respectively. ***Carbocations*** occur when a carbon has only three bonds and no lone pairs of electrons. Carbocations have only 6 valence electrons and a formal charge of +1. ***Carbanions*** occur when the carbon atom has three bonds plus one lone pair of electrons. Carbanions have 8 valence electrons and a formal charge of -1.



3 bonds, no lone pair: carbocation

3 bonds + lone pair: carbanion

3 bonds + unpaired electron: carbon radical

Two other possibilities are carbpon radicals and carbenes, both of which have a formal charge of zero. A ***carbon radical*** has three bonds and a single, unpaired electron. Carbon radicals have 7 valence electrons and a formal charge of zero. ***Carbenes*** are a highly reactive species, in which a carbon atom has two bonds and one lone pair of electrons, giving it a formal charge of zero. You may encounter carbenes in more advanced chemistry courses, but they will not be discussed any further in this book.

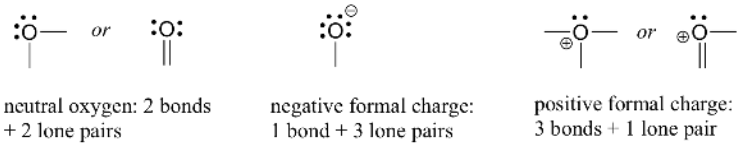
You should certainly use the methods you have learned to check that these formal charges are correct for the examples given above. More importantly, you will need, before you progress much further in your study of organic chemistry, to simply recognize these patterns (and the patterns described below for other atoms) and be able to identify carbons that bear positive and negative formal charges by a quick inspection.

HYDROGEN

The common bonding pattern for hydrogen is easy: hydrogen atoms in organic molecules typically have only one bond, no unpaired electrons and a formal charge of zero. The exceptions to this rule are the proton, H^+, the hydride ion, H^-, and the hydrogen radical, $H\cdot$. The ***proton*** is a hydrogen with no bonds and no lone pairs and a formal charge of +1. The ***hydride ion*** is a is a hydrogen with no bonds, a pair of electrons, and a formal charge of -1. The ***hydrogen radical*** is a hydrogen atom with no bonds, a single unpaired electron and a formal charge of 0. Because this book concentrates on organic chemistry as applied to living things, however, we will not be seeing 'naked' protons and hydrides as such, because they are too reactive to be present in that form in aqueous solution. Nonetheless, the *idea* of a proton will be very important when we discuss acid-base chemistry, and the *idea* of a hydride ion will become very important much later in the book when we discuss organic oxidation and reduction reactions. As a rule, though, all hydrogen atoms in organic molecules have one bond, and no formal charge.

OXYGEN

The common arrangement of oxygen that has a formal charge of zero is when the oxygen atom has 2 bonds and 2 lone pairs. Other arrangements are oxygen with 1 bond and 3 lone pairs, that has a -1 formal charge, and oxygen with 3 bonds and 1 lone pair that has a formal charge of +1. All three patterns of oxygen fulfill the octet rule.



neutral oxygen: 2 bonds + 2 lone pairs

negative formal charge: 1 bond + 3 lone pairs

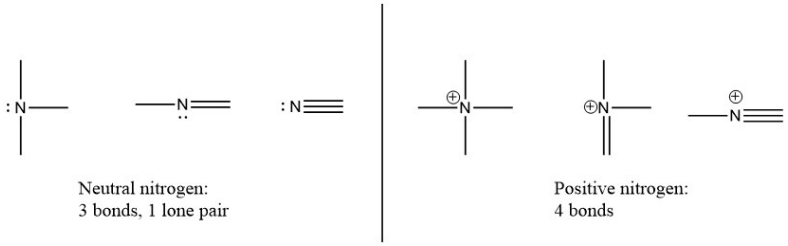
positive formal charge: 3 bonds + 1 lone pair

If it has two bonds and two lone pairs, as in water, it will have a formal charge of zero. If it has one bond and three lone pairs, as in hydroxide ion, it will have a formal charge of-1. If it has three bonds and one lone pair, as in hydronium ion, it will have a formal charge of +1.

When we get to our discussion of free radical chemistry in chapter 17, we will see other possibilities, such as where an oxygen atom has one bond, one lone pair, and one unpaired (free radical) electron, giving it a formal charge of zero. For now, however, concentrate on the three main non-radical examples, as these will account for virtually everything we see until chapter 17.

NITROGEN

Nitrogen has two major bonding patterns, both of which fulfill the octet rule:



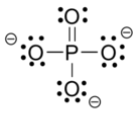
Neutral nitrogen: 3 bonds, 1 lone pair

Positive nitrogen: 4 bonds

If a nitrogen has three bonds and a lone pair, it has a formal charge of zero. If it has four bonds (and no lone pair), it has a formal charge of +1. In a fairly uncommon bonding pattern, negatively charged nitrogen has two bonds and two lone pairs.

PHOSPHORUS AND SULFUR

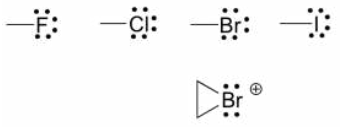
Two third row elements are commonly found in biological organic molecules: phosphorus and sulfur. Although both of these elements have other bonding patterns that are relevant in laboratory chemistry, in a biological context sulfur almost always follows the same bonding/formal charge pattern as oxygen, while phosphorus is present in the form of phosphate ion (PO_4^{3-}), where it has five bonds (almost always to oxygen), no lone pairs, and a formal charge of zero. Remember that elements in the third row of the periodic table have *d* orbitals in their valence shell as well as *s* and *p* orbitals, and thus are not bound by the octet rule.



phosphate

HALOGENS

The halogens (fluorine, chlorine, bromine, and iodine) are very important in laboratory and medicinal organic chemistry, but less common in naturally occurring organic molecules. Halogens in organic compounds usually are seen with one bond, three lone pairs, and a formal charge of zero. Sometimes, especially in the case of bromine, we will encounter reactive species in which the halogen has two bonds (usually in a three-membered ring), two lone pairs, and a formal charge of +1.



These rules, if learned and internalized so that you don't even need to think about them, will allow you to draw large organic structures, complete with formal charges, quite quickly.

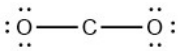
Once you have gotten the hang of drawing Lewis structures, it is not always necessary to draw lone pairs on heteroatoms, as you can assume that the proper number of electrons are present around each atom to match the indicated formal charge (or lack thereof). Occasionally, though, lone pairs are drawn if doing so helps to make an explanation more clear.

USING FORMAL CHARGES TO DISTINGUISH BETWEEN LEWIS STRUCTURES

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for CO_2. Both structures conform to the rules for Lewis electron structures.

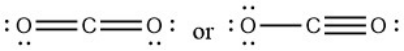
- CO_2

1. C is less electronegative than O, so it is the central atom.
2. C has 4 valence electrons and each O has 6 valence electrons, for a total of 16 valence electrons.
3. Placing one electron pair between the C and each O gives O–C–O, with 12 electrons left over.
4. Dividing the remaining electrons between the O atoms gives three lone pairs on each atom:



This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

5. No electrons are left for the central atom.
6. To give the carbon atom an octet of electrons, we can convert two of the lone pairs on the oxygen atoms to bonding electron pairs. There are, however, two ways to do this. We can either take one electron pair from each oxygen to form a symmetrical structure or take both electron pairs from a single oxygen atom to give an asymmetrical structure:



Both Lewis electron structures give all three atoms an octet. How do we decide between these two possibilities? The formal charges for the two Lewis electron structures of CO_2 are as follows:



Both Lewis structures have a net formal charge of zero, but the structure on the right has a +1 charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.

NOTE

The Lewis structure with the set of formal charges closest to zero is usually the most stable.

EXAMPLE 2.3.2

The thiocyanate ion (SCN^-), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which is the preferred arrangement of electrons.

Given: chemical species

Asked for: Lewis electron structures, formal charges, and preferred arrangement

Strategy:

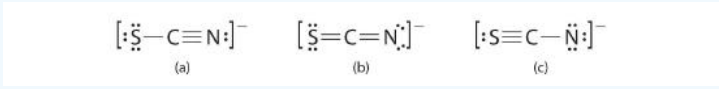
A Use the step-by-step procedure to write two plausible Lewis electron structures for SCN^-.

B Calculate the formal charge on each atom using Equation 2.3.1.

C Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

Solution:

A Possible Lewis structures for the SCN^- ion are as follows:



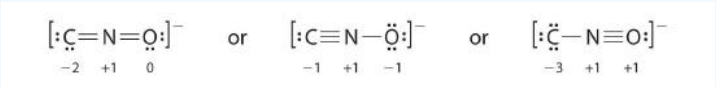
B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore 6 - (6 + 2/2) = -1. In (b), the sulfur atom has a formal charge of 0. In (c), the sulfur atom has a formal charge of +1. Continuing with the nitrogen, we observe that in (a) the nitrogen atom shares three bonding pairs and has one lone pair and has a total of 5 valence electrons. The formal charge on the nitrogen atom is therefore 5 - (2 + 6/2) = 0. In (b), the nitrogen atom has a formal charge of -1. In (c), the nitrogen atom has a formal charge of -2.

C Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, −1 versus +1, −2.

EXERCISE \PageIndex2

Salts containing the fulminate ion (CNO^-) are used in explosive detonators. Draw three Lewis electron structures for CNO^- and use formal charges to predict which is more stable. (Note: N is the central atom.)

Answer



The second structure is predicted to be the most stable.

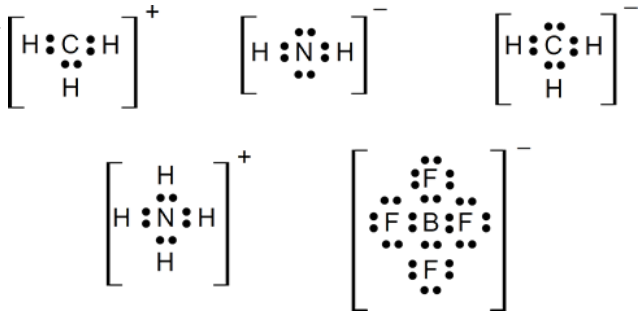
EXERCISES

1. Draw the Lewis structure of each of the molecules listed below.

   CH_3^+, NH_2^-, CH_3^-, NH_4^+, BF_4^-

   In each case, use the method of calculating formal charge described to satisfy yourself that the structures you have drawn do in fact carry the charges shown.

Answer:

1. 

QUESTIONS

Q2.3.1

Give the formal charges for all non-hydrogen atoms in the following molecules: BH_4^-, H_2O, CH_3O^-

SOLUTIONS

S2.3.1

BH_4^- (B = −1)

H_2O (O = 0)

CH_3O^- (C = 0, O = −1)

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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2.4: RESONANCE

OBJECTIVE

After completing this section, you should be able to understand the concept of resonance.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- resonance form

RESONANCE STRUCTURES

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

O_3

1. We know that ozone has a V-shaped structure, so one O atom is central:



2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



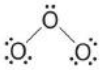
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

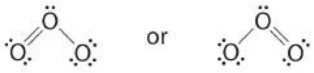


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. If the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Edit section

Equivalent Lewis dot structures, such as those of ozone, are called resonance structures . The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



Before the development of quantum chemistry it was thought that the double-headed arrow indicates that the actual electronic structure is an *average* of those shown, or that the molecule oscillates between the two structures. Today we know that the electrons involved in the double bonds occupy an orbital that extends over all three oxygen molecules, combining *p* orbitals on all three.

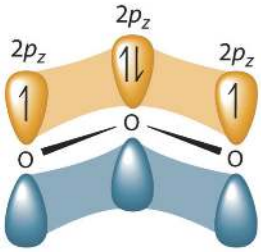


Figure 5.3.4: *The resonance structure of ozone involves a molecular orbital extending all three oxygen atoms.In ozone, a molecular orbital extending over all three oxygen atoms is formed from three atom centered p_z orbitals. Similar molecular orbitals are found in every resonance structure.*Edit section

We will discuss the formation of these molecular orbitals in the next chapter but it is important to understand that resonance structures are based on molecular orbitals not averages of different bonds between atoms. We describe the electrons in such molecular orbitals as being delocalized, that is they cannot be assigned to a bond between two atoms.

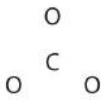
NOTE

When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure involves a molecular orbital which is a linear combination of atomic orbitals from each of the atoms.

CO_3^{2-}

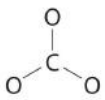
Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the Lewis structures describing CO_3^{2-} has *three* equivalent representations.

1. Because carbon is the least electronegative element, we place it in the central position:

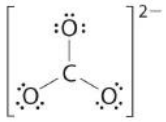


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

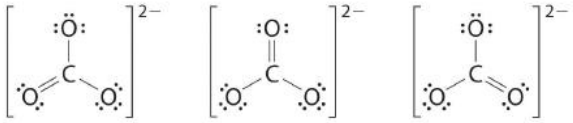


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:

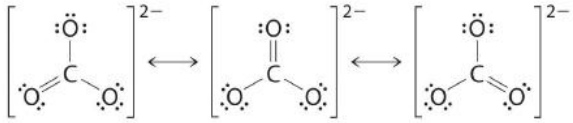


5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



As the case for ozone, the actual structure involves the formation of a molecular orbital from p_z orbitals centered on each atom and sitting above and below the plane of the CO_3^{2-} ion. Edit section

EXAMPLE 2.4.1

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

Asked for: resonance structures

Strategy:

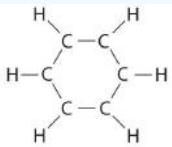
A Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

B Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.

C Draw the resonance structures for benzene.

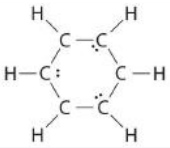
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



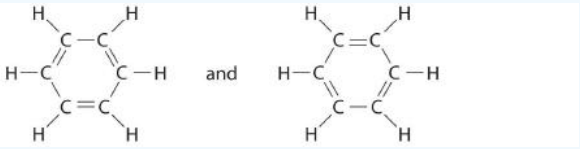
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

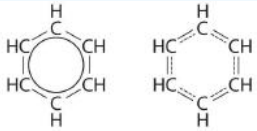


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



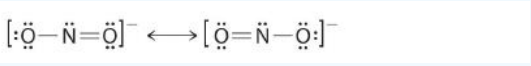
Benzene

This combination of *p* orbitals for benzene can be visualized as a ring with a node in the plane of the carbon atoms.

? EXERCISE 2.4.1

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer

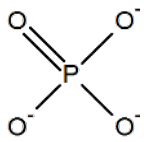


Resonance structures are particularly common in oxoanions of the p-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

QUESTIONS

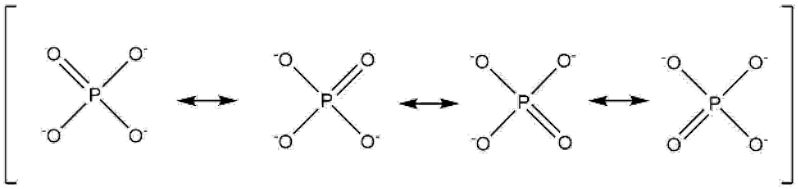
Q2.4.1

Draw the resonance structures for the following molecule:



SOLUTIONS

S2.4.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

2.4: Resonance is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

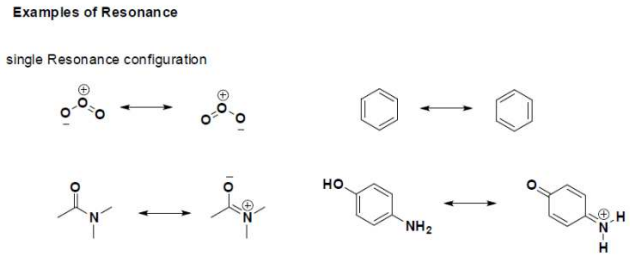
2.5: RULES FOR RESONANCE FORMS

Objective

After completing this section, you should be able to use the concept of resonance to explain structural features of certain species; for example, why all of the carbon-oxygen bonds in the carbonate ion are the same length. This particular compound is discussed in further detail in Section 2.6.

Rules for estimating stability of resonance structures

1. The **greater the number of covalent bonds**, the greater the stability since more atoms will have complete octets
2. The structure with the **least number of formal charges** is more stable
3. The structure with the **least separation of formal charge** is more stable
4. A structure with a **negative charge on the more electronegative atom** will be more stable
5. **Positive charges on the least electronegative atom** (most electropositive) is more stable
6. **Resonance forms that are equivalent have no difference in stability and contribute equally.** (eg. benzene)



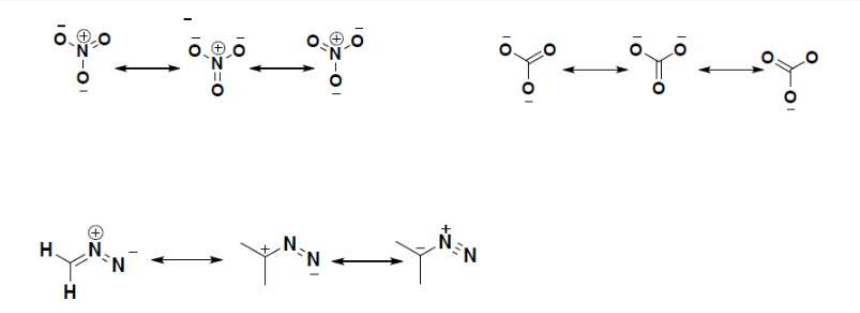
The above resonance structures show that the electrons are delocalized within the molecule and through this process the molecule gains extra stability. Ozone with both of its opposite charges creates a neutral molecule and through resonance it is a stable molecule. The extra electron that created the negative charge on either terminal oxygen can be delocalized by resonance through the terminal oxygens.

Benzene is an extremely stable molecule and it is accounted for its geometry and molecular orbital interaction, but most importantly it's due to its resonance structures. The delocalized electrons in the benzene ring make the molecule very stable and with its characteristics of a nucleophile, it will react with a strong electrophile only and after the first reactivity, the substituted benzene will depend on its resonance to direct the next position for the reaction to add a second substituent.

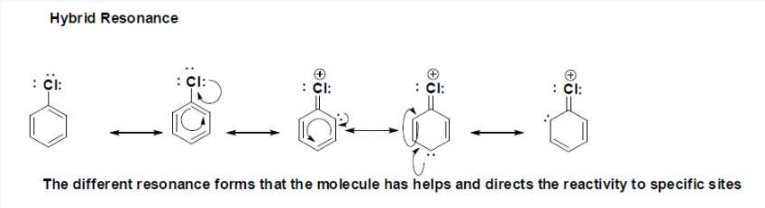
The next molecule, the Amide, is a very stable molecule that is present in most biological systems, mainly in proteins. By studies of NMR spectroscopy and X-Ray crystallography it is confirmed that the stability of the amide is due to resonance which through molecular orbital interaction creates almost a double bond between the nitrogen and the carbon.

✔ EXAMPLE 2.5.1: MULTIPLE RESONANCE OF OTHER MOLECULES

Molecules with more than one resonance form



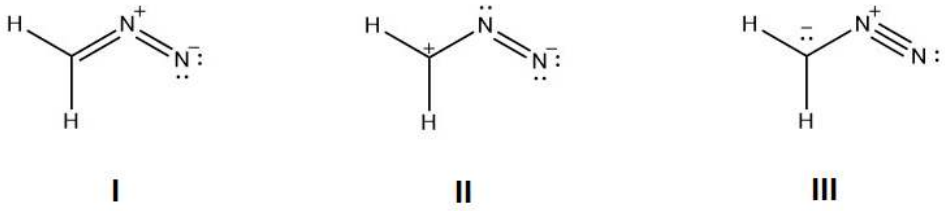
Some structural resonance conformations are the major contributor or the dominant forms that the molecule exists. For example, if we look at the above rules for estimating the stability of a molecule, we see that for the third molecule the first and second forms are the major contributors for the overall stability of the molecule. The nitrogen is more electronegative than carbon so, it can handle the negative charge more than carbon. A carbon with a negative charge is the least favorable conformation for the molecule to exist, so the last resonance form contributes very little for the stability of the Ion.



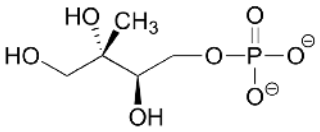
The Hybrid Resonance forms show the different Lewis structures with the electron been delocalized. This is very important for the reactivity of chloro-benzene because in the presence of an electrophile it will react and the formation of another bond will be directed and determine by resonance. The long pair of electrons delocalized in the aromatic substituted ring is where it can potentially form a new bond with an electrophile, as it is shown there are three possible places that reactivity can take place, the first to react will take place at the *para* position with respect to the chloro substituent and then to either *ortho* position.

EXERCISES

1) For the following resonance structures please rank them in order of stability. Indicate which would be the major contributor to the resonance hybrid.

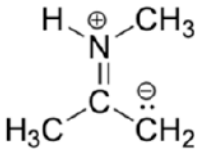


2) Draw four additional resonance contributors for the molecule below. Label each one as major or minor (the structure below is of a major contributor).

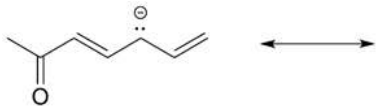


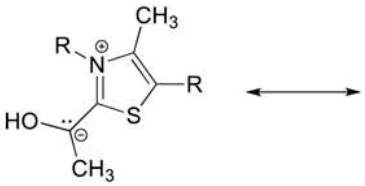
3) Draw three resonance contributors of methyl acetate (an ester with the structure CH_3COOCH_3), and order them according to their relative importance to the bonding picture of the molecule. Explain your reasoning.

4) Below is a minor resonance contributor of a species known as an ‘enamine’, which we will study more in Section 19.8 (formation of enamines) Section 23.12 (reactions of enamines). Draw the major resonance contributor for the enamine, and explain why your contributor is the major one.



5) Draw the major resonance contributor for each of the anions below:

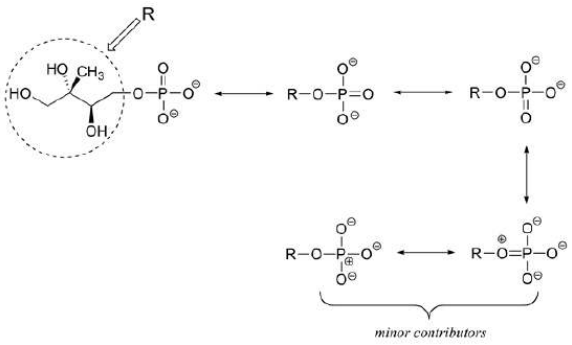




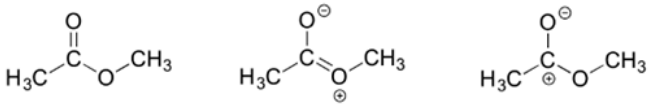
SOLUTIONS

1) Structure I would be the most stable because all the non-hydrogen atoms have a full octet and the negative charge is on the more electronegative nitrogen. Structure III would be the next in stability because all of the non-hydrogen atoms have full octets. Structrure II would be the least stable because it has the violated octet of a carbocation.

2)



3)

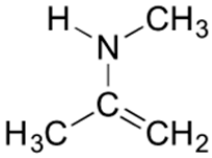


The contributor on the left is the most stable: there are no formal charges.

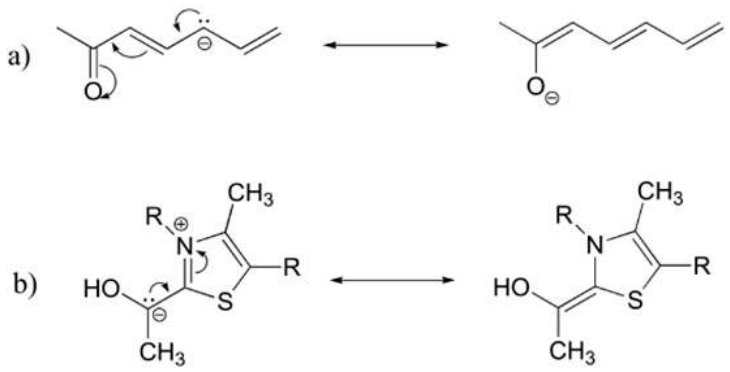
The contributor on the right is least stable: there are formal charges, and a carbon has an incomplete octet.

The contributor in the middle is intermediate stability: there are formal charges, but all atoms have a complete octet.

4) This contributor is major because there are no formal charges.



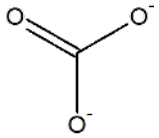
5)



QUESTIONS

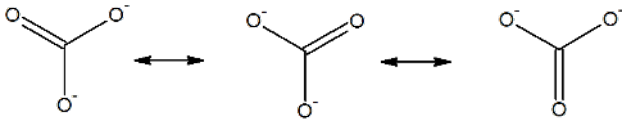
Q2.5.1

Are all the bond lengths the same in the carbonate ion, CO_3^{2-}?



SOLUTIONS

S2.5.1 Yes, the bond lengths in carbonate ion are all the same. Carbonate ion exists as the resonance hybrid of the three resonance forms below.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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2.6: DRAWING RESONANCE FORMS

Objective

After completing this section, you should be able to draw all possible resonance structures for a given species.

Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. It compares and contrasts two or more possible Lewis structures that can represent a particular molecule. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

INTRODUCTION

Electrons have no fixed position in atoms, compounds and molecules (see image below) but have probabilities of being found in certain spaces (orbitals). Resonance forms illustrate areas of higher probabilities (electron densities). This is like holding your hat in either your right hand or your left. The term Resonance is applied when there are two or more possibilities available. Resonance structures do not change the relative positions of the atoms like your arms in the metaphor. The skeleton of the Lewis Structure remains the same, only the electron locations change. A double headed arrow on both ends of the arrow ($\leftrightarrow$) between Lewis structures is used to show their inter-connectivity. It is different from the double harpoons ($\rightleftharpoons$) used for designating equilibria. A double headed arrow on only one end ($\rightarrow$) is used to indicate the movement of two electrons in a single resonance structure.

EXAMPLE 2.6.1: OZONE

Consider ozone (O_3)

Solution

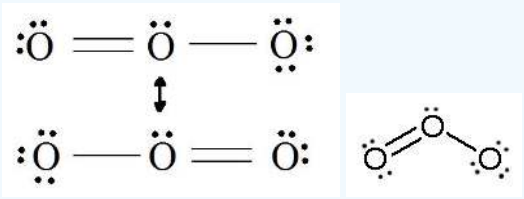


Figure: This is an animation of how one can do a resonance with ozone by moving electrons.

DELOCALIZATION AND RESONANCE STRUCTURES RULES

In resonance structures, the electrons are able to move to help stabilize the molecule. This movement of the electrons is called delocalization.

1. Resonance structures should have the same number of electrons, do not add or subtract any electrons. (You can check the number of electrons by counting them)
2. All resonance structures must follow the rules of writing Lewis Structures.
3. The hybridization of the structure must stay the same.
4. The skeleton of the structure can not be changed (only the electrons move).
5. Resonance structures must also have the same amount of lone pairs.

FORMAL CHARGE

Even though the structures look the same, the formal charge (FC) may not be. Formal charges are charges that are assigned to a specific atom in a molecule. If computed correctly, the overall formal charge of the molecule should be the same as the oxidation charge of the molecule (the charge when you write out the empirical and molecular formula) We want to choose the resonance structure with the least formal charges that add up to zero or the charge of the overall molecule.

The equation for finding Formal Charge is:

Formal Charge = (number of valence electrons in free orbital) - (number of lone-pair electrons) - ($\frac{1}{2}$ number bond pair electrons)

The formal charge has to equal the molecule's overall charge.

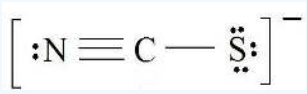
Ex.) CNS^- has an overall charge of -1, so the Lewis structure's formal charge has to equal -1. See Lewis Structure for more information.

EXAMPLE 2.6.2: THIOCYANATE ION

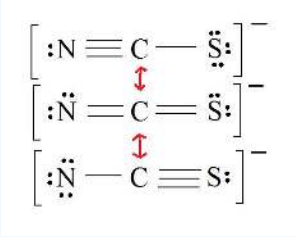
Consider the thiocyanate (CNS^-) ion.

Solution

1. Find the Lewis Structure of the molecule. (Remember the Lewis Structure rules.)



2. Resonance: All elements want an octet, and we can do that in multiple ways by moving the terminal atom's electrons around (bonds too).

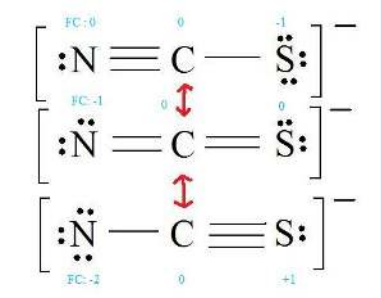


3. Assign Formal Charges

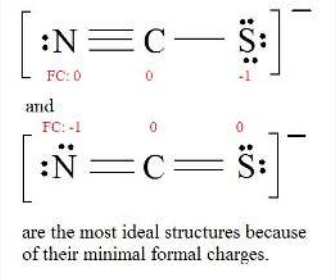
Formal Charge = (number of valence electrons in free orbital) - (number of lone-pair electrons) - ($\frac{1}{2}$ number bond pair electrons)

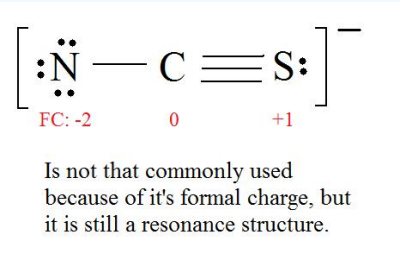
Remember to determine the number of valence electron each atom has before assigning Formal Charges

C = 4 valence e^-, N = 5 valence e^-, S = 6 valence e^-, also add an extra electron for the (-1) charge. The total of valence electrons is 16.



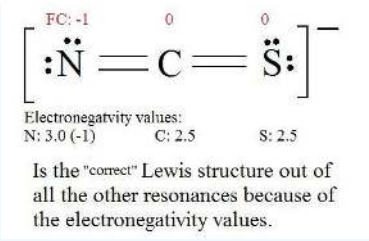
4. Find the most ideal resonance structure. (Note: It is the one with the least formal charges that adds up to zero or to the molecule's overall charge.)





5. Now we have to look at electronegativity for the "Correct" Lewis structure.

The most electronegative atom usually has the negative formal charge, while the least electronegative atom usually has the positive formal charges.



RESONANCE HYBRIDS

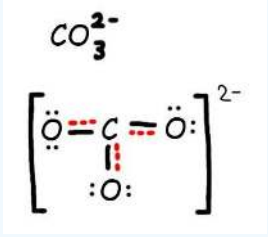
Resonance Structures are a representation of a *Resonance Hybrid*, which is the combination of all resonance structures. Though the Formal Charge closest to zero is the most accepted structure, in reality the correct Lewis structure is actually a combination of all the resonance structures (and hence is not solely describe as one).

1. Draw the Lewis Structure & Resonance for the molecule (using solid lines for bonds).
2. Where there **can** be a double or triple bond, draw a dotted line (-----) for a bond.
3. Draw only the lone pairs found in all resonance structures, do not include the lone pairs that are not on all of the resonance structures.

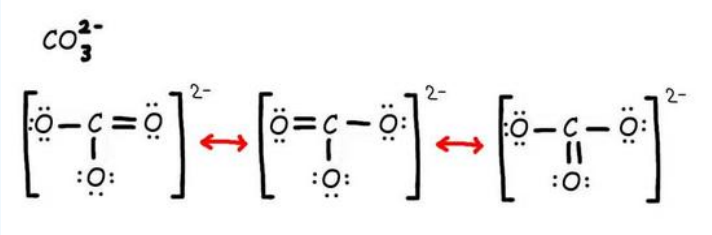
EXAMPLE 2.6.3: CARBONATE ION

Consider the carbonate ion: CO_3^{2-}

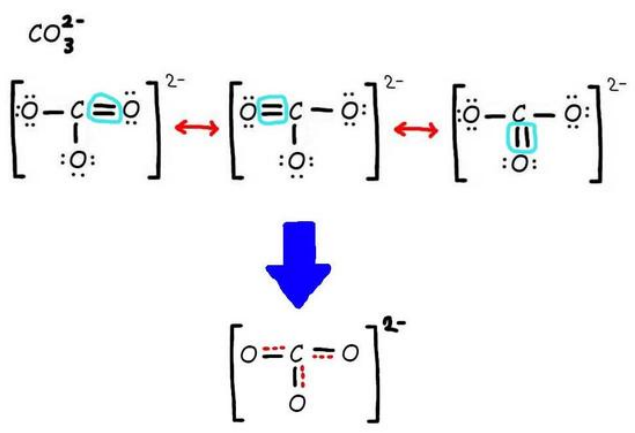
Solution



Step 1: Draw the Lewis Structure & Resonance.

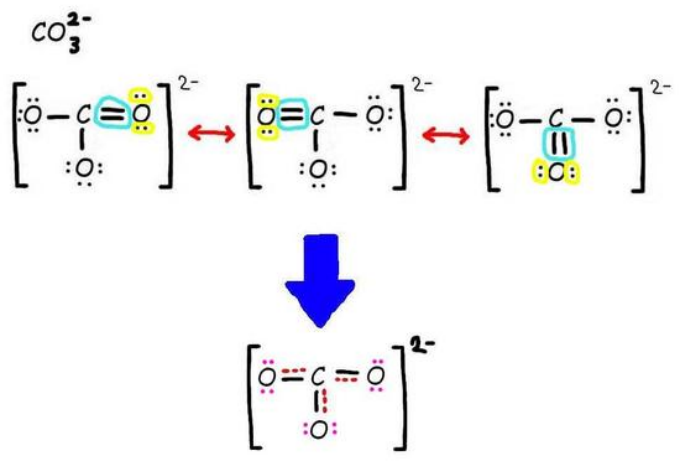


Step 2: Combine the resonance structures by adding (dotted) bonds where other resonance bonds can be formed.



Step 3: Add only the lone pairs found on **ALL** resonance structures.

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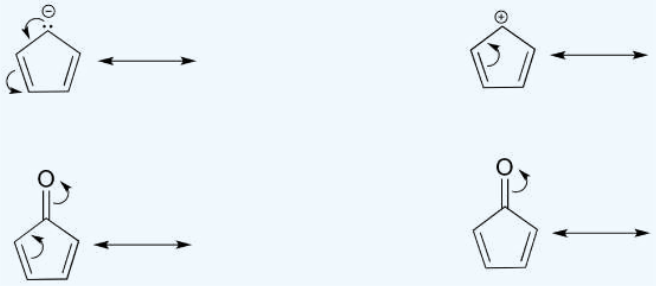
The bottom is the finished resonance hybrid for $\mathbf{CO_3^{2-}}$.

Rules for estimating stability of resonance structures

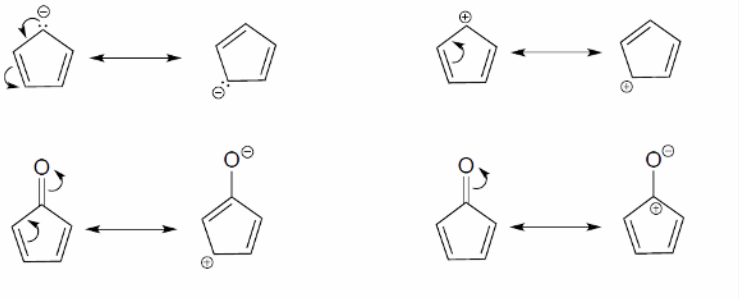
1. The **greater the number of covalent bonds**, the greater the stability since more atoms will have complete octets
2. The structure with the **least number of formal charges** is more stable
3. The structure with the **least separation of formal charge** is more stable
4. A structure with a **negative charge on the more electronegative atom** will be more stable
5. **Positive charges on the least electronegative atom** (most electropositive) is more stable
6. Resonance forms that are equivalent have no difference in stability and contribute equally. (eg. benzene)

EXERCISE 2.6.1

Draw the resonance contributors that correspond to the curved, two-electron movement arrows in the resonance expressions below. Then identify the type of resonance motion in each structure below.

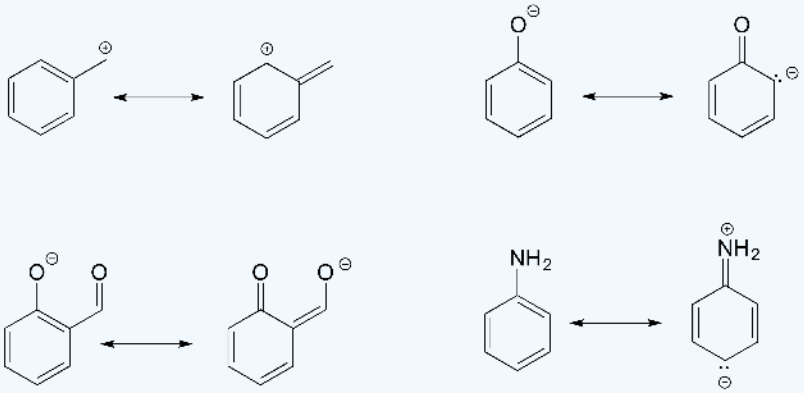


Answer

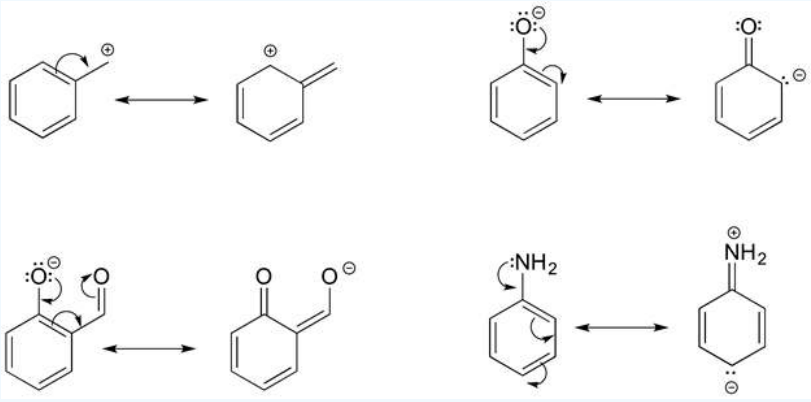


EXERCISE 2.6.2

In each resonance expression, identify the type of resonance motion. Then draw curved arrows on the left-side contributor that shows how we get to the right-side contributor.



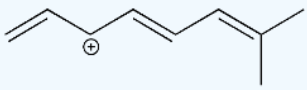
Answer



bond.

EXERCISE 2.6.3

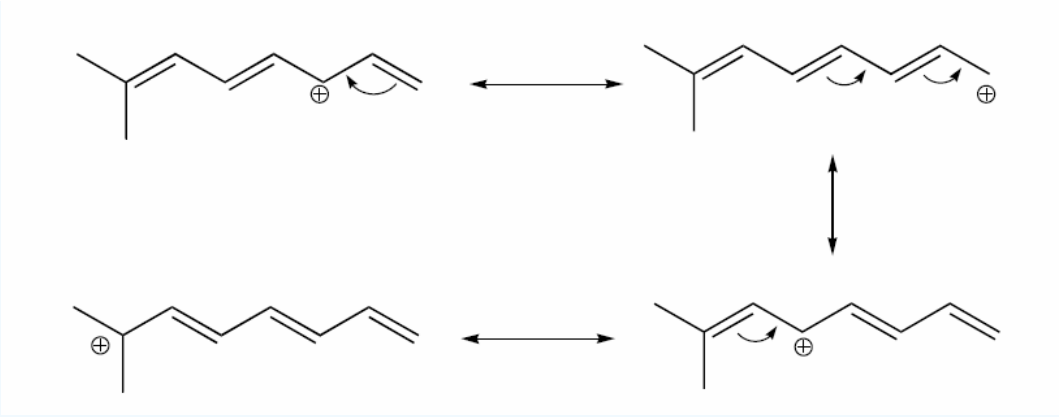
a) Draw three additional resonance contributors for the carbocation below. Include in your figure the appropriate curved arrows showing how one contributor is converted to the next.



b) Fill in the blanks: the conjugated pi system in this carbocation is composed of _____ *2p* orbitals sharing _____ delocalized pi electrons.

Answer

a)



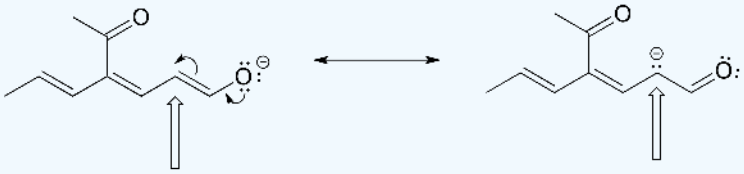
b) The conjugated pi system in this carbocation is composed of seven p orbitals containing six delocalized pi electrons.

EXERCISE 2.6.4

The figure below shows how the negative formal charge on an oxygen (of an enol) can be delocalized to the carbon indicated by an arrow. More resonance contributors can be drawn in which negative charge is delocalized to three other atoms on the molecule.

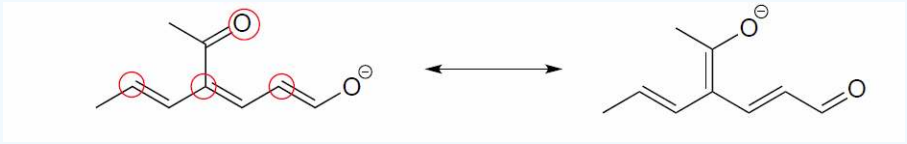
a) Circle these atoms that can also have a resonance structure with a negative charge.

b) Draw the two most important resonance contributors for the enolate ion.



Answer

The two major contributors are those in which the negative formal charge is located on an oxygen rather than on a carbon.



REFERENCES

1. Petrucci, Ralph H., et al. *General Chemistry: Principles and Modern Applications*. New Jersey: Pearson Prentice Hall, 2007. Print.
2. Ahmad, Wan-Yaacob and Zakaria, Mat B. "Drawing Lewis Structures from Lewis Symbols: A Direct Electron Pairing Approach." Journal of Chemical Education: Journal 77.3: n. pag. Web. March 2000. Link to this journal: pkukmweb.ukm.my/~mbz/c_penerbitan/jurnal/jce2k77%283%29/p329.pdf

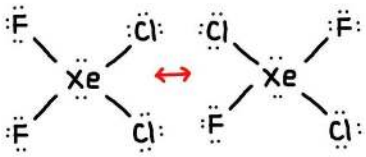
OUTSIDE LINKS

1. http://en.Wikipedia.org/wiki/Resonance_(chemistry)
2. http://www.absoluteastronomy.com/topics/Resonance_(chemistry)#encyclopedia
3. http://www.nku.edu/~russellk/tutorial/reson/resonance.html
4. http://en.Wikipedia.org/wiki/Formal_charge
5. http://commons.wikimedia.org/wiki/Main_Page (for the electronegatvity chart)
6. http://misterguch.brinkster.net/PRA037.pdf (for problem 5)
7. http://commons.wikimedia.org/wiki/File:Phosphite-ion-resonance-structures-2D.png (for the (HPO_3^{2-}) problem 4 answer)
8. http://commons.wikimedia.org/wiki/File:Sulfate-resonance-2D.png (for the Sulfate answer)
9. http://www.mpcfaculty.net/mark_bishop/resonance.htm

10. www.chem.ucla.edu/harding/tutorials/resonance/draw_res_str.html

PROBLEMS

1. True or False, The picture below is a resonance structure?

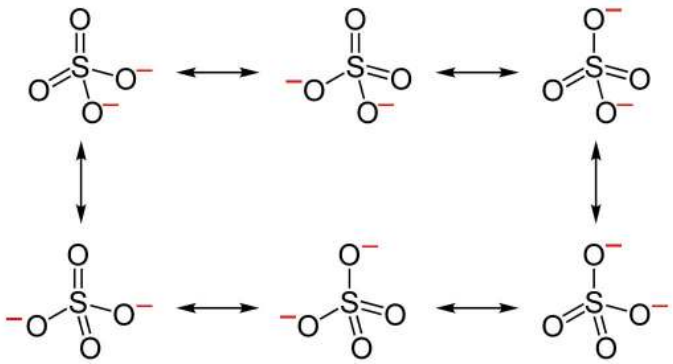


2. Draw the Lewis Dot Structure for $\mathbf{SO_4^{2-}}$ and all possible resonance structures. Which of the following resonance structure is not favored among the Lewis Structures? Explain why. Assign Formal Charges.
3. Draw the Lewis Dot Structure for $\mathbf{CH_3COO^-}$ and all possible resonance structures. Assign Formal Charges. Choose the most favorable Lewis Structure.
4. Draw the Lewis Dot Structure for $\mathbf{HPO_3^{2-}}$ and all possible resonance structures. Assign Formal Charges.
5. Draw the Lewis Dot Structure for $\mathbf{CHO_2^{1-}}$ and all possible resonance structures. Assign Formal Charges.
6. Draw the Resonance Hybrid Structure for $\mathbf{PO_4^{3-}}$.
7. Draw the Resonance Hybrid Structure for $\mathbf{NO_3^-}$.

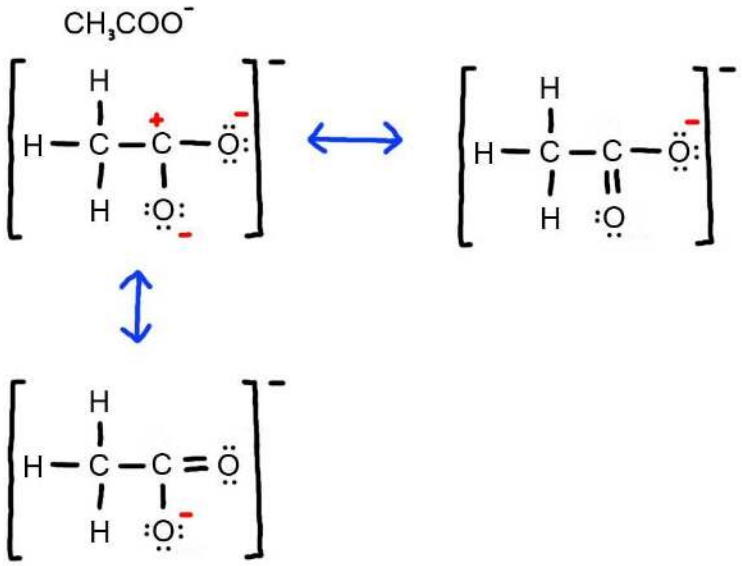
ANSWERS

1. False, because the electrons were not moved around, only the atoms (this violates the Resonance Structure Rules).

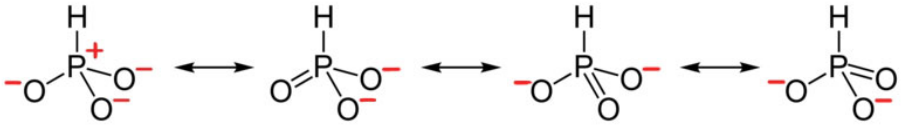
2. Below are the all Lewis dot structure with formal charges (in red) for Sulfate ($\mathbf{SO_4^{2-}}$). There isn't a most favorable resonance of the Sulfate ion because they are all identical in charge and there is no change in Electronegativity between the Oxygen atoms.



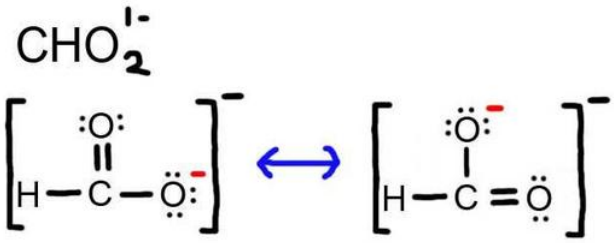
3. Below is the resonance for $\mathbf{CH_3COO^-}$, formal charges are displayed in red. The Lewis Structure with the most formal charges is not desirable, because we want the Lewis Structure with the least formal charge.



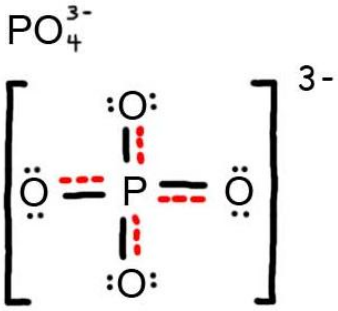
4. The resonance for **HPO_3^{2-}**, and the formal charges (in red).



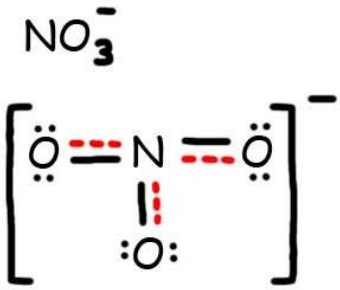
5. The resonance for **CHO_2^{1-}**, and the formal charges (in red).



6. The resonance hybrid for **PO_4^{3-}**, hybrid bonds are in red.



7. The resonance hybrid for **NO_3^-**, hybrid bonds are in red.



CONTRIBUTORS AND ATTRIBUTIONS

- Sharon Wei (UCD), Liza Chu (UCD)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

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2.7: ACIDS AND BASES- THE BRØNSTED-LOWRY DEFINITION

OBJECTIVES

After completing this section, you should be able to

1. state the Brønsted-Lowry definition of an acid and a base.
2. identify the Brønsted-Lowry acid and base in a given acid-base reaction.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- acid (Brønsted-Lowry)
- base (Brønsted-Lowry)
- conjugate acid
- conjugate base

STUDY NOTES

You should be familiar with the Brønsted-Lowry concept of acidity and the differences between strong and weak acids. You may wish to review this topic before proceeding.

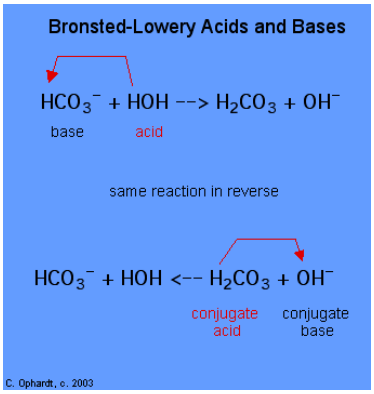
In 1923, chemists Johannes Brønsted and Martin Lowry independently developed definitions of acids and bases based on compounds abilities to either donate or accept protons (H^+ ions). Here, acids are defined as being able to donate protons in the form of hydrogen ions; whereas bases are defined as being able to accept protons. This took the Arrhenius definition one step further as water is no longer required to be present in the solution for acid and base reactions to occur.

BRØNSTED-LOWERY DEFINITION EDIT SECTION

J.N. Brønsted and T.M. Lowry independently developed the theory of proton donors and proton acceptors in acid-base reactions, coincidentally in the same region and during the same year. The Arrhenius theory where acids and bases are defined by whether the molecule contains hydrogen and hydroxide ion is too limiting. The main effect of the Brønsted-Lowry definition is to identify the proton (H^+) transfer occurring in the acid-base reaction. This is best illustrated in the following equation:

Acid	Base	
Donates hydrogen ions	**Accepts hydrogen ions.**	
HCl^+	HOH →	$H_3O^+ + Cl^-$
HOH^+	NH_3 →	$NH_4^+ + OH^-$

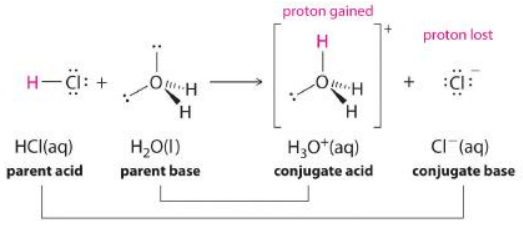
The determination of a substance as a Brønsted-Lowery acid or base can only be done by observing the reaction. In the case of the HOH it is a base in the first case and an acid in the second case.



To determine whether a substance is an acid or a base, count the hydrogens on each substance before and after the reaction. If the number of hydrogens has decreased that substance is the acid (donates hydrogen ions). If the number of hydrogens has increased that substance is the base (accepts hydrogen ions). These definitions are normally applied to the reactants on the left. If the reaction is viewed in reverse a new acid and base can be identified. The substances on the right side of the equation are called conjugate acid and conjugate base compared to those on the left. Also note that the original acid turns in the conjugate base after the reaction is over.

CONJUGATE ACID–BASE PAIRS

We discussed the concept of conjugate acid–base pairs in Chapter 4, using the reaction of ammonia, the base, with water, the acid, as an example. In aqueous solutions, acids and bases can be defined in terms of the transfer of a proton from an acid to a base. Thus for every acidic species in an aqueous solution, there exists a species derived from the acid by the loss of a proton. These two species that differ by only a proton constitute a conjugate acid–base pair. For example, in the reaction of *HCl* with water (Equation 16.1), *HCl* , the parent acid, donates a proton to a water molecule, the parent base, thereby forming Cl^-. Thus *Cl* and Cl^- constitute a conjugate acid–base pair. By convention, we always write a conjugate acid–base pair as the acid followed by its conjugate base. In the reverse reaction, the Cl^- ion in solution acts as a base to accept a proton from H_3O^+, forming H_2O and *HCl*. Thus H_3O^+ and H_2O constitute a second conjugate acid–base pair. In general, any acid–base reaction must contain two conjugate acid–base pairs, which in this case are HCl/Cl^- and H_3O^+/H_2O.

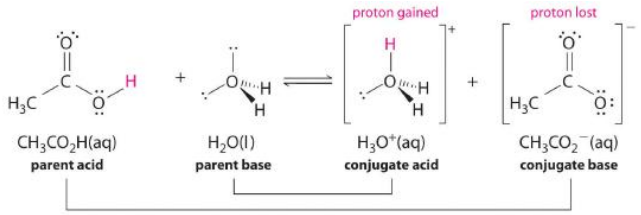


\

NOTE

All acid–base reactions contain two conjugate acid–base pairs.

Similarly, in the reaction of acetic acid with water, acetic acid donates a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base. Once again, we have two conjugate acid–base pairs: the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and the parent base and its conjugate acid (H_3O^+/H_2O).



In the reaction of ammonia with water to give ammonium ions and hydroxide ions (Equation 16.3), ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-. Some common conjugate acid–base pairs are shown in Figure 2.7.1.

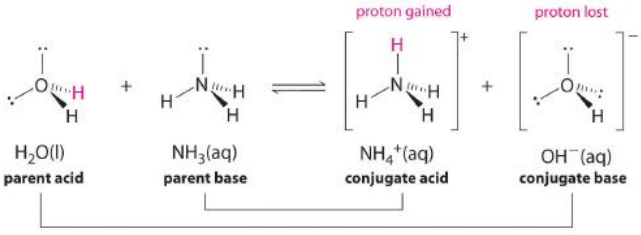
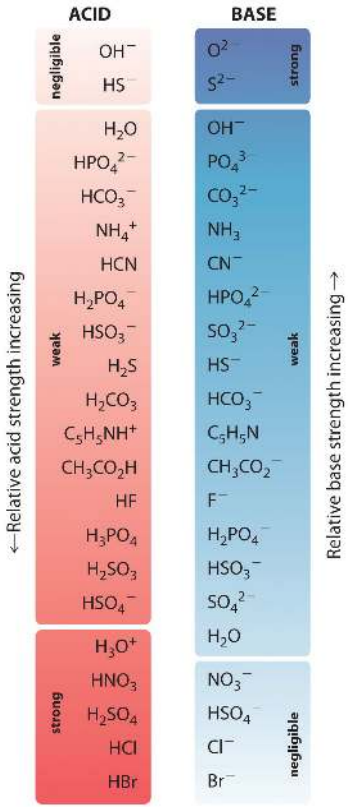


Figure 2.7.1 *The Relative Strengths of Some Common Conjugate Acid–Base Pairs*



The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

EXERCISES

1. Identify the Brønsted-Lowry acids and bases in the reactions given below.

   a. $CH_3CH_2O^- + H_2O \rightleftharpoons CH_3CH_2OH + OH^-$

   b. $CH_3CH_2OH + H_2SO_4 \rightleftharpoons CH_3CH_2OH_2^+ + HSO_4^-$

Answer:

1. a. $CH_3CH_2O^- + H_2O \rightleftharpoons CH_3CH_2OH + OH^-$

   b. $\underset{\text{base}}{CH_3CH_2OH} + \underset{\text{acid}}{H_2SO_4} \rightleftharpoons \underset{\text{acid}}{CH_3CH_2OH_2^+} + \underset{\text{base}}{HSO_4^-}$

   base acid acid base

QUESTIONS

Q2.7.1

Is the following molecule a Brønsted acid or base?

HSO_4^-

SOLUTIONS

S2.7.1

It can be both, consider the following schemes:

$HSO_4^- + H_3O^+ \longrightarrow H_2SO_4 + H_2O$

$HSO_4^- + OH^- \longrightarrow SO_4^{2-} + H_2O$

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Prof. Steven Farmer (Sonoma State University)

2.7: Acids and Bases- The Brønsted-Lowry Definition is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

2.8: ACID AND BASE STRENGTH

Objectives

After completing this section, you should be able to

1. write the expression for the K_a of any given weak acid, HA.
2. convert a given K_a value into a pK_a value, and *vice versa*.
3. arrange a series of acids in order of increasing or decreasing strength, given their K_a or pK_a values.
4. arrange a series of bases in order of increasing or decreasing strength, given the K_a or pK_a values of their conjugate acids.

KEY TERMS

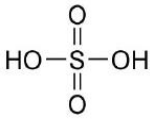
Make certain that you can define, and use in context, the key terms below.

- acidity constant, K_a
- equilibrium constant, K_{eq}

STUDY NOTES

Calculations and expressions involving K_a and pK_a were covered in detail in your first-year general chemistry course. Note that acidity constant is also known as the acid dissociation constant.

You are no doubt aware that some acids are stronger than others. Sulfuric acid is strong enough to be used as a drain cleaner, as it will rapidly dissolve clogs of hair and other organic material.

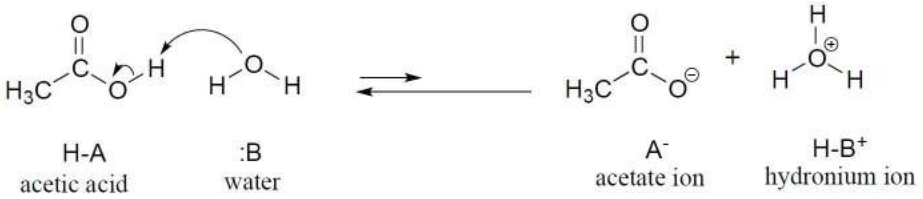


sulfuric acid

Not surprisingly, concentrated sulfuric acid will also cause painful burns if it touches your skin, and permanent damage if it gets in your eyes (there's a good reason for those safety goggles you wear in chemistry lab!). Acetic acid (vinegar), will also burn your skin and eyes, but is not nearly strong enough to make an effective drain cleaner. Water, which we know can act as a proton donor, is obviously not a very strong acid. Even hydroxide ion could *theoretically* act as an acid – it has, after all, a proton to donate – but this is not a reaction that we would normally consider to be relevant in anything but the most extreme conditions.

The relative acidity of different compounds or functional groups – in other words, their relative capacity to donate a proton to a common base under identical conditions – is quantified by a number called the **dissociation constant**, abbreviated $\mathbf{K_a}$. The common base chosen for comparison is water.

We will consider acetic acid as our first example. When a small amount of acetic acid is added to water, a proton-transfer event (acid-base reaction) occurs to some extent.



H-A acetic acid | :B water | A^- acetate ion | $H\text{-}B^+$ hydronium ion

Notice the phrase 'to some extent' – this reaction does *not* run to completion, with all of the acetic acid converted to acetate, its conjugate base. Rather, a *dynamic equilibrium* is reached, with proton transfer going in both directions (thus the two-way arrows) and finite concentrations of all four species in play. The nature of this equilibrium situation, as you recall from General Chemistry, is expressed by an equilibrium constant, K_{eq}.

$$K_{eq} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]} \tag{2.8.1}$$

We added a small amount of acetic acid to a large amount of water: water is the *solvent* for this reaction. Therefore, in the course of the reaction, the concentration of water (approximately 55.6 mol/L) changes very little, and can be treated as constant. The acid dissociation constant, or K_a, for acetic acid is defined as:

$$K_a = K_{eq}[H_2O] = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.75 \times 10^{-5} \tag{2.8.2}$$

In more general terms, the dissociation constant for a given acid is expressed as:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \tag{2.8.3}$$

or

$$K_a = \frac{[A][H_3O^+]}{[HA^+]} \tag{2.8.4}$$

Equation 2.8.3 applies to a neutral acid such as like HCl or acetic acid, while Equation 2.8.4 applies to a cationic acid like ammonium (NH_4^+).

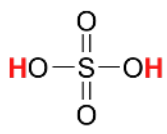
The value of K_a = 1.75 x 10^{-5} for acetic acid is very small - this means that very little dissociation actually takes place, and there is much more acetic acid in solution at equilibrium than there is acetate ion. Acetic acid is a relatively weak acid, at least when compared to sulfuric acid ($K_a = 10^9$) or hydrochloric acid ($K_a = 10^7$), both of which undergo essentially complete dissociation in water.

A number like 1.75 x 10^{-5} is not very easy either to say or to remember. Chemists have therefore come up with a more convenient term to express relative acidity: the **pK_a** value.

$$pK_a = -\log K_a \tag{2.8.5}$$

Doing the math, we find that the pK_a of acetic acid is 4.8. The use of pK_a values allows us to express the acidity of common compounds and functional groups on a numerical scale of about –10 (very strong acid) to 50 (not acidic at all). Table 2.8.1 at the end of the text lists exact or approximate pK_a values for different types of protons that you are likely to encounter in your study of organic and biological chemistry. Looking at Table **2.8.1**, you see that the pK_a of carboxylic acids are in the 4-5 range, the pK_a of sulfuric acid is –10, and the pK_a of water is 15.7. Alkenes and alkanes, which are not acidic at all, have pK_a values above 30. *The lower the pK_a value, the stronger the acid.*

***Table* 2.8.1:** *Representative acid constants*



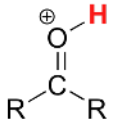
sulfuric acid
pK_a -10, 2.0



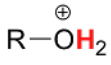
hydrochloric acid
pK_a -7



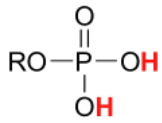
hydronium
pK_a -1.7



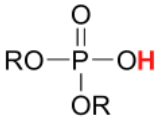
protonated ketone
pK_a ~ -7



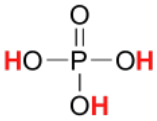
protonated alcohol
pK_a ~ -3



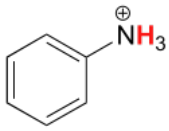
phosphate monoester [1]
pK_a ~ 1, 6.5



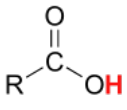
phosphate diester [1]
pK_a ~ 1.5



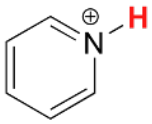
phosphoric acid
pK_a = 2.2, 7.2, 12.3



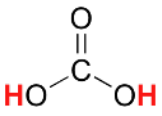
aniline
pK_a = 4.6



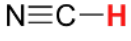
carboxylic acid
pK_a ~ 4-5



pyridinium
pK_a 5.3



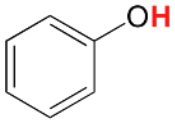
carbonic acid
pK_a 6.4, 10.3



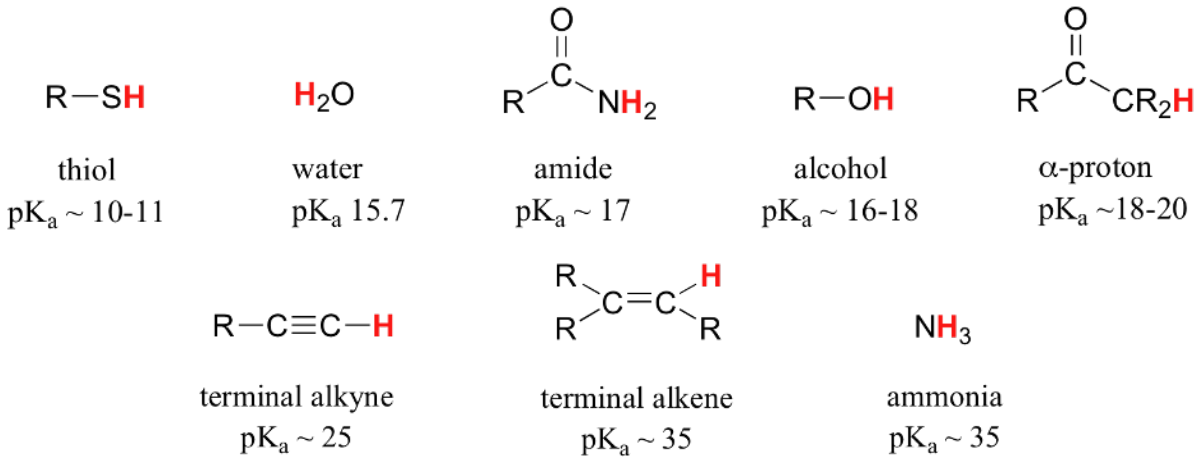
hydrogen cyanide
pK_a 9.2



ammonium
pK_a 9.2



phenol
pK_a 9.9



It is important to realize that pK_a is not at all the same thing as pH: the former is an inherent property of a compound or functional group, while the latter is the measure of the hydronium ion concentration in a particular aqueous solution:

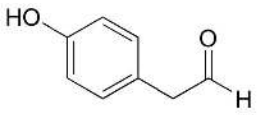
$$pH = -\log[H_3O^+] \tag{2.8.6}$$

Any particular acid will always have the same pK_a (assuming that we are talking about an aqueous solution at room temperature) but different aqueous solutions of the acid could have different pH values, depending on how much acid is added to how much water.

Our table of pK_a values will also allow us to compare the strengths of different bases by comparing the pK_avalues of their conjugate acids. The key idea to remember is this: *the stronger the conjugate acid, the weaker the conjugate base*. Sulfuric acid is the strongest acid on our list with a pK_a value of –10, so HSO_4^- is the weakest conjugate base. You can see that hydroxide ion is a stronger base than ammonia (NH_3), because ammonium (NH_4^+, pK_a = 9.2) is a stronger acid than water (pK_a = 15.7).

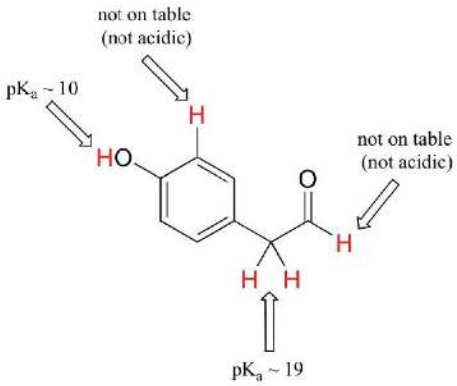
> *The stronger the conjugate acid, the weaker the conjugate base.*

While Table **2.8.1** provides the pK_a values of only a limited number of compounds, it can be very useful as a starting point for estimating the acidity or basicity of just about any organic molecule. Here is where your familiarity with organic functional groups will come in very handy. What, for example, is the $pK_a$of cyclohexanol? It is not on the table, but as it is an alcohol it is probably somewhere near that of ethanol (pK_a = 16). Likewise, we can use Table **2.8.1** to predict that para-hydroxyphenyl acetaldehyde, an intermediate compound in the biosynthesis of morphine, has a pK_a in the neighborhood of 10, close to that of our reference compound, phenol.



p=hydroxyphenyl acetaldehyde

Notice in this example that we need to evaluate the potential acidity at *four* different locations on the molecule.



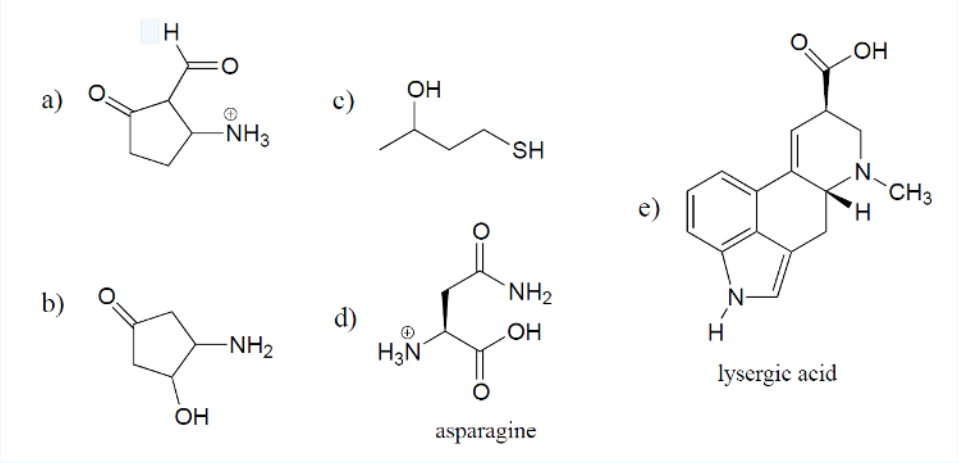
Aldehyde and aromatic protons are not at all acidic (pK_avalues are above 40 – not on our table). The two protons on the carbon next to the carbonyl are slightly acidic, with pK_a values around 19-20 according to the table. The most acidic proton is on the phenol group, so if the compound were to be subjected to a single molar equivalent of strong base, this is the proton that would be donated.

As you continue your study of organic chemistry, it will be a very good idea to commit to memory the approximate pK_a ranges of some important functional groups, including water, alcohols, phenols, ammonium, thiols, phosphates, carboxylic acids and carbons next to carbonyl groups (so-called a-carbons). These are the groups that you are most likely to see acting as acids or bases in biological organic reactions.

A word of caution: when using the pK_a table, be absolutely sure that you are considering the correct conjugate acid/base pair. If you are asked to say something about the basicity of ammonia (NH_3) compared to that of ethoxide ion ($CH_3CH_2O^-$), for example, the relevant pK_a values to consider are 9.2 (the pK_a of ammonium ion) and 16 (the pK_a of ethanol). From these numbers, you know that ethoxide is the stronger base. Do not make the mistake of using the pK_a value of 38: this is the pK_a of ammonia *acting as an acid*, and tells you how basic the NH_2^- ion is (very basic!)

EXAMPLE 2.8.1

Using the pK_a table, estimate pK_a values for the most acidic group on the compounds below, and draw the structure of the conjugate base that results when this group donates a proton. Use the pKa table above and/or from the Reference Tables.



Answer

a. The most acidic group is the protonated amine, pKa ~ 5-9

b. Alpha proton by the C=O group, pKa ~ 18-20

c. Thiol, pKa ~ 10

d. Carboxylic acid, pKa ~ 5

e. Carboxylic acid, pKa ~ 5

EXERCISES

1. Write down an expression for the acidity constant of acetic acid, CH_3COOH.
2. The pK_a of acetic acid is 4.72; calculate its K_a.
3. The K_a of benzoic acid is 6.5×10^{-5}; determine its pK_a.
4. From your answers to the questions above, determine whether acetic acid or benzoic acid is stronger.

ANSWERS:

1. $K_a = \dfrac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]}$ or $K_a = \dfrac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]}$
2. $pK_a = -\log_{10} K_a$
   $= 4.74$
   $\text{Thus, } \log_{10} K_a = -4.72 \text{ and } K_a = \text{anti-log}(-4.72) = 1.9 \times 10^{-5}$

3. $$\begin{aligned} pK_a &= -\log_{10} K_a \\ &= -\log_{10}(6.5 \times 10^{-5}) \\ &= -(-4.19) \\ &= 4.19 \end{aligned}$$
4. Benzoic acid is stronger than acetic acid. [Benzoic acid has a higher K_a and a lower pK_a.]

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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2.9: PREDICTING ACID-BASE REACTIONS FROM PKA VALUES

Objective

After completing this section, you should be able to predict the acid-base reactivity of a system using pK_a values.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- pK_a

USING PK$_A$ VALUES TO PREDICT REACTION EQUILIBRIA

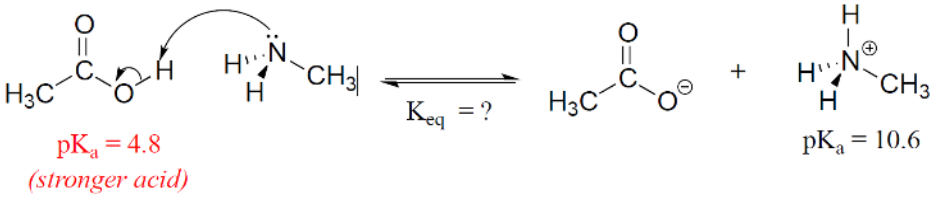
EDIT SECTION

By definition, the pK_a value tells us the extent to which an acid will react with water as the base, but by extension, we can also calculate the equilibrium constant for a reaction between any acid-base pair. Mathematically, it can be shown that:

$$K_{eq} \text{ (for the acid base reaction in question)} = 10^{\Delta pKa}$$

where ΔpK_a = pK_a of product acid minus pK_a of reactant acid

Consider a reaction between methylamine and acetic acid:



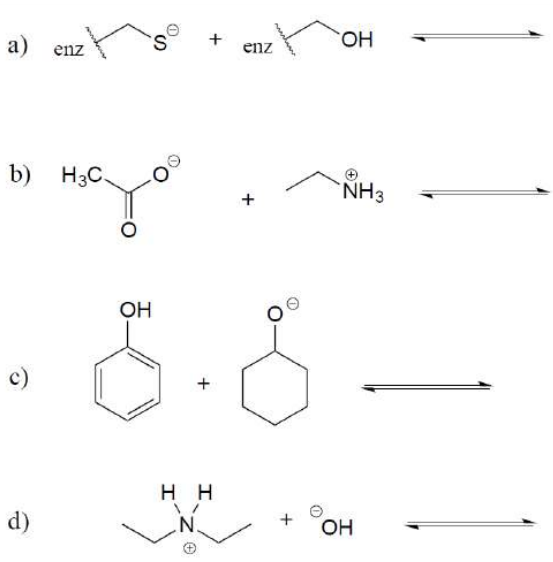
First, we need to identify the acid species on either side of the equation. On the left side, the acid is of course acetic acid, while on the right side the acid is methyl ammonium. The specific pK_a values for these acids are not on our very generalized pK_a table, but are given in the figure above. Without performing any calculations, you should be able to see that this equilibrium lies far to the right-hand side: acetic acid has a lower pK_a, is a stronger acid, and thus it wants to give up its proton more than methyl ammonium does. Doing the math, we see that

$$K_{eq} = 10^{\Delta pKa} = 10^{(10.6 - 4.8)} = 10^{5.8} = 6.3 \times 10^5$$

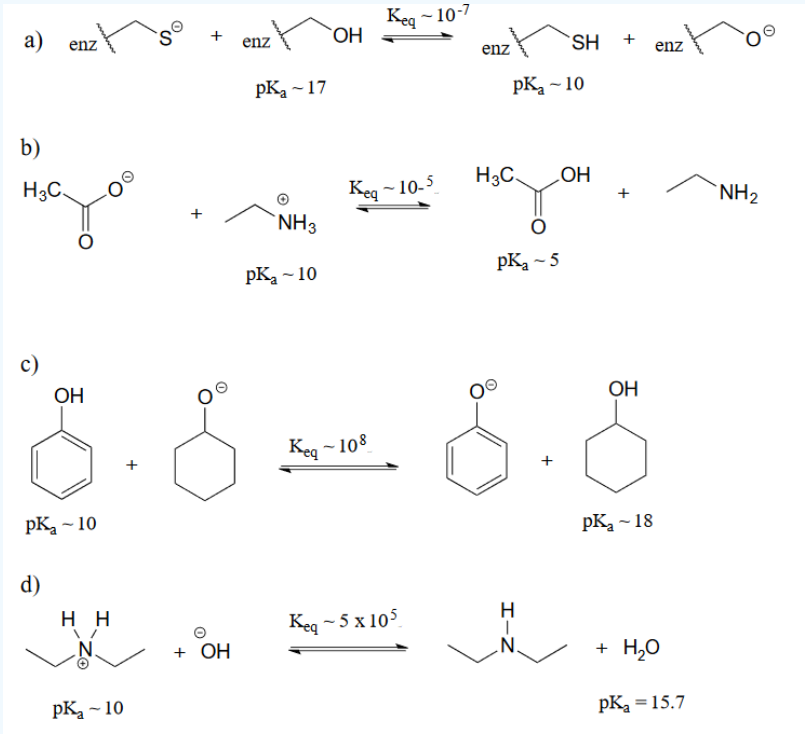
So $K_{eq}$is a very large number (much greater than 1) and the equilibrium lies far to the right-hand side of the equation, just as we had predicted. If you had just wanted to approximate an answer without bothering to look for a calculator, you could have noted that the difference in pK_a values is approximately 6, so the equilibrium constant should be somewhere in the order of 10^6, or one million. Using the pK_a table in this way, and making functional group-based pK_a approximations for molecules for which we don't have exact values, we can easily estimate the extent to which a given acid-base reaction will proceed.

EXERCISE 2.9.1

Show the products of the following acid-base reactions, and estimate the value of K_{eq}. Use the pKa table from Section 2.8 and/or from the Reference Tables.



Answer



QUESTIONS

Q2.9.1

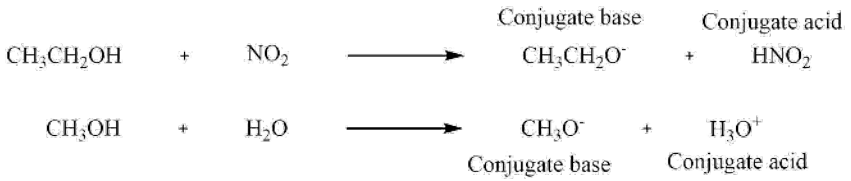
In the following reactions give the resulting products and label the conjugate acid and bases.

CH_3CH_2OH NO_2 ⟶

CH_3OH H_2O ⟶

SOLUTIONS

S2.9.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
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2.10: ORGANIC ACIDS AND ORGANIC BASES

Objective

After completing this section, you should be able to identify an organic compound as being acidic or basic, given its structure.

This page explains the acidity of simple organic acids and looks at the factors which affect their relative strengths.

ORGANIC ACIDS AS WEAK ACIDS

For the purposes of this topic, we are going to take the definition of an acid as "a substance which donates hydrogen ions (protons) to other things". We are going to get a measure of this by looking at how easily the acids release hydrogen ions to water molecules when they are in solution in water.

An acid in solution sets up this equilibrium:

$$AH_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)} \tag{2.10.1}$$

A hydronium ion is formed together with the anion (negative ion) from the acid. This equilibrium is sometimes simplified by leaving out the water to emphasize the ionization of the acid.

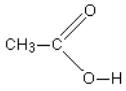
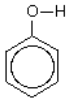
$$AH_{(aq)} \rightleftharpoons A^-_{(aq)} + H^+_{(aq)} \tag{2.10.2}$$

If you write it like this, you must include the state symbols - "(aq)". Writing $H^+_{(aq)}$ implies that the hydrogen ion is attached to a water molecule as H_3O^+. Hydrogen ions are always attached to something during chemical reactions.

The organic acids are weak in the sense that this ionization is very incomplete. At any one time, most of the acid will be present in the solution as un-ionized molecules. For example, in the case of dilute ethanoic acid, the solution contains about 99% of ethanoic acid molecules - at any instant, only about 1% have actually ionised. The position of equilibrium therefore lies well to the left.

COMPARING THE STRENGTHS OF WEAK ACIDS

The strengths of weak acids are measured on the pK_a scale. The smaller the number on this scale, the stronger the acid is. Three of the compounds we shall be looking at, together with their pK_a values are:

		pK_a
ethanoic acid		4.76
phenol		10.00
ethanol	$CH_3—CH_2—O—H$	about 16

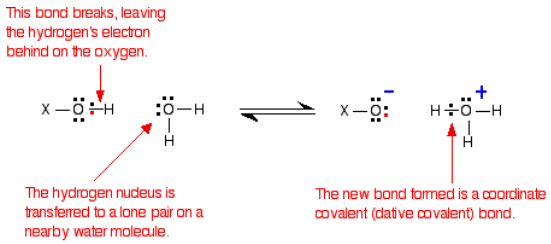
Remember - the smaller the number the stronger the acid. Comparing the other two to ethanoic acid, you will see that phenol is very much weaker with a pK_a of 10.00, and ethanol is so weak with a pK_a of about 16 that it hardly counts as acidic at all!

NOTE

The smaller the pK_a, the stronger the acid

WHY ARE THESE ACIDS ACIDIC?

In each case, the same bond gets broken - the bond between the hydrogen and oxygen in an -OH group. Writing the rest of the molecule as "X":



If the same bond is being broken in each case, why do these three compounds have such widely different acid strengths?

DIFFERENCES IN ACID STRENGTHS BETWEEN CARBOXYLIC ACIDS, PHENOLS AND ALCOHOLS

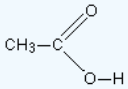
Two of the factors which influence the ionization of an acid are:

- the strength of the bond being broken,
- the stability of the ions being formed.

In these cases, you seem to be breaking the same oxygen-hydrogen bond each time, and so you might expect the strengths to be similar. The most important factor in determining the relative acid strengths of these molecules is the nature of the ions formed. You always get a hydroxonium ion - so that's constant - but the nature of the anion (the negative ion) varies markedly from case to case.

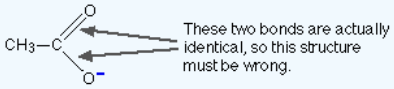
EXAMPLE 2.10.1: **ETHANOIC ACID (ACETIC ACID)**

Ethanoic acid has the structure:



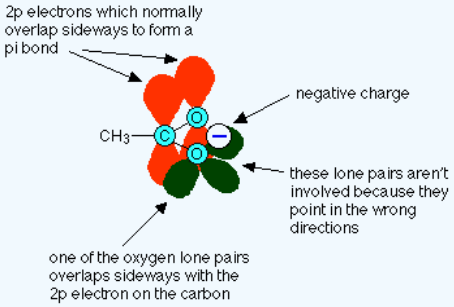
The acidic hydrogen is the one attached to the oxygen. When ethanoic acid ionises it forms the ethanoate ion, CH_3COO^-.

You might reasonably suppose that the structure of the ethanoate ion was as below, but measurements of bond lengths show that the two carbon-oxygen bonds are identical and somewhere in length between a single and a double bond.

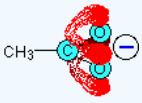


To understand why this is, you have to look in some detail at the bonding in the ethanoate ion. Like any other double bond, a carbon-oxygen double bond is made up of two different parts. One electron pair is found on the line between the two nuclei - this is known as a sigma bond. The other electron pair is found above and below the plane of the molecule in a pi bond. Pi bonds are made by sideways overlap between p orbitals on the carbon and the oxygen.

In an ethanoate ion, one of the lone pairs on the negative oxygen ends up almost parallel to these p orbitals, and overlaps with them

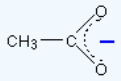


This leads to a delocalised pi system over the whole of the $-COO^-$ group, rather like that in benzene.



All the oxygen lone pairs have been left out of this diagram to avoid confusion. Because the oxygens are more electronegative than the carbon, the delocalised system is heavily distorted so that the electrons spend much more time in the region of the oxygen atoms.

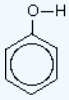
So where is the negative charge in all this? It has been spread around over the whole of the -COO^- group, but with the greatest chance of finding it in the region of the two oxygen atoms. Ethanoate ions can be drawn simply as:



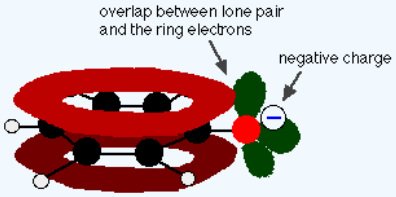
The dotted line represents the delocalisation. The negative charge is written centrally on that end of the molecule to show that it isn't localised on one of the oxygen atoms. The more you can spread charge around, the more stable an ion becomes. In this case, if you delocalise the negative charge over several atoms, it is going to be much less attractive to hydrogen ions - and so you are less likely to re-form the ethanoic acid.

EXAMPLE 2.10.2: PHENOL

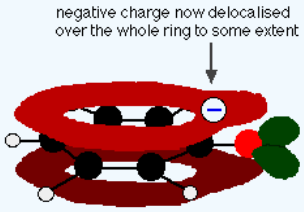
Phenols have an -OH group attached directly to a benzene ring. Phenol itself is the simplest of these with nothing else attached to the ring apart from the -OH group.



When the hydrogen-oxygen bond in phenol breaks, you get a phenoxide ion, $C_6H_5O^-$. Delocalization also occurs in this ion. This time, one of the lone pairs on the oxygen atom overlaps with the delocalised electrons on the benzene ring.

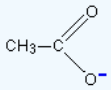


This overlap leads to a delocalisation which extends from the ring out over the oxygen atom. As a result, the negative charge is no longer entirely localised on the oxygen, but is spread out around the whole ion.

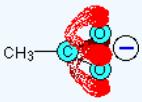


Why then is phenol a much weaker acid than ethanoic acid?

Think about the ethanoate ion again. If there wasn't any delocalization, the charge would all be on one of the oxygen atoms, like this:



But the delocalisation spreads this charge over the whole of the COO group. Because oxygen is more electronegative than carbon, you can think of most of the charge being shared between the two oxygens (shown by the heavy red shading in this diagram).



If there wasn't any delocalisation, one of the oxygens would have a full charge which would be very attractive towards hydrogen ions. With delocalisation, that charge is spread over two oxygen atoms, and neither will be as attractive to a hydrogen ion as if one of the oxygens carried the whole charge.

That means that the ethanoate ion won't take up a hydrogen ion as easily as it would if there wasn't any delocalisation. Because some of it stays ionised, the formation of the hydrogen ions means that it is acidic.

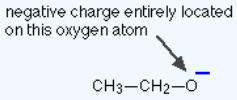
In the phenoxide ion, the single oxygen atom is still the most electronegative thing present, and the delocalised system will be heavily distorted towards it. That still leaves the oxygen atom with most of its negative charge.

What delocalisation there is makes the phenoxide ion more stable than it would otherwise be, and so phenol is acidic to an extent.

However, the delocalisation hasn't shared the charge around very effectively. There is still lots of negative charge around the oxygen to which hydrogen ions will be attracted - and so the phenol will readily re-form. Phenol is therefore only very weakly acidic.

EXAMPLE 2.10.3: ETHANOL

Ethanol, CH_3CH_2OH, is so weakly acidic that you would hardly count it as acidic at all. If the hydrogen-oxygen bond breaks to release a hydrogen ion, an ethoxide ion is formed:



This has nothing at all going for it. There is no way of delocalizing the negative charge, which remains firmly on the oxygen atom. That intense negative charge will be highly attractive towards hydrogen ions, and so the ethanol will instantly re-form. Since ethanol is very poor at losing hydrogen ions, it is hardly acidic at all.

VARIATIONS IN ACID STRENGTHS BETWEEN DIFFERENT CARBOXYLIC ACIDS

You might think that all carboxylic acids would have the same strength because each depends on the delocalization of the negative charge around the $-COO^-$ group to make the anion more stable, and so more reluctant to re-combine with a hydrogen ion. In fact, the carboxylic acids have widely different acidities. One obvious difference is between methanoic acid, HCOOH, and the other simple carboxylic acids:

	pK_a
HCOOH	3.75
CH_3COOH	4.76
CH_3CH_2COOH	4.87
$CH_3CH_2CH_2COOH$	4.82

NOTE

Remember that the higher the value for pK_a, the weaker the acid is.

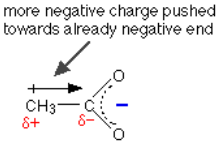
Why is ethanoic acid weaker than methanoic acid? It again depends on the stability of the anions formed - on how much it is possible to delocalise the negative charge. The less the charge is delocalised, the less stable the ion, and the weaker the acid.

The methanoate ion (from methanoic acid) is:

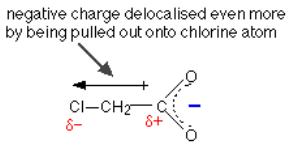


The only difference between this and the ethanoate ion is the presence of the CH_3 group in the ethanoate. But that's important! Alkyl groups have a tendency to "push" electrons away from themselves. That means that there will be a small amount of extra negative charge built up on the $-COO^-$ group. Any build-up of charge will make the ion less stable, and more attractive to hydrogen ions.

Ethanoic acid is therefore weaker than methanoic acid, because it will re-form more easily from its ions.



The other alkyl groups have "electron-pushing" effects very similar to the methyl group, and so the strengths of propanoic acid and butanoic acid are very similar to ethanoic acid. The acids can be strengthened by pulling charge away from the $-COO^-$ end. You can do this by attaching electronegative atoms like chlorine to the chain.



As the next table shows, the more chlorines you can attach the better:

	pK_a
CH_3COOH	4.76
$CH_2ClCOOH$	2.86
$CHCl_2COOH$	1.29
CCl_3COOH	0.65

Trichloroethanoic acid is quite a strong acid.

Attaching different halogens also makes a difference. Fluorine is the most electronegative and so you would expect it to be most successful at pulling charge away from the -COO^- end and so strengthening the acid.

	pK_a
CH_2FCOOH	2.66
$CH_2ClCOOH$	2.86
$CH_2BrCOOH$	2.90
CH_2ICOOH	3.17

The effect is there, but isn't as great as you might expect.

Finally, notice that the effect falls off quite quickly as the attached halogen gets further away from the -COO^- end. Here is what happens if you move a chlorine atom along the chain in butanoic acid.

	pK_a
$CH_3CH_2CH_2COOH$	4.82
$CH_3CH_2CHClCOOH$	2.84
$CH_3CHClCH_2COOH$	4.06
$CH_2ClCH_2CH_2COOH$	4.52

The chlorine is effective at withdrawing charge when it is next-door to the -COO^- group, and much less so as it gets even one carbon further away.

This page explains why simple organic bases are basic and looks at the factors which affect their relative strengths. For A'level purposes, all the bases we are concerned with are primary amines - compounds in which one of the hydrogens in an ammonia molecule, NH_3, is replaced either by an alkyl group or a benzene ring.

AMMONIA AS A WEAK BASE

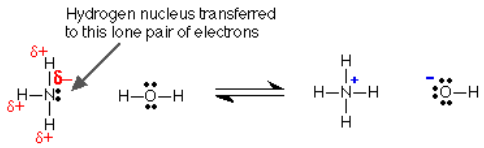
All of the compounds we are concerned with are derived from ammonia and so we'll start by looking at the reason for its basic properties. For the purposes of this topic, we are going to take the definition of a base as "a substance which combines with hydrogen ions (protons)". We are going to get a measure of this by looking at how easily the bases take hydrogen ions from water molecules when they are in solution in water.

Ammonia in solution sets up this equilibrium:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad (2.10.1)$$

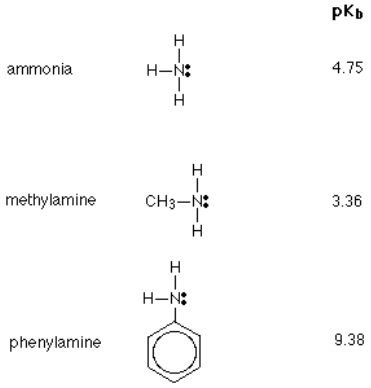
An ammonium ion is formed together with hydroxide ions. Because the ammonia is only a weak base, it doesn't hang on to the extra hydrogen ion very effectively and so the reaction is reversible. At any one time, about 99% of the ammonia is present as unreacted molecules. The position of equilibrium lies well to the left.

The ammonia reacts as a base because of the active lone pair on the nitrogen. Nitrogen is more electronegative than hydrogen and so attracts the bonding electrons in the ammonia molecule towards itself. That means that in addition to the lone pair, there is a build-up of negative charge around the nitrogen atom. That combination of extra negativity and active lone pair attracts the new hydrogen from the water.



COMPARING THE STRENGTHS OF WEAK BASES

The strengths of weak bases are measured on the pK_b scale. The smaller the number on this scale, the stronger the base is. Three of the compounds we shall be looking at, together with their pK_b values are:



Remember - the smaller the number the stronger the base. Comparing the other two to ammonia, you will see that methylamine is a stronger base, whereas phenylamine is very much weaker.

- Methylamine is typical of aliphatic primary amines - where the $-NH_2$ group is attached to a carbon chain. All aliphatic primary amines are stronger bases than ammonia.
- Phenylamine is typical of aromatic primary amines - where the $-NH_2$ group is attached directly to a benzene ring. These are very much weaker bases than ammonia.

EXPLAINING THE DIFFERENCES IN BASE STRENGTHS

Two of the factors which influence the strength of a base are:

- the ease with which the lone pair picks up a hydrogen ion,
- the stability of the ions being formed.

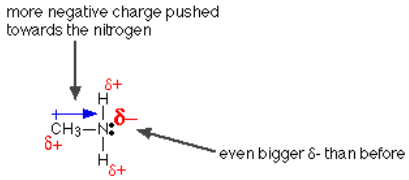
WHY ARE ALIPHATIC PRIMARY AMINES STRONGER BASES THAN AMMONIA?

METHYLAMINE

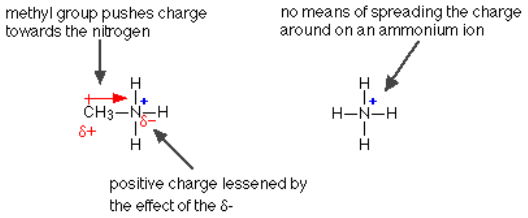
Methylamine has the structure:



The only difference between this and ammonia is the presence of the CH_3 group in the methylamine. But that's important! Alkyl groups have a tendency to "push" electrons away from themselves. That means that there will be a small amount of extra negative charge built up on the nitrogen atom. That extra negativity around the nitrogen makes the lone pair even more attractive towards hydrogen ions.



Making the nitrogen more negative helps the lone pair to pick up a hydrogen ion. What about the effect on the positive methylammonium ion formed? Is this more stable than a simple ammonium ion? Compare the methylammonium ion with an ammonium ion:



In the methylammonium ion, the positive charge is spread around the ion by the "electron-pushing" effect of the methyl group. The more you can spread charge around, the more stable an ion becomes. In the ammonium ion there is not any way of spreading the charge.

To summarize:

- The nitrogen is more negative in methylamine than in ammonia, and so it picks up a hydrogen ion more readily.
- The ion formed from methylamine is more stable than the one formed from ammonia, and so is less likely to shed the hydrogen ion again.

Taken together, these mean that methylamine is a stronger base than ammonia.

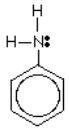
THE OTHER ALIPHATIC PRIMARY AMINES

The other alkyl groups have "electron-pushing" effects very similar to the methyl group, and so the strengths of the other aliphatic primary amines are very similar to methylamine. For example:

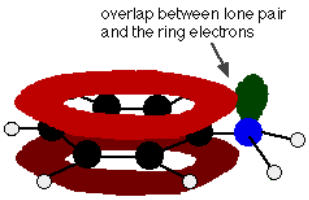
	pK_b
CH_3NH_2	3.36
$CH_3CH_2NH_2$	3.27
$CH_3CH_2CH_2NH_2$	3.16
$CH_3CH_2CH_2CH_2NH_2$	3.39

WHY ARE AROMATIC PRIMARY AMINES MUCH WEAKER BASES THAN AMMONIA?

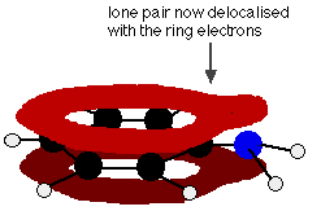
An aromatic primary amine is one in which the $-NH_2$ group is attached directly to a benzene ring. The only one you are likely to come across is phenylamine. Phenylamine has the structure:



The lone pair on the nitrogen touches the delocalized ring electrons . . .



. . . and becomes delocalized with them:



That means that the lone pair is no longer fully available to combine with hydrogen ions. The nitrogen is still the most electronegative atom in the molecule, and so the delocalized electrons will be attracted towards it, but the intensity of charge around the nitrogen is nothing like what it is in, say, an ammonia molecule.

The other problem is that if the lone pair is used to join to a hydrogen ion, it is no longer available to contribute to the delocalisation. That means that the delocalization would have to be disrupted if the phenylamine acts as a base. Delocalization makes molecules more stable,

and so disrupting the delocalization costs energy and will not happen easily.

Taken together - the lack of intense charge around the nitrogen, and the need to break some delocalization - this means that phenylamine is a very weak base indeed.

? EXERCISE 2.10.1

The 4-methylbenzylammonium ion has a pK_a of 9.51, and the butylammonium ion has a pK_a of 10.59. Which is more basic? What's the pK_b for each compound?

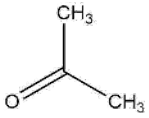
Answer

The butylammonium is more basic. Remember that $pK_a+pK_b = 14$. The pK_b for butylammonium is 3.41, the pK_b for 4-methylbenzylammonium is 4.49.

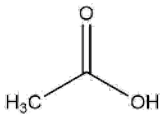
QUESTIONS

Q2.10.1

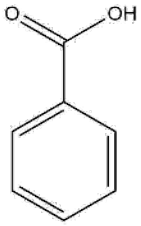
Determine which of the one of the molecules is an acid or a base.



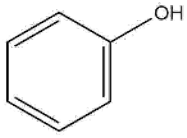
1



2



3



4

SOLUTIONS

S2.10.1

1 = Base

2 = Acid

3 = Acid

4 = Acid

CONTRIBUTORS AND ATTRIBUTIONS

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- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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2.11: ACIDS AND BASES- THE LEWIS DEFINITION

Objectives

After completing this section, you should be able to

1. state the Lewis definition of an acid and a base.
2. identify a given compound as being a Lewis acid or Lewis base, given its Lewis structure or its Kekulé structure.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- Lewis acid
- Lewis base

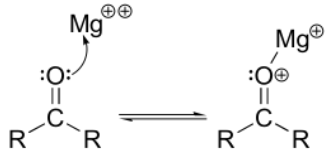
STUDY NOTES

The Lewis concept of acidity and basicity will be of great use to you when you study reaction mechanisms. The realization that an ion such as

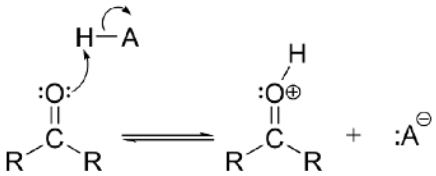


is electron deficient, and is therefore a Lewis acid, should help you understand why this ion reacts with substances which are Lewis bases (e.g., H_2O).

The Brønsted-Lowry picture of acids and bases as proton donors and acceptors is not the only definition in common use. A broader definition is provided by the **Lewis theory** of acids and bases, in which a Lewis acid is an electron-pair acceptor and a Lewis base is an electron-pair donor. This definition covers Brønsted-Lowry proton transfer reactions, but also includes reactions in which no proton transfer is involved. The interaction between a magnesium cation (Mg^{+2}) and a carbonyl oxygen is a common example of a Lewis acid-base reaction. The carbonyl oxygen (the Lewis base) donates a pair of electrons to the magnesium cation (the Lewis acid).



As we will see in CHEM 360 (Chapter 19) when we begin the study of reactions involving carbonyl groups, this interaction has the very important effect of increasing the polarity of the carbon-oxygen double bond. The Brønsted-Lowry equivalent of the reaction above is simply protonation of the carbonyl group. This, too, has the effect of increasing the polarity of the carbonyl double bond.



While it is important to be familiar with the Lewis definition, the focus throughout the remainder of this chapter will be on acid-base reactions of the Brønsted-Lowry type, where an actual proton transfer event takes place.

LEWIS ACIDS

Borane is unusual because it is a compound without an octet. The central boron atom has only six valence electrons. It needs one more pair of electrons to obtain an octet. The boron is a Lewis acid.

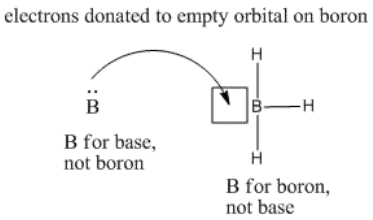


Figure 2.11.1: *Borane is a Lewis acid. It can accept electrons from a donor atom. The square drawn beside the boron is used to reinforce the idea that there is a vacant site for electrons there.*

- Lewis acids are often short of a complete octet.

In the main group of the periodic table, atoms in the Group 13 column (including boron and aluminum) have three valence electrons to share in order to make bonds. Sharing these electrons with three electrons from neighbors would make three bonds, and provide six electrons, not eight, in the valence shell. Another pair of electrons must be accepted from a donor to achieve an octet.

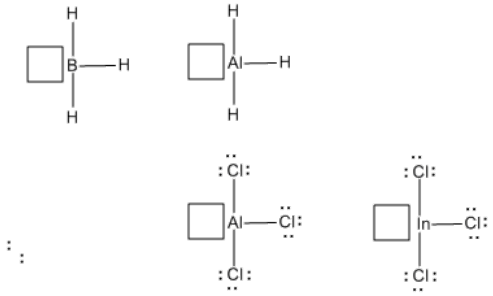


Figure 2.11.2*: Boron, aluminum and indium are from the same column of the periodic table. All three are often Lewis acidic; they can accept electrons from donors.*

- Boron, aluminum and indium compounds are often Lewis acids.

The eight-electron rule does not hold throughout the periodic table. In order to obtain noble gas configurations, some atoms may need eighteen electrons in their valence shell. For example, transition metals such as titanium often follow an eighteen-electron rule. Titanium has four valence electrons and can form four bonds in compounds such as titanium tetrakis (isopropoxide), below, or titanium tetrachloride, $TiCl_4$. However, the titanium atom in that compound has only eight valence electrons, not eighteen. It can easily accept electrons from donors.

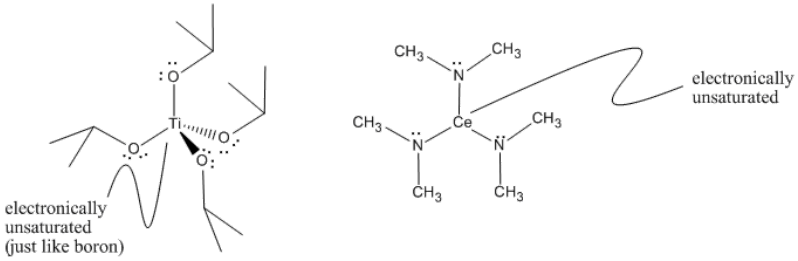


Figure 2.11.3*: Although titanium has eight electrons in this molecule, titanium tetrakis(isopropoxide), it can accommodate up to eighteen. It is a Lewis acid. The cerium atom in cerium tris(dimethylamide) comes from a similar part of the periodic table and is also a Lewis acid.*

- Transition metals such as titanium, iron and nickel may have up to eighteen electrons and can frequently accept electron pairs from Lewis bases. Transition metals are often Lewis acids.
- Lanthanides such as cerium and samarium could conceivably have up to thirty-two electrons in their valence shells! They never do. However, they are usually strong Lewis acids.

Positive ions are often Lewis acids because they have an electrostatic attraction for electron donors. Examples include alkali and alkaline earth metals in the group IA and IIA columns. K^+, Mg^{2+} and Ca^{2+} are sometimes seen as Lewis acidic sites in biology, for example. These ions are very stable forms of these elements because of their low electron ionization potentials. However, their positive charges do attract electron donors.



Figure 2.11.4*. A calcium ion essentially has a noble gas configuration. Nevertheless, its positive charge can attract electrons from a donor atom.*

In a similar way, "early" transition metals -- those that are close to the left hand side of the periodic table, especially in groups IIIB, IVB and VB -- have low ionization potentials and have high positive charges or oxidation states. For example, Sc^{3+}, Zr^{4+} and V^{5+} are common forms of some early transition metals, and they are strong Lewis acids.



Figure 2.11.5*: A few alkali, alkaline earth and transition metals that are commonly found as cations.*

- Many cations such as Ca^{2+} or Sc^{3+} are good Lewis acids. Their positive charges attract electrons.

THE PROTON AS A COMMON LEWIS ACID

Perhaps the most common example of a Lewis acid or electrophile is also the simplest. It is the hydrogen cation or proton. It is called a proton because, in most hydrogen atoms, the only particle in the nucleus is a proton. If an electron is removed to make a cation, a proton is all that is left.

- H^+ is a very common Lewis acid or electrophile.

A proton is electrophilic for a couple of reasons. It has a positive charge, and so it will attract electrons, which are negative. Also, it lacks the electron configuration of its noble gas neighbor, helium. Helium has two electrons. If a Lewis base or nucleophile donates a pair of electrons to a proton, the proton will obtain a Noble gas configuration. That's part of the reason why, in some periodic tables, hydrogen is shown in two places: at the very left, illustrating its potential to lose an electron, like sodium and lithium; and at the right, illustrating its potential to take on helium's configuration.



Figure 2.11.6: *Proton as Lewis acid.*

There is something about hydrogen cations that is not so simple, however. They are actually not so common. Instead, protons are generally always bound to a Lewis base. Hydrogen is almost always covalently (or datively / coordinately) bonded to another atom.

Many of the other elements commonly found in compounds with hydrogen are more electronegative than hydrogen. As a result, hydrogen often has a partial positive charge. Remember, that is one of the reasons that atoms can act as Lewis acids: with a partial positive charge, an atom becomes electrophilic.

Our statement about protons might better be expressed as:

- H^+ is a very common Lewis acid or electrophile.

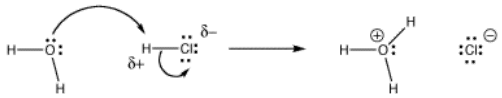


Figure 2.11.7. *Proton transfer from one site to another.*

If hydrogens are almost always bonded to other atoms, then the Lewis acid-base interactions we have looked at so far are slightly different here. Instead of two compounds coming together and forming a bond, we have one Lewis base replacing another at a proton.

- Protons are transferred from one basic site to another.
- Transfer occurs by donation of a lone pair to the proton.

LEWIS BASES

What makes a molecule (or an atom or ion) a Lewis base? It must have a pair of electrons available to share with another atom to form a bond. The most readily available electrons are those that are not already in bonds. Bonding electrons are low in energy. Non-bonding electrons are higher in energy and may be stabilized when they are delocalized in a new bond.

Lewis bases usually have non-bonding electrons or lone pairs.

NOTE 1: AMMONIA

Ammonia, NH_3, has a lone pair and is a Lewis base. It can donate to compounds that will accept electrons.



Ammonia donating to an electron acceptor or Lewis acid.

Lewis bases may be anionic or neutral. The basic requirement is that they have a pair of electrons to donate. Examples of Lewis bases include halide ions such as bromide or chloride. To the right of the halides in the periodic table are Noble gases such as neon. Noble gases do have lone pairs, but are stable enough that they do not usually react. They are not very good Lewis bases. To the left of the halides, however, are other examples in oxygen and nitrogen compounds. Water also has lone pairs and is a common Lewis base, and so is hydroxide ion, HO-.

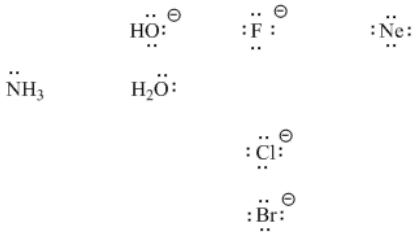


***Figure 2.11.8**: Some examples of Lewis basic ions and molecules. Note that neon, although it has non-bonding electron pairs or lone pairs, does not usually act as a Lewis base.*

- Halides, water, ammonia and hydroxide ion are examples of Lewis bases.

One column further to the left in the periodic table from nitrogen is carbon. Carbon does not normally have a lone pair. For example, methane, CH_4, has all of its valence electrons in bonding pairs. These bonding pairs are too stable to donate under normal conditions. Methane is not a Lewis base. Even further to the left is boron. A simple boron compound is borane, BH_3. Borane has no lone pairs; all its valence electrons are in bonds. Boron is not a good Lewis base.

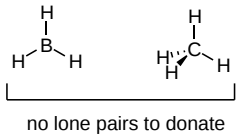


***Figure 2.11.9**. Carbon and boron compounds with all sigma bonds do not have lone pairs, and do not act as Lewis bases.*

EXERCISE 2.11.1

Which of the following compounds would you expect to be Lewis bases?

a) SiH_4 b) AlH_3 c) PH_3 d) SH_2 e) ^-SH

Answer

a) No, silicon has 4 valence electrons (like carbon) and all 4 are involved in sigma bonds

b) No, aluminum has 3 valence electrons and all 3 are involved in sigma bonds

c) Yes, phosphorus has 5 valence electrons, so there is one lone pair available

d) Yes, sulfur has 6 valence electrons, so there are two lone pairs available

e) Yes, this ion has 3 lone pairs available

LEWIS ACID-BASE COMPLEXES

What happens when a Lewis base donates a pair of electrons to a Lewis acid? The arrow formulism we have been using to illustrate the behaviour of Lewis acids and Lewis bases is meant to show the direction of electron movement from the donor to the acceptor. However, given that a bond can be thought of as a pair of electrons that are shared between two atoms (in this case, between the donor and the acceptor), these arrows also show where bonds are forming.

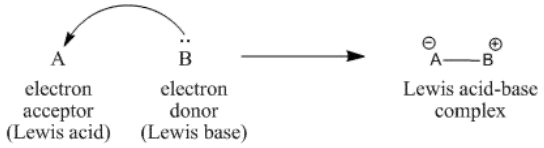


Figure 2.11.10. Donation of electrons from a Lewis base to a Lewis acid.

The electrons donated from a Lewis base to a Lewis acid form a new bond. A new, larger compound is formed from the smaller Lewis acid and Lewis base. This compound is called a Lewis acid-base complex.

A simple example of Lewis acid-base complexation involves ammonia and boron trifluoride. The nitrogen atom has a lone pair and is an electron donor. The boron has no octet and is an electron acceptor. The two compounds can form a Lewis acid-base complex or a coordination complex together.

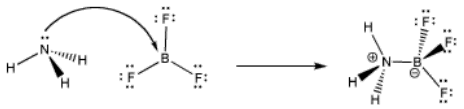


Figure 2.11.11*: Formation of a Lewis acid-base complex from ammonia and boron trifluoride.*

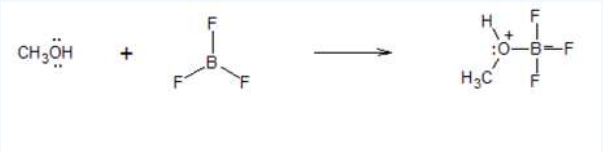
When the nitrogen donates a pair of electrons to share with the boron, the bond that forms is sometimes called a coordinate bond. Another term for this kind of bond is a dative bond. A coordinate or dative bond is any covalent bond that arose because one atom brought a pair of its electrons and donated them with another.

There is another piece of terminology you should get used to here. Sometimes, the electron donor is called a **nucleophile** and the electron acceptor is called an **electrophile**. Ammonia is a nucleophile and boron trifluoride is an electrophile.

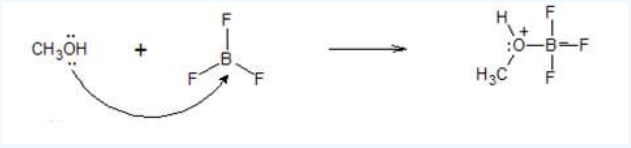
- Because Lewis bases are attracted to electron-deficient atoms, and because positive charge is generally associated with the nucleus of an atom, Lewis bases are sometimes refered to as "nucleophiles". Nucleophile means nucleus-loving.
- Because Lewis acids attract electron pairs, Lewis acids are sometimes called "electrophiles". Electrophile means electron-loving.

? EXERCISE 2.11.2

For the following reaction, add curved arrows (electron pushing formalism) to indicate the electron flow.



Answer



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EXERCISE 2.11.3

A Lewis acid-base complex is formed between THF (tetrahyrofuran) and borane, BH_3.

a) Which compound is the Lewis acid? Which one is the Lewis base?

b) Which atom in the Lewis acid is the acidic site? Why?

c) Which atom in the Lewis base is the basic site? Why?

d) How many donors would be needed to satisfy the acidic site?

e) Show, using arrow notation, the reaction to form a Lewis acid-base complex.

f) Borane is highly pyrophoric; it reacts violently with air, bursting into flames. Show, using arrow notation, what might be happening when borane contacts the air.

g) Borane-THF complex is much less pyrophoric than borane. Why do you suppose that is so?

Add exercises text here.

Answer

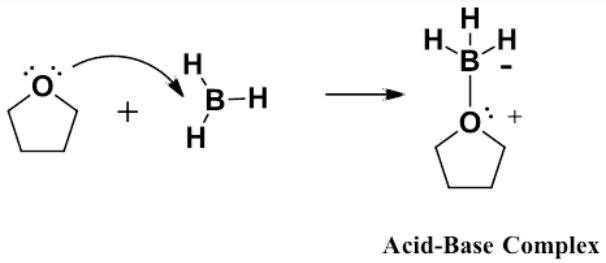
a) Borane is the Lewis acid. THF has lone pair electrons so it is the Lewis base.

b) The Boron atom has an unfilled octet so it has an empty p orbital that can accept electrons.

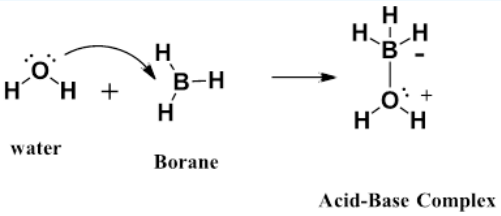
c) The oxygen atom in THF has lone pair electrons contained in a sp^3 hybridized orbital.

d) The boron in borane has six electrons around it so it would only need one lone pair donor to reach an octet.

e) Show, using arrow notation, the reaction to form a Lewis acid-base complex.



f) The Borane initially reacts with water in air.

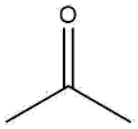


g) After the Borane-THF complex is formed, the boron atom has a complete octet making it less reactive.

QUESTIONS

Q2.11.1

For the following molecules state wither they are Lewis acid or base and wither or not they are a Brønsted acid or base.



NH_4^+

https://chem.libretexts.org/@go/page/67062

SOLUTIONS

S2.11.1

Acetone is a Lewis base and a Brønsted base. Ammonium cation is both a Lewis acid and a weak Brønsted acid.

CONTRIBUTORS AND ATTRIBUTIONS

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2.12: NONCOVALENT INTERACTIONS BETWEEN MOLECULES

Objectives

After completing this section, you should be able to

1. identify the various intermolecular forces that may be at play in a given organic compound.
2. describe how intermolecular forces influence the physical properties, 3-dimensional shape and structure of compounds.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- dipole-dipole forces
- London dispersion forces
- hydrogen bond
- intermolecular forces
- noncovalent interaction
- van der Waals forces

STUDY NOTES

Much of the material in this section should be familiar to you from your pre-requisite general chemistry course. Nonetheless, this section is important, as it covers some of the fundamental factors that influence many physical and chemical properties.

INTRODUCTION

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

NOTE

The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures. (For more information on the behavior of real gases and deviations from the ideal gas law,.)

In this section, we explicitly consider three kinds of intermolecular interactions: dipole-dipole, London dispersion, and hydrogen bond. The first two are often described collectively as van der Waals forces. There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water.

DIPOLE–DIPOLE INTERACTIONS

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Figure 2.12.1. These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (part (c) in Figure 2.12.1). Hence dipole–dipole interactions, such as those in part (b) in Figure 2.12.1, are *attractive intermolecular interactions*, whereas those in part (d) in Figure 2.12.1 are *repulsive intermolecular interactions.*

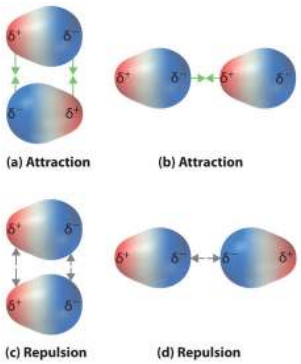


Figure 2.12.1 *Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.*

Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 2.12.2. On average, however, the attractive interactions dominate.

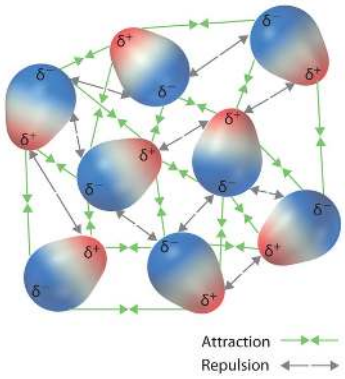


Figure 2.12.2 *Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules*

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6, or 64-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 2.12.1. Using what we learned about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

Table 2.12.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

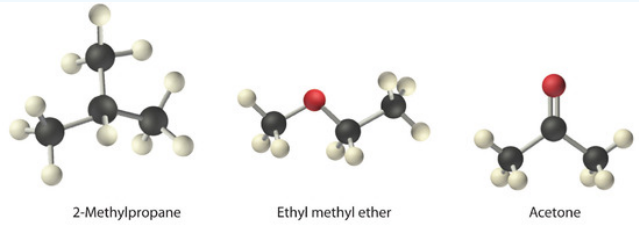
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

NOTE

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

EXAMPE 2.12.2.12.1

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

EXERCISE 2.12.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer: dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

LONDON DISPERSION FORCES

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 11.3).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 11.3: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 11.5.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

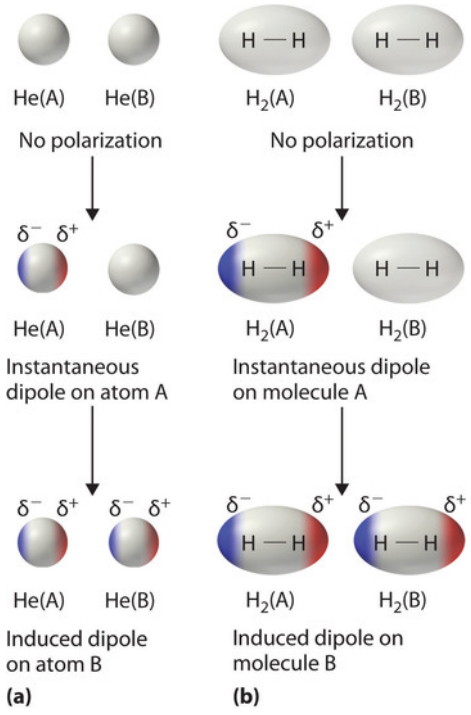


Figure 11.5.3 *Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.*

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 11.5.3, tends to become more pronounced as atomic and molecular masses increase (Table 11.3). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and

electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

NOTE

For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 2.12.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 2.12.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

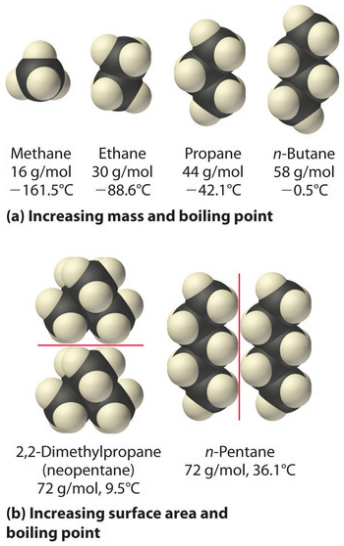


Figure 2.12.4 *Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear n-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas n-pentane is a volatile liquid.*

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

EXAMPE 2.12.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

? EXERCISE 2.12.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer: $GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

HYDROGEN BONDS

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 2.12.5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

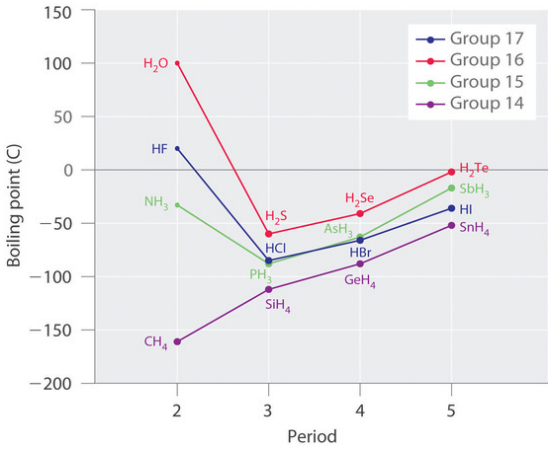


***Figure 2.12.5**: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.*

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 2.12.6. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O···H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

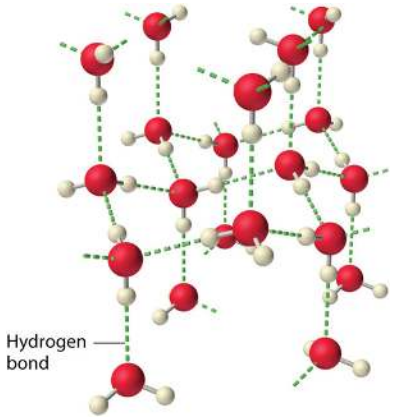


Figure 2.12.6: *The Hydrogen-Bonded Structure of Ice*

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

NOTE

Hydrogen bond formation requires *both* a hydrogen bond donor *and* a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

EXAMPE 2.12.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

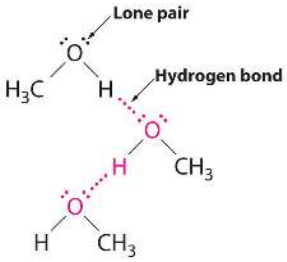
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

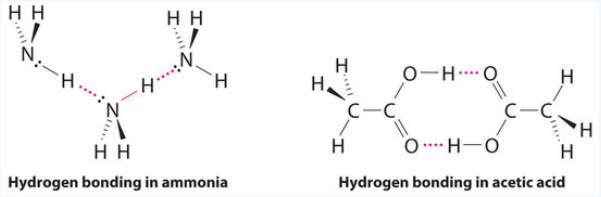
B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



EXERCISE 2.12.3

Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer: CH_3CO_2H and NH_3;



EXAMPLE 2.12.4

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses: He (−269°C) < Ar (−185.7°C) < N_2O (−88.5°C) < C_{60} (>280°C) < NaCl (1465°C).

EXERCISE 2.12.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer: KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

SUMMARY

Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between

dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O · · · Hhydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

KEY TAKEAWAY

- Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds.

PROBLEMS

1. Which are stronger—dipole–dipole interactions or London dispersion forces? Which are likely to be more important in a molecule with heavy atoms? Explain your answers.
2. Liquid water is essential for life as we know it, but based on its molecular mass, water should be a gas under standard conditions. Why is water a liquid rather than a gas under standard conditions?
3. Why are intermolecular interactions more important for liquids and solids than for gases? Under what conditions must these interactions be considered for gases?
4. In group 17, elemental fluorine and chlorine are gases, whereas bromine is a liquid and iodine is a solid. Why?
5. Identify the most important intermolecular interaction in each of the following.

   a) SO_2

   b) HF

   c) CO_2

   d) CCl_4

   e) CH_2Cl_2
6. Both water and methanol have anomalously high boiling points due to hydrogen bonding, but the boiling point of water is greater than that of methanol despite its lower molecular mass. Why? Draw the structures of these two compounds, including any lone pairs, and indicate potential hydrogen bonds.
7. Do you expect the boiling point of H_2S to be higher or lower than that of H_2O? Justify your answer.
8. Some recipes call for vigorous boiling, while others call for gentle simmering. What is the difference in the temperature of the cooking liquid between boiling and simmering? What is the difference in energy input?

SOLUTIONS

1. Dipole-Diple interactions are stronger because molecules polarity is permanent. Molecules involved in London dispersion forces are only temporarily polar

2. Water is a liquid under standard conditions because of its unique ability to form four strong hydrogen bonds per molecule.

3. In solids and liquids the molecules are in direct contact. In gases the molecules only contact during collisions. Intermolecules forces become inmportant when gases are cooled to the point where they form a liquid. 4. As the atomic mass of the halogens increases, so does the number of electrons and the average distance of those electrons from the nucleus. Larger atoms with more electrons are more easily polarized than smaller atoms, and the increase in polarizability with atomic number increases the strength of London dispersion forces. These intermolecular interactions are strong enough to favor the condensed states for bromine and iodine under normal conditions of temperature and pressure. 5. a) The V-shaped SO2 molecule has a large dipole moment due to the polar S=O bonds, so dipole–dipole interactions will be most important.

b) The H–F bond is highly polar, and the fluorine atom has three lone pairs of electrons to act as hydrogen bond acceptors; hydrogen bonding will be most important.

c) Although the C=O bonds are polar, this linear molecule has no net dipole moment; hence, London dispersion forces are most important.

d) This is a symmetrical molecule that has no net dipole moment, and the Cl atoms are relatively polarizable; thus, London dispersion forces will dominate.

e) This molecule has a small dipole moment, as well as polarizable Cl atoms. In such a case, dipole–dipole interactions and London dispersion forces are often comparable in magnitude.

6) Water has two polar O–H bonds with H atoms that can act as hydrogen bond donors, plus two lone pairs of electrons that can act as hydrogen bond acceptors, giving a net of four hydrogen bonds per H2O molecule. Although methanol also has two lone pairs of electrons on oxygen that can act as hydrogen bond acceptors, it only has one O–H bond with an H atom that can act as a hydrogen bond donor. Consequently, methanol can only form two hydrogen bonds per molecule on average, versus four for water. Hydrogen bonding therefore has a much greater effect on the boiling point of water.

7) H2O would have the higher boiling point because it can form the stronger hydrogen bonding intermolecular force. 8) Vigorous boiling causes more water molecule to escape into the vapor phase, but does not affect the temperature of the liquid. Vigorous boiling requires a higher energy input than does gentle simmering.

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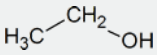
2.13: MOLECULAR MODELS

Objective

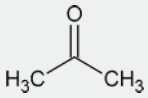
After completing this section, you should be able to use ball-and-stick molecular models to make models of simple organic compounds (e.g., ethane, ethylene, acetylene, ethanol, formaldehyde, acetone, acetic acid), given their Kekulé structures or molecular formulas.

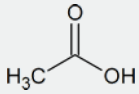
STUDY NOTES

You will have noticed that we have given two names for most of the compounds discussed up to this point. In general we shall be using systematic (i.e., IUPAC—International Union of Pure and Applied Chemistry) names throughout the course. However, simple compounds are often known principally by their common names, which may be more familiar to you than their IUPAC counterparts. We shall address the subject of nomenclature (naming) in Chapter 3.

ethanol, 

formaldehyde (methanal), 

acetone (propanone), 

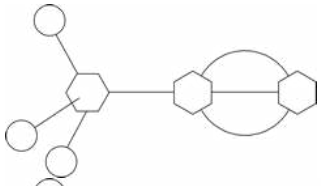
acetic (ethanoic) acid, 

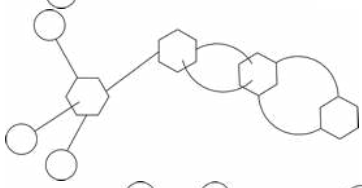
EXERCISES

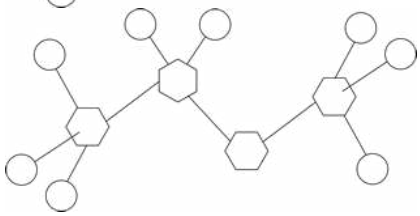
1. Construct a molecular model of each of the compounds listed below.
   a. CH_3-CN
   b. $CH_3-N=C=O$
   c. $CH_3-CH_2-O-CH_3$

Hint: Use the curved sticks to form the multiple bonds and the straight sticks for single bonds.

ANSWERS:

A. 

B. 

C. 

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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2.S: POLAR COVALENT BONDS; ACIDS AND BASES (SUMMARY)

CONCEPTS & VOCABULARY

2.1 Polar Covalent Bonds: Electronegativity

- The difference in electronegativity values of two atoms determines whether the bond between those atoms is classified as either **ionic**, **polar covalent**, or **non-polar covalent**.
- **Ionic bonds** result from large differences in electronegativity values, such as that between a metal and non-metal atom (Na and Cl).
- Covalent bonding generally results when both atoms are non-metals, like C, H, O, N and the halides.
- When both atoms the same and/or have the same electronegativity value, then the bonding electrons are shared equally and the bond is classified as **non-polar covalent**.
- **Polar covalent** bonds occur when the difference in electronegativity values is small, and the bonding electrons are not shared equally.

2.2 Polar Covalent Bonds: Dipole Moments

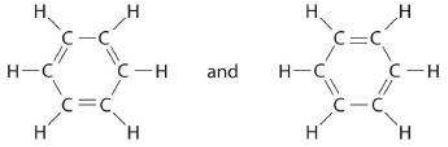
- The **molecular dipole moment** is the sum of all the bond dipoles within a molecule and depends on both the molecular geometry and the bond polarity.
- Molecules that contain no polar bonds, like CH_4, and/or completely symmetrical molecules, like CO_2, generally have no net dipole moment.
- Asymmetrical molecules that contain bonds of different polarities or non-bonding lone pairs typically have a molecular dipole moment.

2.3 Formal Charges

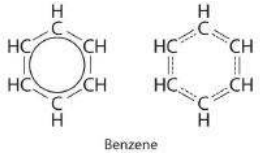
- Formal Charge compares how many valence electrons surround a free atom versus how many surround that same type of atom bonded with a molecule or ion.
- **Formal Charge = (# of valence electrons in free atom) - (# of lone-pair electrons) - (1/2 # of bond pair electrons)** *Eqn. 2.3.1*
- Formal charges of zero generally represent the most stable structures.
- These bonding patterns for the atoms commonly found in organic molecules result in a formal charge of zero
  - Carbon - 4 bonds, no lone pairs
  - Hydrogen - 1 bond, no lone pairs
  - Nitrogen - 3 bonds, 1 lone pair
  - Oxygen - 2 bonds, 2 lone pairs
  - Halogens - 1 bond, 3 lone pairs.

2.4 Resonance

- Resonance Theory is often used when the observed chemical and physical properties of a molecule or ion cannot be adequately described by a single Lewis Structure. A classic example is the benzene molecule, C_6H_6. The Lewis Structure of benzene could be drawn in two different ways. Both structures have alternating double bond and single bonds between the carbons. The only difference is the location of the pi bonds.



If these structures are correct, then the benzene molecule should have two different C-C bond lengths and bond energies, corresponding to a C-C single bond and to a C=C double bond. However, analysis shows that benzene contains only one type of carbon-carbon bond and it's bond length and energy are half between those of a single bond and double bond. Resonance theory states that benzene exists as the "average" of the two structures called a **resonance hybrid**, in which the six pi electrons **delocalized** over all six carbon atoms. Each C-C bond in benzene would be the average of a single bond and double bond or a "bond and a half". Dashed lines are often used to show type of "partial" bonding in a resonance hybrid of benzene

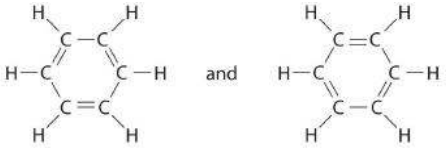


2.5 Rules for Resonance Forms

- The rules for estimating stability of resonance structures are
  - The resonance form in which all atoms have complete valence shells is more stable.

- The **greater the number of covalent bonds**, the greater the stability since more atoms will have complete octets
- The structure with the **least number of formal charges** is more stable
- The structure with the **least separation of formal charges** is more stable
- A structure with a **negative charge on the more electronegative atom** will be more stable
- **Positive charges on the least electronegative atom** (most electropositive) is more stable
- **Resonance forms that are equivalent have no difference in stability and contribute equally.** (eg. benzene)

- If these rules are applied to the two Lewis Structures of benzene, the result would be that both structures will have the same relative stability and will both contribute equally to the character of the resonance hybrid.



2.6 Drawing Resonance Forms

- In resonance structures, the electrons are able to move to help stabilize the molecule. This movement of the electrons is called delocalization.
- The rules for drawing resonance structures are:
  - Resonance structures should have the same number of electrons, do not add or subtract any electrons. (You can check the number of electrons by counting them)
  - All resonance structures must follow the rules of writing Lewis Structures.
  - The hybridization of the structure must stay the same.
  - The skeleton of the structure can not be changed (only the electrons move).
  - Resonance structures must also have the same amount of lone pairs.

2.7 Acids and Bases - The Brønsted-Lowry Definition

- A Brønsted-Lowry acid is a proton (H^+) donor and a Brønsted-Lowry base is a proton acceptor.

2.8 Acid and Base Strength

- The strength of Brønsted-Lowry acids is measured indicated by its pKa value. The lower the pKa - the stronger the acid.
- A strong acid will have a weak conjugate base. A strong base will have a weak conjugate acid.

2.9 Predicting Acid-Base Reactions from pKa Values

- The equilibrium of an acid-base reaction favors the formation of weaker acids from stronger acids. To predict the direction of the equilibrium, identify Brønsted-Lowry acid on each side of the reaction. Assign/look up pKa values for each acid. The equilibrium will favor the side that has the weakest acid (the highest pKa).

2.10 Organic Acids and Organic Bases

- Organic acids are stronger when the conjugate base that is formed upon loss of a proton is more stable.
- Some factors that effect the stability of the conjugate base (often an anion) are the anionic atom's size and electronegativity, resonance effects, inductive effects, and solvation.

2.11: Acids and Bases - The Lewis Definition

- A Lewis acid is a lone pair acceptor and a Lewis base is a lone pair donor.

2.12: Non-covalent Interactions between Molecules

- Non-covalent Interactions, also known as Intermolecular Forces, significantly effect the physical properties of organic molecules. Hydrogen bonding is the most important of these interactions, but others include ion-dipole, dipole-dipole, and London Dispersion Forces.

2.MM: Molecular Models

SKILLS TO MASTER

- Skill 2.1 Predict whether a bond is ionic, polar covalent, or non-polar covalent based on the position of the atoms in the periodic table.
- Skill 2.2 Identify the partial positive and partial negative atoms of a polar covalent bond based on relative electronegativity.

- Skill 2.3 Determine the dipole moment of a molecule based on molecular geometry and bond polarity.
- Skill 2.4 Identify the chemicals in a reaction as Brønsted-Lowry acids or bases, and conjugate acids and bases.
- Skill 2.5 Predict the products of an acid-base reaction.
- Skill 2.6 Use pKa values to predict the equilibrium direction of an acid-base reaction.
- Skill 2.7 Predict the relative strength of an organic acid by examining the stability of the conjugate base.
- Skill 2.8 Use molecular structure and analysis of intermolecular forces to rank a series of organic molecules with respect to physical properties like melting point and boiling point.
- Skill 2.9 Identify the chemicals in a reaction as Lewis acids or bases.

MEMORIZATION TASKS (MT)

MT 2.1 Memorize that the C-H bond is considered to be non-polar.

MT 2.2 Memorize the common bonding patterns for C, H, N, O and the halogens that have a zero formal charge.

MT 2.3 Memorize the factors that affect the relativity stability of conjugate bases.

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CHAPTER OVERVIEW

3: ORGANIC COMPOUNDS- ALKANES AND THEIR STEREOCHEMISTRY

LEARNING OBJECTIVES

After you have completed Chapter 3, you should be able to

1. fulfill the detailed objectives listed under each section.
2. identify some of the commonest functional groups.
3. write the structures and names of the first ten straight-chain alkanes.
4. recognize and name the simple alkyl substituents, and give the systematic names for branched-chain alkanes.
5. briefly describe some of the processes used during the refining of petroleum.
6. briefly describe the physical properties of alkanes.
7. draw a number of possible conformations of some simple alkanes and alkane-like compounds, and represent the energies of such conformations on energy versus rotation diagrams.
8. define, and use in context, the key terms introduced in this chapter.

This chapter begins with an introduction to the concept of the functional group, a concept that facilitates the systematic study of organic chemistry. Next, we introduce the fundamentals of organic nomenclature (i.e., the naming of organic chemicals) through examination of the alkane family of compounds. We then discuss, briefly, the occurrence and properties of alkanes, and end with a description of *cis-trans* isomerism in cycloalkanes.

3.0: Prelude
3.1: Functional Groups
3.2: Alkanes and Alkane Isomers
3.3: Alkyl Groups
3.4: Naming Alkanes
3.5: Properties of Alkanes
3.6: Conformations of Ethane
3.7: Conformations of Other Alkanes
3.8: Gasoline- A Deeper Look
3.S: Organic Compounds- Alkanes and Their Stereochemistry (Summary)

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3.0: Prelude

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3.1: FUNCTIONAL GROUPS

Objectives

After completing this section, you should be able to

1. explain why the properties of a given organic compound are largely dependent on the functional group or groups present in the compound.
2. identify the functional groups present in each of the following compound types: alkenes, alkynes, arenes, (alkyl and aryl) halides, alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, (carboxylic) acid chlorides, amides, amines, nitriles, nitro compounds, sulfides and sulfoxides.
3. identify the functional groups present in an organic compound, given its structure.
4. Given the structure of an organic compound containing a single functional group, identify which of the compound types listed under Objective 2, above, it belongs to.
5. draw the structure of a simple example of each of the compound types listed in Objective 2.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- functional group

STUDY NOTES

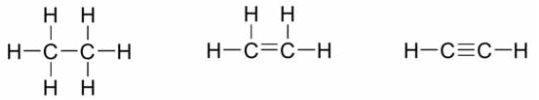
The concept of functional groups is a very important one. We expect that you will need to refer back to tables at the end of Section 3.1 quite frequently at first, as it is not really feasible to learn the names and structures of all the functional groups and compound types at one sitting. Gradually they will become familiar, and eventually you will recognize them automatically.

Functional groups are atoms or small groups of atoms (two to four) that exhibit a characteristic reactivity. A particular functional group will almost always display its characteristic chemical behavior when it is present in a compound. Because of their importance in understanding organic chemistry, functional groups have characteristic names that often carry over in the naming of individual compounds incorporating specific groups

As we progress in our study of organic chemistry, it will become extremely important to be able to quickly recognize the most common functional groups, because they are the key structural elements that define how organic molecules react. For now, we will only worry about drawing and recognizing each functional group, as depicted by Lewis and line structures. Much of the remainder of your study of organic chemistry will be taken up with learning about how the different functional groups tend to behave in organic reactions.

HYDROCARBONS AND HALIDES

We have already seen some examples of very common functional groups: ethene, for example, contains a carbon-carbon double bond. This double bond is referred to, in the functional group terminology, as an **alkene**.



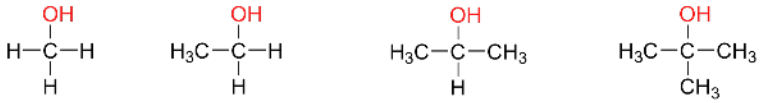
ethane (an alkane) | ethene (an alkene) | ethyne (an alkyne)

The carbon-carbon triple bond in ethyne is the simplest example of an **alkyne** function group.

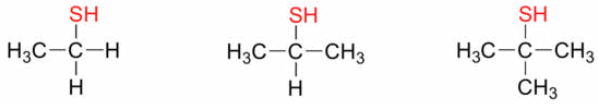
What about ethane? All we see in this molecule is carbon-hydrogen and carbon-carbon single bonds, so in a sense we can think of ethane as lacking a functional group entirely. However, we do have a general name for this ‘default’ carbon bonding pattern: molecules or parts of molecules containing only carbon-hydrogen and carbon-carbon single bonds are referred to as **alkanes**. If the carbon of an alkane is bonded to a halogen, the group is now referred to as a **haloalkane** (fluoroalkane, chloroalkane, etc.). Chloroform, $CHCl_3$, is an example of a simple haloalkane.

ALCOHOLS AND THIOLS

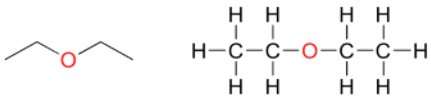
We have already seen the simplest possible example of an **alcohol** functional group in methanol. In the alcohol functional group, a carbon is single-bonded to an OH group (this OH group, by itself, is referred to as a **hydroxyl**). If the central carbon in an alcohol is bonded to only one other carbon, we call the group a primary alcohol. In secondary alcohols and tertiary alcohols, the central carbon is bonded to two and three carbons, respectively. Methanol, of course, is in class by itself in this respect.



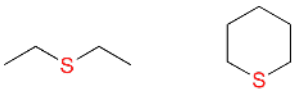
The sulfur analog of an alcohol is called a **thiol** (the prefix *thio*, derived from the Greek, refers to sulfur).



In an **ether** functional group, a central oxygen is bonded to two carbons. Below are the line and Lewis structures of diethyl ether, a common laboratory solvent and also one of the first medical anaesthesia agents.

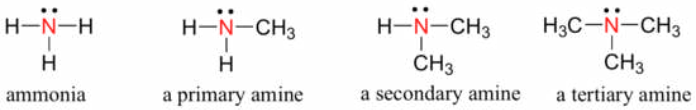


In **sulfides**, the oxygen atom of an ether has been replaced by a sulfur atom.

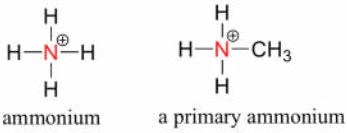


AMINES AND PHOSPHATES

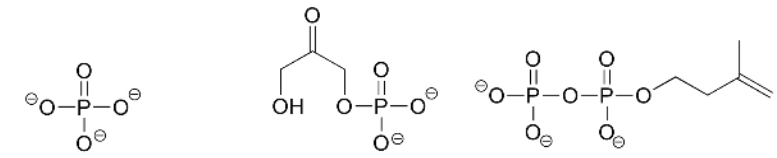
Ammonia is the simplest example of a functional group called **amines**. Just as there are primary, secondary, and tertiary alcohols, there are primary, secondary, and tertiary amines.



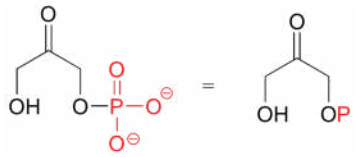
One of the most important properties of amines is that they are basic, and are readily protonated to form **ammonium** cations.

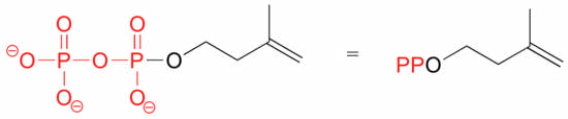


Phosphorus is a very important element in biological organic chemistry, and is found as the central atom in the **phosphate** group. Many biological organic molecules contain phosphate, diphosphate, and triphosphate groups, which are linked to a carbon atom by the **phosphate ester** functionality.



Because phosphates are so abundant in biological organic chemistry, it is convenient to depict them with the abbreviation 'P'. Notice that this 'P' abbreviation includes the oxygen atoms and negative charges associated with the phosphate groups.

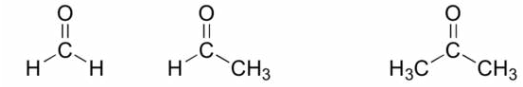




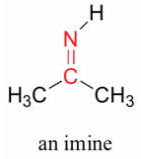
CARBONYL CONTAINING FUNCTIONAL GROUPS

ALDEHYDES AND KETONES

There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.



Molecules with carbon-nitrogen double bonds are called **imines**, or **Schiff bases**.

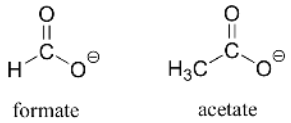


CARBOXYLIC ACIDS AND ACID DERIVATIVES

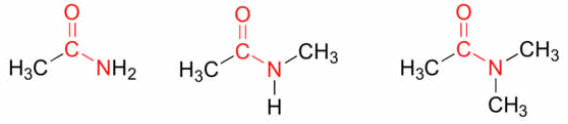
If a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to a **heteroatom** (in organic chemistry, this term generally refers to oxygen, nitrogen, sulfur, or one of the halogens), the functional group is considered to be one of the '**carboxylic acid derivatives'**, a designation that describes a grouping of several functional groups. The eponymous member of this grouping is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl (OH) group.



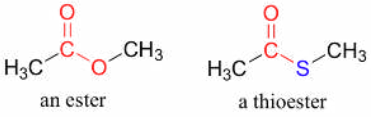
As the name implies, carboxylic acids are acidic, meaning that they are readily deprotonated to form the conjugate base form, called a **carboxylate** (much more about carboxylic acids in the acid-base chapter!).



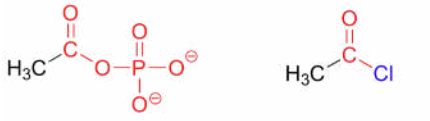
In **amides**, the carbonyl carbon is bonded to a nitrogen. The nitrogen in an amide can be bonded either to hydrogens, to carbons, or to both. Another way of thinking of an amide is that it is a carbonyl bonded to an amine.



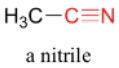
In **esters**, the carbonyl carbon is bonded to an oxygen which is itself bonded to another carbon. Another way of thinking of an ester is that it is a carbonyl bonded to an alcohol. **Thioesters** are similar to esters, except a sulfur is in place of the oxygen.



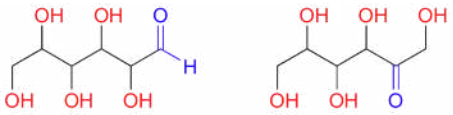
In an **acyl phosphate**, the carbonyl carbon is bonded to the oxygen of a phosphate, and in an **acid chloride**, the carbonyl carbon is bonded to a chlorine.



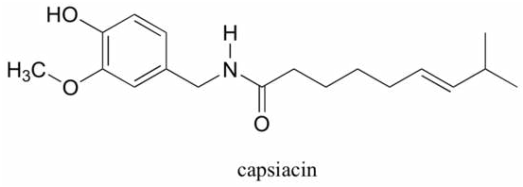
Finally, in a **nitrile** group, a carbon is triple-bonded to a nitrogen. Nitriles are also often referred to as **cyano** groups.



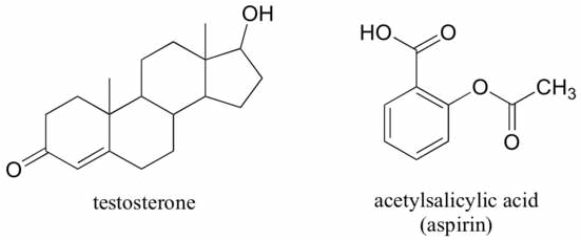
A single compound often contains several functional groups. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').



Capsaicin, the compound responsible for the heat in hot peppers, contains phenol, ether, amide, and alkene functional groups.



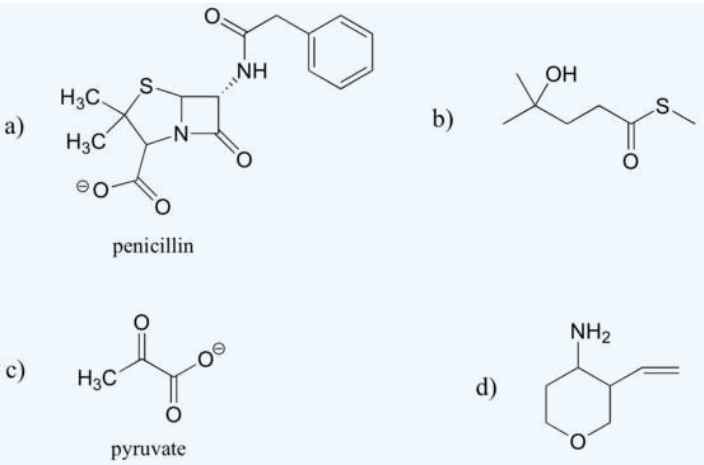
The male sex hormone testosterone contains ketone, alkene, and secondary alcohol groups, while acetylsalicylic acid (aspirin) contains aromatic, carboxylic acid, and ester groups.



While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological and laboratory organic chemistry. The table on the inside back cover provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

? EXERCISE 3.1.1

Identify the functional groups in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.



Answer

a) carboxylate, sulfide, aromatic, two amide groups (one of which is cyclic)

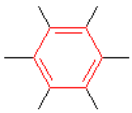
b) tertiary alcohol, thioester

c) carboxylate, ketone

d) ether, primary amine, alkene

FUNCTIONAL GROUP TABLES

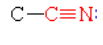
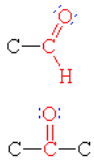
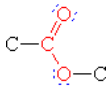
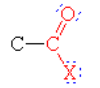
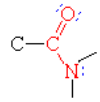
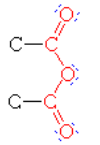
EXCLUSIVELY CARBON FUNCTIONAL GROUPS

Group Formula	Class Name	Specific Example	IUPAC Name	Common Name
	Alkene	$H_2C{=}CH_2$	Ethene	Ethylene
	Alkyne	$HC{\equiv}CH$	Ethyne	Acetylene
	Arene	C_6H_6	Benzene	Benzene

FUNCTIONAL GROUPS WITH SINGLE BONDS TO HETEROATOMS

Group Formula	Class Name	Specific Example	IUPAC Name	Common Name
	Halide	H_3C-I	Iodomethane	Methyl iodide
	Alcohol	CH_3CH_2OH	Ethanol	Ethyl alcohol
	Ether	$CH_3CH_2OCH_2CH_3$	Diethyl ether	Ether
	Amine	H_3C-NH_2	Aminomethane	Methylamine
	Nitro Compound	H_3C-NO_2	Nitromethane	
	Thiol	H_3C-SH	Methanethiol	Methyl mercaptan
	Sulfide	H_3C-S-CH_3	Dimethyl sulfid	

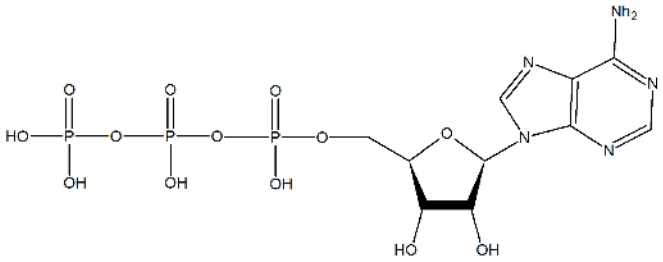
FUNCTIONAL GROUPS WITH MULTIPLE BONDS TO HETEROATOMS

Group Formula	Class Name	Specific Example	IUPAC Name	Common Name
	Nitrile	H_3C-CN	Ethanenitrile	Acetonitrile
	Aldehyde	H_3CCHO	Ethanal	Acetaldehyde
	Ketone	H_3CCOCH_3	Propanone	Acetone
	Carboxylic Acid	H_3CCO_2H	Ethanoic Acid	Acetic acid
	Ester	$H_3CCO_2CH_2CH_3$	Ethyl ethanoate	Ethyl acetate
	Acid Halide	H_3CCOCl	Ethanoyl chloride	Acetyl chloride
	Amide	$H_3CCON(CH_3)_2$	N,N-Dimethylethanamide	N,N-Dimethylacetamide
	Acid Anhydride	$(H_3CCO)_2O$	Ethanoic anhydride	Acetic anhydride

QUESTIONS

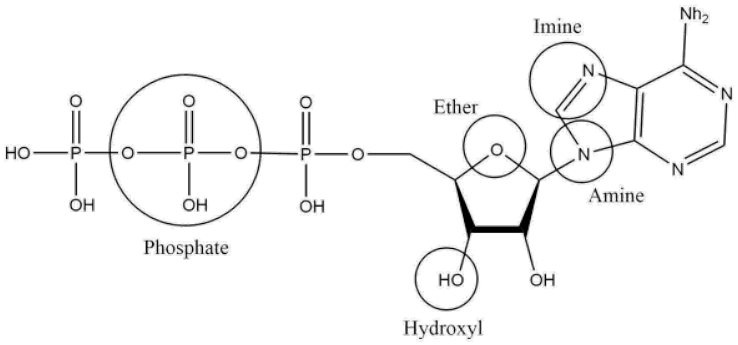
Q3.1.1

The following is the molecule for ATP, or the molecule responsible for energy in human cells. Identify the functional groups for ATP.



SOLUTIONS

S3.1.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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3.2: ALKANES AND ALKANE ISOMERS

Objectives

After completing this section, you should be able to

1. draw the Kekulé structure, condensed structure and shorthand structure of each of the first ten straight-chain alkanes.
2. name each of the first ten straight-chain alkanes, given its molecular formula, Kekulé structure, condensed structure or shorthand structure.
3. explain the difference in structure between a straight- and a branched-chain alkane, and illustrate the difference using a suitable example.
4. explain why the number of possible isomers for a given molecular formula increases as the number of carbon atoms increases.
5. draw all the possible isomers that correspond to a given molecular formula of the type $C_n H_{2n+2}$, where n is ≤ 7.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- branched-chain alkane
- constitutional or structural isomer
- homologous series
- isomer
- saturated hydrocarbon
- straight-chain alkane (or normal alkane)

STUDY NOTES

A series of compounds in which successive members differ from one another by a CH_2 unit is called a homologous series. Thus, the series CH_4, C_2H_6, C_3H_8 . . . C_nH_{2n+2}, is an example of a homologous series.

It is important that you commit to memory the names of the first 10 straight-chain alkanes (i.e., from CH_4 to $C_{10}H_{22}$). You will use these names repeatedly when you begin to learn how to derive the systematic names of a large variety of organic compounds. You need not remember the number of isomers possible for alkanes containing more than seven carbon atoms. Such information is available in reference books when it is needed. When drawing isomers, be careful not to deceive yourself into thinking that you can draw more isomers than you are supposed to be able to. Remember that it is possible to draw each isomer in several different ways and you may inadvertently count the same isomer more than once.

Alkanes are organic compounds that consist entirely of single-bonded carbon and hydrogen atoms and lack any other functional groups. Alkanes have the general formula C_nH_{2n+2} and can be subdivided into the following three groups: the linear straight-chain alkanes, branched alkanes, and cycloalkanes. Alkanes are also saturated hydrocarbons.

Cycloalkanes are cyclic hydrocarbons, meaning that the carbons of the molecule are arranged in the form of a ring. Cycloalkanes are also saturated, meaning that all of the carbons atoms that make up the ring are single bonded to other atoms (no double or triple bonds). There are also polycyclic alkanes, which are molecules that contain two or more cycloalkanes that are joined, forming multiple rings.

This is an introductory page about alkanes, such as methane, ethane, propane, butane and the remainder of the common alkanes. This page addresses their formulae and isomerism, their physical properties, and an introduction to their chemical reactivity.

MOLECULAR FORMULAS

Alkanes are the simplest family of hydrocarbons - compounds containing carbon and hydrogen only. Alkanes only contain carbon-hydrogen bonds and carbon-carbon single bonds. The first six alkanes are as follows:

methane	CH_4
ethane	C_2H_6
propane	C_3H_8
butane	C_4H_{10}
pentane	C_5H_{12}
hexane	C_6H_{14}

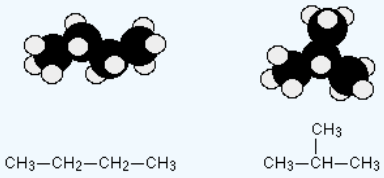
You can work out the formula of any of the alkanes using the general formula C_nH_{2n+2}

ISOMERISM

All of the alkanes containing 4 or more carbon atoms show structural isomerism, meaning that there are two or more different structural formulae that you can draw for each molecular formula.

EXAMPLE: BUTANE OR METHYLPROPANE

C_4H_{10} could be either of these two different molecules:



These are named butane and 2-methylpropane, respectively

WHAT IS STRUCTURAL ISOMERISM?

Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. That excludes any different arrangements which are simply due to the molecule rotating as a whole, or rotating about particular bonds. For example, both of the following are the same molecule. They are not isomers; both are butane.

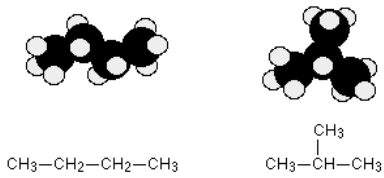


There are also endless other possible ways that this molecule could twist itself. There is completely free rotation around all the carbon-carbon single bonds. If you had a model of a molecule in front of you, you would have to take it to pieces and rebuild it if you wanted to make an isomer of that molecule. If you can make an apparently different molecule just by rotating single bonds, it's not different - it's still the same molecule.

In structural isomerism, the atoms are arranged in a completely different order. This is easier to see with specific examples. What follows looks at some of the ways that structural isomers can arise. The names of the various forms of structural isomerism probably do not matter all that much, but you must be aware of the different possibilities when you come to draw isomers.

CHAIN ISOMERISM

These isomers arise because of the possibility of branching in carbon chains. For example, there are two isomers of butane, C_4H_{10}. In one of them, the carbon atoms lie in a "straight chain" whereas in the other the chain is branched.



Be careful not to draw "false" isomers which are just twisted versions of the original molecule. For example, this structure is just the straight chain version of butane rotated about the central carbon-carbon bond.

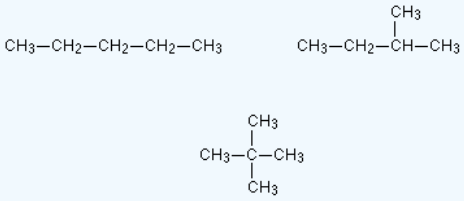


You could easily see this with a model. This is the example we've already used at the top of this page.



EXAMPLE 1: CHAIN ISOMERS IN PENTANE

Pentane, C_5H_{12}, has three chain isomers. If you think you can find any others, they are simply twisted versions of the ones below. If in doubt make some models.



Examples of Simple Unbranched Alkanes

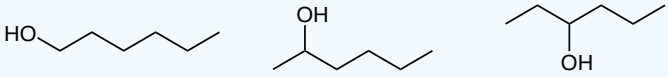
Name	Molecular Formula	Structural Formula	Isomers		Name	Molecular Formula	Structural Formula	Isomers
methane	CH_4	CH_4	1		hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
ethane	C_2H_6	CH_3CH_3	1		heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
propane	C_3H_8	$CH_3CH_2CH_3$	1		octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2		nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3		decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

EXERCISES

EXERCISE 3.2.1

Draw all of the isomers for $C_6H_{14}O$ that contain a 6 carbon chain and an alcohol (-OH) functional group.

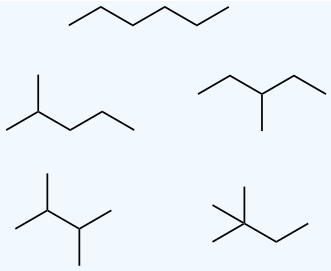
Answer



EXERCISE 3.2.2

Draw all possible isomers for C_6H_{14} (There are five total).

Answer



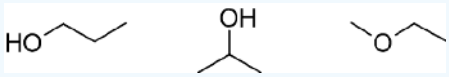
The top structure is when it is a 6 carbon chain. The middle row contains the 5 carbon chained isomers with branching at the 2nd and 3rd carbon. The bottom row contains the two 4 carbon chain isomers that can be drawn.

EXERCISE 3.2.3

Draw all possible isomers for C_3H_8O.

Answer

The first structure is when an alcohol comes off the first carbon. The second structure is when the alcohol is coming off the central carbon. The third structure is the only possible ether form of C_3H_8O.

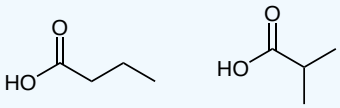


EXERCISE 3.2.4

Draw all possible isomers for $C_4H_8O_2$ that contain a carboxylic acid.

Answer

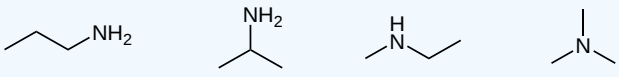
There are only 2 possibilities.



EXERCISE 3.2.5

Draw all possible isomers for C_3H_9N and indicate whether each amine is primary, secondary, or tertiary.

Answer

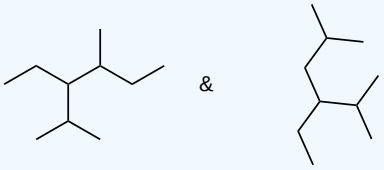


The first and second structures are primary amines. The third structure is a secondary amine. The last structure is a tertiary amine.

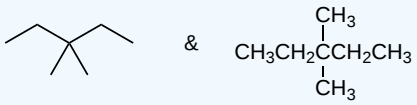
EXERCISE 3.2.6

Indicate whether each of the following sets are constitutional isomers, the same compound, or different compounds.

a)



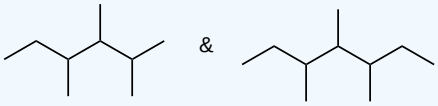
b)



c)



d)



Answer

a) Both structures have formulas of $C_{10}H_{22}$ and have different connectivity which makes these **constitutional isomers**.

b) Both structures have formulas of C_7H_{16} and have the same connectivity which makes these the **same compound**.

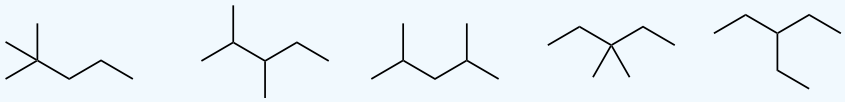
c) Both structure have formulas of C_7H_{16} and have different connectivity which makes these **constitutional isomers**.

d) The structure on the left has a formula of C_9H_{20} and the structure on the right has a formula of $C_{10}H_{22}$ so these are **different compounds**.

? EXERCISE 3.2.7

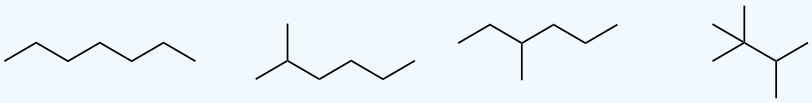
Draw the 5 constitutional isomers of C_7H_{16} (of the 9 total isomers possible) that have 5 carbons as the longest carbon chain length.

Answer



The 5 constitutional isomers with a 5 carbon chain length are shown above. Since there needs to be 7 carbons total, the 2 extra carbons are added as substituents. From left to right, the methyl group substitution pattern is 2,2, 2,3, 2,4, and 3,3, and the last one (on right) has a 3-ethyl substituent.

The other 4 possible constitutional isomers (with different length carbon chains) are shown below.



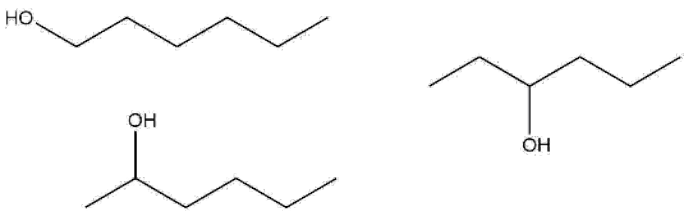
QUESTIONS

Q3.2.1

Give all the isomers for a straight chain hexanol.

SOLUTIONS

S3.2.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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3.3: ALKYL GROUPS

OBJECTIVES

After completing this section, you should be able to

1. recognize and name any alkyl group that can be considered to have been formed by the removal of a terminal hydrogen atom from a straight-chain alkane containing ten or fewer carbon atoms.
2. explain what is meant by a primary, secondary, tertiary or quaternary carbon atom.
3. represent the various types of organic compounds using the symbol “R” to represent any alkyl group.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- alkyl group
- methyl group
- primary carbon
- quaternary carbon
- secondary carbon
- tertiary carbon

STUDY NOTES

The differences among primary, secondary, tertiary and quaternary carbon atoms are explained in the following discussion. A convenient way of memorizing this classification scheme is to remember that a primary carbon atom is attached directly to only one other carbon atom, a secondary carbon atom is attached directly to two carbon atoms, and so on.

The **IUPAC** system requires first that we have names for simple unbranched chains, as noted above, and second that we have names for simple alkyl groups that may be attached to the chains. Examples of some common **alkyl groups** are given in the following table. Note that the "ane" suffix is replaced by "**yl**" in naming groups. The symbol **R** is used to designate a generic (unspecified) alkyl group.

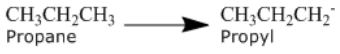
Table **3.3.1**: Alkyl Group names

Group	CH_3–	C_2H_5–	$CH_3CH_2CH_2$–	$(CH_3)_2CH$–	$CH_3CH_2CH_2CH_2$–	$(CH_3)_2CHCH_2$–	$CH_3CH_2CH(CH_3)$–	$(CH_3)_3C$–	R–
Name	Methyl	Ethyl	Propyl	Isopropyl	Butyl	Isobutyl	sec-Butyl	tert-Butyl	Alkyl

ALKYL GROUPS EDIT SECTION

Alkanes can be described by the general formula C_nH_{2n+2}. An alkyl group is formed by removing one hydrogen from the alkane chain and is described by the formula C_nH_{2n+1}. The removal of this hydrogen results in a stem change from **-ane** to **-yl**. Take a look at the following examples.





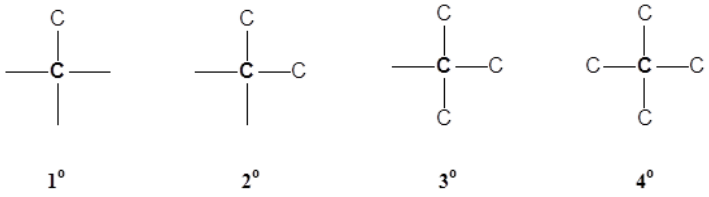
The same concept can be applied to any of the straight chain alkane names provided in Table **3.3.2**.

Table **3.3.2**: straight chain alkane

Name	Molecular Formula	Condensed Structural Formula
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3CH_3
Propane	C_3H_8	$CH_3CH_2CH_3$
Butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$
Undecane	$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$
Dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$
Tridecane	$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$
Tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
Pentadecane	$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$
Hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
Heptadecane	$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$
Octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
Nonadecane	$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$
Eicosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$

CLASSIFICATION OF CARBON ATOMS

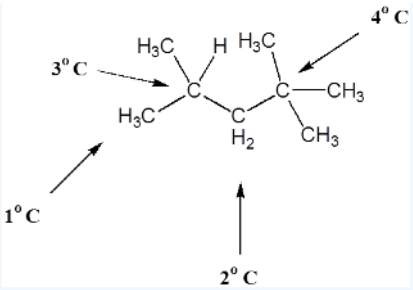
Carbons have a special terminology to describe how many other carbons they are attached to.



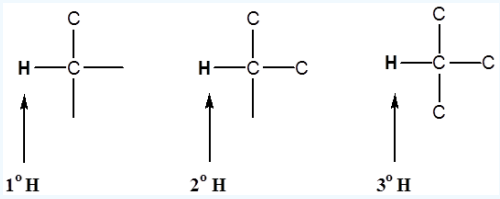
- Primary carbons (1°) attached to one other C atom
- Secondary carbons (2°) are attached to two other C's
- Tertiary carbons (3°) are attached to three other C's
- Quaternary carbons (4°) are attached to four C's

✔ EXAMPLE 3.3.1

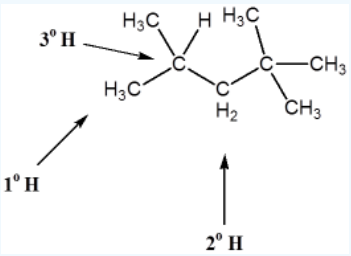
You will find that hydrogen atoms are also classified in this manner. A hydrogen atom attached to a primary carbon atom is called a primary hydrogen; thus, isobutane, has fifteen primary hydrogens and one tertiary hydrogen.



- Primary hydrogens (1°) are attached to carbons bonded to one other C atom
- Secondary hydrogens (2°) are attached to carbons bonded to two other C's
- Tertiary hydrogens (3°) are attached to carbons bonded to three other C's



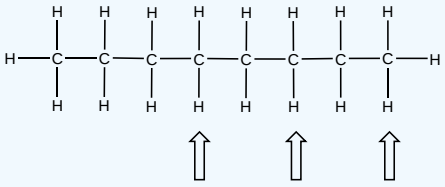
EXAMPLE 3.3.2



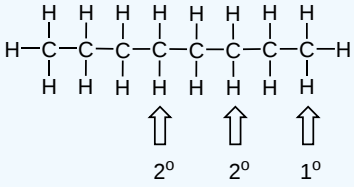
EXERCISES

EXERCISE 3.3.1

Determine whether the H's indicated in the following structure are 1°, 2°, or 3°.



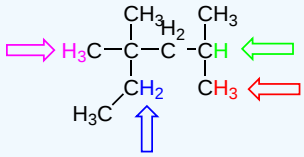
Answer



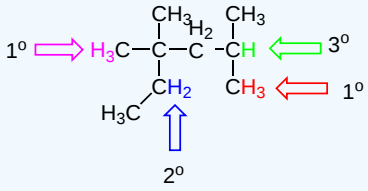
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EXERCISE 3.3.2

Determine whether the H's indicated in the following structure is 1°, 2°, or 3°.

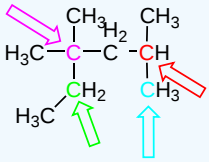


Answer

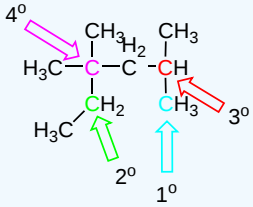


EXERCISE 3.3.3

Determine whether the carbons indicated in the structure below are 1°, 2°, 3°, or 4°.

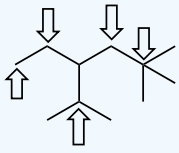


Answer

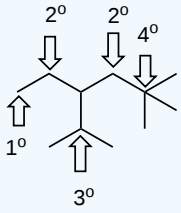


EXERCISE 3.3.4

Determine whether the carbons indicated in the structure below are 1°, 2°, 3°, or 4°.

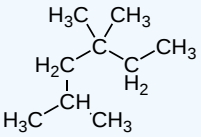


Answer



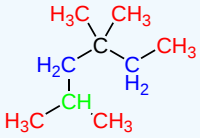
EXERCISE 3.3.5

Please indicate the total number of each type 1°, 2°, 3°, and 4° carbons in the following molecule.



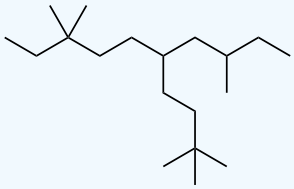
Answer

There are 5 primary (1°) C's, 2 secondary (2°) C's, 1 tertiary (3°) C and 1 quaternary (4°) C in the structure (seen color coded below).



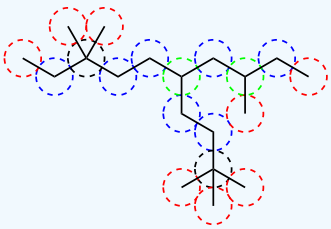
EXERCISE 3.3.6

Please indicate the total number of each type 1°, 2°, 3°, and 4° carbons in the following molecule.



Answer

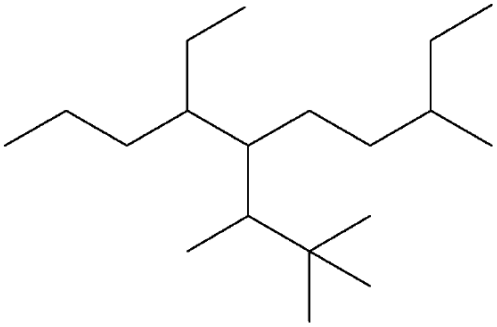
There are 8 primary (1°) C's, 7 secondary (2°) C's, 2 tertiary (3°) C's and 2 quaternary (4°) C's in the structure (seen color coded below).



QUESTIONS

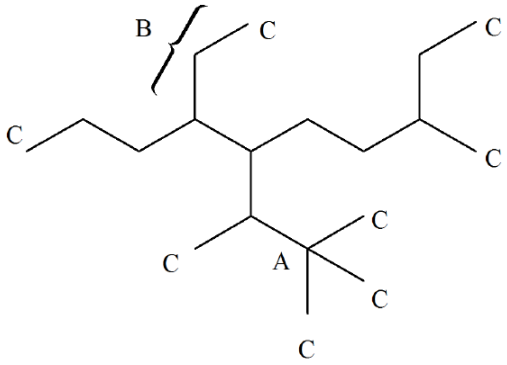
Q3.3.1

Consider the following molecule. How many carbons are in the longest chain? Find a primary and quaternary carbon, and label an ethyl group.



SOLUTIONS

S3.3.1



A = 4° Carbon

B = Ethyl Group

C = 1° Carbon

The longest chain is 10 carbons long

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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3.4: NAMING ALKANES

Objectives

After completing this section, you should be able to

1. provide the correct IUPAC name for any given alkane structure (Kekulé, condensed or shorthand).
2. draw the Kekulé, condensed or shorthand structure of an alkane, given its IUPAC name.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- IUPAC system

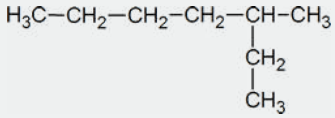
STUDY NOTES

The IUPAC system of nomenclature aims to ensure

1. that every organic compound has a unique, unambiguous name.
2. that the IUPAC name of any compound conveys the structure of that compound to a person familiar with the system.

One way of checking whether the name you have given to an alkane is reasonable is to count the number of carbon atoms implied by the chosen name. For example, if you named a compound 3-ethyl-4-methylheptane, you have indicated that the compound contains a total of 10 carbon atoms—seven carbon atoms in the main chain, two carbon atoms in an ethyl group, and one carbon atom in a methyl group. If you were to check the given structure and find 11 carbon atoms, you would know that you had made a mistake. Perhaps the name you should have written was 3-ethyl-4,4-dimethylheptane!

When naming alkanes, a common error of beginning students is a failure to pick out the longest carbon chain. For example, the correct name for the compound shown below is 3-methylheptane, not 2-ethylhexane.



Remember that every substituent must have a number, and do not forget the prefixes: di, tri, tetra, etc.

You must use commas to separate numbers, and hyphens to separate numbers and substituents. Notice that 3-methylhexane is one word.

Hydrocarbons having no double or triple bond functional groups are classified as **alkanes** or **cycloalkanes**, depending on whether the carbon atoms of the molecule are arranged only in chains or also in rings. Although these hydrocarbons have no functional groups, they constitute the framework on which functional groups are located in other classes of compounds, and provide an ideal starting point for studying and naming organic compounds. The alkanes and cycloalkanes are also members of a larger class of compounds referred to as **aliphatic**. Simply put, aliphatic compounds are compounds that do not incorporate any aromatic rings in their molecular structure.

The following table lists the IUPAC names assigned to simple continuous-chain alkanes from C-1 to C-10. A common "**ane**" suffix identifies these compounds as alkanes. Longer chain alkanes are well known, and their names may be found in many reference and text books. The names **methane** through **decane** should be memorized, since they constitute the root of many IUPAC names. Fortunately, common numerical prefixes are used in naming chains of five or more carbon atoms.

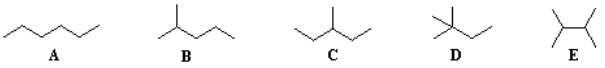
Table **3.4.1**: Simple Unbranched Alkanes

Name	Molecular Formula	Structural Formula	Isomers	Name	Molecular Formula	Structural Formula	Isomers
meth**ane**	CH_4	CH_4	1	hex**ane**	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
eth**ane**	C_2H_6	CH_3CH_3	1	hept**ane**	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
prop**ane**	C_3H_8	$CH_3CH_2CH_3$	1	oct**ane**	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
but**ane**	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2	non**ane**	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
pent**ane**	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3	dec**ane**	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

SOME IMPORTANT BEHAVIOR TRENDS AND TERMINOLOGIES

1. The formulas and structures of these alkanes increase uniformly by a CH_2 increment.
2. A uniform variation of this kind in a series of compounds is called **homologous**.
3. These formulas all fit the $\mathbf{C_nH_{2n+2}}$ rule. This is also the highest possible H/C ratio for a stable hydrocarbon.
4. Since the H/C ratio in these compounds is at a maximum, we call them **saturated** (with hydrogen).

Beginning with butane (C_4H_{10}), and becoming more numerous with larger alkanes, we note the existence of alkane isomers. For example, there are five C_6H_{14} isomers, shown below as abbreviated line formulas (**A** through **E**):



Although these distinct compounds all have the same molecular formula, only one (**A**) can be called hexane. How then are we to name the others?

The **IUPAC** system requires first that we have names for simple unbranched chains, as noted above, and second that we have names for simple alkyl groups that may be attached to the chains. Examples of some common **alkyl groups** are given in the following table. Note that the "ane" suffix is replaced by "**yl**" in naming groups. The symbol **R** is used to designate a generic (unspecified) alkyl group.

Table **3.4.2**: Alkyl Groups Names

Group	CH_3–	C_2H_5–	$CH_3CH_2CH_2$–	$(CH_3)_2CH$–	$CH_3CH_2CH_2CH_2$–	$(CH_3)_2CHCH_2$–	$CH_3CH_2CH(CH_3)$–	$(CH_3)_3C$–	R–
Name	Methyl	Ethyl	Propyl	Isopropyl	Butyl	Isobutyl	sec-Butyl	tert-Butyl	Alkyl

Halogen substituents are easily accommodated, using the names: fluoro (F-), chloro (Cl-), bromo (Br-) and iodo (I-).

IUPAC RULES FOR ALKANE NOMENCLATURE

1. Find and name the longest continuous carbon chain.
2. Identify and name groups attached to this chain.
3. Number the chain consecutively, starting at the end nearest a substituent group.
4. Designate the location of each substituent group by an appropriate number and name.
5. Assemble the name, listing groups in alphabetical order.
6. The prefixes di, tri, tetra etc., used to designate several groups of the same kind, are not considered when alphabetizing.

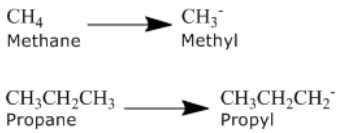
EXAMPLE 3.4.1: HALOGEN SUBSTITUTION

For example, $(CH_3)_2CHCH_2CH_2Br$ would be named 1-bromo-3-methylbutane. If the halogen is bonded to a simple alkyl group an alternative "alkyl halide" name may be used. Thus, C_2H_5Cl may be named chloroethane (no locator number is needed for a two carbon chain) or ethyl chloride.

For the above isomers of hexane the IUPAC names are: **B** 2-methylpentane **C** 3-methylpentane **D** 2,2-dimethylbutane **E** 2,3-dimethylbutane

ALKYL GROUPS

Alkanes can be described by the general formula C_nH_{2n+2}. An alkyl group is formed by removing one hydrogen from the alkane chain and is described by the formula C_nH_{2n+1}. The removal of this hydrogen results in a stem change from **-ane** to **-yl**. Take a look at the following examples.



The same concept can be applied to any of the straight chain alkane names provided in the table above.

Table **3.4.3**: Alkyl Groups Names

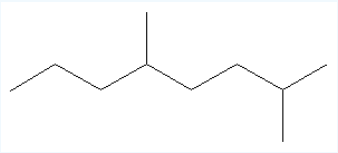
Name	Molecular Formula	Condensed Structural Formula
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3CH_3
Propane	C_3H_8	$CH_3CH_2CH_3$
Butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$
Pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$
Hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$
Heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$
Octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$
Nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$
Decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$
Undecane	$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$
Dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$
Tridecane	$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$
Tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
Pentadecane	$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$
Hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
Heptadecane	$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$
Octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
Nonadecane	$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$
Eicosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$

THREE RULES OF NAMING ALKANES

1. Choose the longest, most substituted carbon chain containing a functional group.
2. A carbon bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number.
3. Take the alphabetical order into consideration; that is, after applying the first two rules given above, make sure that your substitutes and/or functional groups are written in alphabetical order.

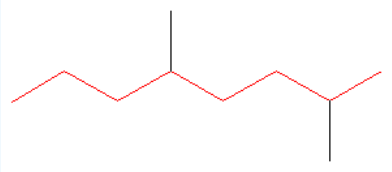
✔ EXAMPLE 3.4.2

What is the name of the follow molecule?

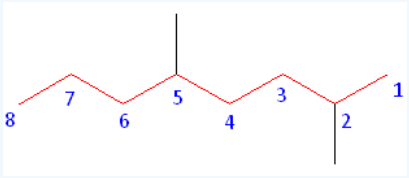


Solution

Rule #1: Choose the longest, most substituted carbon chain containing a functional group. This example does not contain any functional groups, so we only need to be concerned with choosing the longest, most substituted carbon chain. The longest carbon chain has been highlighted in red and consists of eight carbons.



Rule #2: Carbons bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number. Because this example does not contain any functional groups, we only need to be concerned with the two substitutes present, that is, the two methyl groups. If we begin numbering the chain from the left, the methyls would be assigned the numbers 4 and 7, respectively. If we begin numbering the chain from the right, the methyls would be assigned the numbers 2 and 5. Therefore, to satisfy the second rule, numbering begins on the right side of the carbon chain as shown below. This gives the methyl groups the lowest possible numbering.

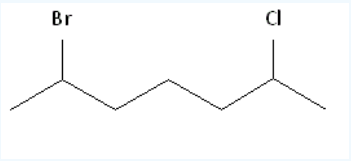


Rule 3: In this example, there is no need to utilize the third rule. Because the two substitutes are identical, neither takes alphabetical precedence with respect to numbering the carbons. This concept will become clearer in the following examples.

The name of this molecule is thus: **2,5-dimethyloctane**

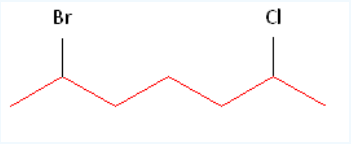
EXAMPLE 3.4.3:

What is the name of the follow molecule?

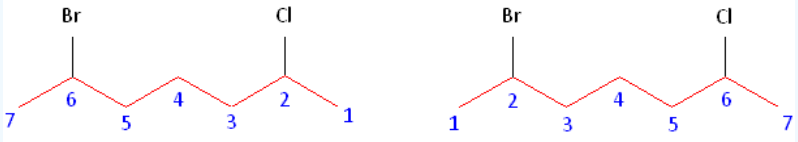


Solution

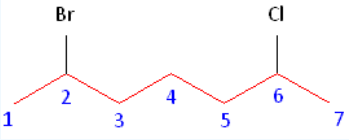
Rule #1: Choose the longest, most substituted carbon chain containing a functional group. This example contains two functional groups, bromine and chlorine. The longest carbon chain has been highlighted in red and consists of seven carbons.



Rule #2: Carbons bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substitute present must have the lowest possible number. In this example, numbering the chain from the left or the right would satisfy this rule. If we number the chain from the left, bromine and chlorine would be assigned the second and sixth carbon positions, respectively. If we number the chain from the right, chlorine would be assigned the second position and bromine would be assigned the sixth position. In other words, whether we choose to number from the left or right, the functional groups occupy the second and sixth positions in the chain. To select the correct numbering scheme, we need to utilize the third rule.



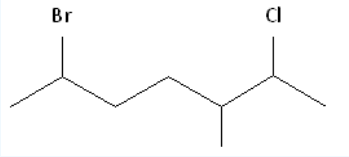
Rule #3: After applying the first two rules, take the alphabetical order into consideration. Alphabetically, bromine comes before chlorine. Therefore, bromine is assigned the second carbon position, and chlorine is assigned the sixth carbon position.



The name of this molecule is thus: **2-bromo-6-chloroheptane**

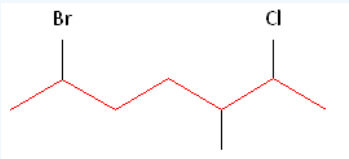
EXAMPLE 3.4.4

What is the name of the follow molecule?

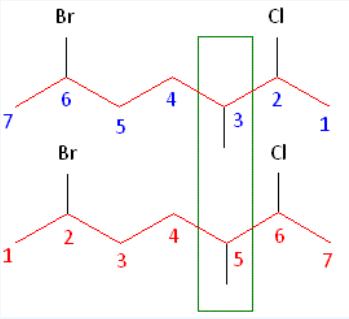


Solution

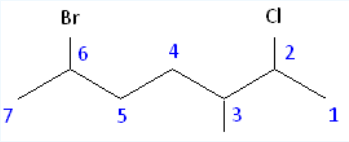
Rule #1: Choose the longest, most substituted carbon chain containing a functional group. This example contains two functional groups, bromine and chlorine, and one substitute, the methyl group. The longest carbon chain has been highlighted in red and consists of seven carbons.



Rule #2: Carbons bonded to a functional group must have the lowest possible carbon number. After taking functional groups into consideration, any substitutes present must have the lowest possible carbon number. This particular example illustrates the **point of difference principle**. If we number the chain from the left, bromine, the methyl group and chlorine would occupy the second, fifth and sixth positions, respectively. This concept is illustrated in the second drawing below. If we number the chain from the right, chlorine, the methyl group and bromine would occupy the second, third and sixth positions, respectively, which is illustrated in the first drawing below. The position of the methyl, therefore, becomes a **point of difference**. In the first drawing, the methyl occupies the third position. In the second drawing, the methyl occupies the fifth position. To satisfy the second rule, we want to choose the numbering scheme that provides the lowest possible numbering of this substitute. Therefore, the first of the two carbon chains shown below is correct.



Therefore, the first numbering scheme is the appropriate one to use.



Once you have determined the correct numbering of the carbons, it is often useful to make a list, including the functional groups, substitutes, and the name of the parent chain.

Rule #3: After applying the first two rules, take the alphabetical order into consideration. Alphabetically, bromine comes before chlorine. Therefore, bromine is assigned the second carbon position, and chlorine is assigned the sixth carbon position.

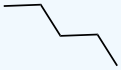
Parent chain: heptane 2-Chloro 3-Methyl 6-Bromo

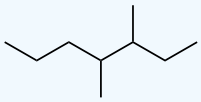
The name of this molecule is thus: **6-bromo-2-chloro-3-methylheptane**

EXERCISES

? EXERCISE 3.4.1

Give the proper IUPAC names of the following compounds.

a) 

b) 

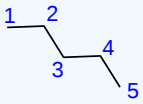
c) 

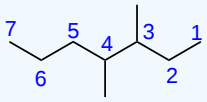
Answer

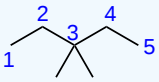
a) Since this structure is an unbranched alkane (all single bonds) with a 5 carbon chain length, its name would be **pentane**.

b) This alkane has a 7 carbon longest continuous chain length that we number from right to left to get the first methyl substituent we encounter to have the lowest possible number (3 versus being 4 if numbering from left to right). This causes it to have 2 methyl substituents at positions 3 & 4 so we would name it indicating those numbers and the prefix dimethyl which gives a proper IUPAC name of **3,4-dimethylheptane**.

c) This alkane has a 5 carbon longest continuous chain length (which could be numbered from left to right or right to left due to the symmetry at C-3). It has two methyl substituents off of C-3 so the proper IUPAC name is **3,3-dimethylpentane.**

a) 

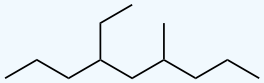
b) 

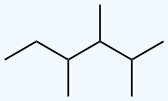
c) 

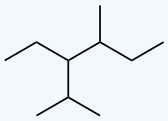
? EXERCISE 3.4.2

Give the proper IUPAC names of the following compounds.

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a) 

b) 

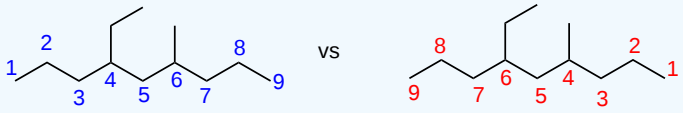
c) 

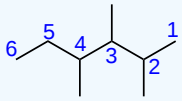
Answer

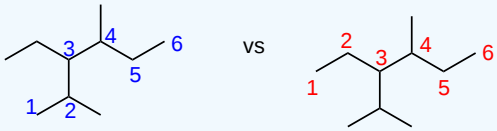
a) This alkane has a 9 carbon longest continuous chain length that we number from left to right (structure on left numbered in blue) to make the ethyl substituent be number 4. For the structure on the right (numbered in red) going from right to left, the methyl substituent is number 4. Since ethyl is higher in the alphabetical order, you want to make it have the lower number so the structure on the left (blue numbering) takes priority and the name is **4-ethyl-6-methylnonane**.

b) This alkane has a 6 carbon longest continuous chain length that we number from right to left to make the first methyl be C-2 (versus the opposite direction which would make the first methyl C-3). Since there are 3 methyl substituents at positions 2,3, & 4, this compound would have the name **2,3,4-trimethylhexane**.

c) This 6 carbon alkane can be numbered along different chains (see below) as well as in the opposite directions. This shows the two different chains that can be drawn (making the first substituent in that chain the lowest number). The structure on the left (numbered in blue) is the correct choice since it causes more substituents to be on the longest continuous chain (3 vs 2 in the structure on the right). This would make the IUPAC name of the structure **3-ethyl-2,4-dimethylhexane**. (Notice how ethyl takes priority over methyl and the di- is not considered for alphabetizing.)

a) 

b) 

c) 

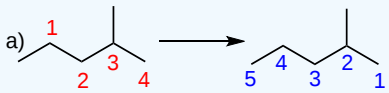
EXERCISE 3.4.3

All of the following names represent a compound that has been named improperly. Draw out the structure from the name and give the proper IUPAC name for the compounds.

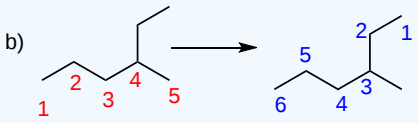
a. 1,3-dimethylbutane
b. 4-ethylpentane
c. 2-ethyl-3-methylpentane

Answer

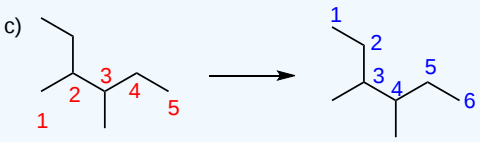
a) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right), the correct name should be **2-methylpentane**.



b) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right), notice that the longest chain is 6 C's and we start the numbering on the end to the right to make the methyl substituent come off at C-3 (instead of beong at C-4 if we numbered it the opposite direction) the correct name should be **3-methyl hexane**.



c) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right), notice that the longest chain is 6 C's and since this molecule is symmetrical (between carbon 3 & 4), you can start the numbers from either end. In this case, we have methyl substituents coming off of carbons 3 & 4 so the proper name is **3,4-dimethyl hexane**.



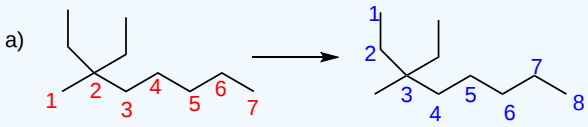
EXERCISE 3.4.4

All of the following names represent a compound that has been named improperly. Draw out the structure from the name and give the proper IUPAC name for the compounds.

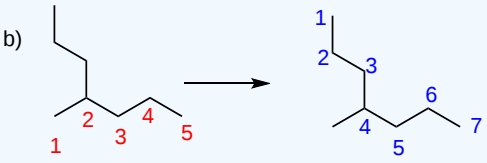
a. 2,2-diethylheptane
b. 2-propylpentane
c. 4,4-diethylbutane

Answer

a) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right), notice that the longest chain is now 8 C's and you have an ethyl substituent at C-3 and a methyl substituent also at C-3 so the proper name is **3- ethyl-3-methyloctane**.

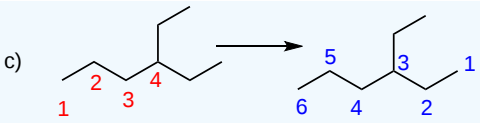


b) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right), notice that the longest chain is now 7 C's and since this molecule is symmetrical (at carbon 4), you can start the numbers from either end. There is a methyl substituent at C-4 so the proper name is **4-methylheptane**.



c) The structure that can be drawn for the improper name is shown below on the left. When you renumber it properly (structure on the right) going from right to left (to make the ethyl substituent have the lowest number possible), the correct name is **3-ethylhexane**

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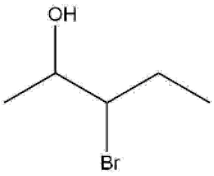


3.4 EXERCISES

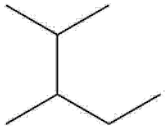
QUESTIONS

Q3.4.1

Are the following structures properly named, and if they are not, what is the correct naming?



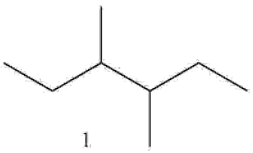
3-bromo-4-hydroxypentane



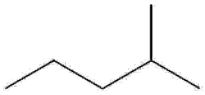
2-isopropylbutane

Q3.4.2

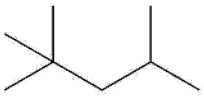
Give the name of the following molecules:



1



2



3

SOLUTIONS

S3.4.1

They are both labeled incorrectly:

3-bromo-2-hydroxypentane

2, 3-dimethylpentane

S3.4.2

1 = 3,4-Dimethyl hexane

2 = 2-methyl pentane

3 = 2,2,4-trimethyl pentane

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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3.5: PROPERTIES OF ALKANES

Objectives

After completing this section, you should be able to

1. arrange a number of given straight-chain alkanes in order of increasing or decreasing boiling point or melting point.
2. arrange a series of isomeric alkanes in order of increasing or decreasing boiling point.
3. explain the difference in boiling points between a given number of alkanes.

KEY TERMS

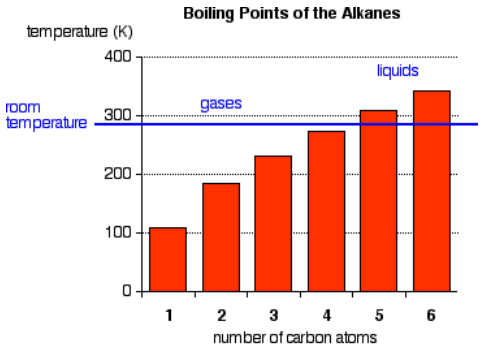
Make certain that you can define, and use in context, the key term below.

- van der Waals force

Alkanes are not very reactive and have little biological activity; all alkanes are colorless and odorless.

BOILING POINTS

The boiling points shown are for the "straight chain" isomers of which there is more than one. The first four alkanes are gases at room temperature, and solids do not begin to appear until about $C_{17}H_{36}$, but this is imprecise because different isomers typically have different melting and boiling points. By the time you get 17 carbons into an alkane, there are unbelievable numbers of isomers!



Cycloalkanes have boiling points that are approximately 20 K higher than the corresponding straight chain alkane.

There is not a significant electronegativity difference between carbon and hydrogen, thus, there is not any significant bond polarity. The molecules themselves also have very little polarity. A totally symmetrical molecule like methane is completely non-polar, meaning that the only attractions between one molecule and its neighbors will be Van der Waals dispersion forces. These forces will be very small for a molecule like methane but will increase as the molecules get bigger. Therefore, the boiling points of the alkanes increase with molecular size.

Where you have isomers, the more branched the chain, the lower the boiling point tends to be. Van der Waals dispersion forces are smaller for shorter molecules and only operate over very short distances between one molecule and its neighbors. It is more difficult for short, fat molecules (with lots of branching) to lie as close together as long, thin molecules.

EXAMPLE 3.5.1: BOILING POINTS OF ALKANES

For example, the boiling points of the three isomers of C_5H_{12} are:

- pentane: 309.2 K
- 2-methylbutane: 301.0 K
- 2,2-dimethylpropane: 282.6 K

The slightly higher boiling points for the cycloalkanes are presumably because the molecules can get closer together because the ring structure makes them tidier and less "wriggly"!

? EXERCISE 3.5.1

For each of the following pairs of compounds, select the substance you expect to have the higher boiling point.

a. octane and nonane.
b. octane and 2,2,3,3-tetramethylbutane.

Answer

Nonane will have a higher boiling point than octane, because it has a longer carbon chain than octane. Octane will have a higher boiling point than 2,2,3,3-tetramethylbutane, because it branches less than 2,2,3,3-tetramethylbutane, and therefore has a larger "surface area" and more van der Waals forces.

Note: The actual boiling points are

nonane, 150.8°C
octane, 125.7°C
2,2,3,3-tetramethylbutane, 106.5°C

SOLUBILITY

Alkanes are virtually insoluble in water, but dissolve in organic solvents. However, liquid alkanes are good solvents for many other non-ionic organic compounds.

SOLUBILITY IN WATER

When a molecular substance dissolves in water, the following must occur:

- break the intermolecular forces within the substance. In the case of the alkanes, these are the Van der Waals dispersion forces.
- break the intermolecular forces in the water so that the substance can fit between the water molecules. In water, the primary intermolecular attractions are hydrogen bonds.

Breaking either of these attractions requires energy, although the amount of energy to break the Van der Waals dispersion forces in something like methane is relatively negligible; this is not true of the hydrogen bonds in water.

As something of a simplification, a substance will dissolve if there is enough energy released when new bonds are made between the substance and the water to compensate for what is used in breaking the original attractions. The only new attractions between the alkane and the water molecules are Van der Waals forces. These forces do not release a sufficient amount of energy to compensate for the energy required to break the hydrogen bonds in water. The alkane does not dissolve.

NOTE

This is a simplification because entropic effects are important when things dissolve.

SOLUBILITY IN ORGANIC SOLVENTS

In most organic solvents, the primary forces of attraction between the solvent molecules are Van der Waals - either dispersion forces or dipole-dipole attractions. Therefore, when an alkane dissolves in an organic solvent, the Van der Waals forces are broken and are replaced by new Van der Waals forces. The two processes more or less cancel each other out energetically; thus, there is no barrier to solubility.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Jim Clark (Chemguide.co.uk)

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3.6: CONFORMATIONS OF ETHANE

OBJECTIVES

After completing this section, you should be able to

1. explain the concept of free rotation about a carbon-carbon single bond.
2. explain the difference between conformational isomerism and the other types of isomerism which you have encountered.
3. represent the conformers of ethane by both sawhorse representation and Newman projection.
4. sketch a graph of energy versus bond rotation for ethane, and discuss the graph in terms of torsional strain.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- conformation (conformer, conformational isomer)
- eclipsed conformation
- Newman projection
- sawhorse representation
- staggered conformation
- strain energy
- torsional strain (eclipsing strain)

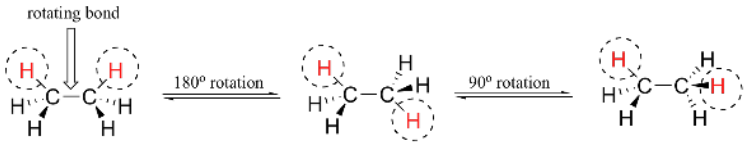
STUDY NOTES

You should be prepared to sketch various conformers using both sawhorse representations and Newman projections. Each method has its own advantages, depending upon the circumstances. Notice that when drawing the Newman projection of the eclipsed conformation of ethane, you cannot draw the rear hydrogens exactly behind the front ones. This is an inherent limitation associated with representing a 3-D structure in two dimensions.

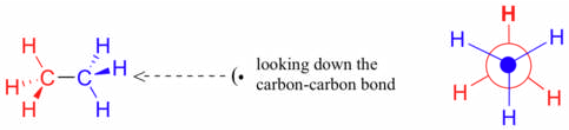
Conformational isomerism involves rotation about sigma bonds, and does not involve any differences in the connectivity or geometry of bonding. Two or more structures that are categorized as conformational isomers, or **conformers**, are really just two of the exact same molecule that differ only in terms of the angle about one or more sigma bonds.

ETHANE CONFORMATIONS

Although there are seven sigma bonds in the ethane molecule, rotation about the six carbon-hydrogen bonds does not result in any change in the shape of the molecule because the hydrogen atoms are essentially spherical. Rotation about the carbon-carbon bond, however, results in many different possible molecular conformations.



In order to better visualize these different conformations, it is convenient to use a drawing convention called the **Newman projection**. In a Newman projection, we look lengthwise down a specific bond of interest – in this case, the carbon-carbon bond in ethane. We depict the 'front' atom as a dot, and the 'back' atom as a larger circle.



'staggered' conformation
(Newman projection)

The six carbon-hydrogen bonds are shown as solid lines protruding from the two carbons at 120°angles, which is what the actual tetrahedral geometry looks like when viewed from this perspective and flattened into two dimensions.

The lowest energy conformation of ethane, shown in the figure above, is called the ‘staggered’ conformation, in which all of the C-H bonds on the front carbon are positioned at dihedral angles of 60°relative to the C-H bonds on the back carbon. In this conformation, the distance between the bonds (and the electrons in them) is maximized.

If we now rotate the front CH_3 group 60° clockwise, the molecule is in the highest energy ‘eclipsed' conformation, where the hydrogens on the front carbon are as close as possible to the hydrogens on the back carbon.



'eclipsed' conformation

This is the highest energy conformation because of unfavorable interactions between the electrons in the front and back C-H bonds. The energy of the eclipsed conformation is approximately 3 kcal/mol higher than that of the staggered conformation. Another 60°rotation returns the molecule to a second staggared conformation. This process can be continued all around the 360°circle, with three possible eclipsed conformations and three staggered conformations, in addition to an infinite number of variations in between.

FREE ROTATIONS DO NOT EXIST IN ETHANE

The carbon-carbon bond is not *completely* free to rotate – there is indeed a small, 3 kcal/mol barrier to rotation that must be overcome for the bond to rotate from one staggered conformation to another. This rotational barrier is not high enough to prevent constant rotation except at extremely cold temperatures. However, at any given moment the molecule is more likely to be in a staggered conformation - one of the rotational ‘energy valleys’ - than in any other state. The potential energy associated with the various conformations of ethane varies with the dihedral angle of the bonds, as shown below.

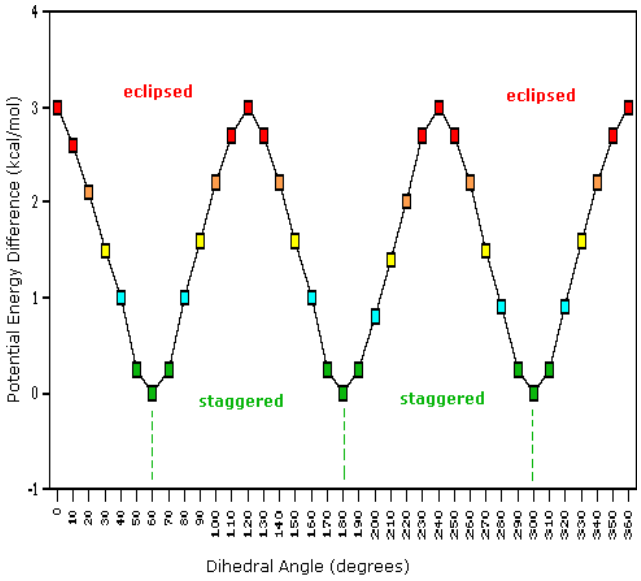


***Figure 3.6.X**: The potential energy associated with the various conformations of ethane varies with the dihedral angle of the bonds.*

Although the conformers of ethane are in rapid equilibrium with each other, the 3 kcal/mol energy difference leads to a substantial preponderance of staggered conformers (> 99.9%) at any given time. The animation below illustrates the relationship between ethane's potential energy and its dihedral angle

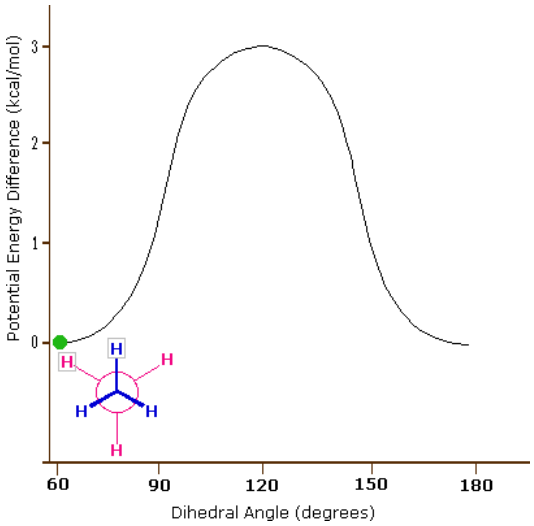


***Figure 3.6.X**: Animation of potential energy vs. dihedral angle in ethane*

EXERCISE

? EXERCISE 3.6.1

What is the most stable rotational conformation of ethane and explain why it is preferred over the other conformation?

Answer

Staggered, as there is less repulsion between the hydrogen atoms.

QUESTIONS

Q3.6.1

What is the most stable rotational conformation of ethane and explain why it is preferred over the other conformation?

SOLUTIONS

S3.6.1

Staggered, as there is less repulsion between the hydrogen atoms.

CONTRIBUTORS AND ATTRIBUTIONS

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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3.7: CONFORMATIONS OF OTHER ALKANES

OBJECTIVES

After completing this section, you should be able to

1. depict the staggered and eclipsed conformers of propane (or a similar compound) using sawhorse representations and Newman projections.
2. sketch a graph of energy versus bond rotation for propane (or a similar compound) and discuss the graph in terms of torsional strain.
3. depict the anti, gauche, eclipsed and fully eclipsed conformers of butane (or a similar compound), using sawhorse representations and Newman projections.
4. sketch a graph of energy versus ($C2-C3$) bond rotation for butane (or a similar compound), and discuss it in terms of torsional and steric repulsion.
5. assess which of two (or more) conformers of a given compound is likely to predominate at room temperature from a semi-quantitative knowledge of the energy costs of the interactions involved.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- anti conformation
- gauche conformation
- eclipsed conformation
- steric repulsion

In butane, there are now three rotating carbon-carbon bonds to consider, but we will focus on the middle bond between C_2 and C_3. Below are two representations of butane in a conformation which puts the two CH_3 groups (C_1 and C_4) in the eclipsed position.

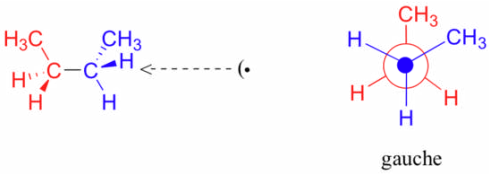


eclipsed (A)

This is the highest energy conformation for butane, due to what is called '**van der Waals repulsion**', or '**steric repulsion'**, between the two rather bulky methyl groups.

What is van der Waals repulsion? Didn't we just learn in Chapter 2 that the van der Waals force between two nonpolar groups is an *attractive* force? Consider this: you probably like to be near your friends, but no matter how close you are you probably don't want to share a one-room apartment with five of them. When the two methyl groups are brought too close together, the overall resulting noncovalent interaction is repulsive rather than attractive. The result is that their respective electron densities repel one another.

If we rotate the front, (blue) carbon by 60°clockwise, the butane molecule is now in a staggered conformation.



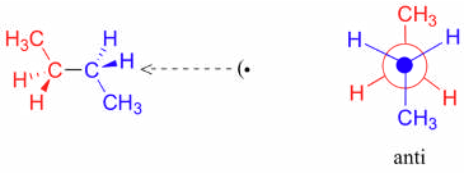
gauche

This is more specifically referred to as the '**gauche'** conformation of butane. Notice that although they are staggered, the two methyl groups are not as far apart as they could possibly be. There is still significant steric repulsion between the two bulky groups. A further rotation of 60°gives us a second eclipsed conformation (B) in which both methyl groups are lined up with hydrogen atoms.



Due to steric repulsion between methyl and hydrogen substituents, this eclipsed conformation B is higher in energy than the gauche conformation. However, because there is no methyl-to-methyl eclipsing, it is lower in energy than eclipsed conformation A.

One more 60 rotation produces the 'anti' conformation, where the two methyl groups are positioned opposite each other and steric repulsion is minimized.



This is the lowest energy conformation for butane.

The diagram below summarizes the relative energies for the various eclipsed, staggered, and gauche conformations.

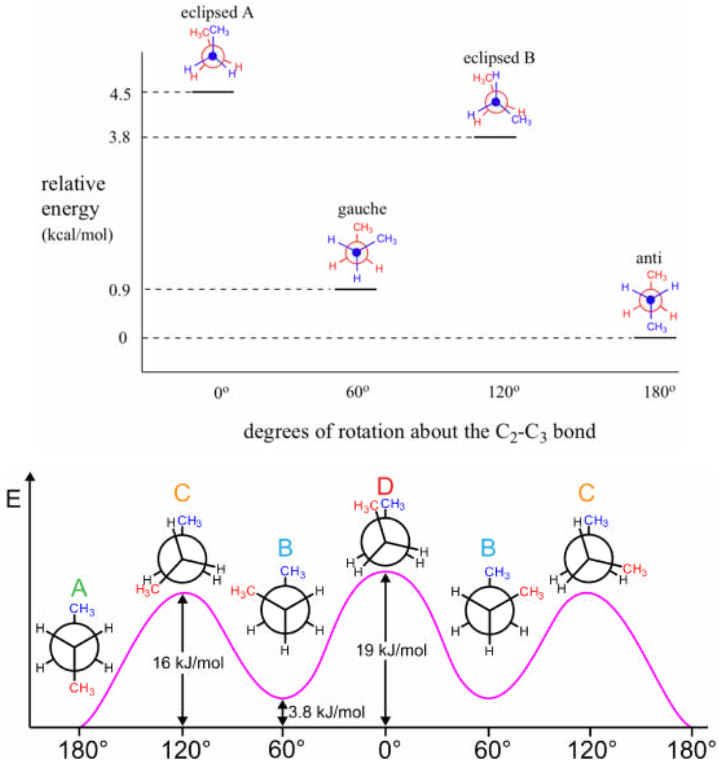
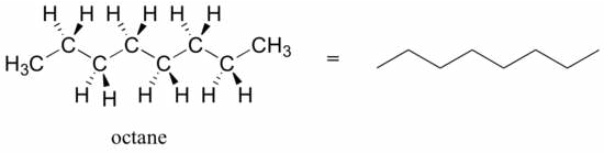


Figure \PageIndex1: Newman projections of butane conformations & their relative energy differences (not total energies). Conformations form when butane rotates about one of its single covalent bond. Torsional/dihedral angle is shown on x-axis. Torsional/dihedral angle is shown on x-axis. Conformation names (according to IUPAC): **A**: anti-periplanar, anti or trans **B**: synclinal or gauche **C**: anticlinal or eclipsed **D**: syn-periplanar or cis. Source for conformation names & conformer classification: Pure & Appl. Chem., Vol. 68, No. 12, pp. 2193-2222, 1996. (Public Domain; Keministi).

At room temperature, butane is most likely to be in the lowest-energy anti conformation at any given moment in time, although the energy barrier between the anti and eclipsed conformations is not high enough to prevent constant rotation except at very low temperatures. For this reason (and also simply for ease of drawing), it is conventional to draw straight-chain alkanes in a zigzag form, which implies anti conformation at all carbon-carbon bonds.



octane

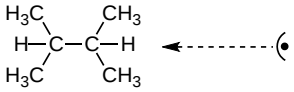
DRAWING NEWMAN PROJECTIONS

Newman projections are a valuable method for viewing the relative positions of groups within molecule. Being able to draw the Newman projection for a given molecule is a valuable skill and will be used repeatedly throughout organic chemistry. Because organic molecules often contain multiple carbon-carbon bonds it is important to precisely know which bond and which direction is being sighted for the Newman projection. The details of the Newman projection change given the molecule but for typical alkanes a full conformational analysis involves a full 360° rotation in 60° increments. This will produce three staggered conformers and three eclipsed conformers. Typically, the staggered conformers are more stable and the eclipsed conformers are less stable. The least stable conformer will have the largest groups eclipsed while the most stable conformer will have the largest groups anti (180°) to each other.

EXAMPLE

Draw the Newman projection of 2,3 dimethylbutane along the C_2-C_3 bond. Then determine the least stable conformation.

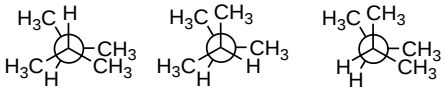
First draw the molecule and locate the indicated bond:



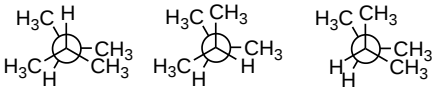
Because the question asks for the least stable conformation, focus on the three possible eclipsed Newman projections. Draw out three eclipsed Newman projections as a template. Because it is difficult to draw a true staggered Newman projection, it is common to show the bonds slightly askew.



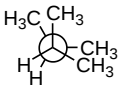
Place the substituents attached to the second carbon (C_3) on the back bonds of all three Newman projections. In this example they are 2 CH_3s and an H. Place the substituents in the same position on all three Newman projections.



Then place the substituents attached to the first carbon (C_2) on the front bonds of the Newman projection. In this example, the substituents are also 2 CH_3s and an H. Move the substituents through two 60° rotations to create the remaining two eclipsed Newman projections. Leave the substituents on the back carbon in place. Attempting to rotate the front and back carbons simultaneously is a common mistake and often leads to incorrect Newman projections.



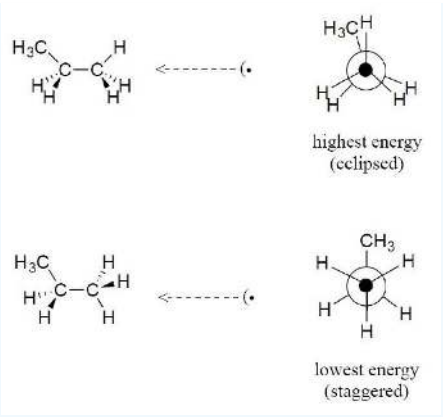
Compare the Newman projections by looking the eclipsed interactions. Remember that the order of torsional strain interactions are CH_3-CH_3 > CH_3-H > H-H. The third structure has two CH_3-CH_3 torsional interactions which will make it the least stable conformer of 2,3 dimethyl butane.



✔ EXAMPLE 3.7.1

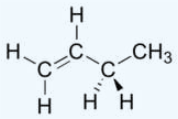
Draw Newman projections of the eclipsed and staggered conformations of propane.

Answer

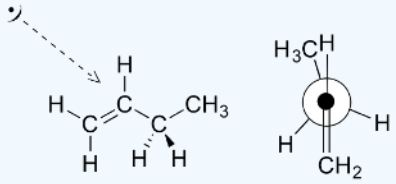


EXAMPLE 3.7.2

Draw a Newman projection, looking down the C_2-C_3 bond, of 1-butene in the conformation shown below.



Answer



QUESTIONS

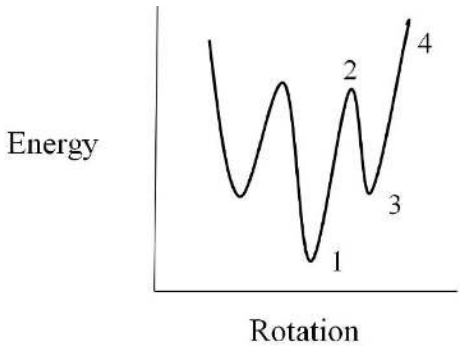
Q3.7.1

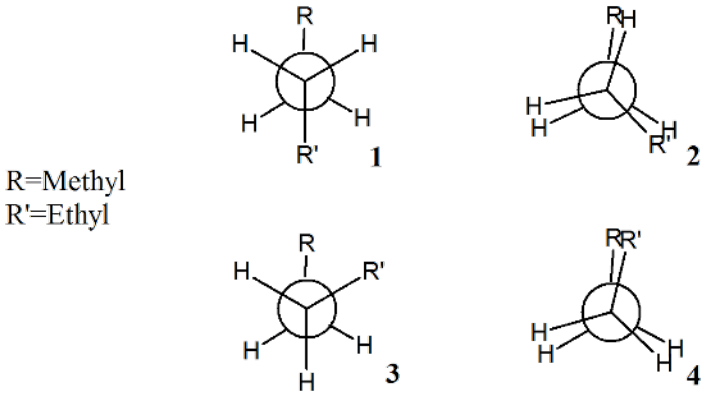
Draw the energy diagram for the rotation of the bond highlighted in pentane.



SOLUTIONS

S3.7.1





CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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3.8: GASOLINE- A DEEPER LOOK

OBJECTIVES

After completing this section, you should be able to

1. describe the general nature of petroleum deposits, and recognize why petroleum is such an important source of organic compounds.
2. explain, in general terms, the processes involved in the refining of petroleum.
3. define the octane number of a fuel, and relate octane number to chemical structure.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- catalytic cracking
- catalytic reforming
- fractional distillation
- octane number (octane rating)

STUDY NOTES

The refining of petroleum into usable fractions is a very important industrial process. In the laboratory component of this course, you will have the opportunity to compare this industrial process to the procedure as it is performed in the laboratory.

PETROLEUM

The petroleum that is pumped out of the ground at locations around the world is a complex mixture of several thousand organic compounds, including straight-chain alkanes, cycloalkanes, alkenes, and aromatic hydrocarbons with four to several hundred carbon atoms. The identities and relative abundances of the components vary depending on the source. So Texas crude oil is somewhat different from Saudi Arabian crude oil. In fact, the analysis of petroleum from different deposits can produce a “fingerprint” of each, which is useful in tracking down the sources of spilled crude oil. For example, Texas crude oil is “sweet,” meaning that it contains a small amount of sulfur-containing molecules, whereas Saudi Arabian crude oil is “sour,” meaning that it contains a relatively large amount of sulfur-containing molecules.

GASOLINE

Petroleum is converted to useful products such as gasoline in three steps: distillation, cracking, and reforming. Recall from Chapter 1 that distillation separates compounds on the basis of their relative volatility, which is usually inversely proportional to their boiling points. Part (a) in Figure 3.8.1 shows a cutaway drawing of a column used in the petroleum industry for separating the components of crude oil. The petroleum is heated to approximately 400°C (750°F), at which temperature it has become a mixture of liquid and vapor. This mixture, called the feedstock, is introduced into the refining tower. The most volatile components (those with the lowest boiling points) condense at the top of the column where it is cooler, while the less volatile components condense nearer the bottom. Some materials are so nonvolatile that they collect at the bottom without evaporating at all. Thus the composition of the liquid condensing at each level is different. These different fractions, each of which usually consists of a mixture of compounds with similar numbers of carbon atoms, are drawn off separately. Part (b) in Figure 3.8.1 shows the typical fractions collected at refineries, the number of carbon atoms they contain, their boiling points, and their ultimate uses. These products range from gases used in natural and bottled gas to liquids used in fuels and lubricants to gummy solids used as tar on roads and roofs.

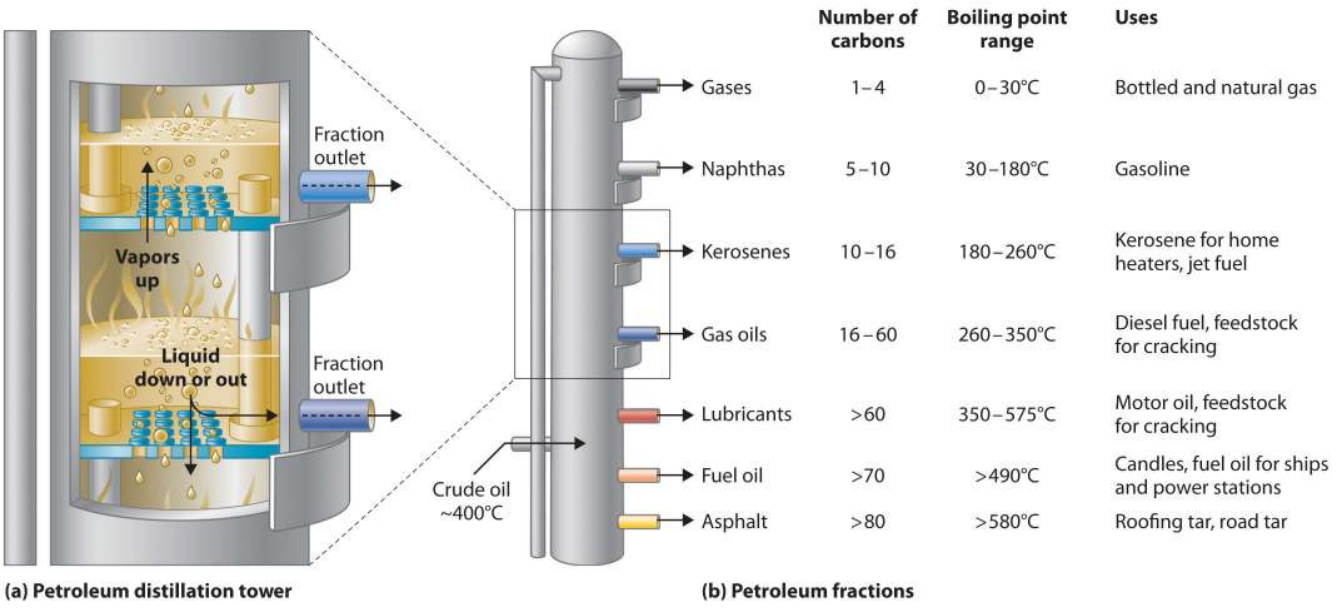


Figure 3.8.1: *The Distillation of Petroleum. (a) This is a diagram of a distillation column used for separating petroleum fractions. (b) Petroleum fractions condense at different temperatures, depending on the number of carbon atoms in the molecules, and are drawn off from the column. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom.*

The economics of petroleum refining are complex. For example, the market demand for kerosene and lubricants is much lower than the demand for gasoline, yet all three fractions are obtained from the distillation column in comparable amounts. Furthermore, most gasolines and jet fuels are blends with very carefully controlled compositions that cannot vary as their original feedstocks did. To make petroleum refining more profitable, the less volatile, lower-value fractions must be converted to more volatile, higher-value mixtures that have carefully controlled formulas. The first process used to accomplish this transformation is cracking, in which the larger and heavier hydrocarbons in the kerosene and higher-boiling-point fractions are heated to temperatures as high as 900°C. High-temperature reactions cause the carbon–carbon bonds to break, which converts the compounds to lighter molecules similar to those in the gasoline fraction. Thus in cracking, a straight-chain alkane with a number of carbon atoms corresponding to the kerosene fraction is converted to a mixture of hydrocarbons with a number of carbon atoms corresponding to the lighter gasoline fraction. The second process used to increase the amount of valuable products is called reforming; it is the chemical conversion of straight-chain alkanes to either branched-chain alkanes or mixtures of aromatic hydrocarbons. Using metals such as platinum brings about the necessary chemical reactions. The mixtures of products obtained from cracking and reforming are separated by fractional distillation.

OCTANE RATINGS

The quality of a fuel is indicated by its octane rating, which is a measure of its ability to burn in a combustion engine without knocking or pinging. Knocking and pinging signal premature combustion (Figure 3.8.2), which can be caused either by an engine malfunction or by a fuel that burns too fast. In either case, the gasoline-air mixture detonates at the wrong point in the engine cycle, which reduces the power output and can damage valves, pistons, bearings, and other engine components. The various gasoline formulations are designed to provide the mix of hydrocarbons least likely to cause knocking or pinging in a given type of engine performing at a particular level.

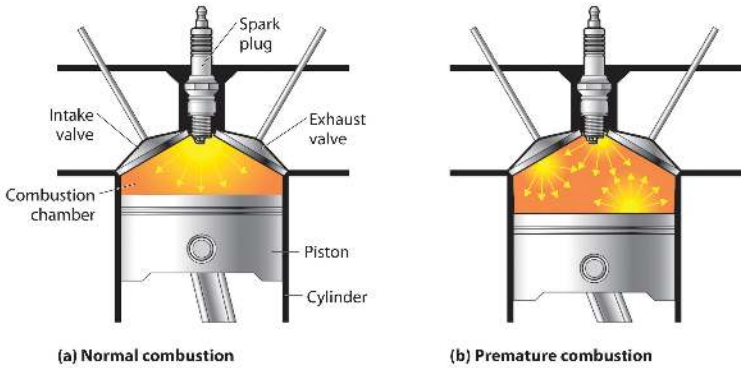


***Figure 3.8.2**: The Burning of Gasoline in an Internal Combustion Engine. (a) Normally, fuel is ignited by the spark plug, and combustion spreads uniformly outward. (b) Gasoline with an octane rating that is too low for the engine can ignite prematurely, resulting in uneven burning that causes knocking and pinging.*

The octane scale was established in 1927 using a standard test engine and two pure compounds: n-heptane and isooctane (2,2,4-trimethylpentane). n-Heptane, which causes a great deal of knocking on combustion, was assigned an octane rating of 0, whereas isooctane, a very smooth-burning fuel, was assigned an octane rating of 100. Chemists assign octane ratings to different blends of gasoline by burning a sample of each in a test engine and comparing the observed knocking with the amount of knocking caused by specific mixtures of n-heptane and isooctane. For example, the octane rating of a blend of 89% isooctane and 11% n-heptane is simply the average of the octane ratings of the components weighted by the relative amounts of each in the blend. Converting percentages to decimals, we obtain the octane rating of the mixture:

$$0.89(100) + 0.11(0) = 89 \tag{3.8.1}$$

As shown in Figure 3.8.3, many compounds that are now available have octane ratings greater than 100, which means they are better fuels than pure isooctane. In addition, antiknock agents, also called octane enhancers, have been developed. One of the most widely used for many years was tetraethyllead [$(C_2H_5)_4Pb$], which at approximately 3 g/gal gives a 10–15-point increase in octane rating. Since 1975, however, lead compounds have been phased out as gasoline additives because they are highly toxic. Other enhancers, such as methyl t-butyl ether (MTBE), have been developed to take their place. They combine a high octane rating with minimal corrosion to engine and fuel system parts. Unfortunately, when gasoline containing MTBE leaks from underground storage tanks, the result has been contamination of the groundwater in some locations, resulting in limitations or outright bans on the use of MTBE in certain areas. As a result, the use of alternative octane enhancers such as ethanol, which can be obtained from renewable resources such as corn, sugar cane, and, eventually, corn stalks and grasses, is increasing.

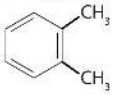
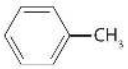
Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
n-heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	0	*o*-xylene		107
n-hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	25	ethanol	CH_3CH_2OH	108
n-pentane	$CH_3CH_2CH_2CH_2CH_3$	62	*t*-butyl alcohol	$(CH_3)_3COH$	113
isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	100	*p*-xylene		116
benzene		106	methyl *t*-butyl ether	$H_3COC(CH_3)_3$	116
methanol	CH_3OH	107	toluene		118

***Figure 3.8.3**: The Octane Ratings of Some Hydrocarbons and Common Additives*

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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3.S: ORGANIC COMPOUNDS- ALKANES AND THEIR STEREOCHEMISTRY (SUMMARY)

CONCEPTS & VOCABULARY

3.1: Functional Groups

- **Functional groups** are atoms or small groups of atoms (two to four) that exhibit a characteristic reactivity.
- Functional groups have characteristic names that often carry over into the naming of compounds.
- The most common organic functional groups that will be encountered is this course are: alkanes, alkenes, alkynes, arenes, (alkyl and aryl) halides, alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, acid chlorides, amides, amines, nitriles, nitro compounds, sulfides and sulfoxides.

3.2: Alkanes and Alkane Isomers

- Hydrocarbons are a common class of organic molecules that contain only carbon and hydrogen atoms.
- Alkanes are one type of hydrocarbon that contains only carbon-carbon and carbon hydrogen single bonds.
- Straight chain and branched alkanes have the generic formula C_nH_{2n+2}, where *n* is equal to the number of carbons. Cycloalkanes have the generic formula C_nH_{2n}.
- Structural isomers are molecules with the same molecular formula, but different structures.

3.3: Alkyl Groups

- Alkyl groups are small hydrocarbon chains attached to the parent alkane chain. The names of alkyl groups use the same prefixes to indicate the number of carbons (meth-, eth-, etc.), but use "-yl" as the ending, instead of "-ane".

3.4: Naming Alkanes

- The IUPAC System of nomenclature provides a set of rules for assigning every molecule a unique name.

3.5: Properties of Alkanes

- The boiling point of an alkane depends upon molecular weight and number of branches in the chain. Boiling points tend to increase with increasing molecular weight. Boiling points tend to decrease within a set of isomers as the number of branches increases.
- Alkanes and cycloalkanes are generally more soluble in organic solvents than in water.

3.6: Conformations of Ethane

- Rotation about the carbon-carbon sigma bonds in ethane results in different **rotational isomers** (also known as **conformational isomers** or **conformers**). **Newman projections** are a very common way of depicting conformers.
- The two most common conformers of ethane are called **staggered** and **eclipsed**. The staggered conformer is lower in energy (more stable) than the eclipsed conformer, because it has less **torsional strain**.

3.7: Conformations of Other Alkanes

- Alkanes more complex than ethane, will have a greater variety of possible conformers. The **anti** and **gauche** conformers of butane are specific types of staggered conformations.

3.8: Gasoline - A Deeper Look

SKILLS TO MASTER

- Skill 3.1 Identify the following functional groups that are present in a given organic molecule: alkanes, alkenes, alkynes, arenes, (alkyl and aryl) halides, alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, acid chlorides, amides, amines, nitriles, and nitro compounds.
- Skill 3.2 Name and draw structures of straight chain alkanes up to ten carbons in length.
- Skill 3.3 Name and draw structures for all the structural isomers of a given molecular formula.
- Skill 3.4 Identify methyl, primary, secondary, tertiary, and quaternary carbons in organic structures.
- Skill 3.5 Provide the IUPAC name of any given alkane or cycloalkane structure.
- Skill 3.6 Draw the structure of an alkane or cycloalkane given its IUPAC name.
- Skill 3.7 Arrange a series of alkanes in order of increasing or decreasing boiling point.
- Skill 3.8 Be able to draw Newman Projections of different conformers of alkanes.

- Skill 3.9 be able evaluate a conformer in terms of torsional and steric strain.
- Skill 3.10 Be able to identify the staggered, eclipsed, anti and gauche conformers of alkanes and to order them with respect to relative energy.

MEMORIZATION TASKS (MT)

- MT 3.1 Memorize the name and structure of each of the common functional groups listed in Skill 3.1.
- MT 3.2 Memorize the names and be able to draw the first ten straight chain alkanes.
- MT 3.3 Memorize the structures and common names of the alkyl substitutent groups - isopropyl, *sec*-butyl, isobutyl,, and *tert*-butyl.

CONTRIBUTORS

- Dr. Kelly Matthews (Senior Professor of Chemistry, Harrisburg Area Community College)

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CHAPTER OVERVIEW

4: ORGANIC COMPOUNDS- CYCLOALKANES AND THEIR STEREOCHEMISTRY

LEARNING OBJECTIVES

After you have completed Chapter 4, you should be able to

- fulfill all of the detailed objectives listed under each individual section.
- draw the *cis-trans* isomers of some simple disubstituted cycloalkanes, and write the IUPAC names of such compounds.
- define, and use in context, the key terms introduced in this chapter.

This chapter deals with the concept of stereochemistry and conformational analysis in cyclic compounds. The causes of various ring strains and their effects on the overall energy level of a cycloalkane are discussed. We shall stress the stereochemistry of alicyclic compounds.

4.0: Prelude
4.1: Naming Cycloalkanes
4.2: Cis-Trans Isomerism in Cycloalkanes
4.3: Stability of Cycloalkanes - Ring Strain
4.4: Conformations of Cycloalkanes
4.5: Conformations of Cyclohexane
4.6: Axial and Equatiorial Bonds in Cyclohexane
4.7: Conformations of Monosubstituted Cyclohexanes
4.8: Conformations of Disubstituted Cyclohexanes
4.9: Conformations of Polycyclic Molecules
4.S: Organic Compounds- Cycloalkanes and their Stereochemistry (Summary)

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4.0: Prelude

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4.1: NAMING CYCLOALKANES

Objectives

After completing this section, you should be able to

1. name a substituted or unsubstituted cycloalkane, given its Kekulé structure, shorthand structure or condensed structure.
2. draw the Kekulé, shorthand or condensed structure for a substituted or unsubstituted cycloalkane, given its IUPAC name.
3. draw all possible cycloalkane structures (substituted or unsubstituted) that correspond to a given molecular formula.

STUDY NOTES

Provided that you have mastered the IUPAC system for naming alkanes, you should find that the nomenclature of cycloalkanes does not present any particular difficulties. Concentrate on the examples in which the substituent or substituents is or are an alkyl group, a halogen, or both.

Cycloalkanes are cyclic hydrocarbons, meaning that the carbons of the molecule are arranged in the form of a ring. Cycloalkanes are also saturated, meaning that all of the carbons atoms that make up the ring are single bonded to other atoms (no double or triple bonds). There are also polycyclic alkanes, which are molecules that contain two or more cycloalkanes that are joined, forming multiple rings.

INTRODUCTION

Many organic compounds found in nature or created in a laboratory contain rings of carbon atoms with distinguishing chemical properties; these compounds are known as cycloalkanes. Cycloalkanes only contain carbon-hydrogen bonds and carbon-carbon single bonds, but in cycloalkanes, the carbon atoms are joined in a ring. The smallest cycloalkane is cyclopropane.

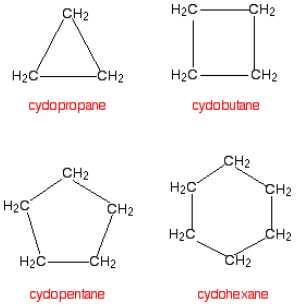


***Figure 4.1.1**:*

If you count the carbons and hydrogens, you will see that they no longer fit the general formula C_nH_{2n+2}. By joining the carbon atoms in a ring,two hydrogen atoms have been lost. The general formula for a cycloalkane is C_nH_{2n}. Cyclic compounds are not all flat molecules. All of the cycloalkanes, from cyclopentane upwards, exist as "puckered rings". Cyclohexane, for example, has a ring structure that looks like this:

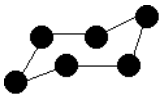
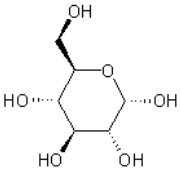
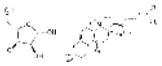


***Figure 4.1.2**: This is known as the "chair" form of cyclohexane from its shape, which vaguely resembles a chair. Note: The cyclohexane molecule is constantly changing, with the atom on the left, which is currently pointing down, flipping up, and the atom on the right flipping down. During this process, another (slightly less stable) form of cyclohexane is formed known as the "boat" form. In this arrangement, both of these atoms are either pointing up or down at the same time*

In addition to being saturated cyclic hydrocarbons, cycloalkanes may have multiple substituents or functional groups that further determine their unique chemical properties. The most common and useful cycloalkanes in organic chemistry are cyclopentane and cyclohexane, although other cycloalkanes varying in the number of carbons can be synthesized. Understanding cycloalkanes and their properties are crucial in that many of the biological processes that occur in most living things have cycloalkane-like structures.



Glucose (6 carbon sugar)



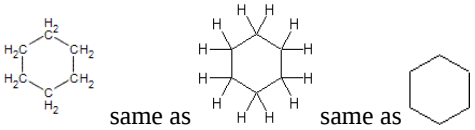
Ribose (5 carbon sugar)

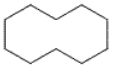
Cholesterol (polycyclic)

Although polycyclic compounds are important, they are highly complex and typically have common names accepted by IUPAC. However, the common names do not generally follow the basic IUPAC nomenclature rules. The general formula of the cycloalkanes is C_nH_{2n} where n is the number of carbons. The naming of cycloalkanes follows a simple set of rules that are built upon the same basic steps in naming alkanes. Cyclic hydrocarbons have the prefix "cyclo-".

CONTENTS

For simplicity, cycloalkane molecules can be drawn in the form of skeletal structures in which each intersection between two lines is assumed to have a carbon atom with its corresponding number of hydrogens.



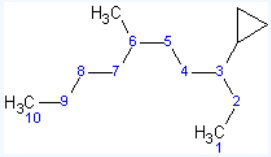
Cycloalkane	Molecular Formula	Basic Structure
Cyclopropane	C_3H_6	
Cyclobutane	C_4H_8	
Cyclopentane	C_5H_{10}	
Cyclohexane	C_6H_{12}	
Cycloheptane	C_7H_{14}	
Cyclooctane	C_8H_{16}	
Cyclononane	C_9H_{18}	
Cyclodecane	$C_{10}H_{20}$	

IUPAC RULES FOR NOMENCLATURE

1. Determine the cycloalkane to use as the parent chain. The parent chain is the one with the highest number of carbon atoms. If there are two cycloalkanes, use the cycloalkane with the higher number of carbons as the parent chain.
2. If there is an alkyl straight chain that has a greater number of carbons than the cycloalkane, then the alkyl chain must be used as the primary parent chain. Cycloalkane acting as a substituent to an alkyl chain has an ending "-yl" and, therefore, must be named as a cycloalkyl.

Cycloalkane	Cycloalkyl
cyclopropane	cyclopropyl
cyclobutane	cyclobutyl
cyclopentane	cyclopentyl
cyclohexane	cyclohexyl
cycloheptane	cycloheptyl
cyclooctane	cyclooctyl
cyclononane	cyclononanyl
cyclodecane	cyclodecanyl

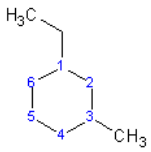
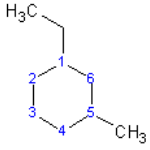
EXAMPLE 4.1.1



The longest straight chain contains 10 carbons, compared with cyclopropane, which only contains 3 carbons. Because cyclopropane is a substituent, it would be named a cyclopropyl-substituted alkane.

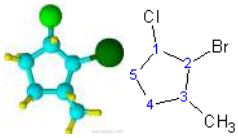
3) Determine any functional groups or other alkyl groups.

4) Number the carbons of the cycloalkane so that the carbons with functional groups or alkyl groups have the lowest possible number. A carbon with multiple substituents should have a lower number than a carbon with only one substituent or functional group. One way to make sure that the lowest number possible is assigned is to number the carbons so that when the numbers corresponding to the substituents are added, their sum is the lowest possible.

1-ethyl-3-methylcyclohexane (1+3=4) **NOT** 1-ethyl-5-methylcyclohexane (1+5=6)

5) When naming the cycloalkane, the substituents and functional groups must be placed in alphabetical order.



(ex: 2-bromo-1-chloro-3-methylcyclopentane)

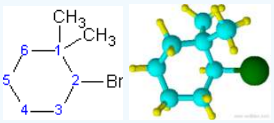
6) Indicate the carbon number with the functional group with the highest priority according to alphabetical order. A dash"-" must be placed between the numbers and the name of the substituent. After the carbon number and the dash, the name of the substituent can follow. When there is only one substituent on the parent chain, indicating the number of the carbon atoms with the substituent is not necessary.

(ex: 1-chlorocyclobutane or cholorocyclobutane is acceptable) 

7) If there is more than one of the same functional group on one carbon, write the number of the carbon two, three, or four times, depending on how many of the same functional group is present on that carbon. The numbers must be separated by commas, and the name of the functional group that follows must be separated by a dash. When there are two of the same functional group, the name must have the prefix "di". When there are three of the same functional group, the name must have the prefix "tri". When there are four of the same functional group, the name must have the prefix "tetra". However, these prefixes cannot be used when determining the alphabetical priorities.

There must always be commas between the numbers and the dashes that are between the numbers and the names.

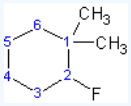
EXAMPLE 4.1.2



(2-bromo-1,1-dimethylcyclohexane)

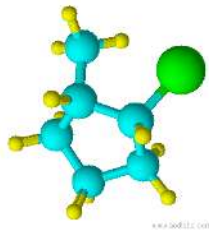
Notice that "f" of fluoro alphabetically precedes the "m" of methyl. Although "di" alphabetically precedes "f", it is not used in determining the alphabetical order.

EXAMPLE 4.1.3



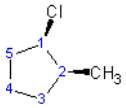
(2-fluoro-1,1,-dimethylcyclohexane **NOT** 1,1-dimethyl-2-fluorocyclohexane)

8) If the substituents of the cycloalkane are related by the cis or trans configuration, then indicate the configuration by placing "cis-" or "trans-" in front of the name of the structure.



Blue=Carbon Yellow=Hydrogen Green=Chlorine

Notice that chlorine and the methyl group are both pointed in the same direction on the axis of the molecule; therefore, they are cis.

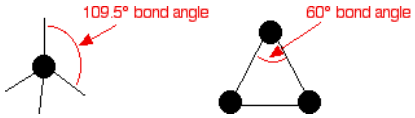


cis-1-chloro-2-methylcyclopentane

9) After all the functional groups and substituents have been mentioned with their corresponding numbers, the name of the cycloalkane can follow.

REACTIVITY

Cycloalkanes are very similar to the alkanes in reactivity, except for the very small ones, especially cyclopropane. Cyclopropane is significantly more reactive than what is expected because of the bond angles in the ring. Normally, when carbon forms four single bonds, the bond angles are approximately 109.5°. In cyclopropane, the bond angles are 60°.



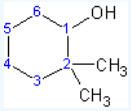
With the electron pairs this close together, there is a significant amount of repulsion between the bonding pairs joining the carbon atoms, making the bonds easier to break.

ALCOHOL SUBSTITUENTS ON CYCLOALKANES

Alcohol (-OH) substituents take the highest priority for carbon atom numbering in IUPAC nomenclature. The carbon atom with the alcohol substituent must be labeled as 1. Molecules containing an alcohol group have an ending "-ol", indicating the presence of an alcohol group. If there are two alcohol groups, the molecule will have a "di-" prefix before "-ol" (diol). If there are three alcohol groups, the molecule will have a "tri-" prefix before "-ol" (triol), etc.

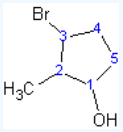
EXAMPLE 4.1.4

The alcohol substituent is given the lowest number even though the two methyl groups are on the same carbon atom and labeling 1 on that carbon atom would give the lowest possible numbers. Numbering the location of the alcohol substituent is unnecessary because the ending "-ol" indicates the presence of one alcohol group on carbon atom number 1.



2,2-dimethylcyclohexanol **NOT** 1,1-dimethyl-cyclohexane-2-ol

EXAMPLE 4.1.5

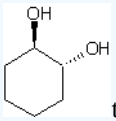


3-bromo-2-methylcyclopentanol **NOT** 1-bromo-2-methyl-cyclopentane-2-ol

EXAMPLE 4.1.6



Blue=Carbon Yellow=Hydrogen Red=Oxygen



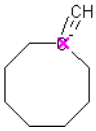
trans-cyclohexane-1,2-diol

OTHER SUBSTITUENTS ON CYCLOALKANES

There are many other functional groups like alcohol, which are later covered in an organic chemistry course, and they determine the ending name of a molecule. The naming of these functional groups will be explained in depth later as their chemical properties are explained.

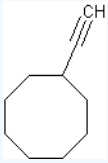
Name	Name ending
alkene	-ene
alkyne	-yne
alcohol	-ol
ether	-ether
nitrile	-nitrile
amine	-amine
aldehyde	-al
ketone	-one
carboxylic acid	-oic acid
ester	-oate
amide	-amide

Although alkynes determine the name ending of a molecule, alkyne as a substituent on a cycloalkane is not possible because alkynes are planar and would require that the carbon that is part of the ring form 5 bonds, giving the carbon atom a negative charge.



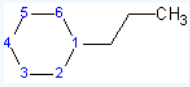
However, a cycloalkane with a triple bond-containing substituent is possible if the triple bond is not directly attached to the ring.

EXAMPLE 4.1.7



ethynylcyclooctane

EXAMPLE 4.1.8



1-propylcyclohexane

SUMMARY

1. Determine the parent chain: the parent chain contains the most carbon atoms.
2. Number the substituents of the chain so that the sum of the numbers is the lowest possible.
3. Name the substituents and place them in alphabetical order.
4. If stereochemistry of the compound is shown, indicate the orientation as part of the nomenclature.
5. Cyclic hydrocarbons have the prefix "cyclo-" and have an "-alkane" ending unless there is an alcohol substituent present. When an alcohol substituent is present, the molecule has an "-ol" ending.

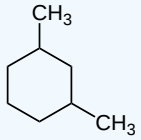
GLOSSARY

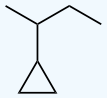
- **alcohol**: An oxygen and hydrogenOH hydroxyl group that is bonded to a substituted alkyl group.
- **alkyl:** A structure that is formed when a hydrogen atom is removed from an alkane.
- **cyclic:** Chemical compounds arranged in the form of a ring or a closed chain form.
- **cycloalkanes:** Cyclic saturated hydrocarbons with a general formula of CnH(2n). Cycloalkanes are alkanes with carbon atoms attached in the form of a closed ring.
- **functional groups:** An atom or groups of atoms that substitute for a hydrogen atom in an organic compound, giving the compound unique chemical properties and determining its reactivity.
- **hydrocarbon:** A chemical compound containing only carbon and hydrogen atoms.
- **saturated**: All of the atoms that make up a compound are single bonded to the other atoms, with no double or triple bonds.
- **skeletal structure:** A simplified structure in which each intersection between two lines is assumed to have a carbon atom with its corresponding number of hydrogens.

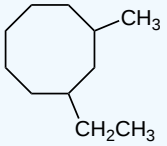
EXERCISES

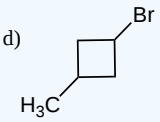
? EXERCISE 4.1.1

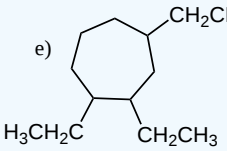
Give the IUPAC names for the following cycloalkane structures.

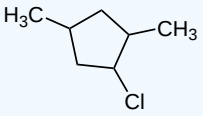
a) 

b) 

c) 

d) 

e) 

f) 

Answer

a) 1,3-Dimethylcyclohexane

b) 2-Cyclopropylbutane

c) 1-Ethyl-3-methylcyclooctane

d) 1-Bromo-3-methylcyclobutane

e) 1,2,4-Triethylcycloheptane

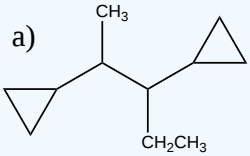
f) 1-Chloro-2,4-dimethylcyclopentane

? EXERCISE 4.1.2

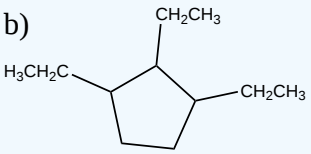
Draw the structures for the IUPAC names below.

a. 2,3-dicyclopropylpentane
b. 1,2,3-triethylcyclopentane
c. 3-cyclobutyl-2-methylhexane
d. 2-bromo-1-chloro-4-methylcyclohexane
e. 1-bromo-5-propylcyclododecane

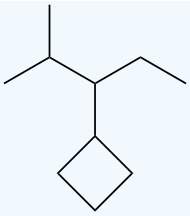
Answer

a) 

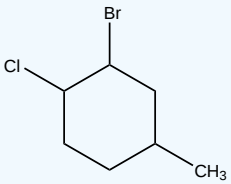
2,3-dicyclopropylpentane

b) 

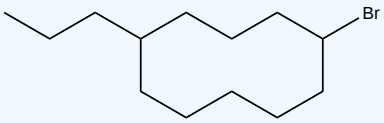
1,2,3-triethylcyclopentane

c) 

3-cyclobutyl-2-methylhexane

d) 

2-bromo-1-chloro-4-methylcyclohexane

e) 

1-bromo-5-propylcyclodecane

OUTSIDE LINKS

- More Practice Problems on Nomenclature of Cycloalkanes
- Vollhardt, Schore. Organic Chemistry. 5th ed.
- Wikipedia: Cycloalkanes
- www.cem.msu.edu/~reusch/VirtualText/nomen1.htm
- http://www.chemguide.co.uk/organicprops/alkanes/background.html
- www.cem.msu.edu/~reusch/VirtualText/nomen1.htm
- science.csustan.edu/nhuy/chem3010/handouts/HandoutIVNamecyal.htm
- en.wikibooks.org/wiki/Organic_Chemistry/Alkanes_and_cycloalkanes/Cycloalkanes

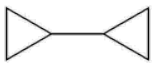
REFERENCES

1. ACD/ChemSketch Freeware, version 11.0, Advanced Chemistry Development, Inc., Toronto, ON, Canada, www.acdlabs.com, 2008.
2. Bruice, Paula Yurkanis. Oragnic Chemistry. 5th. CA. Prentice Hall, 2006.
3. Fryhle, C.B. and G. Solomons. Organic Chemistry. 9th ed. Danvers, MA: Wiley, 2008.
4. McMurry, John. Organic Chemistry. 7th ed. Belmont, California: Thomson Higher Education, 2008.
5. Sadava, Heller, Orians, Purves, Hillis. Life The Science of Biology. 8th ed. Sunderland, MA: W.H. Freeman, 2008.
6. Vollhardt, K. Peter C., and Neil E. Schore. Organic Chemistry. 5th ed. New York: W.H. Freeman, 2007.

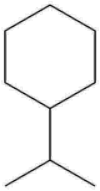
QUESTIONS

Q4.1.1

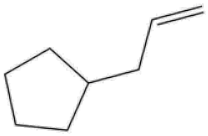
Name the following compounds:



1



2



3

Q4.1.2

Draw the following structures

1 = 1,2-dimethylcyclohexane

2 = 2-cyclopropyl butane

3 = 1,2,3-trimethyl cyclopentane

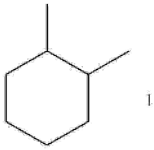
SOLUTIONS

S4.1.1

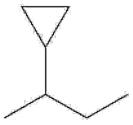
1 = 1-cyclopropyl cyclopropane

2 = 1-isopropyl cyclohexane

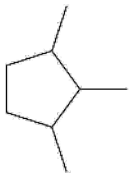
3 = 2-propenyl cyclopentane



1



2



3

CONTRIBUTORS AND ATTRIBUTIONS

- Pwint Zin
- Jim Clark (ChemGuide)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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4.2: CIS-TRANS ISOMERISM IN CYCLOALKANES

Objectives

After completing this section, you should be able to

1. recognize that a formula of the type $C_n H_{2n}$ may represent a cycloalkane.
2. draw structural formulas that distinguish between *cis* and *trans* disubstituted cycloalkanes.
3. construct models of *cis* and *trans* disubstituted cycloalkanes using ball-and-stick molecular models.

KEY TERMS

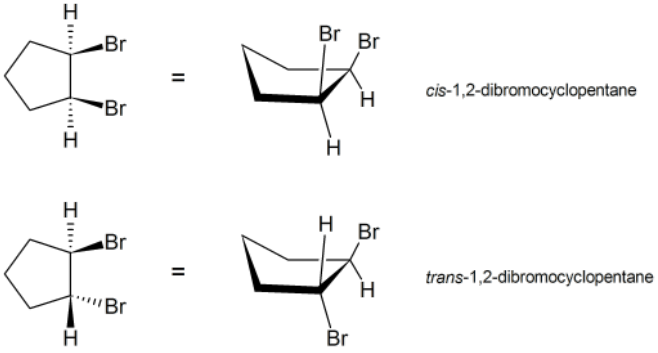
Make certain that you can define, and use in context, the key terms below.

- *cis-trans* isomers
- cycloalkane
- stereoisomer

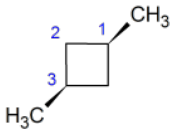
STUDY NOTES

Compounds in which the carbon atoms are joined in a ring, and in which no multiple bonds or other functional groups are present, are called cycloalkanes. A cycloalkane containing only one ring will correspond to the general formula C_nH_{2n}, but alkenes containing only one double bond also correspond to this formula. Cycloalkanes containing more than one ring are not considered in this section.

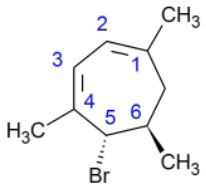
Stereoisomers are also observed in certain disubstituted (and higher substituted) cyclic compounds. Unlike the relatively flat molecules of alkenes, substituted cycloalkanes must be viewed as three-dimensional configurations in order to appreciate the spatial orientations of the substituents. By agreement, chemists use heavy, wedge-shaped bonds to indicate a substituent located above the average plane of the ring, and a hatched line for bonds to atoms or groups located below the ring. As in the case of the 2-butene stereoisomers, disubstituted cycloalkane stereoisomers may be designated by nomenclature prefixes such as *cis* and *trans*. The stereoisomeric 1,2-dibromocyclopentanes below are an example.



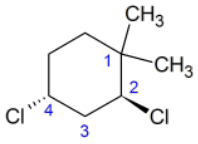
In general, if any two sp^3 carbons in a ring have two different substituent groups (not counting other ring atoms) stereoisomerism is possible. This is similar to the substitution pattern that gives rise to stereoisomers in alkenes; indeed, one might view a double bond as a two-membered ring. Four other examples of this kind of stereoisomerism in cyclic compounds are shown below.



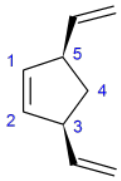
cis-1,3-dimethylcyclobutane



trans-5-bromo-1,4,6-trimethyl-1,3-cycloheptadiene

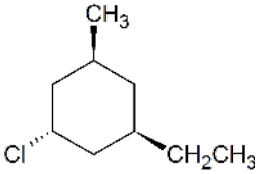


trans-2,4-dichloro-1,1-dimethylcyclohexane



cis-3,5-divinylcyclopentene

If more than two ring carbons have different substituents (not counting other ring atoms) the stereochemical notation distinguishing the various isomers becomes more complex. However, we can always state the relationship of any two substituents using cis or trans. For example, in the trisubstitutued cyclohexane below, we can say that the methyl group is *cis* to the ethyl group, and *trans* to the chlorine. We can also say that the ethyl group is *trans* to the chlorine. We cannot, however, designate the entire molecule as a *cis* or trans *isomer*.



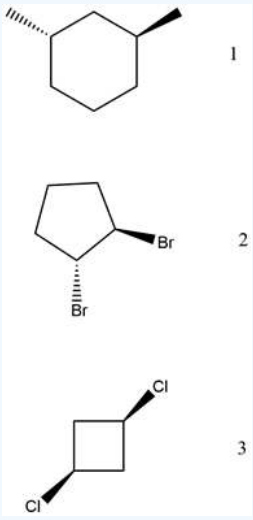
EXERCISES

? EXERCISE 4.2.1

Draw the following molecules:

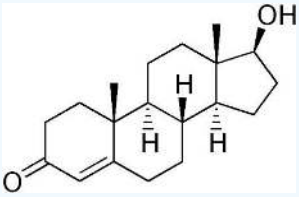
1. *trans*-1,3-dimethylcyclohexane
2. *trans*-1,2-dibromocyclopentane
3. *cis*-1,3-dichlorocyclobutane

Answer



EXERCISE 4.2.2

Cis/Trans nomenclature can be used to describe the relative positioning of substituents on molecules with more complex ring structures. The molecule below is tesosterone, the primary male sex hormone. Is the OH and the adjacent methyl group cis or trans to each other? What can you deduce about the relative positions of the indicated hydrogens?

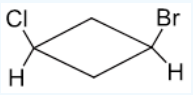


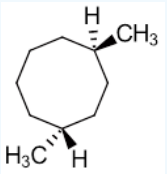
Answer

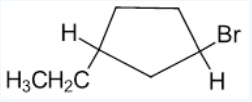
Both the OH and the methyl group have wedge bonds. This implies that they are both on the same side of the testosterone ring making them cis. Two of the hydrogens have wedge bonds while one has a wedge. This means two of the hydrogens are on one side of the testosterone ring while one is on the other side.

EXERCISE 4.2.3

Name the following compounds:







Answer

Cis-1-Bromo-3-Chlorocyclobutane

Trans-1,4-Dimethylcyclooctane

Trans-1-Bromo-3-ethylcyclopentane

QUESTIONS

Q4.2.1

Draw the following molecules:

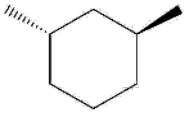
trans-1,3-dimethylcyclohexane

trans-1,2-dibromocyclopentane

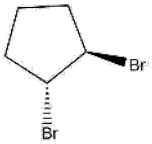
cis-1,3-dichlorocyclobutane

SOLUTIONS

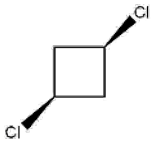
S4.2.1



1



2



3

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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4.3: STABILITY OF CYCLOALKANES - RING STRAIN

Objectives

After completing this section, you should be able to

1. describe the Baeyer strain theory.
2. describe how the measurement of heats of combustion can be used to provide information about the amount of strain present in an alicyclic ring.
3. explain the inadequacies of the Baeyer strain theory.
4. determine which of two similar compounds is likely to be the most stable, by assessing such factors as angle strain, torsional strain and steric strain.

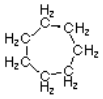
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- angle strain
- heat of combustion
- steric strain
- torsional strain

Cycloalkanes have one or more rings of carbon atoms. The simplest examples of this class consist of a single, unsubstituted carbon ring, and these form a homologous series similar to the unbranched alkanes. The IUPAC names of the first five members of this series are given in the following table. The last (yellow shaded) column gives the general formula for a cycloalkane of any size. If a simple unbranched alkane is converted to a cycloalkane two hydrogen atoms, one from each end of the chain, must be lost. Hence the general formula for a cycloalkane composed of **n** carbons is $\mathbf{C_nH_{2n}}$. Although a cycloalkane has two fewer hydrogens than the equivalent alkane, each carbon is bonded to four other atoms so such compounds are still considered to be **saturated** with hydrogen.

Table 4.3.1: Examples of Simple Cycloalkanes

Name	Cyclopropane	Cyclobutane	Cyclopentane	Cyclohexane	Cycloheptane	Cycloalkane
Molecular Formula	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}	C_7H_{14}	C_nH_{2n}
Structural Formula						$(CH_2)_n$
Line Formula						

THE BAEYER THEORY ON THE STRAIN IN CYCLOALKANE RINGS

Many of the properties of cyclopropane and its derivatives are similar to the properties of alkenes. In 1890, the famous German organic chemist, A. Baeyer, suggested that cyclopropane and cyclobutane derivatives are different from cyclopentane and cyclohexane, because their C—C—C angles cannot have the tetrahedral value of 109.5°. At the same time, Baeyer hypothesized that the difficulties encountered in synthesizing cycloalkane rings from C7 upward was the result of the angle strain that would be expected if the large rings were regular planar polygons (see Table 12-3). Baeyer also believed that cyclohexane had a planar structure like that shown in Figure 12-2, which would mean that the bond angles would have to deviate 10.5° from the tetrahedral value. However, in 1895, the then unknown chemist H. Sachse suggested that cyclohexane exists in the strain-free chair and boat forms discussed in Section 12-3. This suggestion was not accepted at the time because it led to the prediction of several possible isomers for compounds such as chlorocyclohexane (cf. Exercise 12-4). The idea that such isomers might act as a single substance, as the result of rapid equilibration, seemed like a needless complication, and it was not until 1918 that E. Mohr proposed a definitive way to distinguish between the Baeyer and Sachse cyclohexanes. As will be discussed in Section 12-9, the result, now known as the Sachse-Mohr theory, was complete confirmation of the idea of nonplanar large rings.

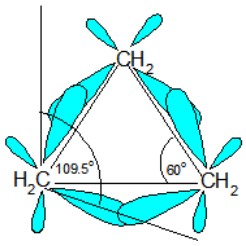
Table 4.3.2: Strain in Cycloalkane Rings and Heats of Combustion of Cycloalkanes

Compound	n	Angle Strain at each CH2	Heat of Combustion ΔHo (kcal/mol)	Heat of Combustion ΔHo per CH2/N (kcal/mol)	Total Strain (kcal/mol)
ethene	2	109.5	337.2	168.6	22.4
cyclopropane	3	49.5	499.9	166.6	27.7
cyclobutane	4	19.5	655.9	164.0	26.3
cyclopentane	5	1.5	793.4	158.7	6.5
cyclohexane	6	10.5	944.8	157.5	0.4
cycloheptane	7	19.1	1108.1	158.4	6.3
cyclooctane	8	25.5	1268.9	158.6	9.7
cyclononane	9	30.5	1429.5	158.8	12.9
cyclodecane	10	34.5	1586.1	158.6	12.1
cyclopentadecane	15	46.5	2362.5	157.5	1.5
open chain alkane				157.4	-

One of the most interesting developments in ‘the stereochemistry of organic compounds in recent years has been the demonstration that transcyclooctene (but not the cis isomer) can be resolved into stable chiral isomers (enantiomers, Section 5-IB). In general, a trans-cycloalkene would not be expected to be resolvable because of the possibility for formation of achiral conformations with a plane of symmetry. Any conformation with all of the carbons in a plane is such an achiral conformation (Figure 12-20a). However, when the chain connecting the ends of the double bond is short, as in trans-cyclooctene, steric hindrance and steric strain prevent easy.

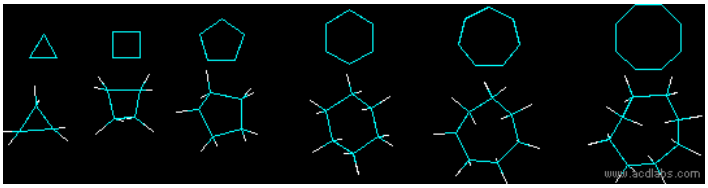
RING STRAIN IN CYCLOALKANES

Ring Strain occurs because the carbons in cycloalkanes are sp^3 hybridized, which means that they do not have the expected ideal bond angle of 109.5º ; this causes an increase in the potential energy because of the desire for the carbons to be at an ideal 109.5º. An example of ring strain can be seen in the diagram of cyclopropane below in which the bond angle is 60º between the carbons.



The reason for ring strain can be seen through the tetrahedral carbon model. The C-C-C bond angles in cyclopropane (diagram above) (60º) and cyclobutane (90º) are much different than the ideal bond angle of 109.5º. This bond angle causes cyclopropane and cyclobutane to have a high ring strain. However, molecules, such as cyclohexane and cyclopentane, would have a much lower ring strain because the bond angle between the carbons is much closer to 109.5º.

Below are some examples of cycloalkanes. Ring strain can be seen more prevalently in the cyclopropane and cyclobutane models.



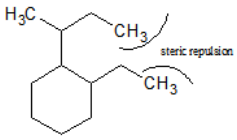
Below is a chart of cycloalkanes and their respective heats of combustion (ΔH_{comb}). The ΔH_{comb} value increases as the number of carbons in the cycloalkane increases (higher membered ring), and the $\Delta H_{comb}/CH_2$ ratio decreases. The increase in ΔH_{comb} can be attributed to the greater amount of London Dispersion forces. However, the decrease in $\Delta H_{comb}/CH_2$can be attributed to a decrease in the ring strain.

Cycloalkane	$\triangle H_{comb}$ (KJ/Mol)	$\triangle H_{comb}/CH_2$ (KJ/mol)
	-499.8	-166.6
	-655.9	-164.0
	-793.5	-158.7
	-944.5	-157.4

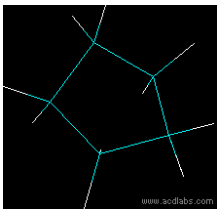
Certain cycloalkanes, such as cyclohexane, deal with ring strain by forming conformers. A conformer is a stereoisomer in which molecules of the same connectivity and formula exist as different isomers, in this case, to reduce ring strain. The ring strain is reduced in conformers due to the rotations around the sigma bonds. More about cyclohexane and its conformers can be seen here.

DIFFERENT TYPES OF STRAIN

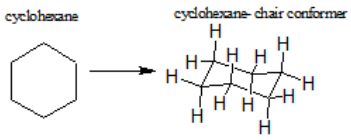
There are many different types of strain that occur with cycloalkanes. In addition to ring strain, there is also transannular (or steric) strain, torsional (or eclipsing) strain, and bond angle strain. Transannular strain exists when there is steric repulsion between atoms. Eclipsing (torsional) strain exists when a cycloalkane is unable to adopt a staggered conformation around a C-C bond, and bond angle strain is the energy needed to distort the tetrahedral carbons enough to close the ring. The presence of angle strain in a molecule indicates that there are bond angles in that particular molecule that deviate from the ideal bond angles required (i.e., that molecule has conformers).



Transannular Strain



This is an example of torsional strain through cylcopentane. The torsional strain is caused by the hudrogen bonds in the ring (shown in yellow)



this conformer is more stable

EXERCISES

? EXERCISE 4.3.1

trans-1,2-Dimethylcyclobutane is more stable than *cis*-1,2-dimethylcyclobutane. Explain this observation.

Answer

The trans form does not have eclipsing methyl groups, therefore lowering the energy within the molecule. It does however have hydrogen-methyl eclipsing interactions which are not as high in energy as methyl-methyl interactions.

EXERCISE 4.3.2

While cyclobutane has less angle strain than cyclopropane, it has more torsional strain than cyclopropane. Explain this observation.

Answer

Cyclobutane has bond angles of about 90° which is closer to the ideal sp^3 hybridized angle of 109.5^o than cyclopropane (60°). However, cyclobutane has 4 CH_2 groups while cyclopropane only has 3. More CH_2 groups means cyclobutane has more eclipsing H-H interactions and therefore has more torsional strain. [The total strain for the two compounds is nearly the same - 110 kJ/mol for cyclobutane and 115 kJ/mol for cyclopropane.]

QUESTIONS

Q4.3.1

trans-1,2-Dimethylcyclobutane is more stable than *cis*-1,2-dimethylcyclobutane. Explain this observation.

SOLUTIONS

S4.3.1

The trans form does not have eclipsing methyl groups, therefore lowering the energy within the molecule. It does however have hydrogen-methyl interactions, but are not as high in energy than methyl-methyl interactions.

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4.4: CONFORMATIONS OF CYCLOALKANES

OBJECTIVES

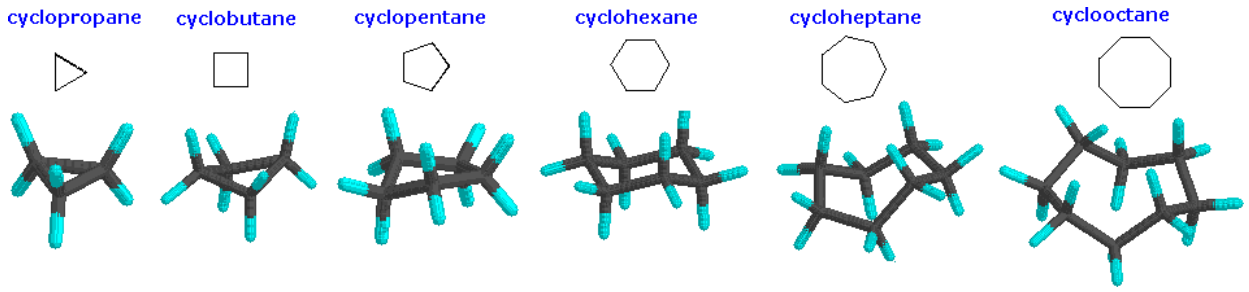
After completing this section, you should be able to

1. describe, and sketch the conformation of, cyclopropane, cyclobutane and cyclopentane.
2. describe the bonding in cyclopropane, and hence account for the high reactivity of this compound.
3. analyse the stability of cyclobutane, cyclopentane and their substituted derivatives in terms of angular strain, torsional strain and steric interactions.

STUDY NOTES

Notice that in both cyclobutane and cyclopentane, torsional strain is reduced at the cost of increasing angular (angle) strain.

Although the customary line drawings of simple cycloalkanes are geometrical polygons, the actual shape of these compounds in most cases is very different.



Cyclopropane is necessarily planar (flat), with the carbon atoms at the corners of an equilateral triangle. The 60º bond angles are much smaller than the optimum 109.5º angles of a normal tetrahedral carbon atom, and the resulting angle strain dramatically influences the chemical behavior of this cycloalkane. Cyclopropane also suffers substantial eclipsing strain, since all the carbon-carbon bonds are fully eclipsed. Cyclobutane reduces some bond-eclipsing strain by folding (the out-of-plane dihedral angle is about 25º), but the total eclipsing and angle strain remains high. Cyclopentane has very little angle strain (the angles of a pentagon are 108º), but its eclipsing strain would be large (about 10 kcal/mol) if it remained planar. Consequently, the five-membered ring adopts non-planar puckered conformations whenever possible.

Rings larger than cyclopentane would have angle strain if they were planar. However, this strain, together with the eclipsing strain inherent in a planar structure, can be relieved by puckering the ring. Cyclohexane is a good example of a carbocyclic system that virtually eliminates eclipsing and angle strain by adopting non-planar conformations. Cycloheptane and cyclooctane have greater strain than cyclohexane, in large part due to transannular crowding (steric hindrance by groups on opposite sides of the ring).

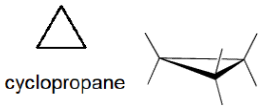
Cyclic systems are a little different from open-chain systems. In an open chain, any bond can be rotated 360 degrees, going through many different conformations. That complete rotation isn't possible in a cyclic system, because the parts that you would be trying to twist away from each other would still be connected together. Cyclic systems have fewer "degrees of freedom" than aliphatic systems; they have "restricted rotation".

Because of the restricted rotation of cyclic systems, most of them have much more well-defined shapes than their aliphatic counterparts. Let's take a look at the basic shapes of some common rings.

- Many biologically important compounds are built around structures containing rings, so it's important that we become familiar with them.
- In nature, three- to six-membered rings are frequently encountered, so we'll focus on those.

CYCLOPROPANE

A three membered ring has no rotational freedom whatsoever. A plane is defined by three points, so the three carbon atoms in cyclopropane are all constrained to lie in the same plane. This lack of flexibility does not allow cyclopropane to form more stable conformers which are non-planar.



The main source of ring strain in cyclopropane is angle strain. All of the carbon atoms in cyclopropane are tetrahedral and would prefer to have a bond angle of 109.5^{o} The angles in an equilateral triangle are actually 60°, about half as large as the optimum angle. The large deviation from the optimal bond angle means that the C-C sigma bonds forming the cyclopropane ring are bent. Maximum bonding occurs when the overlapping orbitals are pointing directly toward each other. The severely strained bond angles in cyclopropane means that the orbitals forming the C-C bonds overlap at a slight angle making them weaker. This strain is partially overcome by using so-called “banana bonds”, where the overlap between orbitals is no longer directly in a line between the two nuclei, as shown here in three representations of the bonding in cyclopropane:

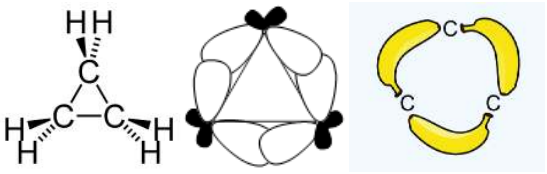
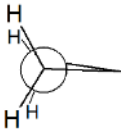


Figure **4.4.1**: Paste Caption Here

The constrained nature of cyclopropane causes neighboring C-H bonds to all be held in eclipsed conformations. Cyclopropane is always at maximum torsional strain. This strain can be illustrated in a Newman projections of cyclopropane as shown from the side.



Newman Projection of cyclopropane

Cyclopropane isn't large enough to introduce any steric strain. Steric strain does not become a factor until we reach six membered rings. Before that point, rings are not flexible enough to allow for two ring substituents to interact with each other.

The combination of torsional and angle strain creates a large amount of ring strain in cyclopropane which weakens the C-C ring bonds (255 kJ/mol) when compared to C-C bonds in open-chain propane (370 kJ/mol).

CYCLOBUTANE

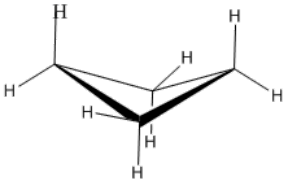
Cyclobutane is a four membered ring. The larger number of ring hydrogens would cause a substantial amount of torsional strain if cyclobutane were planar.



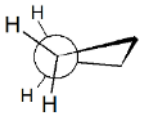
cyclobutane

In three dimensions, cyclobutane is flexible enough to buckle into a "puckered" shape which causes the C-H ring hydrogens to slightly deviate away from being completely eclipsed. This conformation relives some of the torsional strain but increases the angle strain because the ring bond angles decreases to 88°.

In a line drawing, this butterfly shape is usually shown from the side, with the near edges drawn using darker lines.



The deviation of cyclobutane's ring C-H bonds away from being fully eclipsed can clearly be seen when viewing a Newman projections signed down one of the C-C bond.



Newman projection of cyclobutane

- With bond angles of 88º rather than 109.5º degrees, cyclobutane has significant amounts of angle strain, but less than in cyclopropane.
- Although torsional strain is still present, the neighboring C-H bonds are not exactly eclipsed in the cyclobutane's puckered conformation.
- Steric strain is very low. Cyclobutane is still not large enough that substituents can reach around to cause crowding.
- Overall the ring strain in cyclobutane (110 kJ/mol) is slightly less than cyclopropane (115 kJ/mol).
-

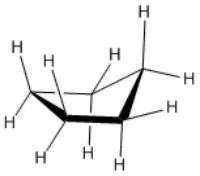
CYCLOPENTANE

Cyclopentanes are even more stable than cyclobutanes, and they are the second-most common cycloalkane ring in nature, after cyclohexanes. Planar cyclopentane has virtually no angle strain but an immense amount of torsional strain. To reduce torsional strain, cyclopentane addops a non-planar conformation even though it slightly increases angle strain.



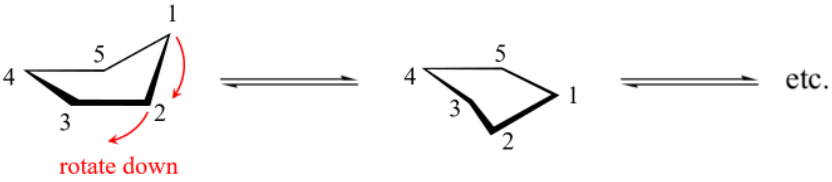
cyclopentane

The lowest energy conformation of cyclopentane is known as the ‘envelope’, with four of the ring atoms in the same plane and one out of plane (notice that this shape resembles an envelope with the flap open). The out-of-plane carbon is said to be in the ***endo*** position (‘*endo*’ means ‘inside’). The envelope removes torsional strain along the sides and flap of the envelope. However, the neighboring carbons are eclipsed along the "bottom" of the envelope, away from the flap.

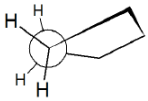


3D structure of cyclopentane (notice that the far top right carbon is the endo position).

At room temperature, cyclopentane undergoes a rapid bond **rotation** process in which each of the five carbons takes turns being in the *endo* position (alternating above and below the plane: 1 up, 2 down, 3 up, 4 down, 5 up, 1 down, 2 up, 3 down, 4 up, 5 down, etc.).



Cyclopentane distorts only very slightly into an "envelope" shape in which one corner of the pentagon is lifted up above the plane of the other four. The envelope removes torsional strain along the sides and flap of the envelope by allowing the bonds to be in an almost completely staggered position. However, the neighboring bonds are eclipsed along the "bottom" of the envelope, away from the flap. Viewing a Newman projections of cyclopentane sighting along one of the C-C bond show the staggered C-H bonds.



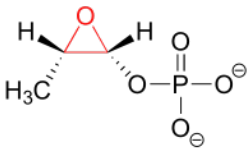
Newman projection of cyclopentane

- The angle strain in the envelope conformation of cyclopentane is low. The ideal angle in a regular pentagon is about 107º, very close to the preferred 109.5º tetrahedral bond angle.
- There is some torsional strain in cyclopentane. The envelope conformation reduces torsional strain by placing some bonds in nearly staggered positions. However, other bonds are still almost fully eclipsed.

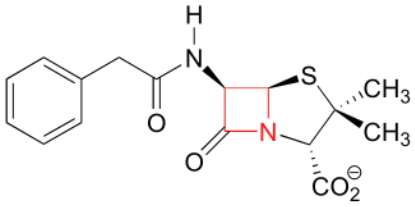
- Cyclopentane is not large enough to allow for steric strain to be created.
- Overall, cyclopentane has very little ring strain (26 kJ/mol) when compared to cyclopropane and cyclobutane.

C_3-C_5 CYCLOALKANES IN NATURE

If one of the carbon-carbon bonds is broken in cyclopropane or cyclobutane, the ring will 'spring' open, releasing energy as the bonds reassume their preferred tetrahedral geometry. The effectiveness of two antibiotic drugs, fosfomycin and penicillin, is due in large part to the high reactivity of the three- and four-membered rings in their structures.

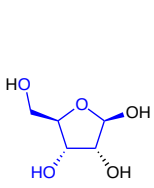


fosfomycin

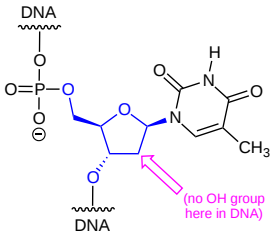


penicillin G

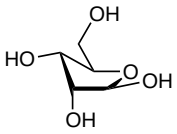
One of the most important five-membered rings in nature is a sugar called ribose – DNA and RNA are both constructed upon 'backbones' derived from ribose. Pictured below is one thymidine (T) deoxy-nucleotide from a stretch of DNA. Since the ribose has lost one of the OH groups (at carbon 2 of the ribose ring), this is part of a deoxyribonucleic acid (DNA). If the OH at carbon 2 of the ribose ring was present, this would be part of a ribonucleic acid (RNA).



ribose



The lowest-energy conformations for ribose are envelope forms in which either C_3 or C_2 are *endo*, on the same side as the C_5 substituent.



EXERCISES

? EXERCISE 4.4.1

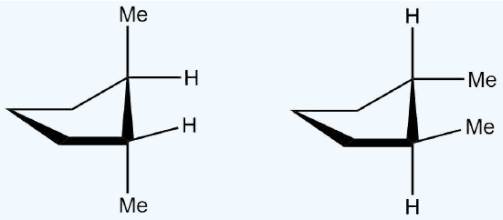
If cyclobutane were to be planar, how many H-H eclipsing interactions would there be? Assuming 4 kJ/mol per H-H eclipsing interaction what would the strain be on this "planar" molecule?

Answer

There are 8 eclipsing interactions (two per C-C bond). The extra strain on this molecule would be 32 kJ/mol (4 kJ/mol x 8).

? EXERCISE 4.4.2

In the two conformations of *trans*-1,2-Dimethylcyclopentane one is more stable than the other. Explain why this is.



Answer

The first conformation is more stable. Even though the methyl groups are *trans* in both models, they are anti to one another in the first structure (which is lower energy) while they are gauche in the second structure increasing strain within the molecule.

? EXERCISE 4.4.3

In methylcyclopentane, which carbon would most likely be in the *endo* position?

Answer

The ring carbon attached to the methyl group would most likely be the endo carbon. The large methyl group would create the most torsional strain if eclipsed. Being in the *endo* position would place the bonds is a more staggered position which would reduce strain.

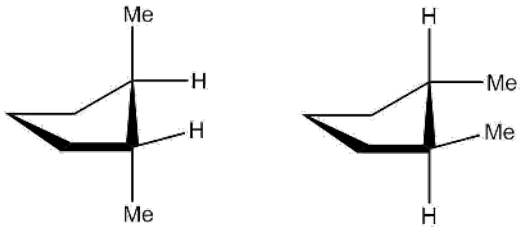
QUESTIONS

Q4.4.1

If cyclobutane were to be planar how many H-H eclipsing interactions would there be, and assuming 4 kJ/mol per H-H eclipsing interaction what is the strain on this “planar” molecule?

Q4.4.2

In the two conformations of *trans*-cyclopentane one is more stable than the other. Explain why this is.



SOLUTIONS

S4.4.1

There are 8 eclipsing interactions (two per C-C bond). The extra strain on this molecule would be 32 kJ/mol (4 kJ/mol x 8).

S4.4.2

The first conformation is more stable. Even though the methyl groups are *trans* in both models, in the second structure they are eclipsing one another, therefore increasing the strain within the molecule compared to the first structure where the larger methyl groups are anti to one another.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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4.5: CONFORMATIONS OF CYCLOHEXANE

OBJECTIVES

After completing this section, you should be able to

1. explain why cyclohexane rings are free of angular strain.
2. draw the conventional shorthand structure of a cyclohexane ring.

KEY TERMS

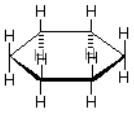
Make certain that you can define, and use in context, the key terms below.

- chair conformation
- twist-boat conformation

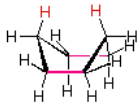
Rings larger than cyclopentane would have angle strain if they were planar. However, this strain, together with the eclipsing strain inherent in a planar structure, can be relieved by puckering the ring. Cyclohexane is a good example of a carbocyclic system that virtually eliminates eclipsing and angle strain by adopting non-planar conformations. Cycloheptane and cyclooctane have greater strain than cyclohexane, in large part due to transannular crowding (steric hindrance by groups on opposite sides of the ring).

CONFORMATIONS OF CYCLOHEXANE

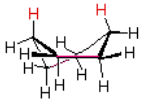
A planar structure for cyclohexane is clearly improbable. The bond angles would necessarily be 120º, 10.5º larger than the ideal tetrahedral angle. Also, every carbon-carbon bond in such a structure would be eclipsed. The resulting angle and eclipsing strains would severely destabilize this structure. If two carbon atoms on opposite sides of the six-membered ring are lifted out of the plane of the ring, much of the angle strain can be eliminated.



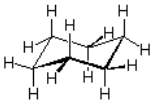
Planar Structure
severe angle strain (120°)
severe eclipsing strain (all bonds)
small steric strain



Boat Conformation
slight angle strain
eclipsing strain at two bonds
steric crowding of two hydrogens



Twist Boat Conformation
slight angle strain
small eclipsing strain
small steric strain



Chair Conformation
no angle strain
no eclipsing strain
small steric strain

This boat structure still has two eclipsed bonds and severe steric crowding of two hydrogen atoms on the "bow" and "stern" of the boat. This steric crowding is often called steric hindrance. By twisting the boat conformation, the steric hindrance can be partially relieved, but the twist-boat conformer still retains some of the strains that characterize the boat conformer. Finally, by lifting one carbon above the ring plane and the other below the plane, a relatively strain-free 'chair' conformer is formed. This is the predominant structure adopted by molecules of cyclohexane.

EXERCISE

EXERCISE 4.5.1

Consider the conformations of cyclohexane: planar, chair, boat, twist boat. Order them in increasing ring strain in the molecule.

Answer

Chair < Twist Boat < Boat < Planar (most ring strain)

QUESTIONS

Q4.5.1

Consider the conformations of cyclohexane, chair, boat, twist boat. Order them in increasing strain in the molecule.

SOLUTIONS

S4.5.1

Chair < Twist Boat < Boat (most strain)

CONTRIBUTORS AND ATTRIBUTIONS

>Robert Bruner (http://bbruner.org)

William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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4.6: AXIAL AND EQUATIORIAL BONDS IN CYCLOHEXANE

Objectives

After completing this section, you should be able to

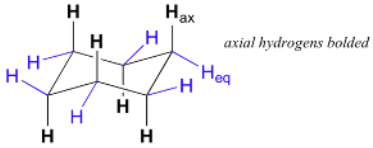
1. sketch the shorthand structure of cyclohexane, with axial and equatorial hydrogen atoms clearly shown and identified.
2. identify the axial and equatorial hydrogens in a given sketch of the cyclohexane molecule.
3. explain how chair conformations of cyclohexane and its derivatives can interconvert through the process of ring flip.

KEY TERMS

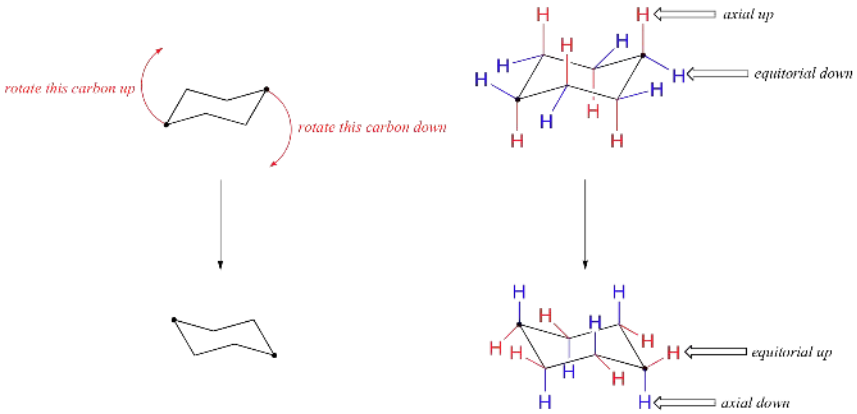
Make certain that you can define, and use in context, the key terms below.

- axial position
- equatorial position
- ring flip

On careful examination of a chair conformation of cyclohexane, we find that the twelve hydrogens are not structurally equivalent. Six of them are located about the periphery of the carbon ring, and are termed equatorial. The other six are oriented above and below the approximate plane of the ring (three in each location), and are termed axial because they are aligned parallel to the symmetry axis of the ring.



In the figure above, the equatorial hydrogens are colored blue, and the axial hydrogens are in bold. Since there are two equivalent chair conformations of cyclohexane in rapid equilibrium, all twelve hydrogens have 50% equatorial and 50% axial character. The figure below illustrates how to convert a molecular model of cyclohexane between two different chair conformations - this is something that you should practice with models. Notice that a 'ring flip' causes equatorial hydrogens to become axial, and vice-versa.



HOW TO DRAW STEREO BONDS ("UP" AND "DOWN" BONDS) EDIT SECTION

There are various ways to show these orientations. The solid (dark) "up wedge" I used is certainly common. Some people use an analogous "down wedge", which is light, to indicate a down bond; unfortunately, there is no agreement as to which way the wedge should point, and you are left relying on the lightness of the wedge to know it is "down". The "down bond" avoids this wedge ambiguity, and just uses some kind of light line. The down bond I used (e.g., in Figure 5B) is a dashed line; IUPAC encourages a series of parallel lines, something like A down bond of the type IUPAC prefers. It is a series of parallel lines.. What I did is a variation of what is recommended by IUPAC: http://www.chem.qmul.ac.uk/iupac/stereo/intro.html.

> *In **ISIS/Draw**, the "up wedge" and "down bond" that I used, along with other variations, are available from a tool button that may be labeled with any of them, depending on most recent use. It is located directly below the tool button for ordinary C-C bonds.*
>
> *In **Symyx Draw**, the "up wedge" and "down bond", along with other variations, are available from a tool button that may be labeled with any of them, depending on most recent use. It is located directly below the "Chain" tool button.*
>
> ***ChemSketch** provides up and down wedges, but not the simple up and down bonds discussed above. The wedges are available from the second toolbar across the top. For an expanded discussion of using these wedges, see the section of my ChemSketch Guide on Stereochemistry: Wedge bonds.*
>
> *As always, the information provided on these pages in intended to help you get started. Each program has more options for drawing bonds than discussed here. When you feel the need, look around!*

HOW TO DRAW CHAIRS EDIT SECTION

Most of the structures shown on this page were drawn with the free program **ISIS/Draw**. I have posted a guide to help you get started with ISIS/Draw. ISIS/Draw provides a simple cyclohexane (6-ring) hexagon template on the toolbar across the top. It provides templates for various 6-ring chair structures from the Templates menu; choose Rings. There are templates for simple chairs, without substituents (e.g., Fig 1B), and for chairs showing all the substituents (e.g., Fig 2B). In either case, you can add, delete, or change things as you wish. Various kinds of stereo bonds (wedges and bars) are available by clicking the left-side tool button that is just below the regular C-C single bond button. It may have a wedge shown on it, but this will vary depending on how it has been used. To choose a type of stereo bond, click on the button and hold the mouse click; a new menu will appear to the right of the button.

The free drawing program **Symyx Draw**, the successor to ISIS/Draw, provides similar templates and tools. A basic chair structure is provided on the default template bar that is shown. More options are available by choosing the Rings template. See my page Symyx Draw for a general guide for getting started with this program.

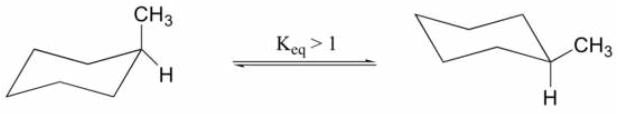
The free drawing program **ChemSketch** provides similar templates and tools. To find the special templates for chairs, go to the **Templates** menu, choose **Template Window**, and then choose "Rings" from the drop-down menu near upper left. See my page ChemSketch for a general guide for getting started with this program.

If you want to draw chair structures by hand (and if you are going on in organic chemistry, you should)... Be careful. The precise zigs and zags, and the angles of substituents are all important. Your textbook may offer you some hints for how to draw chairs. A short item in the Journal of Chemical Education offers a nice trick, showing how the chair can be thought of as consisting of an M and a W. The article is V Dragojlovic, A method for drawing the cyclohexane ring and its substituents. J Chem Educ 78:923, 7/01. (I thank M Farooq Wahab, Chemistry, Univ Karachi, for suggesting that this article be noted here.)

Aside from drawing the basic chair, the key points in adding substituents are:

- Axial groups alternate up and down, and are shown "vertical".
- Equatorial groups are approximately horizontal, but actually somewhat distorted from that, so that the angle from the axial group is a bit more than a right angle -- reflecting the common 109 degree bond angle.
- As cautioned before, it is usually easier to draw and see what is happening at the four corners of the chair than at the two middle positions. Try to use the corners as much as possible.

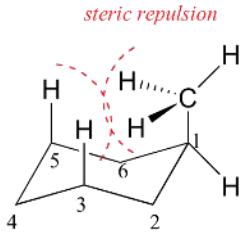
Because axial bonds are parallel to each other, substituents larger than hydrogen generally suffer greater steric crowding when they are oriented axial rather than equatorial. Consequently, ***substituted cyclohexanes will preferentially adopt conformations in which the larger substituents assume equatorial orientation***.



methyl group axial

methyl group equitorial (more stable)

When the methyl group in the structure above occupies an axial position it suffers steric crowding by the two axial hydrogens located on the same side of the ring.



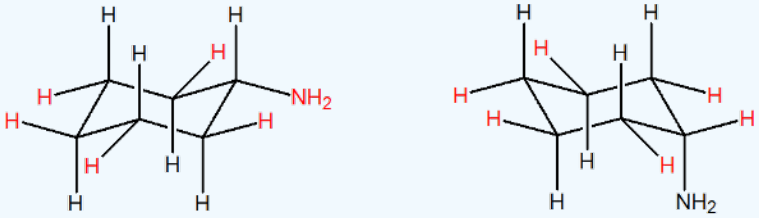
The conformation in which the methyl group is equatorial is more stable, and thus the equilibrium lies in this direction

EXERCISES

? EXERCISE 4.6.1

Draw two conformations of cyclohexyl amine ($C_6H_{11}NH_2$). Indicate axial and equatorial positions.

Answer



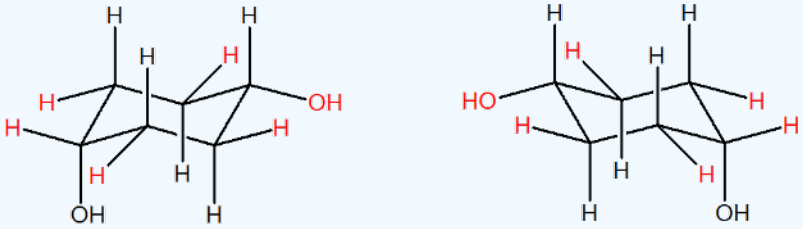
Axial

Equatorial

? EXERCISE 4.6.2

Draw the two isomers of 1,4-dihydroxylcyclohexane, identify which are equatorial and axial.

Answer



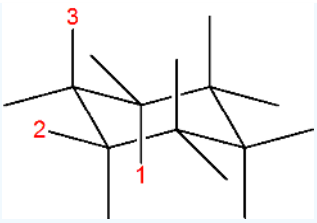
Axial

Equatorial

? EXERCISE 4.6.3

In the following molecule, label which are equatorial and axial, then draw the chair flip.

https://chem.libretexts.org/@go/page/67082



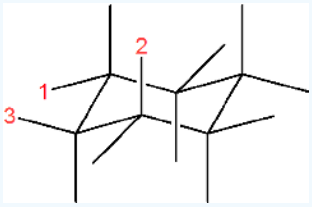
Answer

1 = axial

2 = equatorial

3 = axial

. . . chair flip



QUESTIONS

Q4.6.1

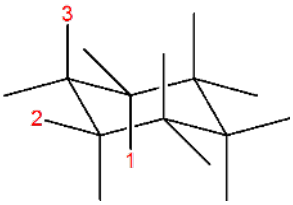
Draw two conformations of cyclohexyl amine ($C_6H_{11}NH_2$). Indicate axial and equatorial positions.

Q4.6.2

Draw the two isomers of 1,4-dihydroxylcyclohexane, identify which are equatorial and axial.

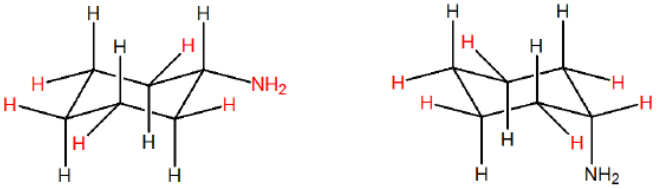
Q4.6.3

In the following molecule, label which are equatorial and which are axial, then draw the chair flip (showing labels 1,2,3).



SOLUTIONS

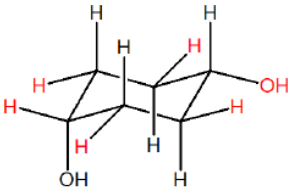
S4.6.1

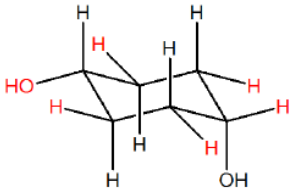


Axial

Equatorial

S4.6.2





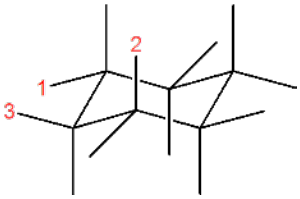
Axial

Equatorial

S4.6.3

Original conformation: 1 = axial, 2 = equatorial, 3 = axial

Flipped chair now looks like this.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

Prof. Steven Farmer (Sonoma State University)

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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4.7: CONFORMATIONS OF MONOSUBSTITUTED CYCLOHEXANES

Objectives

After completing this section, you should be able to

1. account for the greater stability of the equatorial conformers of monosubstituted cyclohexanes compared to their axial counterparts, using the concept of 1,3-diaxial interaction.
2. compare the gauche interactions in butane with the 1,3-diaxial interactions in the axial conformer of methylcyclohexane.
3. arrange a given list of substituents in increasing or decreasing order of 1,3-diaxial interactions.

KEY TERMS

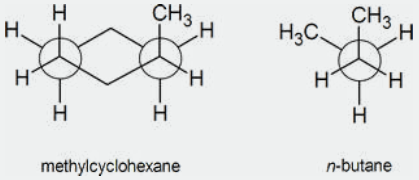
Make certain that you can define, and use in context, the key term below.

- 1,3-diaxial interaction

STUDY NOTES

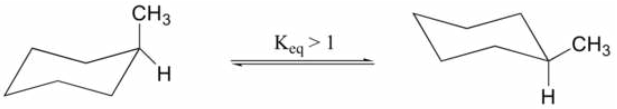
1,3-Diaxial interactions are steric interactions between an axial substituent located on carbon atom 1 of a cyclohexane ring and the hydrogen atoms (or other substituents) located on carbon atoms 3 and 5.

Be prepared to draw Newman-type projections for cyclohexane derivatives as the one shown for methylcyclohexane. Note that this is similar to the Newman projections from chapter 3 such as *n*-butane.

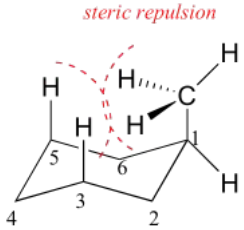


Newman projections of methylcyclohexane and *n*-butane

Because axial bonds are parallel to each other, substituents larger than hydrogen generally suffer greater steric crowding when they are oriented axial rather than equatorial. Consequently, ***substituted cyclohexanes will preferentially adopt conformations in which the larger substituents assume equatorial orientation***.



When the methyl group in the structure above occupies an axial position it suffers steric crowding by the two axial hydrogens located on the same side of the ring.



The conformation in which the methyl group is equatorial is more stable, and thus the equilibrium lies in this direction.

The relative steric hindrance experienced by different substituent groups oriented in an axial versus equatorial location on cyclohexane may be determined by the conformational equilibrium of the compound. The corresponding equilibrium constant is related to the energy difference between the conformers, and collecting such data allows us to evaluate the relative tendency of substituents to exist in an equatorial or axial location.A table of these free energy values (sometimes referred to as A values) may be examined by clicking here.

Looking at the energy values in this table, it is clear that the apparent "size" of a substituent (in terms of its preference for equatorial over axial orientation) is influenced by its width and bond length to cyclohexane, as evidenced by the fact that an axial vinyl group is less hindered than ethyl, and iodine slightly less than chlorine.

We noted earlier that cycloalkanes having two or more substituents on different ring carbon atoms exist as a pair (sometimes more) of configurational stereoisomers. Now we must examine the way in which favorable ring conformations influence the properties of the configurational isomers. Remember, configurational stereoisomers are stable and do not easily interconvert, whereas, conformational isomers normally interconvert rapidly. In examining possible structures for substituted cyclohexanes, it is useful to follow two principles:

i. Chair conformations are generally more stable than other possibilities.
ii. Substituents on chair conformers prefer to occupy equatorial positions due to the increased steric hindrance of axial locations.

Strain values for other cyclohexane substituents can also be considered. The relative steric hindrance experienced by different substituent groups oriented in an axial versus equatorial location on cyclohexane determined the amount of strain generated. The strain generated can be used to evaluate the relative tendency of substituents to exist in an equatorial or axial location. Looking at the energy values in this table, it is clear that as the size of the substituent increases, the 1,3-diaxial energy tends to increase, also. Note that it is the size and not the molecular weight of the group that is important. Table 4.7.1 summarizes some of these strain values values.

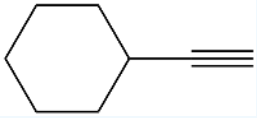
Table 4.7.1: A Selection of ΔG° *Values for the Change from Axial to Equatorial Orientation of Substituents for Monosubstituted Cyclohexanes*

Substituent	-ΔG° (kJ/mol)	Substituent	-ΔG° (kJ/mol)
CH_3–	7.4	HO–	3.9
CH_2H_5–	7.6	N≡C–	0.8
$(CH_3)_2CH$–	9.2	CH_3O–	2.1
$(CH_3)_3C$–	20.0	HO_2C–	5.9
F–	1.4	H_2C=CH–	2.0
Cl–	2.4	C_6H_5–	12.0
Br–	2.4		
I–	2.4		

EXERCISES

? EXERCISE 4.7.1

In the molecule, cyclohexyl ethyne there is little steric strain, why?



Answer

The ethyne group is linear and therefore does not affect the hydrogens in the 1,3 positions to say to the extent as a bulkier or a bent group (e.g. ethene group) would. This leads to less of a strain on the molecule.



EXERCISE 4.7.2

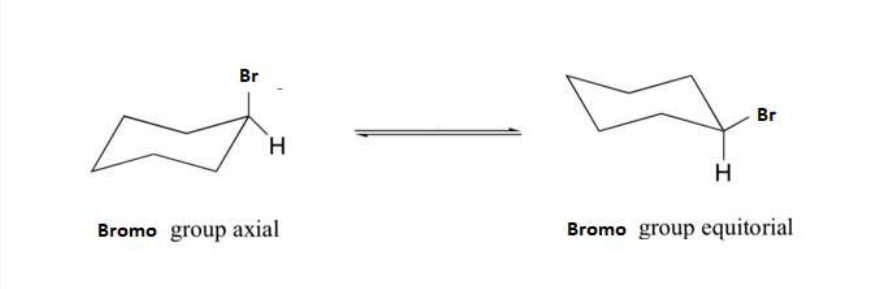
Calculate the energy difference between the axial and equatorial conformations of bromocyclohexane?

Answer

Bromocyclohexane will have two 1,3 diaxial interactions. The table above states that the total strain between axial and equatorial bromocyclohexane will be 2.4 kJ/mol.

EXERCISE 4.7.3

Using your answer from the previous question estimate the percentages of axial and equatorial conformations of bromocyclohexane at 25° C.



Answer

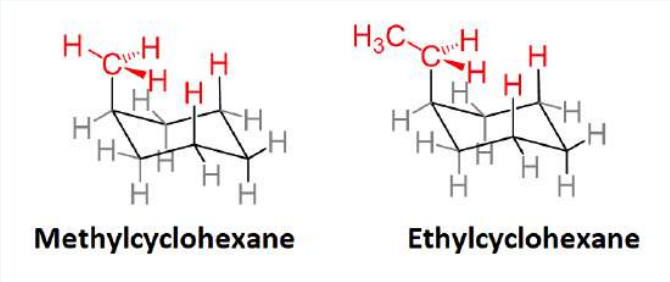
Remembering that the axial conformation is higher in energy, the energy difference between the two conformations is ΔE = (E equatorial - E axial) = (0 - 2.4 kJ/mol) = -2.4 kJ/mol. After converting ^{o}C to Kelvin and kJ/mol to J/mol we can use the equation ΔE = -RT lnK to find that -ΔE/RT = lnK or (2.4 x 10^{3} J/mol) / (8.313 kJ/mol K • 298 K) = lnK. From this we calculate that K = 2.6. Because the ring flip reaction is an equilibrium we can say that K = [Equatorial] / [Axial]. If assumption is made that [Equatorial] = X then [Axial] must be 1-X. Plugging these values into the equilibrium expression produces K = [X] / [1-X]. After plugging in the calculated value for K, X can be solved algebraically. 2.6 = [X] / [1-X] → 2.6 - 2.6X = X → 2.6 = 3.6X → 2.6/3.6 = X = 0.72. This means that bromocyclohexane is in the equatorial position 72% of the time and in the axial position 28% of the time.

EXERCISE 4.7.4

There very little in 1,3-diaxial strain when going from a methyl substituent (3.8 kJ/mol) to an ethyl substituent (4.0 kJ/mol), why? It may help to use molecular model to answer this question.

Answer

The fact that C-C sigma bonds can freely rotate allows the ethyl subsistent to obtain a conformation which places the bulky CH_3 group away from the cyclohexane ring. This forces the ethyl substituent to have only have 1,3- diaxial interactions between hydrogens, which only provides a slight difference to a methyl group.



QUESTIONS

Q4.7.1

In the molecule, cyclohexyl ethyne there is little steric strain, why?

SOLUTIONS

S4.7.1

The ethyne group is linear and therefore does not affect the hydrogens in the 1,3 positions to say to the extent as a bulkier or a bent group (e.g. ethene group) would. This leads to less of a strain on the molecule.



CONTRIBUTORS AND ATTRIBUTIONS

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- Prof. Steven Farmer (Sonoma State University)

>Robert Bruner (http://bbruner.org)

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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4.8: CONFORMATIONS OF DISUBSTITUTED CYCLOHEXANES

OBJECTIVE

After completing this section, you should be able to use conformational analysis to determine the most stable conformation of a given disubstituted cyclohexane.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- conformational analysis

STUDY NOTES

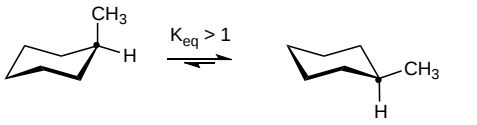
When faced with the problem of trying to decide which of two conformers of a given disubstituted cyclohexane is the more stable, you may find the following generalizations helpful.

1. A conformation in which both substituents are equatorial will always be more stable than a conformation with both groups axial.
2. When one substituent is axial and the other is equatorial, the most stable conformation will be the one with the bulkiest substituent in the equatorial position. Steric bulk decreases in the order

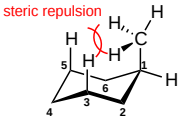
   tert-butyl > isopropyl > ethyl > methyl > hydroxyl > halogens

MONOSUBSTITUTED CYCLOHEXANES

In the previous section, it was stated that the chair conformation in which the methyl group is equatorial is more stable because it minimizes steric repulsion, and thus the equilibrium favors the more stable conformer. This is true for all monosubstituted cyclohexanes. The chair conformation which places the substituent in the equatorial position will be the most stable and be favored in the ring flip equilibrium.



methyl group axial — methyl group equatorial (more stable by **7 kJ/mol**)



DISUBSTITUTED CYCLOHEXANES

Determining the more stable chair conformation becomes more complex when there are two or more substituents attached to the cyclohexane ring. To determine the stable chair conformation, the steric effects of each substituent, along with any additional steric interactions, must be taken into account for both chair conformations.

In this section, the effect of conformations on the relative stability of disubstituted cyclohexanes is examined using the two principles:

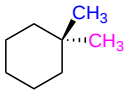
i. Substituents prefer equatorial rather than axial positions in order to minimize the steric strain created of 1,3-diaxial interactions.
ii. The more stable conformation will place the larger substituent in the equatorial position.

1,1-DISUBSTITUTED CYCLOHEXANES

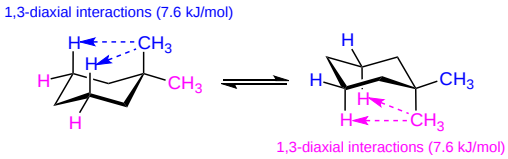
The more stable chair conformation can often be determined empirically or by using the energy values of steric interactions previously discussed in this chapter. Note, in some cases there is no discernable energy difference between the two chair conformations which means they are equally stable.

1,1-dimethylcyclohexane does not have *cis* or *trans* isomers, because both methyl groups are on the same ring carbon. Both chair conformers have one methyl group in an axial position and one methyl group in an equatorial position giving both the same relative stability. The steric strain created by the 1,3-diaxial interactions of a methyl group in an axial position (versus equatorial) is 7.6 kJ/mol (from Table 4.7.1), so both conformers will have equal amounts of steric strain. Thus, the equilibrium between the two conformers does not

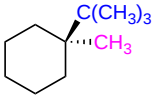
favor one or the other. Note, that both methyl groups cannot be equatorial at the same time without breaking bonds and creating a different molecule.



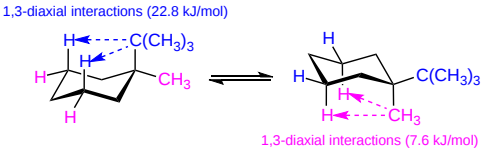
1,1-dimethylcyclohexane



However, if the two groups are different, as in 1-*tert*-butyl-1-methylcyclohexane, then the equilibrium favors the conformer in which the larger group (*tert*-butyl in this case) is in the more stable equatorial position. The energy cost of having one tert-butyl group axial (versus equatorial) can be calculated from the values in table 4.7.1 and is approximately 22.8 kJ/mol. The conformer with the *tert*-butyl group axial is approximately 15.2 kJ/mol (22.8 kJ/mol - 7.6 kJ/mol) less stable then the conformer with the *tert*-butyl group equatorial. Solving for the equilibrium constant K shows that the equatorial is preferred about 460:1 over axial. This means that 1-*tert*-butyl-1-methylcyclohexane will spend the majority of its time in the more stable conformation, with the *tert*-butyl group in the equatorial position.

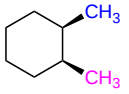


1-(*tert*-butyl)-1-methylcyclohexane

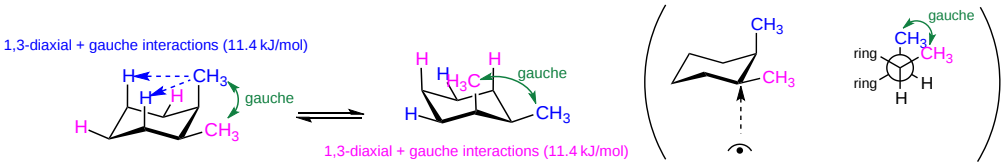


CIS AND *TRANS* STEREOISOMERS OF 1,2-DIMETHYLCYCLOHEXANE

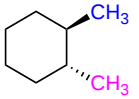
In *cis*-1,2-dimethylcyclohexane, both chair conformations have one methyl group equatorial and one methyl group axial. As previously discussed, the axial methyl group creates 7.6 kJ/mol of steric strain due to 1,3-diaxial interactions. It is important to note, that both chair conformations also have an additional 3.8 kJ/mol of steric strain created by a gauche interaction between the two methyl groups. Overall, both chair conformations have 11.4 kJ/mol of steric strain and are of equal stability.



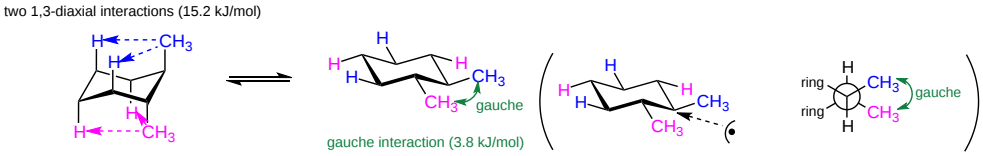
cis-1,2-dimethylcyclohexane



In *trans*-1,2-dimethylcyclohexane, one chair conformer has both methyl groups axial and the other conformer has both methyl groups equatorial. The conformer with both methyl groups equatorial has no 1,3-diaxial interactions however there is till 3.8 kJ/mol of strain created by a gauche interaction. The conformer with both methyl groups axial has four 1,3-Diaxial interactions which creates 2 x 7.6 kJ/mol (15.2 kJ/mol) of steric strain. This conformer is (15.2 kJ/mol -3.8 kJ/mol) 11.4 kJ/mol less stable than the other conformer. The equilibrium will therefore favor the conformer with both methyl groups in the equatorial position.

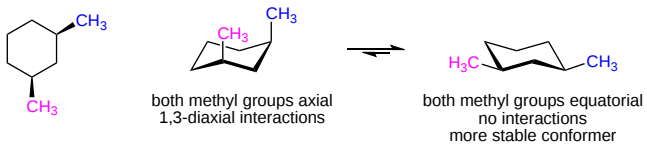


trans-1,2-dimethylcyclohexane

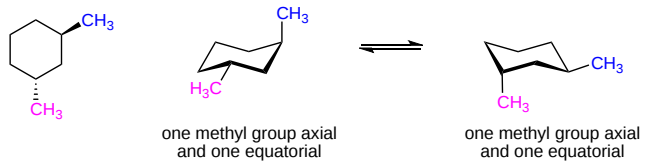


CIS AND *TRANS* STEREOISOMERS OF 1,3-DIMETHYLCYCLOHEXANE

A similar conformational analysis can be made for the *cis* and *trans* stereoisomers of 1,3-dimethylcyclohexane. For *cis*-1,3-dimethylcyclohexane one chair conformation has both methyl groups in axial positions creating 1,3-diaxial interactions. The other conformer has both methyl groups in equatorial positions thus creating no 1,3-diaxial interaction. Because the methyl groups are not on adjacent carbons in the cyclohexane rings gauche interactions are not possible. Even without energy calculations it is simple to determine that the conformer with both methyl groups in the equatorial position will be the more stable conformer.



For *trans*-1,3-dimethylcyclohexane both conformations have one methyl axial and one methyl group equatorial. Each conformer has one methyl group creating a 1,3-diaxial interaction so both are of equal stability.



SUMMARY OF DISUBSTITUED CYCLOHEXANE CHAIR CONFORMATIONS

When considering the conformational analyses discussed above a pattern begins to form. There are only two possible relationships which can occur between ring-flip chair conformations:

1) AA/EE: One chair conformation places both substituents in axial positions creating 1,3-diaxial interactions. The other conformer places both substituents in equatorial positions creating no 1,3-diaxial interactions. This diequatorial conformer is the more stable regardless of the substituents.

2) AE/EA: Each chair conformation places one substituent in the axial position and one substituent in the equatorial position. If the substituents are the same, there will be equal 1,3-diaxial interactions in both conformers making them equal in stability. However, if the substituents are different then different 1,3-diaxial interactions will occur. The chair conformation which places the larger substituent in the equatorial position will be favored.

Substitution type	Chair Conformation Relationship
cs-1,2-disubstituted cyclohexanes	AE/EA
trans-1,2-disubstituted cyclohexanes	AA/EE
cis-1,3-disubstituted cyclohexanes	AA/EE
trans-1,3-disubstituted cyclohexanes	AE/EA
cis-1,4-disubstituted cyclohexanes	AE/EA
trans-1,4-disubstituted cyclohexanes	AA/EE

✔ EXAMPLE 4.8.1

For *cis*-1-chloro-4-methylcyclohexane, draw the most stable chair conformation and determine the energy difference between the two chair conformers.

Solution

Based on the table above, *cis*-1,4-disubstitued cyclohexanes should have two chair conformations each with one substituent axial and one equatorial. Based on this, we can surmise that the energy difference of the two chair conformations will be based on the difference

in the 1,3-diaxial interactions created by the methyl and chloro substituents.



As predicted, each chair conformer places one of the substituents in the axial position. Because the methyl group is larger and has a greater 1,3-diaxial interaction than the chloro, the most stable conformer will place it the equatorial position, as shown in the structure on the right. Using the 1,3-diaxial energy values given in the previous sections we can calculate that the conformer on the right is (7.6 kJ/mol - 2.0 kJ/mol) 5.6 kJ/mol more stable than the other.

EXAMPLE 4.8.2

For *trans*-1-chloro-2-methylcyclohexane, draw the most stable chair conformation and determine the energy difference between the two chair conformers.

Solution

Based on the table above, *trans*-1,2-disubstitued cyclohexanes should have one chair conformation with both substituents axial and one conformation with both substituents equatorial. Based on this, we can predict that the conformer which places both substituents equatorial will be the more stable conformer. The energy difference of the two chair conformations will be based on the 1,3-diaxial interactions created by both the methyl and chloro substituents.

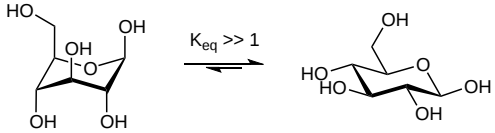


As predicted, one chair conformer places both substituents in the axial position and other places both substituents equatorial. The more stable conformer will place both substituents in the equatorial position, as shown in the structure on the right. Using the 1,3-diaxial energy values given in the previous sections we can calculate that the conformer on the right is (7.6 kJ/mol + 2.0 kJ/mol) 9.6 kJ/mol more stable than the other.

CONFORMATIONAL ANALYSIS OF COMPLEX SIX MEMBERED RING STRUCTURES

Cyclohexane can have more than two substituents. Also, there are multiple six membered rings which contain atoms other than carbon. All of these systems usually form chair conformations and follow the same steric constraints discussed in this section. Because the most commonly found rings in nature are six membered, conformational analysis can often help in understanding the usual shapes of some biologically important molecules. In complex six membered ring structures a direct calculation of 1,3-diaxial energy values may be difficult. In these cases a determination of the more stable chair conformer can be made by empirically applying the principles of steric interactions.

A later chapter will discuss how many sugars can exist in cyclic forms which are often six remembered rings. When in an aqueous solution the six carbon sugar, glucose, is usually a six membered ring adopting a chair conformation. When looking at the two possible ring-clip chair conformations, one has all of the substituents axial and the other has all the substutents equatorial. Even without a calculation, it is clear that the conformation with all equatorial substituents is the most stable and glucose will most commonly be found in this conformation.

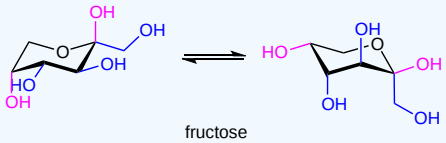


glucose
(β-glucopyranose form)

https://chem.libretexts.org/@go/page/67084

EXAMPLE 4.8.3

The six carbon sugar, fructose, in aqueous solution is also a six-membered ring in a chair conformation. Which of the two possible chair conformations would be expected to be the most stable?



fructose
(β-fructopyranose form)

Solution

The lower energy chair conformation is the one with three of the five substituents (including the bulky $–CH_2OH$ group) in the equatorial position (pictured on the right). The left structure has 3 equatorial substituents while the structure on the right only has two equatorial substituents.

EXERCISES

1. Draw the two chair conformations for *cis*-1-ethyl-2-methylcyclohexane using bond-line structures and indicate the more energetically favored conformation.

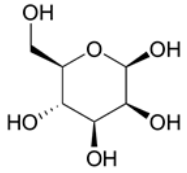
2. Draw the most stable conformation for *trans*-1-ethyl-3-methylcyclohexane using bond-line structures.

3. Draw the most stable conformation for trans-1-*t*-butyl-4-methylcyclohexane using bond-line structures.

4. Draw the most stable conformation fo *trans*-1-isopropyl-3-methylcyclohexane.

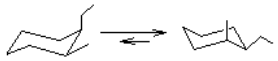
5. Can a 'ring flip' change a *cis*-disubstituted cyclohexane to *trans*? Explain.

6. Draw the two chair conformations of the six-carbon sugar mannose, being sure to clearly show each non-hydrogen substituent as axial or equatorial. Predict which conformation is likely to be more stable, and explain why.

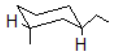


mannose

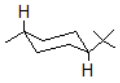
SOLUTIONS

1. 

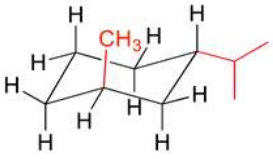
larger ethyl group in equatorial position is favored

2. 

larger ethyl group in equatorial position is favored

3. 

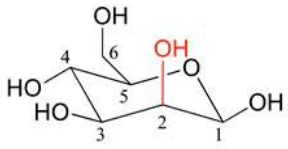
both alkyl groups in equatorial position

4. 

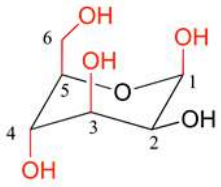
The bulkier isopropyl groups is in the equatorial position.

5. No. In order to change the relationship of two substituents on a ring from *cis* to *trans*, you would need to break and reform two covalent bonds. Ring flips involve only *rotation* of single bonds.

6.



major chair form of mannose
(only one substituent axial)



minor chair form of mannose
(four substituents axial)

EXERCISES

QUESTIONS

Q4.8.1

For the following molecules draw the most stable chair conformation and explain why you chose this as an answer

1 = *trans*-1,2-dimethylcyclohexane

2 = *cis*-1,3-dimethylcyclohexane

SOLUTIONS

S4.8.1

1 – The most stable conformation would be to have the methyl groups equatorial reducing steric interaction

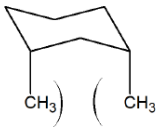
2 – The most stable conformation would be to have the groups equatorial this would reduce the strain if they were axial



1



2



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4.9: CONFORMATIONS OF POLYCYCLIC MOLECULES

Objective

After completing this section, you should be able to draw the structures and construct molecular models of *cis*- and *trans*-decalin and of norbornane.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- bridgehead carbon atom
- polycyclic molecule

STUDY NOTES

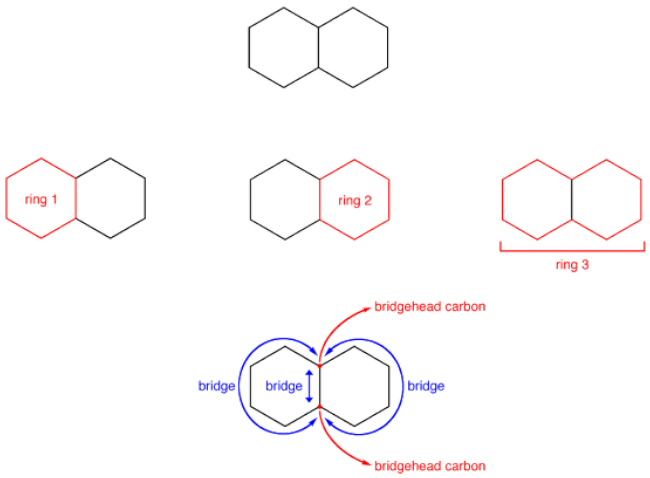
A *bridgehead carbon atom* is a carbon atom which is shared by at least two rings. The hydrogen atom which is attached to a bridgehead carbon may be referred to as a bridgehead hydrogen.

Note that bicyclo[2.2.1]heptane is the systematic name of norborane. You need not be concerned over the IUPAC name of norbornane. The nomenclature of compounds of this type is beyond the scope of this course.

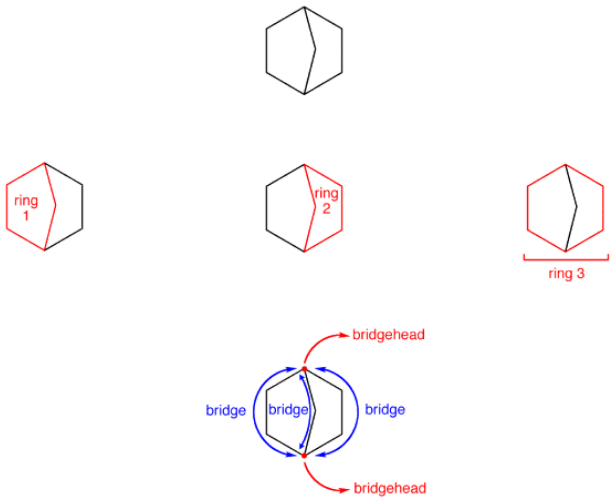
BICYCLIC RING SYSTEMS

A bridged bicycloalkane is a bicycloalkane whose molecule has two carbon atoms shared by all three rings identifiable in the molecule. The two carbon atoms shared by the three rings are called bridgehead carbon atoms. A bond or a chain of bonds connecting the bridgehead carbon atoms is called a bridge.

eg. 1: Decalin



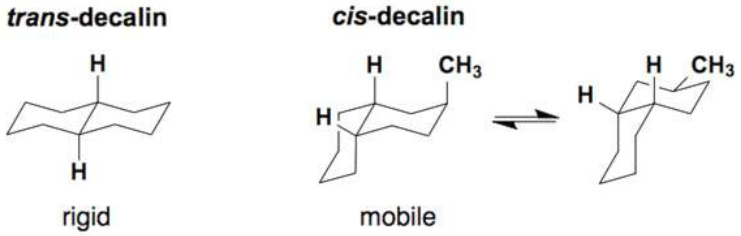
eg. 2: bicyclo[2.2.1]heptane



If in a bridged bicycloalkane, the bridgehead carbons are directly bonded to each other, the compound is called a fused bicycloalkane. In other words, in a fused bicycloalkane, the number of carbon atoms in one of the three bridges is zero. eg: decalin

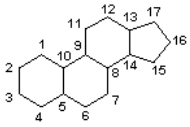
see also spirobicycloalkane

Decalins can come in two diastereomers, the *trans*- or *cis*- diastereomer. The *trans*-diastereomer is a rigid structure which cannot undergo a ring flip. The *cis*-diastereomer is mobile and can ring flip to allow substituents to sit in the equatorial position.



STEROIDS

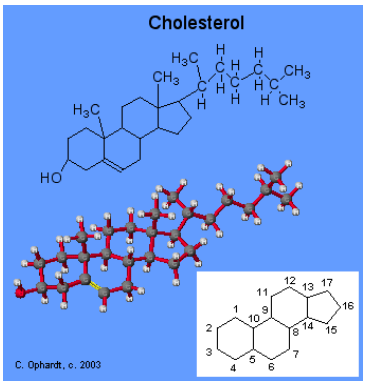
Steroids include such well known compounds as cholesterol, sex hormones, birth control pills, cortisone, and anabolic steroids.



CHOLESTEROL EDIT SECTION

The best known and most abundant steroid in the body is cholesterol. Cholesterol is formed in brain tissue, nerve tissue, and the blood stream. It is the major compound found in gallstones and bile salts. Cholesterol also contributes to the formation of deposits on the inner walls of blood vessels. These deposits harden and obstruct the flow of blood. This condition, known as atherosclerosis, results in various heart diseases, strokes, and high blood pressure.

Much research is currently underway to determine if a correlation exists between cholesterol levels in the blood and diet. Not only does cholesterol come from the diet, but cholesterol is synthesized in the body from carbohydrates and proteins as well as fat. Therefore, the elimination of cholesterol rich foods from the diet does not necessarily lower blood cholesterol levels. Some studies have found that if certain unsaturated fats and oils are substituted for saturated fats, the blood cholesterol level decreases. The research is incomplete on this problem.

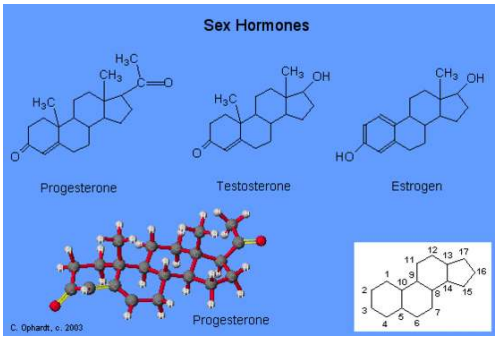


STRUCTURES OF SEX HORMONES

Sex hormones are also steroids. The primary male hormone, testosterone, is responsible for the development of secondary sex characteristics. Two female sex hormones, progesterone and estrogen or estradiol control the ovulation cycle. Notice that the male and female hormones have only slight differences in structures, but yet have very different physiological effects.

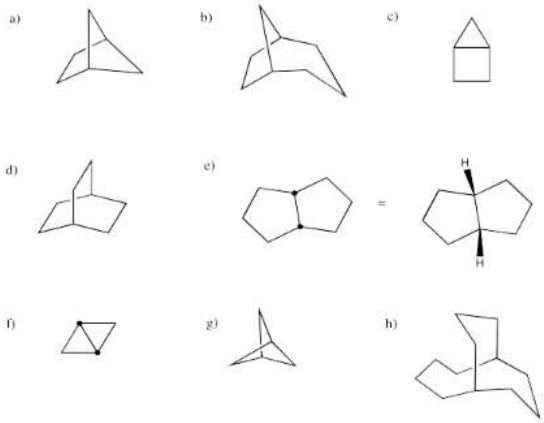
Testosterone promotes the normal development of male genital organs ans is synthesized from cholesterol in the testes. It also promotes secondary male sexual characteristics such as deep voice, facial and body hair.

Estrogen, along with progesterone regulates changes occurring in the uterus and ovaries known as the menstrual cycle. For more details see Birth Control. Estrogen is synthesized from testosterone by making the first ring aromatic which results in mole double bonds, the loss of a methyl group and formation of an alcohol group.

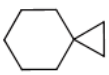


EXERCISES

1) Name the following compounds.



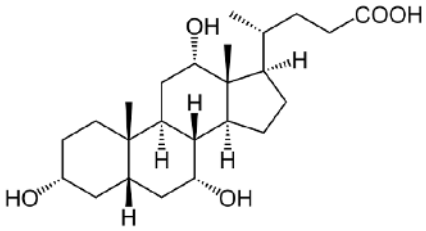
i)



j)



2) The following molecule is cholic acid. Determine if the three fused bonds have a *cis* or *trans* configuration.



SOLUTIONS

1)

a) Bicyclo[2.1.1]hexane

b) Bicyclo[3.2.1]octane

c) Bicyclo[2.1.0]pentane (more commonly called "housane")

d) Bicyclo[2.2.2]octane

e) cis-Bicyclo[3.3.0]octane

f) cis-Bicyclo[1.1.0]butane

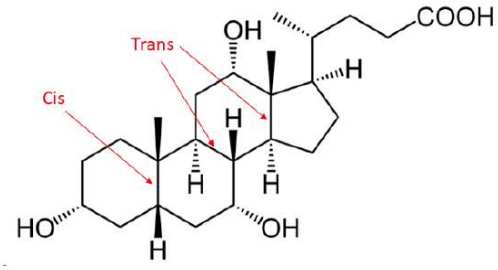
g) Bicyclo[1.1.1]pentane

h) Bicyclo[4.3.3]dodecane

i) Spiro[5.2]octane

j) Spiro[3.3]heptane

2)



QUESTIONS

Q4.9.1

Someone stated that *trans*-decalin is more stable than *cis*-decalin. Explain why this is incorrect.

SOLUTIONS

S4.9.1

Cis-decalin has fewer steric interactions than *trans*-decalin.

CONTRIBUTORS AND ATTRIBUTIONS

- Gamini Gunawardena from the OChemPal site (Utah Valley University)

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

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4.S: ORGANIC COMPOUNDS- CYCLOALKANES AND THEIR STEREOCHEMISTRY (SUMMARY)

CONCEPTS & VOCABULARY

4.1: Naming Cycloalkanes

- Cycloalkanes are saturated hydrocarbons that have the generic formula $\mathbf{C_nH_{2n}}$, where **n** is the number of carbons in the ring.
- The IUPAC rules for naming cycloalkanes is very similar to the rules used for naming alkanes.

4.2: Cis-Trans Isomerism in Cycloalkanes

- **Stereoisomers** are molecules that have the same molecular formula, the same atom connectivity, but they differ in the relative spatial orientation of the atoms.
- Di-substituted cycloalkanes exhibit ***cis***- / ***trans***- stereoisomerism. The ***cis***- isomer has both substituents on the same face of the ring, while the **trans**- isomer has groups on opposite faces of the ring.

4.3: Stability of Cycloalkanes - Ring Strain

- **Ring strain** is the total strain in a ring due to **torsional strain**, **steric strain** and **angle strain**.
- Angle strain is when the C-C-C bond angles in rings are different than 109.5º, the optimal bond angle for sp^3 hybridized carbons.
- Ring strain causes small cycloalkanes, like cyclopropane and cyclobutane, to be much less stable than other cycloalkanes.

4.4: Conformations of Cycloalkanes

- Cyclopentane has less ring strain than cyclopropane and cyclobutane, because its ring carbons have more flexibility to rotate away from planarity, resulting in lower angle and torsional strains.

4.5: Conformations of Cyclohexane

- Cyclohexane has significantly lower ring strain than smaller cycloalkanes, because cyclohexane can adopt non-planar structures, which minimize angle strain and torsional strain.
- The common non-planar structures of cyclohexane are the boat, twist-boat, and chair conformations. The most stable, and hence, the most common, is the chair conformation.

4.6: Axial and Equatorial Bonds in Cyclohexane

- The two chair conformations of cyclohexane interconvert rapidly at room temperature in a process called **chair flip** or **ring flip**.
- In the chair conformation of cyclohexane, of the two groups attached to each ring carbon, one of the groups occupies the **axial** position, while the other group occupies the **equatorial** position.
- A group that was axial will switch to the equatorial position during a ring flip, and vice versa.

4.7: Conformations of Monosubstituted Cyclohexanes

- To minimize the steric effects of **1,3-diaxial interactions**, the single group on a monosubstituted cyclohexane ring will prefer to be in the equatorial position over the axial position. The larger the group, the greater is the preference shifts.

4.8: Conformations of Disubstituted Cyclohexanes

- The preference for large groups to be in the equatorial position effects the relative stability of the *cis* and *trans* isomers of disubstituted cyclohexanes. **Conformational analysis** is the process used to determine which isomer, *cis* or *trans*, is most stable.

4.9: Conformations of Polycyclic Molecules

SKILLS TO MASTER

- Skill 4.1 Be able to name and draw cycloalkanes
- Skill 4.2 Identify and draw the *cis*- and *trans*- stereoisomers of disubstituted cycloalkanes.
- Skill 4.3 Determine the effects of torsional strain, steric strain, and angle strain on the overall ring strain of a cycloalkane.
- Skill 4.4 Draw the chair conformers of cyclohexane.
- Skill 4.5 Draw and identify the axial and equatorial positions in a chair conformer of cyclohexane and its ring-flip conformer.
- Skill 4.6 Use conformational analysis to determine the most stable stereoisomer in disubstituted and polysubstituted cyclohexanes.

CONTRIBUTORS

- Dr. Kelly Matthews, Harrisburg Area Community College

4.S: Organic Compounds- Cycloalkanes and their Stereochemistry (Summary) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

5: STEREOCHEMISTRY AT TETRAHEDRAL CENTRES

LEARNING OBJECTIVES

After you have completed Chapter 5, you should be able to

1. fulfill all of the detailed objectives listed under each individual section.
2. use molecular models in solving problems on stereochemistry.
3. solve road-map problems that include stereochemical information.
4. define, and use in context, the new key terms.

This chapter introduces the concept of chirality, and discusses the structure of compounds containing one or two chiral centers. A convenient method of representing the three-dimensional arrangement of the atoms in chiral compounds is explained; furthermore, throughout the chapter , considerable emphasis is placed on the use of molecular models to assist in the understanding of the phenomenon of chirality. The chapter continues with an examination of stereochemistry—the three-dimensional nature of molecules. The subject is introduced using the experimental observation that certain substances have the ability to rotate plane-polarized light. Finally, certain reactions of alkenes are re-examined in the light of the new material encountered in this chapter.

5.0: Prelude
5.1: Enantiomers and the Tetrahedral Carbon
5.2: The Reason for Handedness in Molecules- Chirality
5.3: Optical Activity
5.4: Pasteur's Discovery of Enantiomers
5.5: Sequence Rules for Specifying Configuration
5.6: Diastereomers
5.7: Meso Compounds
5.8: Racemic Mixtures and the Resolution of Enantiomers
5.9: A Review of Isomerism
5.10: Chirality at Nitrogen, Phosphorus, and Sulfur
5.11: Prochirality
5.12: Chirality in Nature and Chiral Environments
5.S: Stereochemistry at Tetrahedral Centers (Summary)

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5.1: ENANTIOMERS AND THE TETRAHEDRAL CARBON

Objectives

After completing this section, you should be able to

1. use molecular models to show that only a tetrahedral carbon atom satisfactorily accounts for the lack of isomerism in molecules of the type CH_2XY, and for the existence of optical isomerism in molecules of the type CHXYZ.
2. determine whether two differently oriented wedge-and-broken-line structures are identical or represent a pair of enantiomers.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

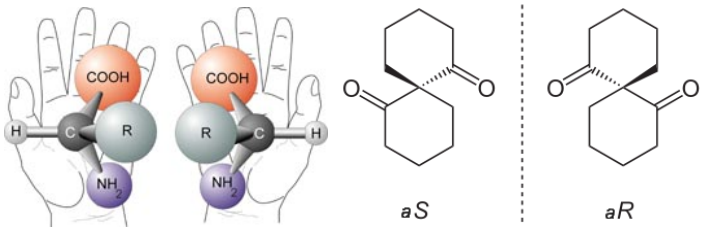
- enantiomer

STUDY NOTES

Stereoisomers are isomers that differ in spatial arrangement of atoms, rather than order of atomic connectivity. One of their most interesting type of isomer is the mirror-image stereoisomers, a non-superimposable set of two molecules that are mirror image of one another. The existance of these molecules are determined by concept known as **chirality**. The word “chiral” was derived from the Greek word for hand, because our hands display a good example of chirality since they are non-superimposable mirror images of each other.

INTRODUCTION

The opposite of chiral is **achiral**. Achiral objects are superimposable with their mirror images. For example, two pieces of paper are achiral. In contrast, chiral molecules, like our hands, are non superimposable mirror images of each other. Try to line up your left hand perfectly with your right hand, so that the palms are both facing in the same directions. Spend about a minute doing this. Do you see that they cannot line up exactly? The same thing applies to some molecules



A Chiral molecule has a mirror image that cannot line up with it perfectly- the mirror images are non superimposable. The mirror images are called **enantiomers**. But why are chiral molecules so interesting? A chiral molecule and its enantiomer have the same chemical and physical properties(boiling point, melting point,polarity, density etc...). It turns out that many of our biological molecules such as our DNA, amino acids and sugars, are chiral molecules.

It is pretty interesting that our hands seem to serve the same purpose but most people are only able to use one of their hands to write. Similarily this is true with chiral biological molecules and interactions. Just like your left hand will not fit properly in your right glove, one of the enantiomers of a molecule may not work the same way in your body.

This must mean that enantiomers have properties that make them unique to their mirror images. One of these properties is that they cannot have a **plane of symmetry** or an internal mirror plane. So, a chiral molecule cannot be divided in two mirror image halves. Another property of chiral molecules is optical activity.

Organic compounds, molecules created around a chain of carbon atom (more commonly known as carbon backbone), play an essential role in the chemistry of life. These molecules derive their importance from the energy they carry, mainly in a form of potential energy between atomic molecules. Since such potential force can be widely affected due to changes in atomic placement, it is important to understand the concept of an isomer, a molecule sharing same atomic make up as another but differing in structural arrangements. This article will be devoted to a specific isomers called stereoisomers and its property of chirality (Figure 5.1.1).

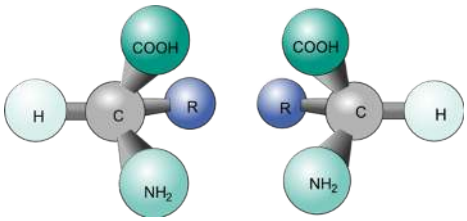


Figure 5.1.1. *Two enantiomers of a tetrahedral complex. from Wikipedia*

The concepts of steroisomerism and chirality command great deal of importance in modern organic chemistry, as these ideas helps to understand the physical and theoretical reasons behind the formation and structures of numerous organic molecules, the main reason behind the energy embedded in these essential chemicals. In contrast to more well-known constitutional isomerism, which develops isotopic compounds simply by different atomic connectivity, stereoisomerism generally maintains equal atomic connections and orders of building blocks as well as having same numbers of atoms and types of elements.

What, then, makes stereoisomers so unique? To answer this question, the learner must be able to think and imagine in not just two-dimensional images, but also three-dimensional space. This is due to the fact that stereoisomers are isomers because their atoms are different from others in terms of spatial arrangement.

SPATIAL ARRANGEMENT

First and foremost, one must understand the concept of spatial arrangement in order to understand stereoisomerism and chirality. Spatial arrangement of atoms concern how different atomic particles and molecules are situated about in the space around the organic compound, namely its carbon chain. In this sense, spatial arrangement of an organic molecule are different another if an atom is shifted in any three-dimensional direction by even one degree. This opens up a very broad possibility of different molecules, each with their unique placement of atoms in three-dimensional space .

STEREOISOMERS

Stereoisomers are, as mentioned above, contain different types of isomers within itself, each with distinct characteristics that further separate each other as different chemical entities having different properties. Type called entaniomer are the previously-mentioned mirror-image stereoisomers, and will be explained in detail in this article. Another type, diastereomer, has different properties and will be introduced afterwards.

ENANTIOMERS

This type of stereoisomer is the essential mirror-image, non-superimposable type of stereoisomer introduced in the beginning of the article. Figure 3 provides a perfect example; note that the gray plane in the middle demotes the mirror plane.

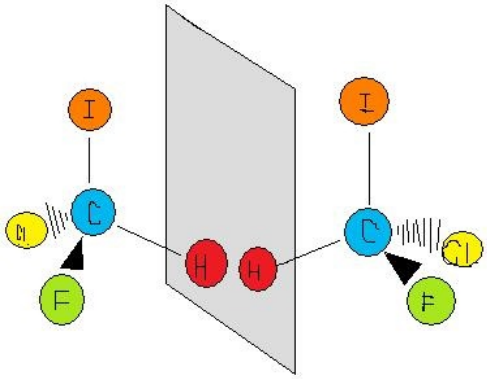


Figure 5.1.2.

Note that even if one were to flip over the left molecule over to the right, the atomic spatial arrangement will not be equal. This is equivalent to the left hand - right hand relationship, and is aptly referred to as 'handedness' in molecules. This can be somewhat counter-intuitive, so this article recommends the reader try the 'hand' example. Place both palm facing up, and hands next to each other. Now flip either side over to the other. One hand should be showing the back of the hand, while the other one is showing the palm. They are not same and non-superimposable. This is where the concept of chirality comes in as one of the most essential and defining idea of stereoisomerism.

CHIRALITY

Chirality essentially means 'mirror-image, non-superimposable molecules', and to say that a molecule is chiral is to say that its mirror image (it must have one) is not the same as it self. Whether a molecule is chiral or achiral depends upon a certain set of overlapping conditions. Figure 5.1.1 shows an example of two molecules, chiral and achiral, respectively. Notice the distinct characteristic of the achiral molecule: it possesses two atoms of same element. In theory and reality, if one were to create a plane that runs through the other two atoms, they will be able to create what is known as bisecting plane: The images on either side of the plan is the same as the other (Figure 5.1.3).

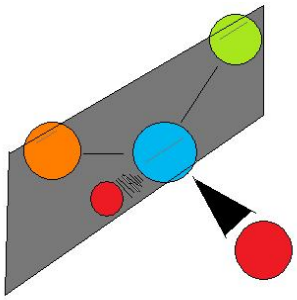


Figure 5.1.3.

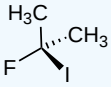
In this case, the molecule is considered 'achiral'. In other words, to distinguish chiral molecule from an achiral molecule, one must search for the existence of the bisecting plane in a molecule. All chiral molecules are deprive of bisecting plane, whether simple or complex. As a universal rule, no molecule with different surrounding atoms are achiral. Chirality is a simple but essential idea to support the concept of stereoisomerism, being used to explain one type of its kind. The chemical properties of the chiral molecule differs from its mirror image, and in this lies the significance of chilarity in relation to modern organic chemistry.

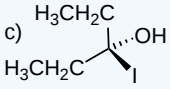
EXERCISES

? EXERCISE 5.1.1

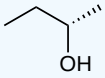
Identify the following molecules as chiral or achiral.

a) 

b) 

c) 

d) 

e) 

f) 

Answer

a) chiral (4 different groups off C)

b) achiral (2 identical -CH_3 substituents off central C)

c) achiral (2 identical -CH_2CH_3 substituents off central C)

d) achiral (2 identical CH_3 substituents off carbon 2)

e) chiral (4 different groups off carbon 2)

f) achiral (2 identical CH_3 substituents off central C)

EXERCISE 5.1.2

Determine if the following sets of compounds in each group are enantiomers or the same compound.

a) 

b) 

c) 

d) 

Answer

a) enantiomers – non superimposable mirror images

b) same compound – when you rotate the molecule on the right it is identical to the one on the left

c) enantiomers – non superimposable mirror images

d) enantiomers – non superimposable mirror images

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)

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5.2: THE REASON FOR HANDEDNESS IN MOLECULES- CHIRALITY

Objectives

After completing this section, you should be able to

1. determine whether or not a compound is chiral, given its Kelulé, condensed or shorthand structure, with or without the aid of molecular models.
2. label the chiral centres (carbon atoms) in a given Kelulé, condensed or shorthand structure.

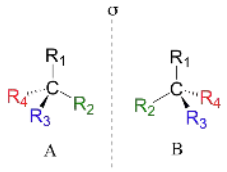
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

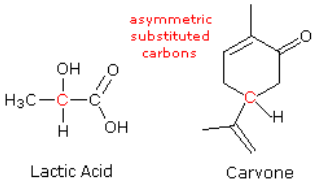
- achiral
- chiral
- chiral (stereogenic) centre
- plane of symmetry

A consideration of the chirality of molecular configurations explains the curious stereoisomerism observed for lactic acid, carvone and a multitude of other organic compounds. Tetravalent carbons have a tetrahedral configuration. If all four substituent groups are the same, as in methane or tetrachloromethane, the configuration is that of a highly symmetric "regular tetrahedron". A regular tetrahedron several planes of symmetry and is achiral.

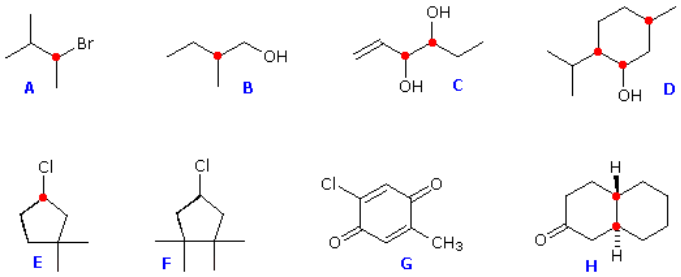
A carbon atom that is bonded to four different atoms or groups loses all symmetry, and is often referred to as an asymmetric carbon. The configuration of such a molecular unit is chiral, and the structure may exist in either a right-handed configuration or a left-handed configuration (one the mirror image of the other). This type of configurational stereoisomerism is termed enantiomorphism, and the non-identical, mirror-image pair of stereoisomers that result are called enantiomers. In the general figure below, A and B are nonsuperposable mirror images of one another, and thus are a pair of enantiomers.



The structural formulas of lactic acid and carvone are drawn on the right with the asymmetric carbon colored red. Consequently, we find that these compounds exist as pairs of enantiomers. The presence of a single asymmetrically substituted carbon atom in a molecule is sufficient to render the whole configuration chiral, and modern terminology refers to such groupings as chiral centers. Most of the chiral centers we shall discuss are asymmetric carbon atoms, but it should be recognized that other tetrahedral or pyramidal atoms may become chiral centers if appropriately substituted. When more than one chiral center is present in a molecular structure, care must be taken to analyze their relationship before concluding that a specific molecular configuration is chiral or achiral. This aspect of stereoisomerism will be treated later.



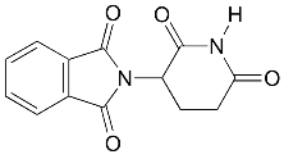
A useful first step in examining structural formulas to determine whether stereoisomers may exist is to identify all stereogenic elements. A stereogenic element is a center, axis or plane that is a focus of stereoisomerism, such that an interchange of two groups attached to this feature leads to a stereoisomer. Stereogenic elements may be chiral or achiral. An asymmetric carbon is often a chiral stereogenic center, since interchanging any two substituent groups converts one enantiomer to the other. Alkenes having two different groups on each double bond carbon constitute an achiral stereogenic element, since interchanging substituents at one of the carbons changes the cis/trans configuration of the double bond.



Some of the structures in the figure above are chiral and some are achiral. First, try to identify all chiral stereogenic centers. Formulas having no chiral centers are necessarily achiral. Formulas having one chiral center are always chiral; and if two or more chiral centers are present in a given structure it is likely to be chiral, but in special cases, to be discussed later, may be achiral.

Structures F and G are achiral. The former has a plane of symmetry passing through the chlorine atom and bisecting the opposite carbon-carbon bond. The similar structure of compound E does not have such a symmetry plane, and the carbon bonded to the chlorine is a chiral center (the two ring segments connecting this carbon are not identical). Structure G is essentially flat. All the carbons except that of the methyl group are sp^2 hybridized, and therefore trigonal-planar in configuration. Compounds C, D & H have more than one chiral center, and are also chiral. Remember, all chiral structures may exist as a pair of enantiomers. Other configurational stereoisomers are possible if more than one stereogenic center is present in a structure.

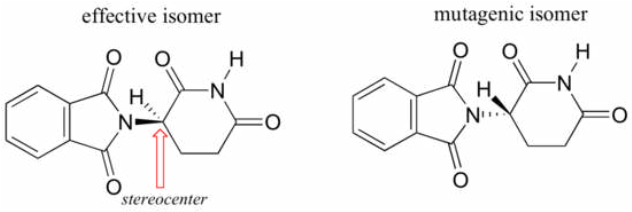
In the 1960's, a drug called thalidomide was widely prescribed in the Western Europe to alleviate morning sickness in pregnant women.



thalidomide

Thalidomide had previously been used in other countries as an antidepressant, and was believed to be safe and effective for both purposes. The drug was not approved for use in the U.S.A. It was not long, however, before doctors realized that something had gone horribly wrong: many babies born to women who had taken thalidomide during pregnancy suffered from severe birth defects.

Researchers later realized the that problem lay in the fact that thalidomide was being provided as a mixture of two different isomeric forms.

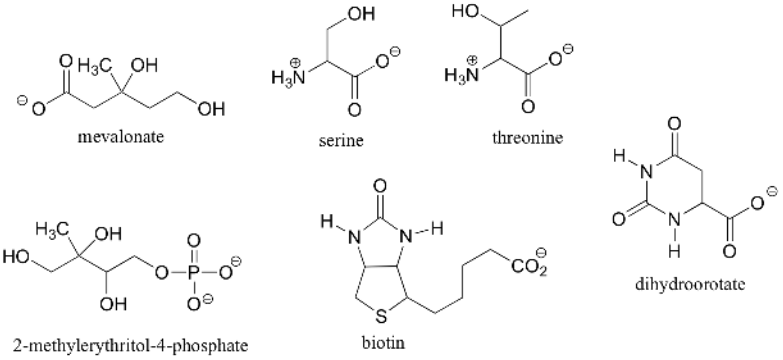


One of the isomers is an effective medication, the other caused the side effects. Both isomeric forms have the same molecular formula and the same atom-to-atom connectivity, so they are not constitutional isomers. Where they differ is in the arrangement in three-dimensional space about one tetrahedral, sp^3-hybridized carbon. These two forms of thalidomide are **stereoisomers**.

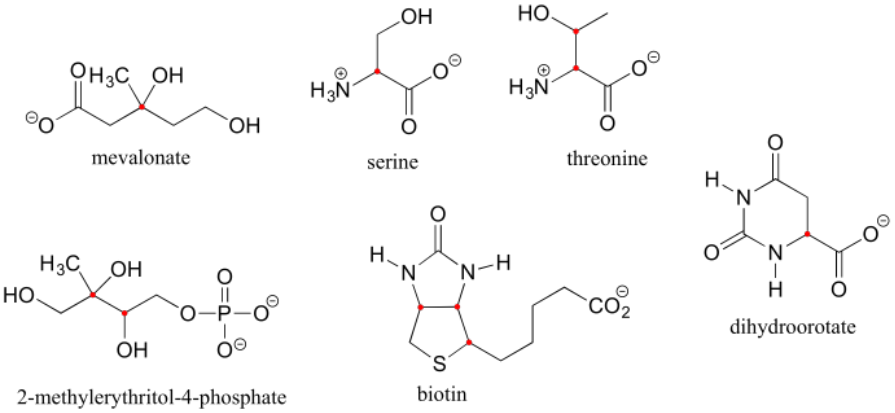
Note that the carbon in question has *four different substituents* (two of these just happen to be connected by a ring structure). Tetrahedral carbons with four different substituent groups are called **stereocenters**.

✔ EXAMPLE 5.2.1

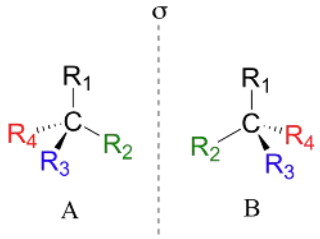
Locate all of the carbon stereocenters in the molecules below.



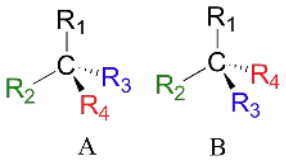
Answer



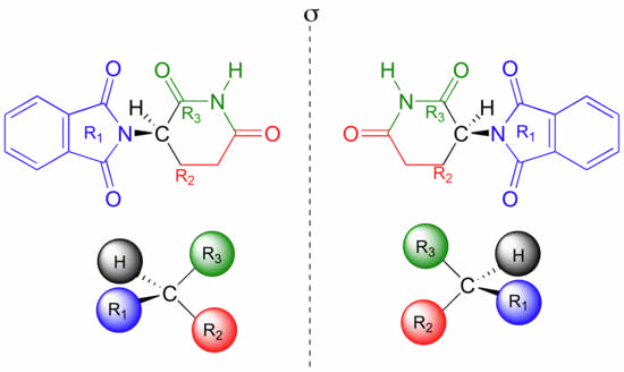
Looking at the structures of what we are referring to as the two isomers of thalidomide, you may not be entirely convinced that they are actually two different molecules. In order to convince ourselves that they are indeed different, let's create a generalized picture of a tetrahedral carbon stereocenter, with the four substituents designated R_1-R_4. The two stereoisomers of our simplified model look like this:



If you look carefully at the figure above, you will notice that molecule A and molecule B are mirror images of each other (the line labeled 's' represents a mirror plane). Furthermore, *they are not superimposable*: if we pick up molecule A, flip it around, and place it next to molecule B, we see that the two structures cannot be superimposed on each other. They are different molecules!



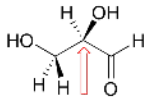
If you make models of the two stereoisomers of thalidomide and do the same thing, you will see that they too are mirror images, and cannot be superimposed (it well help to look at a color version of the figure below).



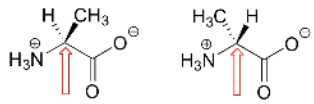
Thalidomide is a **chiral** molecule. Something is considered to be chiral if it cannot be superimposed on its own mirror image – in other words, if it is **asymmetric** (lacking in symmetry). The term 'chiral' is derived from the Greek word for 'handedness' – ie. right-handedness or left-handedness. Your hands are chiral: your right hand is a mirror image of your left hand, but if you place one hand on top of the other, both palms down, you see that they are not superimposable.

A pair of stereoisomers that are non-superimposable mirror images of one another are considered to have a specific type of stereoisomeric relationship – they are a pair of **enantiomers**. Thalidomide exists as a pair of enantiomers. On the macro level, your left and right hands are also a pair of enantiomers.

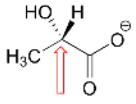
Here are some more examples of chiral molecules that exist as pairs of enantiomers. In each of these examples, there is a single stereocenter, indicated with an arrow. (Many molecules have more than one stereocenter, but we will get to that that a little later!)



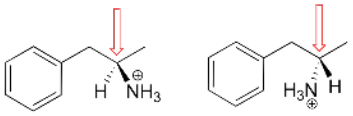
glyceraldehyde



alanine

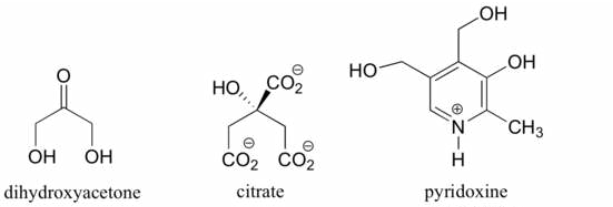


lactate



amphetamine

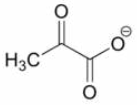
Here are some examples of molecules that are **achiral** (*not* chiral). Notice that none of these molecules has a stereocenter.



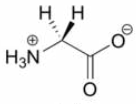
dihydroxyacetone

citrate

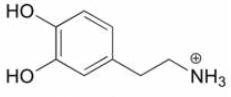
pyridoxine
(vitamin B_6)



pyruvate



glycine
(amino acid)



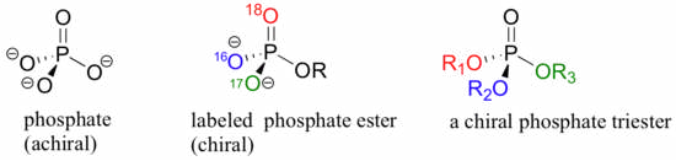
dopamine
(neurotransmitter)

It is difficult to illustrate on the two dimensional page, but you will see if you build models of these achiral molecules that, in each case, there is at least one **plane of symmetry**, where one side of the plane is the mirror image of the other. Chirality is tied conceptually to the idea of asymmetry, and *any molecule that has a plane of symmetry cannot be chiral*. When looking for a plane of symmetry, however, we must consider all possible conformations that a molecule could adopt. Even a very simple molecule like ethane, for example, is asymmetric in many of its countless potential conformations – but it has obvious symmetry in both the eclipsed and staggered conformations, and for this reason it is achiral.

Looking for planes of symmetry in a molecule is useful, but often difficult in practice. In most cases, the easiest way to decide whether a molecule is chiral or achiral is to look for one or more stereocenters - with a few rare exceptions (see section 3.7B), the general rule is that molecules with at least one stereocenter are chiral, and molecules with no stereocenters are achiral. Carbon stereocenters are also referred to quite frequently as **chiral carbons**.

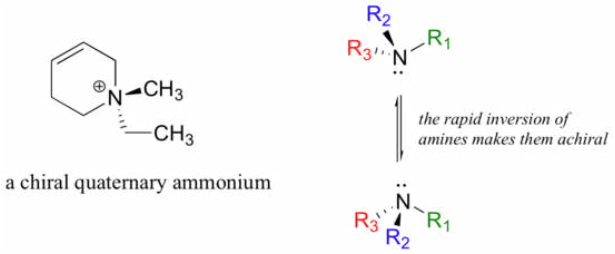
When evaluating a molecule for chirality, it is important to recognize that the question of whether or not the dashed/solid wedge drawing convention is used is irrelevant. Chiral molecules are sometimes drawn without using wedges (although obviously this means that stereochemical information is being omitted). Conversely, wedges may be used on carbons that are not stereocenters – look, for example, at the drawings of glycine and citrate in the figure above. Just because you see dashed and solid wedges in a structure, do not automatically assume that you are looking at a stereocenter.

Other elements in addition to carbon can be stereocenters. The phosphorus center of phosphate ion and organic phosphate esters, for example, is tetrahedral, and thus is potentially a stereocenter.



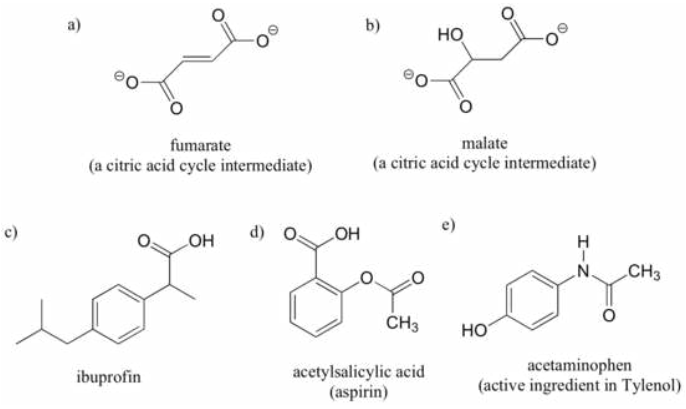
We will see in chapter 10 how researchers, in order to investigate the stereochemistry of reactions at the phosphate center, incorporated sulfur and/or ^{17}O and ^{18}O isotopes of oxygen (the 'normal' isotope is ^{16}O) to create chiral phosphate groups. Phosphate triesters are chiral if the three substituent groups are different.

Asymmetric quaternary ammonium groups are also chiral. Amines, however, are not chiral, because they rapidly invert, or turn 'inside out', at room temperature.

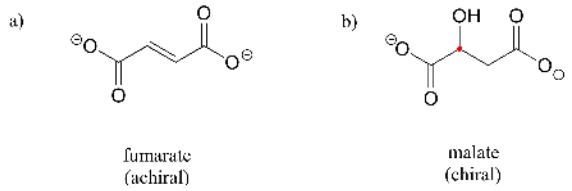


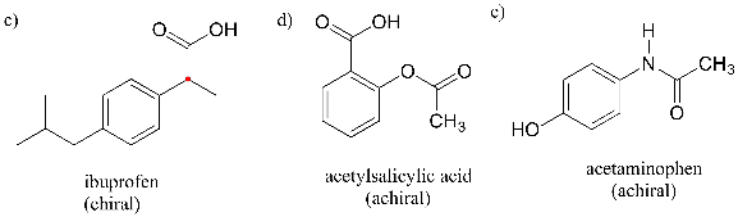
EXAMPLE 5.2.2

Label the molecules below as chiral or achiral, and locate all stereocenters.



Answer

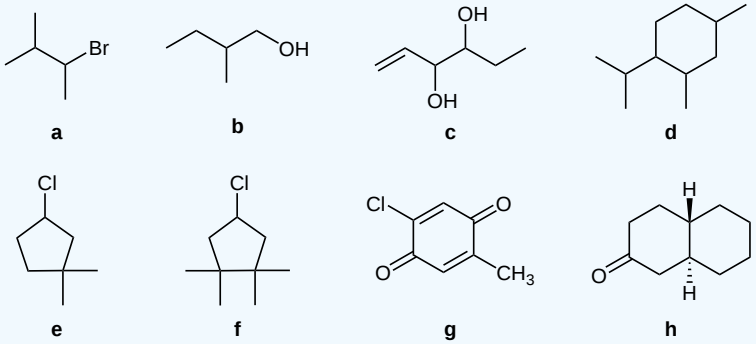




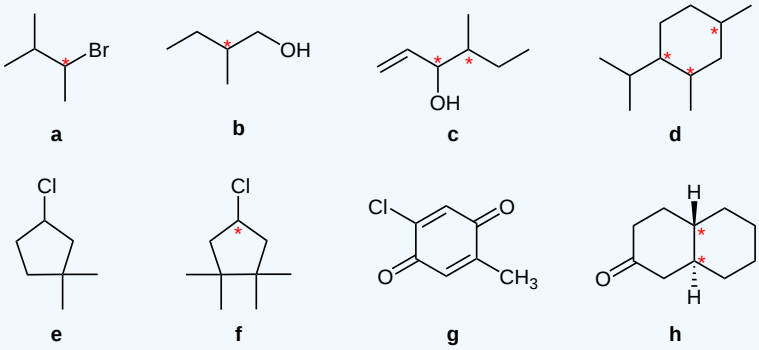
EXERCISES

? EXERCISE 5.2.1

Determine if each of the following molecules are chiral or achiral. For chiral molecules indicate any chiral carbons.



Answer



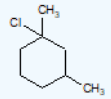
Explanation

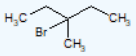
Structures F and G are achiral. The former has a plane of symmetry passing through the chlorine atom and bisecting the opposite carbon-carbon bond. The similar structure of compound E does not have such a symmetry plane, and the carbon bonded to the chlorine is a chiral center (the two ring segments connecting this carbon are not identical). Structure G is essentially flat. All the carbons except that of the methyl group are sp^2 hybridized, and therefore trigonal-planar in configuration. Compounds C, D & H have more than one chiral center, and are also chiral.

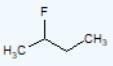
EXERCISE 5.2.2

1) For the following compounds, star (*) each chiral center, if any.

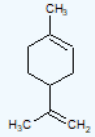
(a) (b) (c)



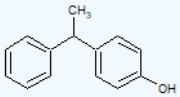




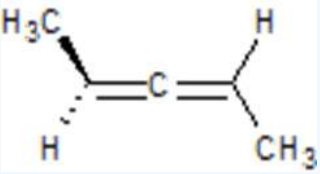
(d) (e) (f)







2) Explain why the following compound is chiral.



3) Determine which of the following objects is chiral.

a) A Glove.

b) A nail.

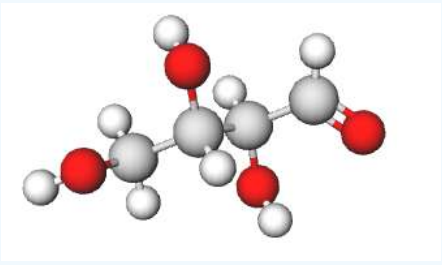
c) A pair of sunglasses.

d) The written word "Chiral".

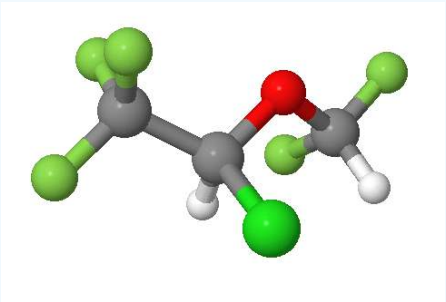
4) Place an "*" by all of the chrial carbons in the following molecules.

a)

Erythrose, a four carbon sugar.

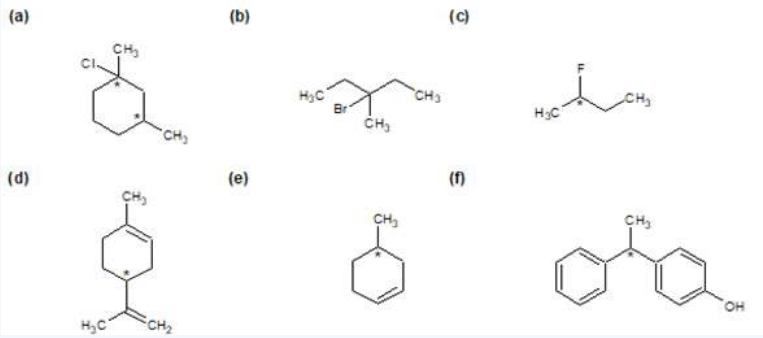


b) Isoflurane, an anestetic. Bright green = Chlorine, Pale green = Fluorine.



Answer

1)



2) Though the molecule does not contain a chiral carbon, it is chiral as it is non-superimposable on its mirror image due to its twisted nature (the twist comes from the structure of the double bonds needing to be at 90° angles to each other, preventing the molecule from being planar).

3)

a) Just as hands are chiral a glove must also be chiral.

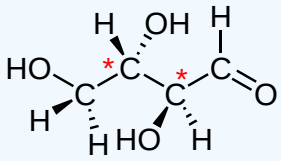
b) A nail has a plane of symmetry which goes down the middle making it a achiral.

c) A pair of sunglasses has a plane of symmetry which goes through the nose making it achiral.

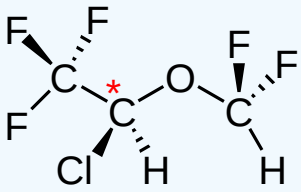
d) Most written words are chiral. Look one in a mirror to confirm this.

4

a)



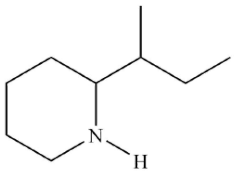
b)

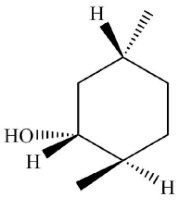


QUESTIONS

Q5.2.1

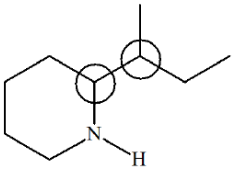
Identify the chiral centers in each of the following:

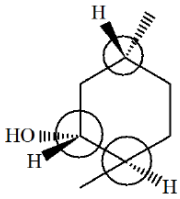




SOLUTIONS

S5.2.1





CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)

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5.3: OPTICAL ACTIVITY

OBJECTIVES

After completing this section, you should be able to

1. describe the nature of plane-polarized light.
2. describe the features and operation of a simple polarimeter.
3. calculate the specific rotation of a compound, given the relevant experimental data.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- analyzer
- dextrorotatory
- levorotatory
- optically active
- plane-polarized light
- polarimeter
- polarizer
- specific rotation, $\ce{\sf{[\alpha]_{D}}}$

STUDY NOTES

A *polarizer* is a device through which only light waves oscillating in a single plane may pass. A *polarimeter* is an instrument used to determine the angle through which plane-polarized light has been rotated by a given sample. You will have the opportunity to use a polarimeter in the laboratory component of the course. An *analyzer* is the component of a polarimeter that allows the angle of rotation of plane-polarized light to be determined.

Specific rotations are normally measured at 20°C, and this property may be indicated by the symbol $\ce{\sf{[\alpha]^20_{D}}}$. Sometimes the solvent is specified in parentheses behind the specific rotation value, for example,

$\ce{\sf{[\alpha]^20_{D} = +12}}$° (chloroform)

For liquids, the specific rotation may be obtained using the neat liquid rather than a solution; in such cases the formula is

$$[\alpha]_{\mathrm{D}}^{\mathrm{temp}}(\mathrm{neat}) = \frac{\alpha}{l \times d}$$

where α is the observed rotation, l is the path length of the cell (measured in decimetres, dm), and d is the density of the liquid.

Identifying and distinguishing enantiomers is inherently difficult, since their physical and chemical properties are largely identical. Fortunately, a nearly two hundred year old discovery by the French physicist Jean-Baptiste Biot has made this task much easier. This discovery disclosed that the right- and left-handed enantiomers of a chiral compound perturb plane-polarized light in opposite ways. This perturbation is unique to chiral molecules, and has been termed **optical activity**.

POLARIMETRY

Plane-polarized light is created by passing ordinary light through a polarizing device, which may be as simple as a lens taken from polarizing sun-glasses. Such devices transmit selectively only that component of a light beam having electrical and magnetic field vectors oscillating in a single plane. The plane of polarization can be determined by an instrument called a **polarimeter**, shown in the diagram below.

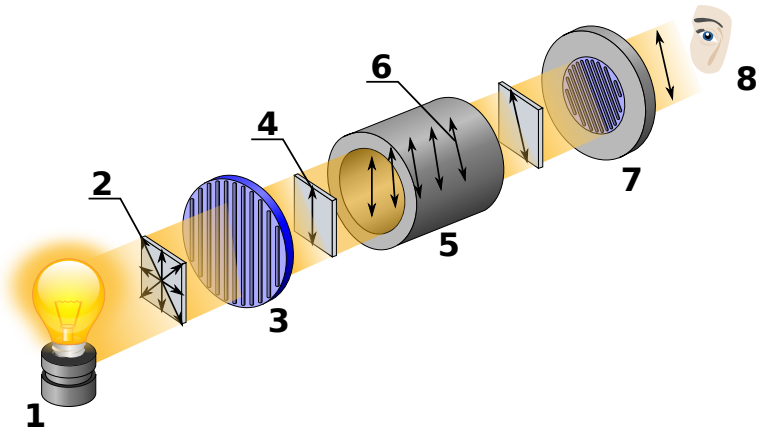


Figure **5.3.1**: Operating principle of an optical polarimeter. 1. Light source 2. Unpolarized light 3. Linear polarizer 4. Linearly polarized light 5. Sample tube containing molecules under study 6. Optical rotation due to molecules 7. Rotatable linear analyzer 8. Detector. (CC BY-SA 3.0 Unported; Kaidor via Wikipedia)

Monochromatic (single wavelength) light, is polarized by a fixed polarizer next to the light source. A sample cell holder is located in line with the light beam, followed by a movable polarizer (the analyzer) and an eyepiece through which the light intensity can be observed. In modern instruments an electronic light detector takes the place of the human eye. In the absence of a sample, the light intensity at the detector is at a maximum when the second (movable) polarizer is set parallel to the first polarizer (α = 0º). If the analyzer is turned 90º to the plane of initial polarization, all the light will be blocked from reaching the detector.

Chemists use polarimeters to investigate the influence of compounds (in the sample cell) on plane polarized light. Samples composed only of achiral molecules (e.g. water or hexane), have no effect on the polarized light beam. However, if a single enantiomer is examined (all sample molecules being right-handed, or all being left-handed), the plane of polarization is rotated in either a clockwise (positive) or counter-clockwise (negative) direction, and the analyzer must be turned an appropriate matching angle, **α**, if full light intensity is to reach the detector. In the above illustration, the sample has rotated the polarization plane clockwise by +90º, and the analyzer has been turned this amount to permit maximum light transmission.

The observed rotations (**α**) of enantiomers are opposite in direction. One enantiomer will rotate polarized light in a clockwise direction, termed **dextrorotatory** or (+), and its mirror-image partner in a counter-clockwise manner, termed **levorotatory** or (–). The prefixes dextro and levo come from the Latin *dexter*, meaning right, and *laevus*, for left, and are abbreviated *d* and *l* respectively. If equal quantities of each enantiomer are examined , using the same sample cell, then the magnitude of the rotations will be the same, with one being positive and the other negative. To be absolutely certain whether an observed rotation is positive or negative it is often necessary to make a second measurement using a different amount or concentration of the sample. In the above illustration, for example, α might be –90º or +270º rather than +90º. If the sample concentration is reduced by 10%, then the positive rotation would change to +81º (or +243º) while the negative rotation would change to –81º, and the correct α would be identified unambiguously.

Since it is not always possible to obtain or use samples of exactly the same size, the observed rotation is usually corrected to compensate for variations in sample quantity and cell length. Thus it is common practice to convert the observed rotation, α, to a **specific rotation**, by the following formula:

$$[\alpha]_D = \frac{\alpha}{lc} \tag{5.3.1}$$

where

- $[\alpha]_D$ is the specific rotation
- l is the cell length in dm
- c is the concentration in g/ml
- D designates that the light used is the 589 line from a sodium lamp

Compounds that rotate the plane of polarized light are termed **optically active**. Each enantiomer of a stereoisomeric pair is optically active and has an equal but opposite-in-sign specific rotation. Specific rotations are useful in that they are experimentally determined constants that characterize and identify pure enantiomers. For example, the lactic acid and carvone enantiomers discussed earlier have the following specific rotations.

Carvone from caraway: $[\alpha]_D = +62.5^o$	this isomer may be referred to as (+)-carvone or *d*-carvone
Carvone from spearmint: $[\alpha]_D = -62.5^o$	this isomer may be referred to as (–)-carvone or *l*-carvone
Lactic acid from muscle tissue: $[\alpha]_D = +2.5^o$	this isomer may be referred to as (+)-lactic acid or *d*-lactic acid
Lactic acid from sour milk: $[\alpha]_D = -2.5^o$	this isomer may be referred to as (–)-lactic acid or *l*-lactic acid

A 50:50 mixture of enantiomers has no observable optical activity. Such mixtures are called **racemates** or racemic modifications, and are designated (±). When chiral compounds are created from achiral compounds, the products are racemic unless a single enantiomer of a chiral co-reactant or catalyst is involved in the reaction. The addition of HBr to either cis- or trans-2-butene is an example of racemic product formation (the chiral center is colored red in the following equation).



Chiral organic compounds isolated from living organisms are usually optically active, indicating that one of the enantiomers predominates (often it is the only isomer present). This is a result of the action of chiral catalysts we call enzymes, and reflects the inherently chiral nature of life itself. Chiral synthetic compounds, on the other hand, are commonly racemates, unless they have been prepared from enantiomerically pure starting materials.

There are two ways in which the condition of a chiral substance may be changed:

1. A racemate may be separated into its component enantiomers. This process is called **resolution**.

2. A pure enantiomer may be transformed into its racemate. This process is called **racemization**.

ENANTIOMERIC EXCESS

The "optical purity" is a comparison of the optical rotation of a pure sample of unknown stereochemistry versus the optical rotation of a sample of pure enantiomer. It is expressed as a percentage. If the sample only rotates plane-polarized light half as much as expected, the optical purity is 50%.

$$\%\ optical\ purity = \frac{specific\ rotation\ of\ mixture}{specific\ rotation\ of\ pure\ enantiomer} \times 100$$

Because *R* and *S* enantiomers have equal but opposite optical activity, it naturally follows that a 50:50 racemic mixture of two enantiomers will have no observable optical activity. If we know the specific rotation for a chiral molecule, however, we can easily calculate the ratio of enantiomers present in a mixture of two enantiomers, based on its measured optical activity. When a mixture contains more of one enantiomer than the other, chemists often use the concept of **enantiomeric excess (ee)** to quantify the difference. Enantiomeric excess can be expressed as:

$$ee = \frac{(\%\ more\ abundant\ enantiomer - 50) \times 100}{50}$$

For example, a mixture containing 60% *R* enantiomer (and 40% *S* enantiomer) has a 20% enantiomeric excess of R: ((60-50) x 100) / 50 = 20 %.

✔ EXAMPLE 5.3.1: CARVONE

The specific rotation of (*S*)-carvone is (+)61°, measured 'neat' (pure liquid sample, no solvent). The optical rotation of a neat sample of a mixture of *R* and *S* carvone is measured at (-)23°. Which enantiomer is in excess, and what is its ee? What are the percentages of (*R*)- and (*S*)-carvone in the sample?

Answer

The observed rotation of the mixture is levorotary (negative, counter-clockwise), and the specific rotation of the pure *S* enantiomer is given as dextrorotary (positive, clockwise), meaning that the pure *R* enantiomer must be levorotary, and the mixture must contain more of the *R* enantiomer than of the *S* enantiomer.

Rotation (*R*/*S* Mix) = [Fraction(*S*) × Rotation (*S*)] + [Fraction(*R*) × Rotation (*R*)]

Let Fraction (*S*) = x, therefore Fraction (*R*) = 1 – x

Rotation (*R*/*S* Mix) = x[Rotation (*S*)] + (1 – x)[Rotation (*R*)]

–23 = x(+61) + (1 – x)(–61)

Solve for x: x = 0.3114 and (1 – x) = 0.6885

Therefore the percentages of (*R*)- and (*S*)-carvone in the sample are 68.9% and 31.1%, respectively.

ee = [(% more abundant enantiomer – 50) × 100]/50

= [68.9 – 50) × 100]/50 = 37.8%

Chiral molecules are often labeled according to the sign of their specific rotation, as in (*S*)-(+)-carvone and (*R*)-(-)-carvone, or (±)-carvone for the racemic mixture. However, there is no relationship whatsoever between a molecule's *R/S* designation and the sign of its specific rotation. Without performing a polarimetry experiment or looking in the literature, we would have no idea that (-)-carvone has the *R* configuration and (+)-carvone has the *S* configuration.

SEPARATION OF CHIRAL COMPOUNDS

As noted earlier, chiral compounds synthesized from achiral starting materials and reagents are generally racemic (i.e. a 50:50 mixture of enantiomers). Separation of racemates into their component enantiomers is a process called resolution. Since enantiomers have identical physical properties, such as solubility and melting point, resolution is extremely difficult. Diastereomers, on the other hand, have different physical properties, and this fact is used to achieve resolution of racemates. Reaction of a racemate with an enantiomerically pure chiral reagent gives a mixture of diastereomers, which can be separated. For example, if a racemic mixture of a chiral alcohol is reacted with a enantiomerically pure carboxylic acid, the result is a mixture of diastereomers: in this case, because the pure (R) entantiomer of the acid was used, the product is a mixture of (R-R) and (R-S) diastereomeric esters, which can, in theory, be separated by their different physical properties. Subsequent hydrolysis of each separated ester will yield the 'resolved' (enantiomerically pure) alcohols. The used in this technique are known as '

EXERCISES

? EXERCISE 5.3.1

A 3.20 g sample of morphine ($[\alpha]_D$ = -132) was dissolved in 10.0 mL of acetic acid ($[\alpha]_D$ = 0). If it is put into a sample tube with a path length of 2.00 cm, what would be its observed rotation (α)?

Answer

The specific rotation, $[\alpha]_D$ = (observed rotation, α (degrees))/ [(pathlength, *l* (dm)) x (concentration, c (g/cm^3))] = α/(*l* x c)

Solving for α, α = $[\alpha]_D$ x *l* x c

($[\alpha]_D$ = -132) x (*l* = 2.00 cm = 0.200 dm) x (c = 3.20 g / 10.0 cm^3 = 0.320 g/cm^3)

α = -132 x 0.200 dm x 0.320 g/cm^3 = -8.45 °

? EXERCISE 5.3.2

Is the morphine in the previous excercise dextrorotatory or levorotatory?

Answer

Since morphine has a (-) rotation, it indicates that it rotates light to the left (counterclockwise) and morphine is levorotatory.

? EXERCISE 5.3.3

Label the following compounds as dextrorotatory or levorotatory.

a. sucrose ($[\alpha]_D$ = + 66.7)
b. cholesterol ($[\alpha]_D$ = - 31.5)
c. cocaine ($[\alpha]_D$ = - 16)
d. chloroform ($[\alpha]_D$ = 0)

Answer

a. sucrose ($[\alpha]_D$ = + 66.7) dextrorotatory

b. cholesterol ($[\alpha]_D$ = - 31.5) levorotatory
c. cocaine ($[\alpha]_D$ = - 16) levorotatory
d. chloroform ($[\alpha]_D$ = 0) neither, not optically active

EXERCISE 5.3.4a

The specific rotation of (*S*)-carvone is (+) 61° when measured neat (pure liquid sample with no solvent). The optical rotation of a neat sample of a mixture of R and S carvone is measured at (-) 23 ^{o}.

a) Which enantiomer is in excess?

Answer

Since the pure *S* enantiomer ((+) 61°) is dextrorotatory (positive, clockwise), the *R* enantiomer must be levorotatory. The observed rotation of the mixture is levorotatory since its negative (counterclockwise). This means the mixture must contain more of the *R* enantiomer than the *S* enantiomer.

EXERCISE 5.3.4b

b) What are the percentages of (*S*)- and (*R*)- carvone in the sample mixture?

Answer

Optical rotation (α) of the (*R*/*S* mixture) = [fraction (*S*) x $[\alpha]_D$ (*S*)] + [fraction (*R*) x $[\alpha]_D$ (*R*)]

To determine the fraction of S and R, we make y = fraction (*S*) and 1 – y = fraction (*R*)

-23° = y x (61°) + (1 – y) x (-61°) solving for y: y = 0.3114 and (1-y) = 0.6885

Therefore the percentage of (*S*)-carvone is 31.1 % and (*R*)-carvone is 68.9 %

EXERCISE 5.3.4c

c) What is the ee (enantiomeric excess)?

Answer

ee = [(% more abundant isomer – 50) x 100]/50 = [(68.9 – 50) x100]/50 = 37.8 % ee

EXERCISE 5.3.5a

Determine the ee's of the following from the percentages

- 95 % (*R*)- tartaric acid and 5.0 % (*S*)- tartaric acid

Answer

[(95 – 50) x 100] / 50 = 90 % ee (*R*)-tartaric acid

EXERCISE 5.3.5b

Determine the ee's of the following from the percentages

- 75 % (*S*)- limonene and 25 % (*R*)- limonene

Answer

[(75 – 50) x 100] / 50 = 50 % ee (*S*)- limonene

EXERCISE 5.3.5c

Determine the ee's of the following from the percentages

- 85 % (*R*) cysteine

Answer

(85 – 50) x 100] / 50 = 70 % ee (*R*)-cysteine

EXERCISE 5.3.5d

Determine the ee's of the following from the percentages

- 50 % (*S*) alanine

Answer

(50 – 50) x 100] / 50 = 0 % ee, racemic mixture

QUESTIONS

Q5.3.1

A sample with a concentration of 0.3 g/mL was placed in a cell with a length of 5 cm. The resulting rotation at the sodium D line was +1.52°. What is the $[\alpha]_D$?

SOLUTIONS

S5.3.1

5 cm = 0.5 dm

$$[\alpha]_D = \alpha/(c \times l) = +1.52/(0.3 \times 0.5) = +10.1°$$

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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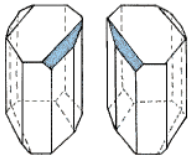
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5.4: PASTEUR'S DISCOVERY OF ENANTIOMERS

Objective

After completing this section, you should be able to discuss how the results of work carried out by Biot and Pasteur contributed to the development of the concept of the tetrahedral carbon atom.

Because enantiomers have identical physical and chemical properties in achiral environments, separation of the stereoisomeric components of a racemic mixture or racemate is normally not possible by the conventional techniques of distillation and crystallization. In some cases, however, the crystal habits of solid enantiomers and racemates permit the chemist (acting as a chiral resolving agent) to discriminate enantiomeric components of a mixture. As background for the following example, it is recommended that the section on crystal properties be reviewed.



Tartaric acid, its potassium salt known in antiquity as "tartar", has served as the locus of several landmark events in the history of stereochemistry. In 1832 the French chemist Jean Baptiste Biot observed that tartaric acid obtained from tartar was optically active, rotating the plane of polarized light clockwise (dextrorotatory). An optically inactive, higher melting, form of tartaric acid, called racemic acid was also known. A little more than a decade later, young Louis Pasteur conducted a careful study of the crystalline forms assumed by various salts of these acids. He noticed that under certain conditions, the sodium ammonium mixed salt of the racemic acid formed a mixture of enantiomorphic hemihedral crystals; a drawing of such a pair is shown on the right. Pasteur reasoned that the dissymmetry of the crystals might reflect the optical activity and dissymmetry of its component molecules. After picking the different crystals apart with a tweezer, he found that one group yielded the known dextrorotatory tartaric acid measured by Biot; the second led to a previously unknown levorotatory tartaric acid, having the same melting point as the dextrorotatory acid. Today we recognize that Pasteur had achieved the first resolution of a racemic mixture, and laid the foundation of what we now call stereochemistry.

Optical activity was first observed by the French physicist Jean-Baptiste Biot. He concluded that the change in direction of plane-polarized light when it passed through certain substances was actually a rotation of light, and that it had a molecular basis. His work was supported by the experimentation of Louis Pasteur. Pasteur observed the existence of two crystals that were mirror images in tartaric acid, an acid found in wine. Through meticulous experimentation, he found that one set of molecules rotated polarized light clockwise while the other rotated light counterclockwise to the same extent. He also observed that a mixture of both, a *racemic mixture* (or *racemic modification*), did not rotate light because the optical activity of one molecule canceled the effects of the other molecule. Pasteur was the first to show the existence of chiral molecules.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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5.5: SEQUENCE RULES FOR SPECIFYING CONFIGURATION

Objectives

After completing this section, you should be able to

1. assign Cahn-Ingold-Prelog priorities to a given set of substituents.
2. determine whether a given wedge-and-broken-line structure corresponds to an *R* or an *S* configuration, with or without the aid of molecular models.
3. draw the wedge-and-broken-line structure for a compound, given its IUPAC name, complete with *R* or *S* designation.
4. construct a stereochemically accurate model of a given enantiomer from either a wedge-and-broken-line structure or the IUPAC name of the compound, complete with *R* or *S* designation.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- absolute configuration
- *R* configuration
- *S* configuration

STUDY NOTES

When designating a structure as *R* or *S*, you must ensure that the atom or group with the lowest priority is pointing away from you, the observer. The easiest way to show this is to use the wedge-and-broken-line representation. You can then immediately determine whether you are observing an *R* configuration or an *S* configuration.

To name the enantiomers of a compound unambiguously, their names must include the "handedness" of the molecule. The method for this is formally known as R/S nomenclature.

INTRODUCTION

The method of unambiguously assigning the handedness of molecules was originated by three chemists: R.S. Cahn, C. Ingold, and V. Prelog and, as such, is also often called the Cahn-Ingold-Prelog rules. In addition to the Cahn-Ingold system, there are two ways of experimentally determining the absolute configuration of an enantiomer:

1. X-ray diffraction analysis. Note that there is no correlation between the sign of rotation and the structure of a particular enantiomer.
2. Chemical correlation with a molecule whose structure has already been determined via X-ray diffraction.

However, for non-laboratory purposes, it is beneficial to focus on the R/S system. The sign of optical rotation, although different for the two enantiomers of a chiral molecule,at the same temperature, **cannot** be used to establish the absolute configuration of an enantiomer; this is because the sign of optical rotation for a particular enantiomer may change when the temperature changes.

STEREOCENTERS ARE LABELED R OR S

The "right hand" and "left hand" nomenclature is used to name the enantiomers of a chiral compound. The stereocenters are labeled as R or S.



Consider the first picture: a curved arrow is drawn from the highest priority (*1*) substituent to the lowest priority *(4*) substituent. If the arrow points in a counterclockwise direction (**left** when leaving the 12 o' clock position), the configuration at stereocenter is considered ***S*** ("Sinister" → Latin= "left"). If, however, the arrow points clockwise,(**Right** when leaving the 12 o' clock position) then the stereocenter is labeled ***R*** ("Rectus" → Latin= "right"). The ***R*** *or* ***S*** is then added as a prefix, in parenthesis, to the name of the enantiomer of interest. For example, (*R*)-2-Bromobutane or (*S*)-2,3- Dihydroxypropanal.

SEQUENCE RULES TO ASSIGN PRIORITIES TO SUBSTITUENTS

Before applying the R and S nomenclature to a stereocenter, the substituents must be prioritized according to the following rules:

RULE 1

First, examine at the atoms directly attached to the stereocenter of the compound. A substituent with a higher atomic number takes precedence over a substituent with a lower atomic number. Hydrogen is the lowest possible priority substituent, because it has the lowest atomic number.

1. When dealing with isotopes, the atom with the higher atomic mass receives higher priority.
2. When visualizing the molecule, the lowest priority substituent should always point away from the viewer (a dashed line indicates this). To understand how this works or looks, imagine that a clock and a pole. Attach the pole to the back of the clock, so that when when looking at the face of the clock the pole points away from the viewer in the same way the lowest priority substituent should point away.
3. Then, draw an arrow from the highest priority atom to the 2nd highest priority atom to the 3rd highest priority atom. Because the 4th highest priority atom is placed in the back, the arrow should appear like it is going across the face of a clock. If it is going clockwise, then it is an R-enantiomer; If it is going counterclockwise, it is an S-enantiomer.

When looking at a problem with wedges and dashes, if the lowest priority atom is not on the dashed line pointing away, the molecule must be rotated.

Remember that

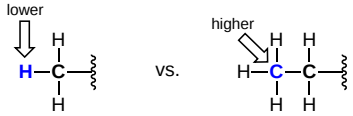
- Wedges indicate coming towards the viewer.
- Dashes indicate pointing away from the viewer.

RULE 2

If there are two substituents with equal rank, proceed along the two substituent chains until there is a point of difference. First, determine which of the chains has the first connection to an atom with the highest priority (the highest atomic number). That chain has the higher priority.

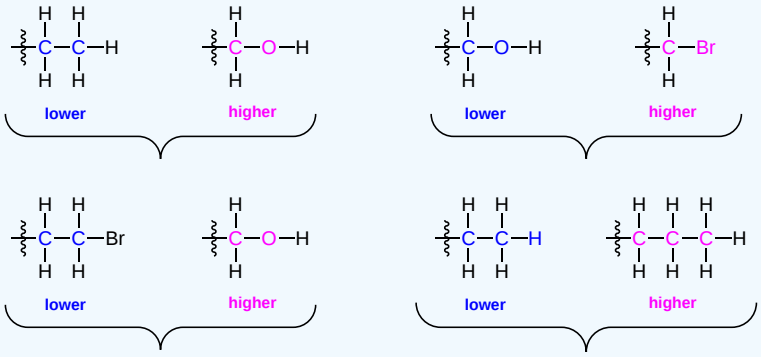
If the chains are similar, proceed down the chain, until a point of difference.

For example: an ethyl substituent takes priority over a methyl substituent. At the connectivity of the stereocenter, both have a carbon atom, which are equal in rank. Going down the chains, a methyl has only has hydrogen atoms attached to it, whereas the ethyl has another carbon atom. The carbon atom on the ethyl is the first point of difference and has a higher atomic number than hydrogen; therefore the ethyl takes priority over the methyl.



The "-H" (left) ranks lower than the "C-" (right) based on the relative molecular weights at the first point of difference.

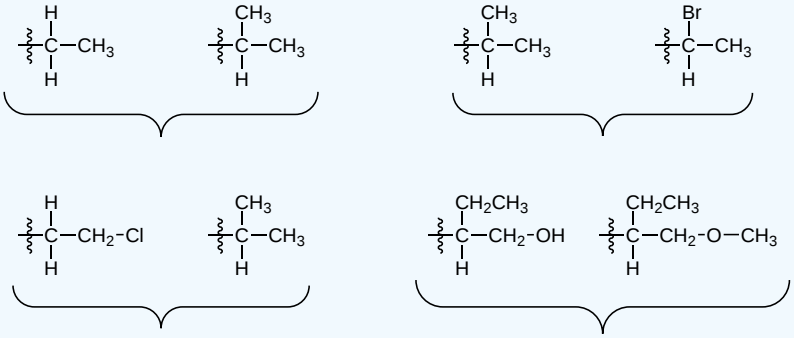
EXAMPLE 5.5.1



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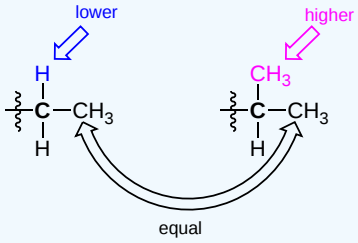
? WORKED EXERCISE 5.5.1

For the following pairs of substituents, determine which would have the higher and lower priority based on the **Cahn-Ingold-Prelog** rules. Explain your answer.



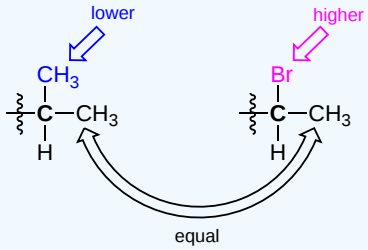
Answer

A 1-methylethyl substituent takes precedence over an ethyl substituent. Connected to the first carbon atom, ethyl only has one other carbon, whereas the 1-methylethyl has two carbon atoms attached to the first; this is the first point of difference. Therefore, 1-methylethyl ranks higher in priority than ethyl, as shown below:



The "C-" (right) ranks higher than the "H-" (left) based on the first point of difference and their relative atomic numbers.

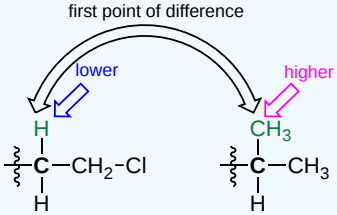
However:



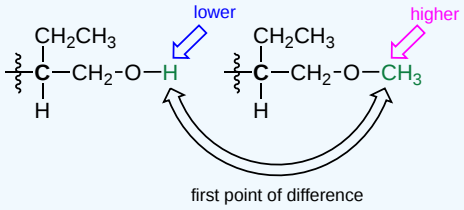
In this case, even though the bold carbon on the right structure has two connections to a non-hydrogen atom (C), it is the lower priority. This is because one of the atoms attached to the bold carbon on the left molecule ranks higher than any of the atoms attached to the bold carbon on the right structure, since Br has a higher atomic number than C.

Caution!!

Keep in mind that priority is determined by the **first** point of difference along the two similar substituent chains. After the first point of difference, the rest of the chain is irrelevant.



When looking for the first point of difference on similar substituent chains, one may encounter branching. If there is branching, choose the branch that is higher in priority. If the two substituents have similar branches, rank the elements within the branches until a point of difference.



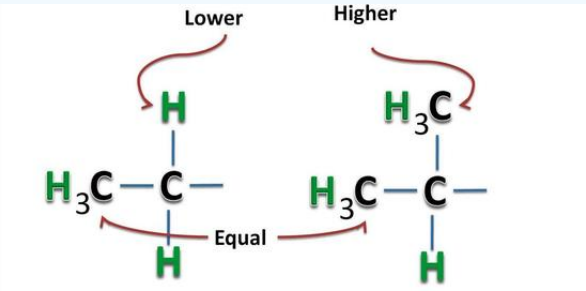
RULE 3

If a chain is connected to the same kind of atom twice or three times, check to see if the atom it is connected to has a greater atomic number than any of the atoms that the competing chain is connected to.

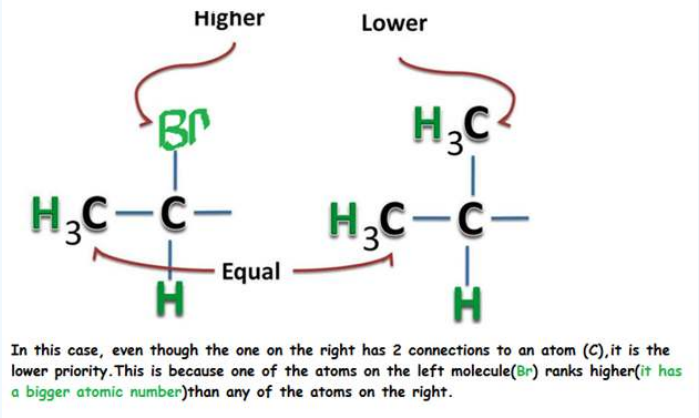
- If none of the atoms connected to the competing chain(s) at the same point has a greater atomic number: the chain bonded to the same atom multiple times has the greater priority
- If however, one of the atoms connected to the competing chain has a higher atomic number: that chain has the higher priority.

EXAMPLE 5.5.2

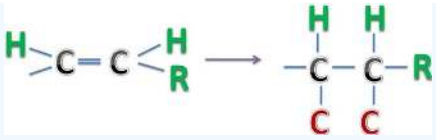
A 1-methylethyl substituent takes precedence over an ethyl substituent. Connected to the first carbon atom, ethyl only has one other carbon, whereas the 1-methylethyl has two carbon atoms attached to the first; this is the first point of difference. Therefore, 1-methylethyl ranks higher in priority than ethyl, as shown below:



However:



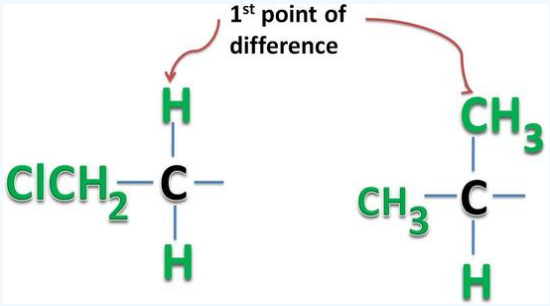
Remember that being double or triple bonded to an atom means that the atom is connected to the same atom twice. In such a case, follow the same method as above.



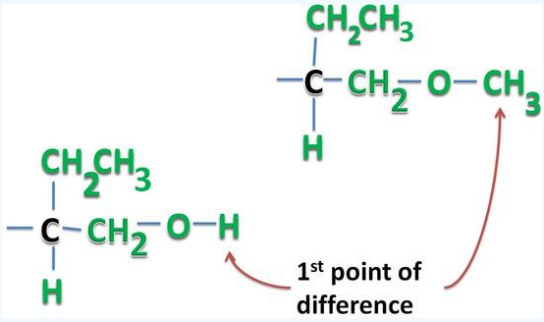


Caution!!

Keep in mind that priority is determined by the **first** point of difference along the two similar substituent chains. After the first point of difference, the rest of the chain is irrelevant.



When looking for the first point of difference on similar substituent chains, one may encounter branching. If there is branching, choose the branch that is higher in priority. If the two substituents have similar branches, rank the elements within the branches until a point of difference.



After all your substituents have been prioritized in the correct manner, you can now name/label the molecule **R** or **S.**

1. Put the lowest priority substituent in the back (dashed line).
2. Proceed from 1 to 2 to 3. (it is helpful to draw or imagine an arcing arrow that goes from 1--> 2-->3)
3. Determine if the direction from 1 to 2 to 3 clockwise or counterclockwise.

i) If it is **clockwise** it is **R.**
ii) if it is **counterclockwise** it is **S**.

USE YOUR MODELING KIT: Models assist in visualizing the structure. When using a model, make sure the lowest priority is pointing away from you. Then determine the direction from the highest priority substituent to the lowest: clockwise (R) or counterclockwise (S).

IF YOU DO NOT HAVE A MODELING KIT: remember that the dashes mean the bond is going into the screen and the wedges means that bond is coming out of the screen. If the lowest priority bond is not pointing to the back, mentally rotate it so that it is. However, it is very useful when learning organic chemistry to use models.

OUTSIDE LINKS

- http://www.youtube.com/watch?v=EphUiPiQiCo
- http://en.Wikipedia.org/wiki/Absolute_configuration

REFERENCES

1. Schore and Vollhardt. *Organic Chemistry Structure and Function*. New York:W.H. Freeman and Company, 2007.
2. McMurry, John and Simanek, Eric. *Fundamentals of Organic Chemistry*. 6th Ed. Brooks Cole, 2006.

EXERCISES

EXERCISE 5.5.1

Orient the following so that the least priority (4) atom is paced behind, then assign stereochemistry ((*R*) or (*S*)).



Answer

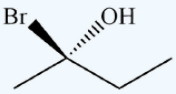
A = *S* and B = *R*



EXERCISE 5.5.2

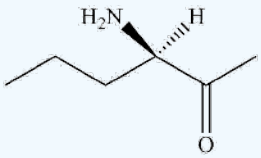
Draw (*R*)-2-bromobutan-2-ol

Answer



EXERCISE 5.5.3

Assign *R/S* to the following molecule:



Answer

The stereo center is (R).

EXERCISE 5.5.4

Identify which substituent in the following sets has a higher ranking.

a. -H or -CH_3

b. -$CH_2CH_2CH_3$ or CH_2CH_3

c. -CH_2Cl or CH_2OH

Answer

a. **-CH_3**
b. **-$CH_2CH_2CH_3$**
c. **-CH_2Cl**

EXERCISE 5.5.5

Identify which substituent in the following sets has a higher ranking.

a. -NH_2 or -N=NH
b. -CH_2CH_2OH or -CH_2OH
c. -$CH{=}CH_2$ or -CH_2CH_3

Answer

a) **-N=NH**

b) **-CH_2OH**

c) **-$CH{=}CH_2$**

EXERCISE 5.5.6

Place the following sets of substituents in each group in order of lowest priority (1st) to highest priority (4th)

a. -NH_2, -F, -Br, -CH_3
b. -SH, -NH_2, -F, -H

Answer

a) -CH_3 < -NH_2 < -F, < -Br

b) -H < -NH_2 < -F, < -SH

EXERCISE 5.5.7

Place the following sets of substituents in each group in order of lowest priority (1st) to highest priority (4th)

a. -CH_2CH_3, -CN, -CH_2CH_2OH, -$CH_2CH_2CH_2OH$
b. -CH_2NH_2, -CH_2SH, -$C(CH_3)_3$, -CN

Answer

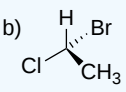
a) -CH_2CH_3 < -$CH_2CH_2CH_2OH$ < -CH_2CH_2OH, < -CN

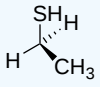
b) -$C(CH_3)_3$ < -CH_2NH_2 < -CN < -CH_2SH

EXERCISE 5.5.8

Assign the following chiral centers as (*R*) or (*S*).

a) 

b) 

c) 

Answer

a) **(*S*)**: I > Br > F > H. The lowest priority substituent is going backwards so following the highest priority, it goes left (counterclockwise).

b) **(*R*)**: Br > Cl > CH_3 > H. Using a model kit, you need to rotate the H to the back position where the Br is. This causes the priority to go to the right (clockwise) when looking at it with the H in the back position. Alternatively, if you do not have a model kit, you can imagine the structure 3-dimensionally and since the lowest priority (H) is facing up (as drawn), if you look at it from below,

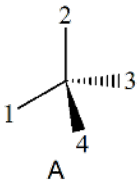
starting with Br (1st priority) and moving towards Cl (2nd priority), you are moving right (clockwise) which represents (*R*) stereochemistry.

c) **Neither (*R*) or (*S*)**: Since there are two identical substituents (H's) the molecule is achiral and cannot be assigned (*R*) or (*S*).

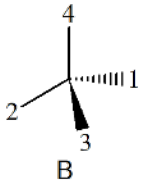
QUESTIONS

Q5.5.1

Orient the following so that the least priority (4) atom is paced behind, then assign stereochemistry (*R* or *S*).



A



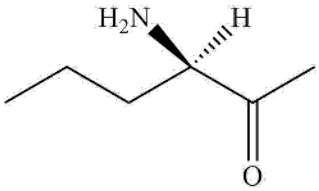
B

Q5.5.2

Draw (*R*)-2-bromobutan-2-ol.

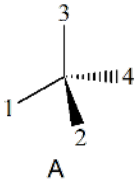
Q5.5.3

Assign *R/S* to the following molecule.

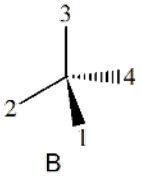


SOLUTIONS

S5.5.1



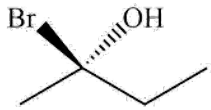
A



B

A = *S*; B = *R*

S5.5.2



S5.5.3

The stereo center is *R*.

CONTRIBUTORS AND ATTRIBUTIONS

- Ekta Patel (UCD), Ifemayowa Aworanti (University of Maryland Baltimore County)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

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5.6: DIASTEREOMERS

OBJECTIVES

After completing this section, you should be able to

1. calculate the maximum number of stereoisomers possible for a compound containing a specified number of chiral carbon atoms.
2. draw wedge-and-broken-line structures for all possible stereoisomers of a compound containing two chiral carbon atoms, with or without the aid of molecular models.
3. assign *R*,*S* configurations to wedge-and-broken-line structures containing two chiral carbon atoms, with or without the aid of molecular models.
4. determine, with or without the aid of molecular models, whether two wedge-and-broken-line structures containing two chiral carbon atoms are identical, represent a pair of enantiomers, or represent a pair of diastereomers.
5. draw the wedge-and-broken-line structure of a specific stereoisomer of a compound containing two chiral carbon atoms, given its IUPAC name and *R*,*S* configuration.

KEY TERMS

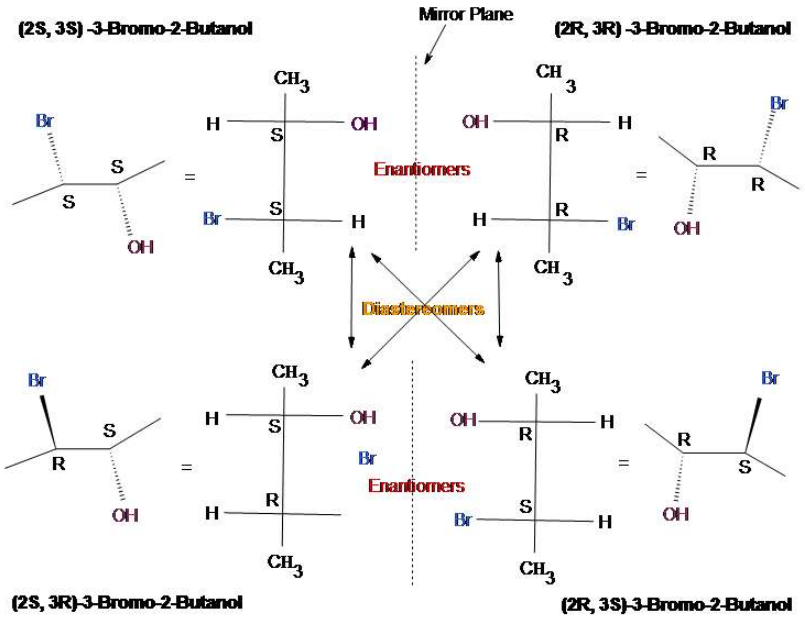
Make certain that you can define, and use in context, the key term below.

- diastereomer

Diastereomers are stereoisomers that are not related as object and mirror image and are not enantiomers. Unlike enatiomers which **are mirror images** of each other and **non-sumperimposable**, diastereomers are **not mirror images** of each other and **non-superimposable**. Diastereomers can have different physical properties and reactivity. They have different melting points and boiling points and different densities. They have **two or more** stereocenters.

INTRODUCTION

It is easy to mistake between diasteromers and enantiomers. For example, we have four steroisomers of 3-bromo-2-butanol. The four possible combination are SS, RR, SR and RS (Figure 5.6.1). One of the molecule is the enantiomer of its mirror image molecule and diasteromer of each of the other two molecule (SS is enantiomer of RR and diasteromer of RS and SR). SS's mirror image is RR and they are not superimposable, so they are enantiomers. RS and SR are not mirror image of SS and are not superimposable to each other, so they are diasteromers.



https://chem.libretexts.org/@go/page/67098

Figure 5.6.1

DIASTEREOMERS VS. ENANTIOMERS

Tartaric acid, $C_4H_6O_6$, is an organic compound that can be found in grape, bananas, and in wine. The structures of tartaric acid itself is really interesting. Naturally, it is in the form of (R,R) stereocenters. Artificially, it can be in the meso form (R,S), which is achiral. R,R tartaric acid is enantiomer to is mirror image which is S,S tartaric acid and diasteromers to meso-tartaric acid (Figure 5.6.2).

(R,R) and (S,S) tartaric acid have similar physical properties and reactivity. However, meso-tartaric acid have different physical properties and reactivity. For example, melting point of (R,R) & (S,S) tartaric is about 170 degree Celsius, and melting point of meso-tartaric acid is about 145 degree Celsius.

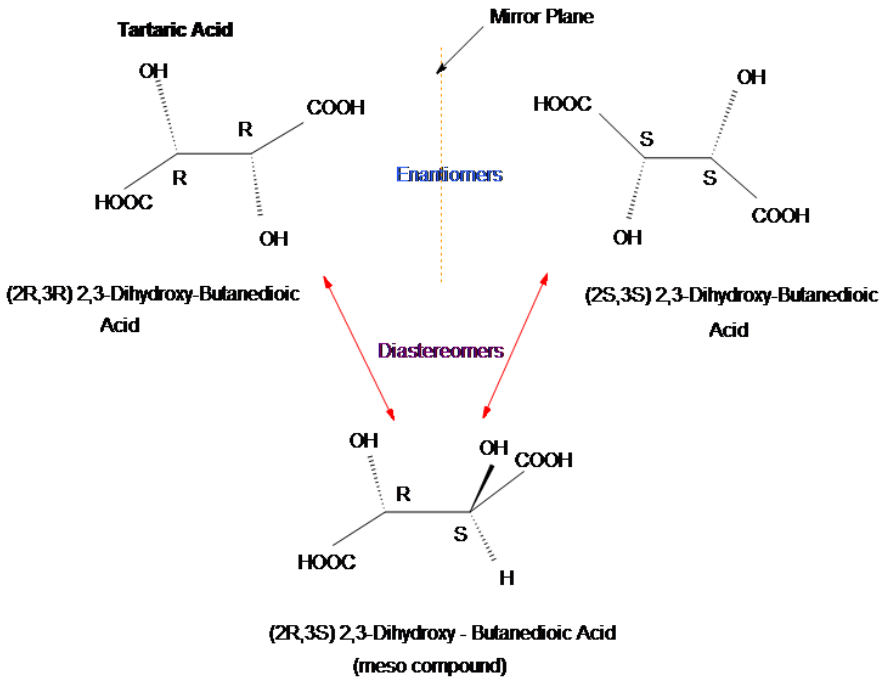
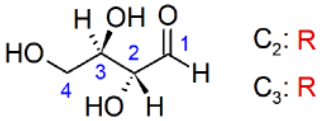


Figure 5.6.2

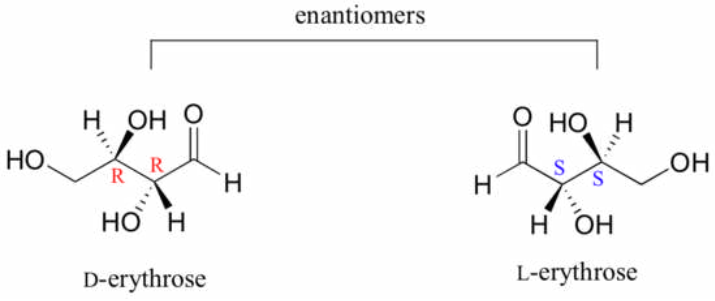
We turn our attention next to molecules which have more than one stereocenter. We will start with a common four-carbon sugar called D-erythrose.



D-erythrose

A note on sugar nomenclature: biochemists use a special system to refer to the stereochemistry of sugar molecules, employing names of historical origin in addition to the designators '*D*' and '*L*'. You will learn about this system if you take a biochemistry class. We will use the *D/L* designations here to refer to different sugars, but we won't worry about learning the system.

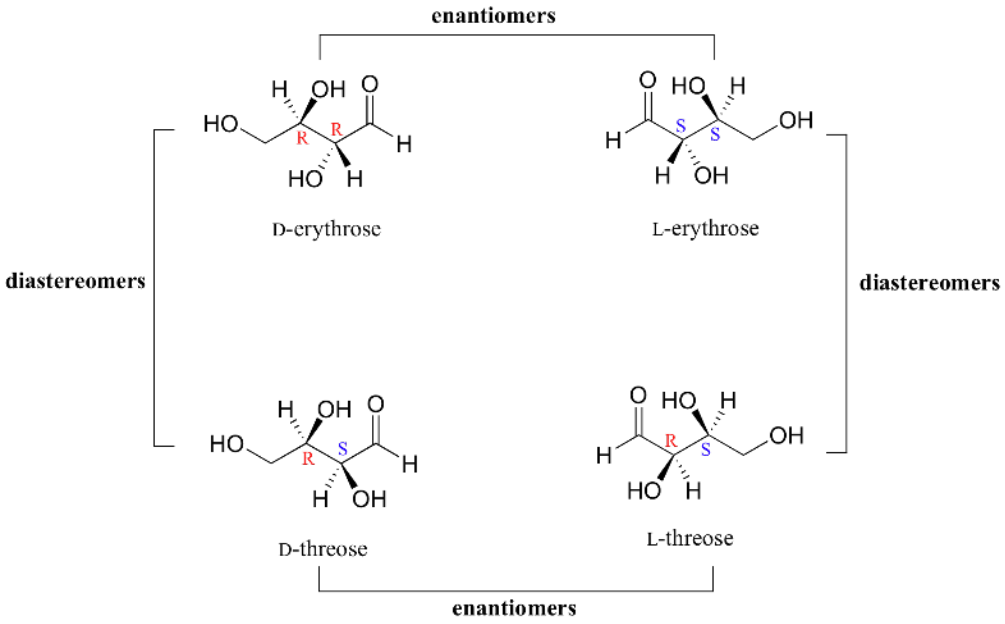
As you can see, *D*-erythrose is a chiral molecule: C_2 and C_3 are stereocenters, both of which have the *R* configuration. In addition, you should make a model to convince yourself that it is impossible to find a plane of symmetry through the molecule, regardless of the conformation. Does D-erythrose have an enantiomer? Of course it does – if it is a chiral molecule, it must. The enantiomer of erythrose is its mirror image, and is named L-erythrose (once again, you should use models to convince yourself that these mirror images of erythrose are not superimposable).



Notice that both chiral centers in L-erythrose both have the *S* configuration.

> NOTE
>
> In a pair of enantiomers, **all** of the chiral centers are of the opposite configuration.

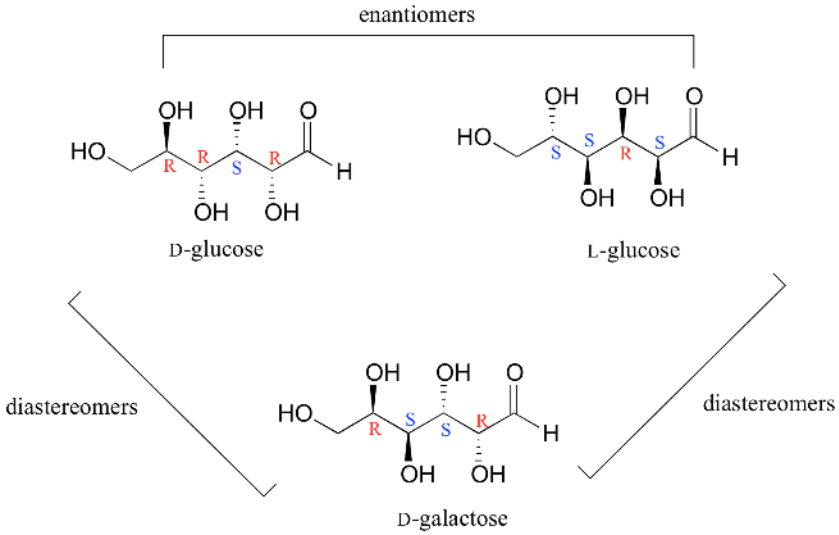
What happens if we draw a stereoisomer of erythrose in which the configuration is *S* at C_2 and *R* at C_3? This stereoisomer, which is a sugar called D-threose, is *not* a mirror image of erythrose. D-threose is a **diastereomer** of both D-erythrose and L-erythrose.



The definition of diastereomers is simple: if two molecules are stereoisomers (same molecular formula, same connectivity, different arrangement of atoms in space) but are *not* enantiomers, then they are diastereomers by default. *In practical terms, this means that at least one - but not all - of the chiral centers are opposite in a pair of diastereomers.* By definition, two molecules that are diastereomers are *not* mirror images of each other.

L-threose, the enantiomer of D-threose, has the *R* configuration at C_2 and the *S* configuration at C_3. L-threose is a diastereomer of both erythrose enantiomers.

In general, a structure with *n* stereocenters will have 2^n different stereoisomers. (We are not considering, for the time being, the stereochemistry of double bonds – that will come later). For example, let's consider the glucose molecule in its open-chain form (recall that many sugar molecules can exist in either an open-chain or a cyclic form). There are two enantiomers of glucose, called D-glucose and L-glucose. The D-enantiomer is the common sugar that our bodies use for energy. It has $n = 4$ stereocenters, so therefore there are $2^n = 2^4 = 16$ possible stereoisomers (including D-glucose itself).



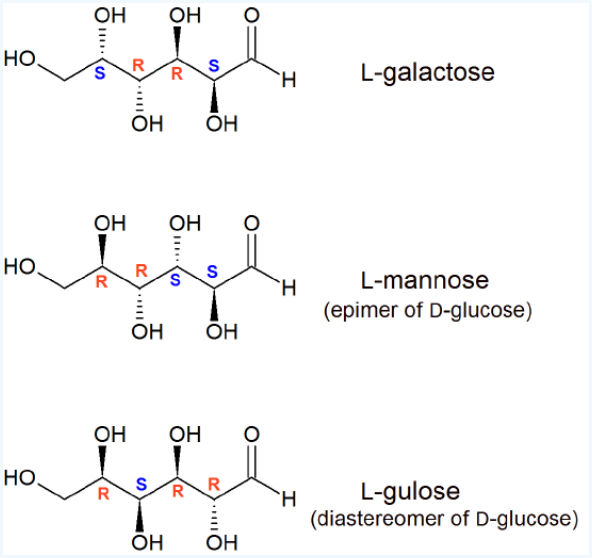
In L-glucose, all of the stereocenters are inverted relative to *D*-glucose. That leaves 14 diastereomers of D-glucose: these are molecules in which at least one, but not all, of the stereocenters are inverted relative to D-glucose. One of these 14 diastereomers, a sugar called *D*-galactose, is shown above: in D-galactose, one of four stereocenters is inverted relative to D-glucose. Diastereomers which differ in only one stereocenter (out of two or more) are called **epimers**. D-glucose and D-galactose can therefore be refered to as epimers as well as diastereomers.

EXAMPLE 5.6.1

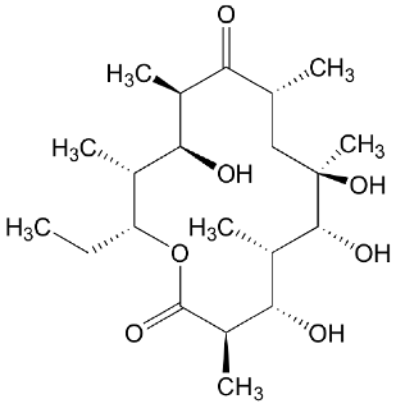
Draw the structure of L-galactose, the enantiomer of D-galactose.

Draw the structure of two more diastereomers of D-glucose. One should be an epimer.

Answer



Erythronolide B, a precursor to the 'macrocyclic' antibiotic erythromycin, has 10 stereocenters. It's enantiomer is that molecule in which all 10 stereocenters are inverted.



erythronolide B

In total, there are 2^{10} = 1024 stereoisomers in the erythronolide B family: 1022 of these are diastereomers of the structure above, one is the enantiomer of the structure above, and the last ***is*** the structure above.

We know that enantiomers have identical physical properties and equal but opposite degrees of specific rotation. Diastereomers, in theory at least, have different physical properties – we stipulate 'in theory' because sometimes the physical properties of two or more diastereomers are so similar that it is very difficult to separate them. In addition, the specific rotations of diastereomers are unrelated – they could be the same sign or opposite signs, and similar in magnitude or very dissimilar.

EXERCISES

? EXERCISE 5.6.1

Determine the number of stereoisomers a molecule can have with…

a. 3 chiral centers
b. 1 chiral center
c. 6 chiral centers

Answer

Since a molecule with n chiral centers can have 2^n stereoisomers…

a. 2^3 = 8 possible stereoisomers
b. 2^1 = 2 possible stereoisomers
c. 2^6 = 64 possible stereoisomers

? EXERCISE 5.6.2*a*

What is the relationship between enantiomers?

Answer

They are mirror images of each other and when 2 or more chiral centers are present, every stereocenter is the opposite in its enantiomer.

? EXERCISE 5.6.2*b*

How does the stereochemistry in diastereomers differ from each other?

Answer

In diastereomers, one or more of the chiral centers is the opposite but they all can't be the opposite or else they'd be enantiomers.

EXERCISE 5.6.2c

What are epimers?

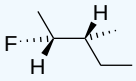
Answer

Epimers are when **only one** chiral center is the opposite (in molecules with 2 or more chiral centers) in its diastereomer.

EXERCISE 5.6.3a

Draw the structure of (2R,3R) 2-fluoro-3-methylpentane.

Answer

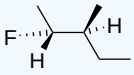


2R,3R

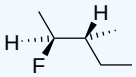
EXERCISE 5.6.3b

Draw both diastereomers of (2R,3R) 2-fluoro-3-methylpentane.

Answer



2R,3S

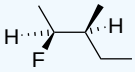


2S,3R

EXERCISE 5.6.3c

Draw the enantiomer of (2R,3R) 2-fluoro-3-methylpentane.

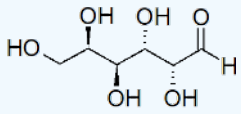
Answer



2S,3S

EXERCISE 5.6.4a

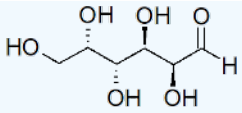
Draw the structure of L-galactose, the enantiomer of D-galactose.



R, S, S, R
D-galactose

Answer

https://chem.libretexts.org/@go/page/67098



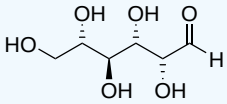
S, *R*, *R*, *S*
L-galactose

EXERCISE 5.6.4*b*

Draw a diastereomer of D-galactose that is an epimer.

Answer

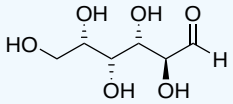
You can draw an epimer by drawing D-galactose with 1 (and only 1) of its chiral centers reversed. Here's an example when you switch only the first chiral center (in red). (There are 3 other epimers that could be drawn as long as you only swap a single chiral center in the diastereomer that you use.)



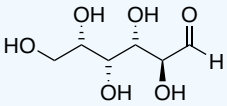
R, *R*, *R*, *S*

EXERCISE 5.6.4*c*

Identify if the following diastereomer of galactose is an epimer of D- galactose or L- galactose.



Answer

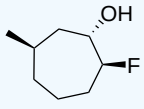


S, *R*, *S*, *S*

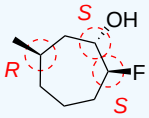
Since the diastereomer above only varies from L-galactose by 1 chiral center, the above is an epimer in relationship to L-galactose. Since it varies from D-galactose by 3 chiral centers, it is not an epimer but a diastereomer. Since not all of the chiral centers are swapped, it is not an enantiomer!

EXERCISE 5.6.5*a*

For the compound shown below, label each chiral center as R or S.



Answer



EXERCISE 5.6.5b

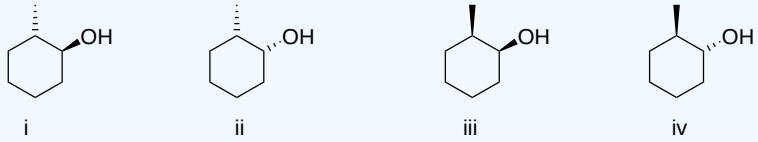
How many stereoisomers are possible for the compound in part a)?

Answer

Since there are 3 chiral centers, $2^3 = 8$ possible stereoisomers.

EXERCISE 5.6.6

Consider the stereoisomers below.



i ii iii iv

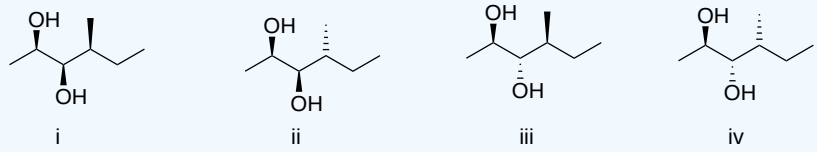
a. Which is/are an enantiomer of i?
b. Which is/are a diastereomer of ii?
c. Which is/are an epimer of i?

Answer

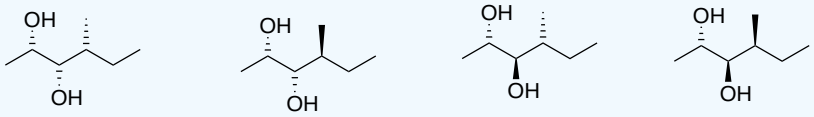
a. iv is an enantiomer of i since both chiral centers are switched and they are non superimposable mirror images.
b. i & iv are diastereomers of ii since they are stereoisomers that are not mirror images.
c. ii and iii are epimers of i since they are diastereomers with only 1 chiral center switched and the other one the same.

EXERCISE 5.6.7

Consider the 8 stereoisomers below.



i ii iii iv



v vi vii viii

a. Which is/are an enantiomer of i?
b. Which is/are a diastereomer of i?
c. Which is/are an epimer of i?

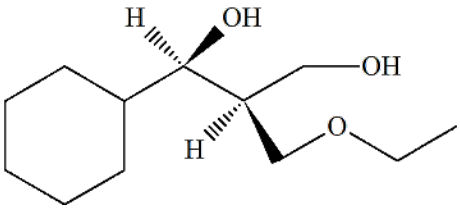
Answer

a. v is an enantiomer since all three chiral centers are switched and they are non superimposable mirror images.
b. ii, iii, iv, vi, vii & viii are diastereomers of i since they are stereoisomers that are not mirror images.
c. ii,iii & viii are epimers of i since they are diastereomers with only 1 chiral center switched and the other chiral centers the same.

QUESTIONS

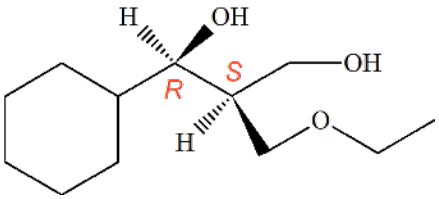
Q5.6.1

Determine the stereochemistry of the following molecule:



SOLUTIONS

S5.6.1



CONTRIBUTORS AND ATTRIBUTIONS

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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5.7: MESO COMPOUNDS

OBJECTIVES

After completing this section, you should be able to

1. determine whether or not a compound containing two chiral carbon atoms will have a meso form, given its Kekulé, condensed or shorthand structure, or its IUPAC name.
2. draw wedge-and-broken-line structures for the enantiomers and meso form of a compound such as tartaric acid, given its IUPAC name, or its Kekulé, condensed or shorthand structure.
3. make a general comparison of the physical properties of the enantiomers, meso form and racemic mixture of a compound such as tartaric acid.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- meso compound

STUDY NOTES

You may be confused by the two sets of structures showing “rotations.” Of course in each case the two structures shown are identical, they represent the same molecule looked at from two different perspectives. In the first case, there is a 120° rotation around the single carbon-carbon bond. In the second, the whole molecule is rotated 180° top to bottom.

Meso Compounds

A meso compound is an achiral compound that has chiral centers. It is superimposed on its mirror image and is optically **inactive** although it contains two or more stereocenters.

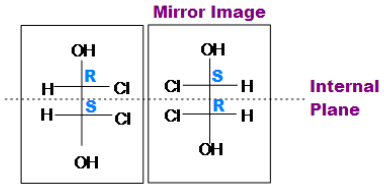
INTRODUCTION

In general, a meso compound should contain two or more identical substituted stereocenters. Also, it has an internal symmetry plane that divides the compound in half. These two halves reflect each other by the internal mirror. The stereochemistry of stereocenters should "cancel out". What it means here is that when we have an internal plane that splits the compound into two symmetrical sides, the stereochemistry of both left and right side should be opposite to each other, and therefore, result in **optically inactive**. Cyclic compounds may also be meso.

IDENTIFICATION

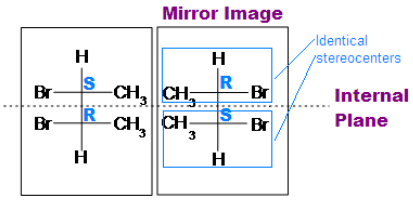
If A is a meso compound, it should have two or more stereocenters, an internal plane, and the stereochemistry should be R and S.

1. Look for an internal plane, or internal mirror, that lies in between the compound.
2. The stereochemistry (e.g. R or S) is very crucial in determining whether it is a meso compound or not. As mentioned above, a meso compound is optically inactive, so their stereochemistry should cancel out. For instance, R cancels S out in a meso compound with two stereocenters.



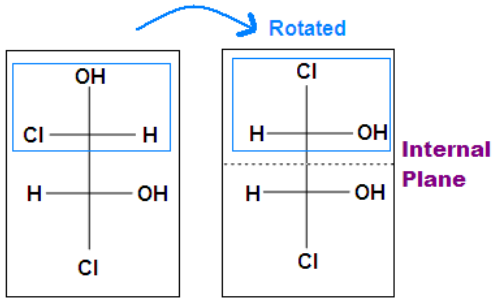
***trans*-1,2-dichloro-1,2-ethanediol**

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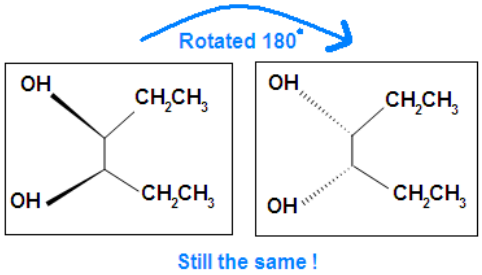


***(meso)*-2,3-dibromobutane**

Tips: An interesting thing about single bonds or sp^3-orbitals is that we can rotate the substituted groups that attached to a stereocenter around to recognize the internal plane. As the molecule is rotated, its stereochemistry does not change. For example:

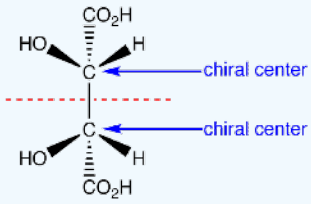


Another case is when we rotate the whole molecule by 180 degree. Both molecules below are still meso.



Remember the internal plane here is depicted on two dimensions. However, in reality, it is three dimensions, so be aware of it when we identify the internal mirror.

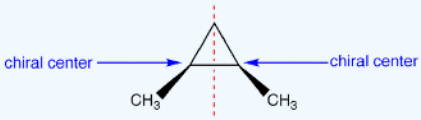
✔ EXAMPLE 5.7.1



1

1 has a plane of symmetry (the horizonatal plane going through the red broken line) and, therefore, is achiral; 1 has chiral centers. Thus, 1 is a meso compound.

EXAMPLE 5.7.2

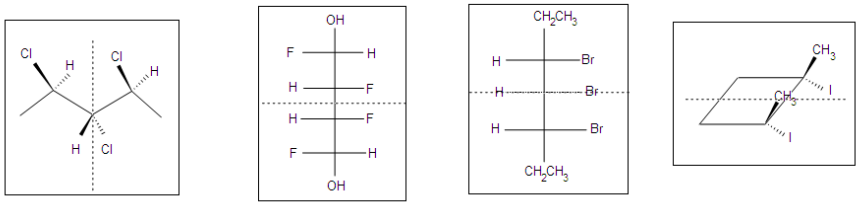


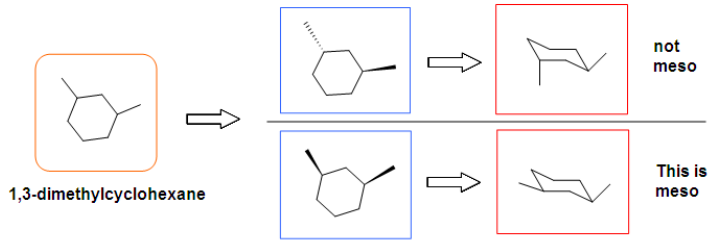
2

This molecules has a plane of symmetry (the vertical plane going through the red broken line perpendicular to the plane of the ring) and, therefore, is achiral, but has has two chiral centers. Thus, its is a meso compound.

OTHER EXAMPLES OF MESO COMPOUNDS

Meso compounds can exist in many different forms such as pentane, butane, heptane, and even cyclobutane. They do not necessarily have to be two stereocenters, but can have more.





OPTICAL ACTIVITY ANALYSIS

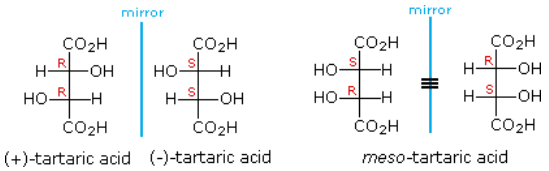
When the optical activity of a meso compound is attempted to be determined with a polarimeter, the indicator will not show (+) or (-). It simply means there is no certain direction of rotation of the polarized light, neither levorotatory (-) and dexorotatory (+).

ACHIRAL DIASTEREOMERS (MESO-COMPOUNDS)

The chiral centers in the preceding examples have all been different. In the case of 2,3-dihydroxybutanedioic acid, known as tartaric acid, the two chiral centers have the same four substituents and are equivalent. As a result, two of the four possible stereoisomers of this compound are identical due to a plane of symmetry, so there are only three stereoisomeric tartaric acids. Two of these stereoisomers are enantiomers and the third is an achiral diastereomer, called a **meso** compound. Meso compounds are achiral (optically inactive) diastereomers of chiral stereoisomers. Investigations of isomeric tartaric acid salts, carried out by Louis Pasteur in the mid 19th century, were instrumental in elucidating some of the subtleties of stereochemistry. Some physical properties of the isomers of tartaric acid are given in the following table.

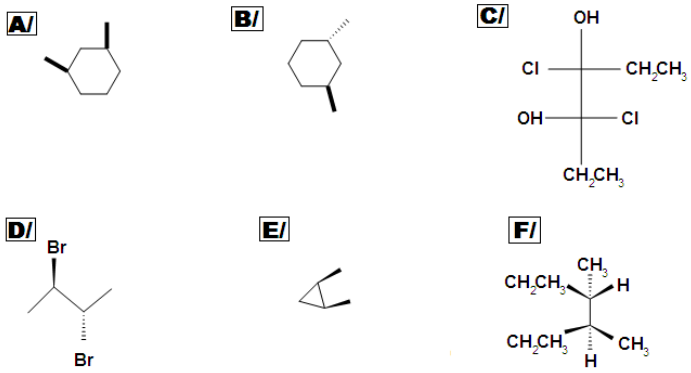
(+)-tartaric acid:	$[\alpha]_D = +13^o$	m.p. 172 ºC
(–)-tartaric acid:	$[\alpha]_D = -13^o$	m.p. 172 ºC
meso-tartaric acid:	$[\alpha]_D = 0^o$	m.p. 140 ºC

Fischer projection formulas provide a helpful view of the configurational relationships within the structures of these isomers. In the following illustration a mirror line is drawn between formulas that have a mirror-image relationship. In demonstrating the identity of the two meso-compound formulas, remember that a Fischer projection formula may be rotated 180º in the plane.



PROBLEMS

Beside meso, there are also other types of molecules: enantiomer, diastereomer, and identical. Determine if the following molecules are meso.

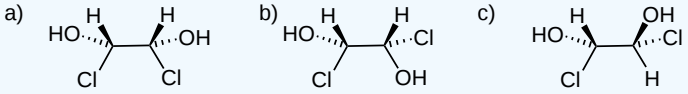


Answer key: A C, D, E are meso compounds.

EXERCISES

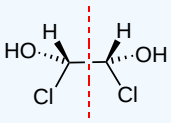
? EXERCISE 5.7.1

Which of the following are meso compounds?



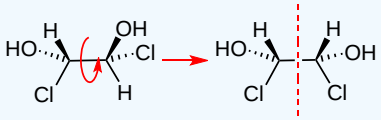
Answer

a) This is a meso compound. There is an internal plane of symmetry (dashed line shown in red) between the C's (and it has stereochemistry of *S* & *R*).



b) This is not a meso compound. No matter how you rotate the C-C bond, you do not see a plane of symmetry (and its stereochemistry is *S* & *S*)

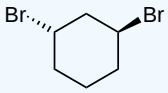
c) This is a meso compound. There is an internal plane of symmetry (dashed line shown in red) that can be seen when you rotate the C-C bond (and it has stereochemistry of *S* & *R*).

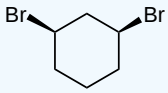


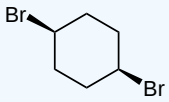
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EXERCISE 5.7.2

Which of the following are meso compounds?

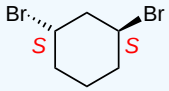
a) 

b) 

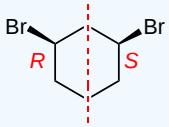
c) 

Answer

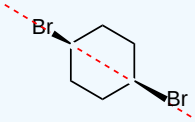
a) This is not a meso compound. There is no plane of symmetry and has stereochemistry of *S* & *S*.



b) This is a meso compound. There is an internal plane of symmetry (dashed line shown in red) and it has stereochemistry of *R* & *S*.

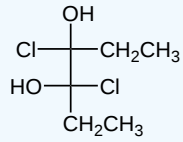


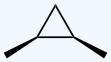
c) This is not a meso compound (even though it has planes of symmetry). The plane of symmetry shown in red makes it so that both chiral centers have symmetrical groups (the ring) and thus the compound is not chiral (so it can't be a meso compound).

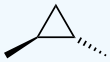


EXERCISE 5.7.3

Which of the following are meso compounds?

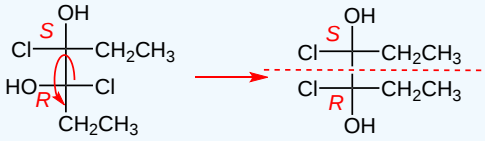
a) 

b) 

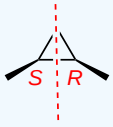
c) 

Answer

a) This is a meso compound. If you rotate between the C-C bond, you can see that it has a mirror plane between the C's (shown in red on the structure to the right). Notice how rotating a C-C bond doesn't change the stereochemistry of the molecule (*S* & *R*).



b) This is a meso compound. You can see the plane of symmetry in red and the compound has stereochemistry of *S* & *R*.



c) This is not a meso compound. There is no plane of symmetry and it has stereochemistry of *S* & *S*.

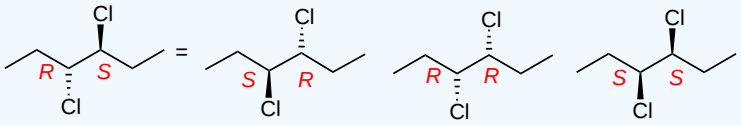


EXERCISE 5.7.4

Determine (and draw) if any of the forms of 3,4-dichlorohexane are a meso compound.

Answer

Looking at the 4 different possibilities below, i & ii are equivalent structures (with R & S stereochemistry) so it is a meso compound. iii & iv are not meso compounds but are enantiomers to each other.

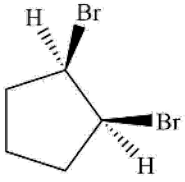


i ii iii iv

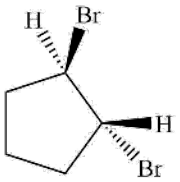
QUESTIONS

Q5.7.1

Which of the following are meso-compounds:



A



B

C – 2,3-dibromobutane

D – 2,3-dibromopentane

SOLUTIONS

S5.7.1

Compounds A and C are meso.

CONTRIBUTORS AND ATTRIBUTIONS

- Duy Dang
- Gamini Gunawardena from the OChemPal site (Utah Valley University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

  Template:HideTOC
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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5.8: RACEMIC MIXTURES AND THE RESOLUTION OF ENANTIOMERS

Objectives

After completing this section, you should be able to

1. describe a common process for separating a mixture of enantiomers.
2. explain why racemic mixtures do not rotate plane-polarized light.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- racemic mixture (or racemate)
- resolve

STUDY NOTES

A *racemic mixture* is a 50:50 mixture of two enantiomers. Because they are mirror images, each enantiomer rotates plane-polarized light in an equal but opposite direction and is optically inactive. If the enantiomers are separated, the mixture is said to have been *resolved*. A common experiment in the laboratory component of introductory organic chemistry involves the resolution of a racemic mixture.

The dramatic biochemical consequences of chirality are illustrated by the use, in the 1950s, of the drug Thalidomide, a sedative given to pregnant women to relieve morning sickness. It was later realized that while the (+)-form of the molecule, was a safe and effective sedative, the (−)-form was an active teratogen. The drug caused numerous birth abnormalities when taken in the early stages of pregnancy because it contained a mixture of the two forms.

As noted earlier, chiral compounds synthesized from achiral starting materials and reagents are generally racemic (i.e. a 50:50 mixture of enantiomers). Separation of racemates into their component enantiomers is a process called resolution. Since enantiomers have identical physical properties, such as solubility and melting point, resolution is extremely difficult. Diastereomers, on the other hand, have different physical properties, and this fact is used to achieve resolution of racemates. Reaction of a racemate with an enantiomerically pure chiral reagent gives a mixture of diastereomers, which can be separated. For example, if a racemic mixture of a chiral alcohol is reacted with a enantiomerically pure carboxylic acid, the result is a mixture of diastereomers: in this case, because the pure (R) entantiomer of the acid was used, the product is a mixture of (R-R) and (R-S) diastereomeric esters, which can, in theory, be separated by their different physical properties. Subsequent hydrolysis of each separated ester will yield the 'resolved' (enantiomerically pure) alcohols. The used in this technique are known as 'Moscher's esters', after Harry Stone Moscher, a chemist who pioneered the method at Stanford University.

As noted earlier, chiral compounds synthesized from achiral starting materials and reagents are generally racemic (i.e. a 50:50 mixture of enantiomers). Separation of racemates into their component enantiomers is a process called **resolution**. Since enantiomers have identical physical properties, such as solubility and melting point, resolution is extremely difficult. Diastereomers, on the other hand, have different physical properties, and this fact is used to achieve resolution of racemates. Reaction of a racemate with an enantiomerically pure chiral reagent gives a mixture of diastereomers, which can be separated. Reversing the first reaction then leads to the separated enantiomers plus the recovered reagent.

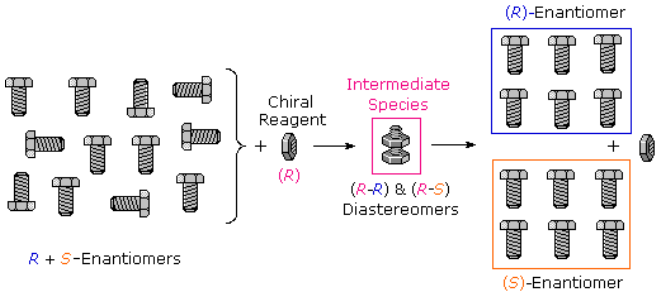


Figure 5.8.1:

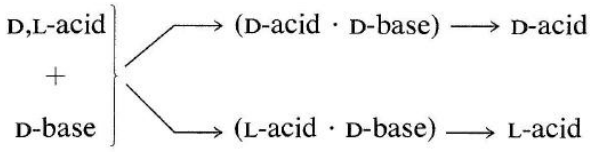
Many kinds of chemical and physical reactions, including salt formation, may be used to achieve the diastereomeric intermediates needed for separation. Figure 5.8.1 illustrates this general principle by showing how a nut having a right-handed thread (R) could serve as a

"reagent" to discriminate and separate a mixture of right- and left-handed bolts of identical size and weight. Only the two right-handed partners can interact to give a fully-threaded intermediate, so separation is fairly simple. The resolving moiety, i.e. the nut, is then removed, leaving the bolts separated into their right and left-handed forms. Chemical reactions of enantiomers are normally not so dramatically different, but a practical distinction is nevertheless possible.

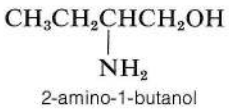
Because the physical properties of enantiomers are identical, they seldom can be separated by simple physical methods, such as fractional crystallization or distillation. It is only under the influence of another chiral substance that enantiomers behave differently, and almost all methods of resolution of enantiomers are based upon this fact. We include here a discussion of the primary methods of resolution

CHIRAL AMINES AS RESOLVING AGENTS AND RESOLUTION OF RACEMIC ACIDS

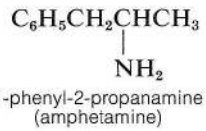
The most commonly used procedure for separating enantiomers is to convert them to a mixture of diastereomers that will have different physical properties: melting point, boiling point, solubility, and so on (Section 5-5). For example, if you have a racemic or D,L mixture of enantiomers of an acid and convert this to a salt with a chiral base having the D configuration, the salt will be a mixture of two diastereomers, (D acid . D base) and (L acid . D base). These diastereomeric salts are *not* identical and they are not mirror images. Therefore they will differ to some degree in their physical properties, and a separation by physical methods, such as crystallization, may be possible. If the diastereomeric salts can be completely separated, the acid regenerated from each salt will be either exclusively the D or the L enantiomer:



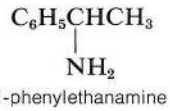
Resolution of chiral acids through the formation of diastereomeric salts requires adequate supplies of suitable chiral bases. Brucine, strychnine, and quinine frequently are used for this purpose because they are readily available, naturally occurring chiral bases. Simpler amines of synthetic origin, such as 2-amino- 1 -butanol, amphetamine, and 1 -phenylethanamine, also can be used, but first they must be resolved themselves.



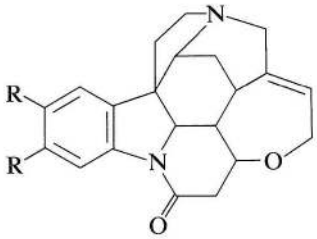
2-amino-1-butanol



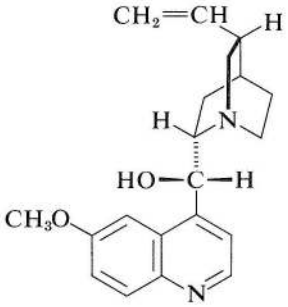
1-phenyl-2-propanamine
(amphetamine)



1-phenylethanamine



R = H, strychnine
R = OCH_3, brucine



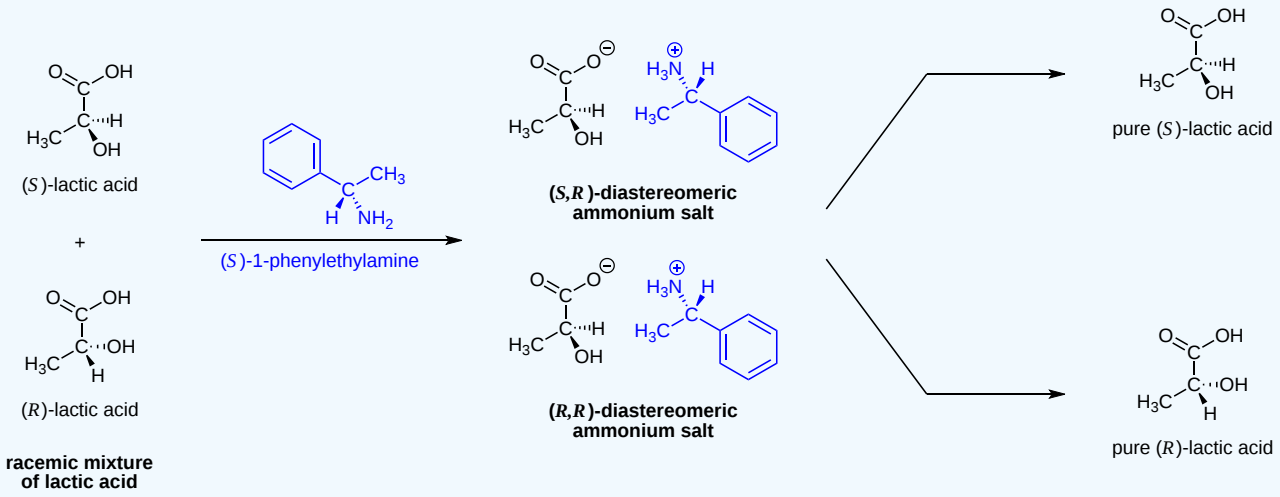
quinine
(antimicrobial)
(antimalarial)

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? WORKED EXAMPLE 5.8.1

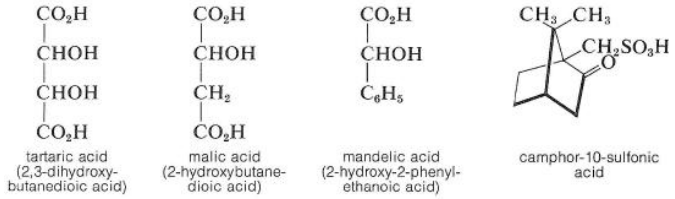
Show how (*S*)-1-phenylethylamine can be used to resolve a racemic mixture of lactic acid. Please draw all the structures involved.

Answer



RESOLUTION OF RACEMIC BASES

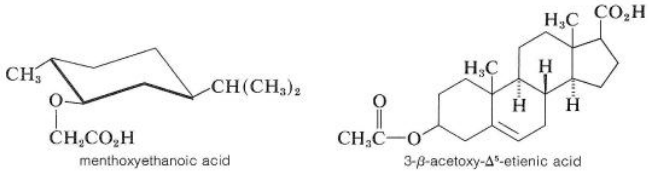
Chiral acids, such as (+)-tartaric acid, (-)-malic acid, (-)-mandelic acid, and (+)-camphor- 10-sulfonic acid, are used for the resolution of a racemic base.



The principle is the same as for the resolution of a racemic acid with a chiral base, and the choice of acid will depend both on the ease of separation of the diastereomeric salts and, of course, on the availability of the acid for the scale of the resolution involved. Resolution methods of this kind can be tedious, because numerous recrystallizations in different solvents may be necessary to progressively enrich the crystals in the less-soluble diastereomer. To determine when the resolution is complete, the mixture of diastereomers is recrystallized until there is no further change in the measured optical rotation of the crystals. At this stage it is hoped that the crystalline salt is a pure diastereomer from which one pure enantiomer can be recovered. The optical rotation of this
enantiomer will be a maximum value if it is "optically" pure because any amount of the other enantiomer could only reduce the magnitude of the measured rotation α.

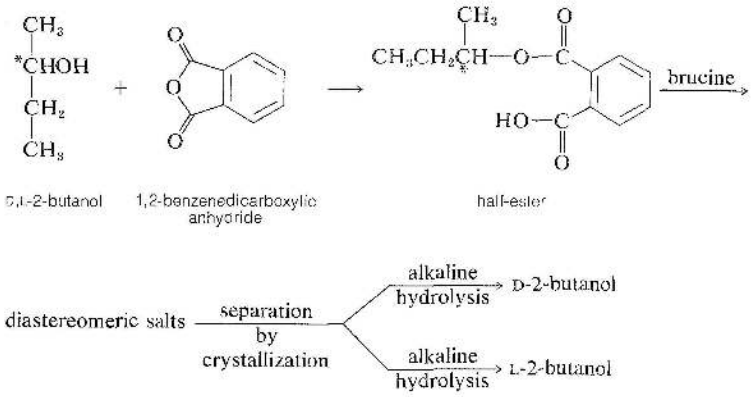
RESOLUTION OF RACEMIC ALCOHOLS

To resolve a racemic alcohol, a chiral acid can be used to convert the alcohol to a mixture of diastereomeric esters. This is not as generally useful as might be thought because esters tend to be liquids unless they are very high-molecularweight compounds. If the diastereomeric esters are not crystalline, they must be separated by some other method than fractional crystallization (for instance, by chromatography methods, Section 9-2). Two chiral acids that are useful resolving agents for alcohols are:



The most common method of resolving an alcohol is to convert it to a half-ester of a dicarboxylic acid, such as butanedioic (succinic) or 1,2-benzenedicarboxylic (phthalic) acid, with the corresponding anhydride. The resulting half-ester has a free carboxyl function and may

then be resolvable with a chiral base, usually brucine:



OTHER METHODS OF RESOLUTION

Qne of the major goals in the field of organic chemistry is the development of reagents with the property of "chiral recognition" such that they can effect a clean separation of enantiomers in one operation without destroying either of the enantiomers. We have not achieved that ideal yet, but it may not be far in the future. Chromatographic methods (Section 9-2), whereby the stationary phase is a chiral reagent that adsorbs one enantiomer more strongly than the other, have been used to resolve racemic compounds, but such resolutions seldom have led to both pure enantiomers on a preparative scale. Other methods, called kinetic resolutions, are excellent when applicable. The procedure takes advantage of differences in reaction rates of enantiomers with chiral reagents. One enantiomer may react more rapidly, thereby leaving an excess of the other enantiomer behind. For example, racemic tartaric acid
can be resolved with the aid of certain penicillin molds that consume the dextrorotatory enantiomer faster than the levorotatory enantiomer. As a result, almost pure (-)-tartaric acid can be recovered from the mixture:

$$(\pm)\text{-tartaric acid} + \text{mold} \rightarrow (-)\text{-tartaric acid} + \text{more mold}$$

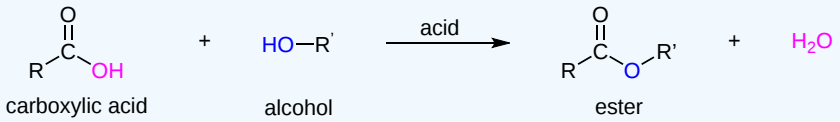
A disadvantage of resolutions of this type is that the more reactive enantiomer usually is not recoverable from the reaction mixture.

The crystallization procedure employed by Pasteur for his classical resolution of (±)-tartaric acid (Section 5-1C) has been successful only in a very few cases. This procedure depends on the formation of individual crystals of each enantiomer. Thus if the crystallization of sodium ammonium tartrate is carried out below 27", the usual racemate salt does not form; a mixture of crystals of the (+) and (-) salts forms instead. The two different kinds of crystals, which are related as an object to its mirror image, can be separated manually with the aid of a microscope and subsequently may be converted to the tartaric acid enantiomers by strong acid. A variation on this method of resolution is the seeding of a saturated solution of a racemic mixture with crystals of one pure enantiomer in the hope of causing crystallization of just that one enantiomer, thereby leaving the other in solution. Unfortunately, very
few practical resolutions have been achieved in this way.

Even when a successful resolution is achieved, some significant problems remain. For instance, the resolution itself does not provide information on the actual configuration of the (+) or (-) enantiomer. This must be determined by other means (see Section 19-5). Also, it is not possible to tell the enantiomeric purity (optical purity) of the resolved enantiomers without additional information. This point is discussed further in the next section.

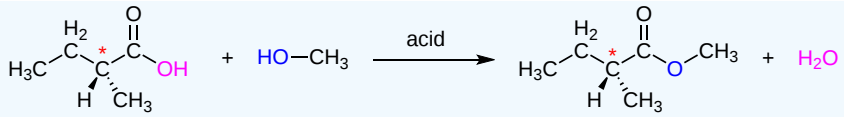
? WORKED EXAMPLE 5.8.2

The following reaction involves the conversion of a carboxylic acid reacting with an alcohol to form an ester. If a pure sample of (R)-2-methylbutanoic acid is reacted with methanol to form an ester, what would be the stereochemistry of the product?



Answer

First it is important to identify the location of the chiral carbon and determine if it is directly involved in the reaction. In this case, the chiral carbon is not involved so the stereochemistry will be carried over into the product unchanged.



(*R*)-2-methylbutanoic acid + methanol → methyl (*R*)-2-methyl butanoate + H_2O

EXERCISES

EXERCISE 5.8.1

Indicate the reagents you could use to resolve the following compounds. Show the reactions involved and specify the physical method you believe would be the best to separate the diastereomers of 1 -phenyl-2-propanamine.

Answer

You could react the 1-phenyl-2-propanamine racemic mixture with a chiral acid such as (+)-tartaric acid (*R*, *R*). The reaction will produce a mixture of diastereomeric salts (i.e. *R*, *R*, *R* and *S*, *R*, *R*). You can separate the diastereomers through crystallization and treat the salt with a strong base (e.g. KOH) to recover the pure enantiomeric amine.

EXERCISE 5.8.2

Indicate the reagents you would use to resolve the following and discuss the reactions involved and specify the physical method you believe would be the best to separate the diastereomers of 2,3-pentadienedioic acid.

Answer

You could react the 2,3-pentadienedioic acid mixture with a chiral base such as (*R*)-1-phenylethylamine. The reaction will produce a mixture of diastereomeric salts. Separate the diastereomers through crystallization and treat the resulting salt with strong acid (e.g. HCl) to recover the pure enantiomeric acid.

EXERCISE 5.8.3

Indicate the reagents you would use to resolve the following and discuss the reactions involved and specify the physical method you believe would be the best to separate the diastereomers of 1-phenylethanol.

Answer

You could react the 1-phenylethanol mixture with 1,2-benzenedicarboxylic anhydride. The reaction will produce a mixture of diastereomeric salts. You could then separate the diastereomers through crystallization and then alkaline hydrolysis treatment should recover the pure enantiomeric alcohol.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

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5.9: A REVIEW OF ISOMERISM

Objective

After completing this section, you should be able to explain the differences among constitutional (structural) isomers and stereoisomers (geometric isomers).

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- constitutional
- (structural) isomers
- stereoisomers

The following flow chart can be used to identify the relationship of two compounds with respect to isomerization:

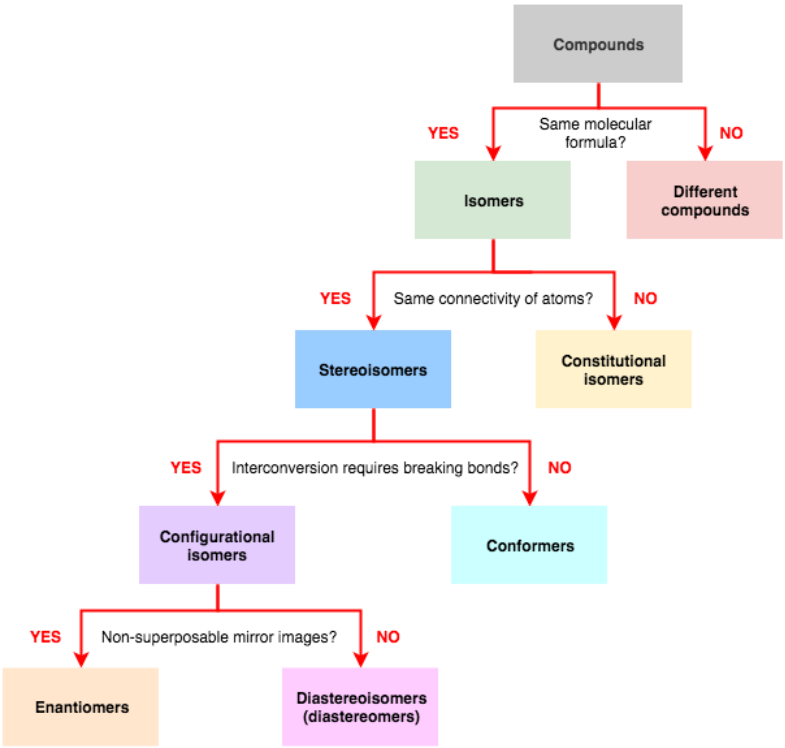


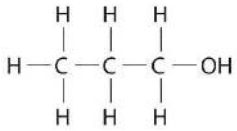
Figure **5.9.1**: Different types of isomers. When using the flow chart, it is really important to remember that each decision on the flow chart is related to comparing two molecules, ie. it doesn't make sense to ask "what is compound A", but it does make sense to ask "how are compounds A and B related"? A molecule may be the enantiomer of another molecule, but a diastereomer of another. (CC-BY-SA 4.0; Mark Coster via StackExchange)

CONFORMATIONAL ISOMERS

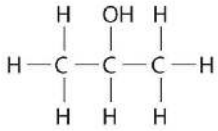
The C–C single bonds in ethane, propane, and other alkanes are formed by the overlap of an sp^3 hybrid orbital on one carbon atom with an sp^3 hybrid orbital on another carbon atom, forming a σ bond. Each sp^3 hybrid orbital is cylindrically symmetrical (all cross-sections are circles), resulting in a carbon–carbon single bond that is also cylindrically symmetrical about the C–C axis. Because rotation about the carbon–carbon single bond can occur without changing the overlap of the sp^3 hybrid orbitals, there is no significant electronic energy barrier to rotation. Consequently, many different arrangements of the atoms are possible, each corresponding to different degrees of rotation. Differences in three-dimensional structure resulting from rotation about a σ bond are called differences in conformation, and each different arrangement is called a conformational isomer (or conformer).

STRUCTURAL ISOMERS

Unlike conformational isomers, which do not differ in connectivity, structural isomers differ in connectivity, as illustrated here for 1-propanol and 2-propanol. Although these two alcohols have the same molecular formula (C_3H_8O), the position of the –OH group differs, which leads to differences in their physical and chemical properties.

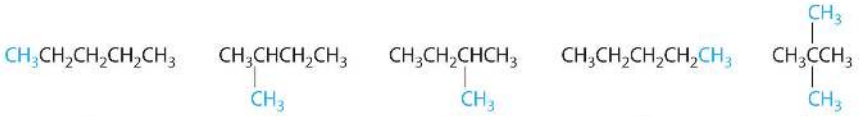


1-Propanol (*n*-propanol)



2-Propanol (isopropanol)

In the conversion of one structural isomer to another, at least one bond must be broken and reformed at a different position in the molecule. Consider, for example, the following five structures represented by the formula C_5H_{12}:



(a) (b) (c) (d) (e)

Of these structures, (a) and (d) represent the same compound, as do (b) and (c). No bonds have been broken and reformed; the molecules are simply rotated about a 180° vertical axis. Only three—n-pentane (a) and (d), 2-methylbutane (b) and (c), and 2,2-dimethylpropane (e)—are structural isomers. Because no bonds are broken in going from (a) to (d) or from (b) to (c), these alternative representations are not structural isomers. The three structural isomers—either (a) or (d), either (b) or (c), and (e)—have distinct physical and chemical properties.

STEREOISOMERS

Molecules with the same connectivity but different arrangements of the atoms in space are called stereoisomers. There are two types of stereoisomers: geometric and optical. Geometric isomers differ in the relative position(s) of substituents in a rigid molecule. Simple rotation about a C–C σ bond in an alkene, for example, cannot occur because of the presence of the π bond. The substituents are therefore rigidly locked into a particular spatial arrangement. Thus a carbon–carbon multiple bond, or in some cases a ring, prevents one geometric isomer from being readily converted to the other. The members of an isomeric pair are identified as either cis or trans, and interconversion between the two forms requires breaking and reforming one or more bonds. Because their structural difference causes them to have different physical and chemical properties, cis and trans isomers are actually two distinct chemical compounds.

NOTE

Stereoisomers have the same connectivity but different arrangements of atoms in space.

Optical isomers are molecules whose structures are mirror images but cannot be superimposed on one another in any orientation. Optical isomers have identical physical properties, although their chemical properties may differ in asymmetric environments. Molecules that are nonsuperimposable mirror images of each other are said to be chiral (pronounced “ky-ral,” from the Greek cheir, meaning “hand”). Examples of some familiar chiral objects are your hands, feet, and ears. As shown in part (a) in Figure 5.9.1, your left and right hands are nonsuperimposable mirror images. (Try putting your right shoe on your left foot—it just doesn’t work.) An achiral object is one that can be superimposed on its mirror image, as shown by the superimposed flasks in part (b) in Figure 5.9.1.

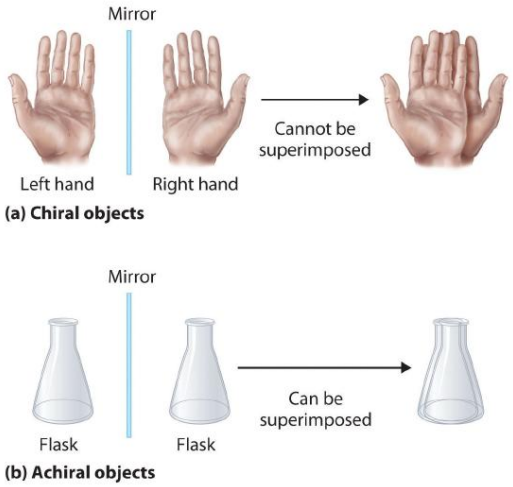


Figure 5.9.1: *Chiral and Achiral Objects/ (a) Objects that are nonsuperimposable mirror images of each other are chiral, such as the left and the right hand. (b) The unmarked flask is achiral because it can be superimposed on its mirror image.*

Most chiral organic molecules have at least one carbon atom that is bonded to four different groups, as occurs in the bromochlorofluoromethane molecule shown in part (a) in Figure 5.9.2. This carbon, often designated by an asterisk in structural drawings, is called a chiral center or asymmetric carbon atom. If the bromine atom is replaced by another chlorine (part (b) in Figure 5.9.2), the molecule and its mirror image can now be superimposed by simple rotation. Thus the carbon is no longer a chiral center. Asymmetric carbon atoms are found in many naturally occurring molecules, such as lactic acid, which is present in milk and muscles, and nicotine, a component of tobacco. A molecule and its nonsuperimposable mirror image are called enantiomers (from the Greek enantiou, meaning "opposite").

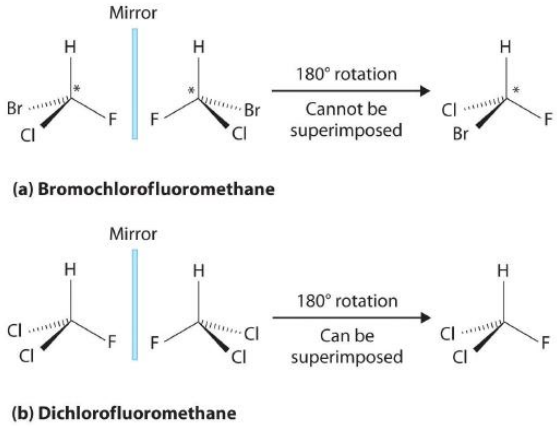
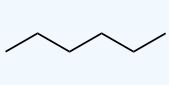
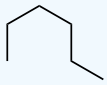


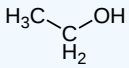
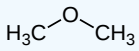
Figure 5.9.2: *Comparison of Chiral and Achiral Molecules. (a) Bromochlorofluoromethane is a chiral molecule whose stereocenter is designated with an asterisk. Rotation of its mirror image does not generate the original structure. To superimpose the mirror images, bonds must be broken and reformed. (b) In contrast, dichlorofluoromethane and its mirror image can be rotated so they are superimposable.*

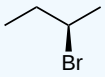
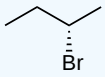
EXERCISES

? EXERCISE 5.9.1

What kind of isomers are the following pairs?

a)  and 

b)  and 

c)  and 

Answer

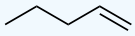
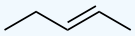
a. Since both structures have the same formula (C_6H_{12}) and they have the same connectivity, but are in a different arrangement of the atoms in space, they are conformational isomers.

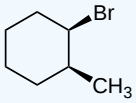
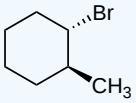
b. Since both structures have the same formula (C_2H_6O) but different connectivity, they are structural isomers.

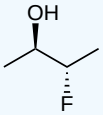
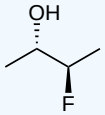
c. Since both structures have the same formula (C_3H_9Br) and the same connectivity but the structure on the left has *R* stereochemistry and the structure on the right has *S* stereochemistry, they are stereoisomers called enantiomers.

EXERCISE 5.9.2

What kind of isomers are the following pairs?

a)  and 

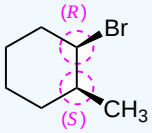
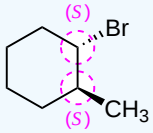
b)  and 

c)  and 

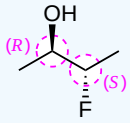
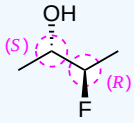
Answer

a) Since both structures have the same formula (C_2H_6O) but different connectivity of where the double bond is, they are structural isomers.

b) Both structures have the same formula and the same connectivity but the structure on the left has (*R*,*S*) stereochemistry and the structure on the right has (S,S) stereochemistry, they are stereoisomers that are diastereomers.

c) Both structures and have the same connectivity but their stereochemistry differs so they are stereoisomers. Since the one on the left is (R,S) and the one on the right is (S,R), they are non-super imposable mirror images of each other and enantiomers.

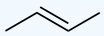
 

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EXERCISE 5.9.3

What is the relationship between the following pairs?

a)  and

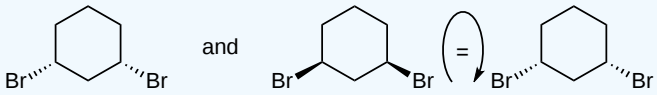
b)  and 

c) (*R*) – 2 chlorohexane & 1-chlorohexane

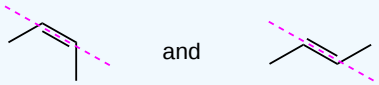
d) (2*R*, 3*R*) dichlorohexane & (2*S*, 3*R*) dichlorohexane

Answer

a) Both structures have the same connectivity and same chemical formula and when you rotate the structure on the right you can see that these are the same compound both with (R,S) stereochemistry.



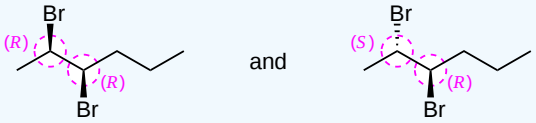
b)) Since both structures have the same formula (C_4H_8) and the same connectivity they are stereoisomers since they differ in what is known as cis/trans isomerism (covered more in Ch 7).Due to the pi bond between carbons 2 & 3, there is not free rotation between the C2-C3 bond so the structure on the left has the carbon chains on the same side of the double bond (cis) and the structure on the right has the carbon chains on opposite sides of the double bond (trans).



c) Looking at the structures below, you can see that they have the same formula ($C_6H_{13}Cl$) and different connectivity, so they are structural isomers.



d) Looking at the structures below, you can see that they have the same formula ($C_6H_{12}Br_2$) and the same connectivity, but the structure on the left is (*R*,*R*) and the structure on the right is (*S*,*R*) so since they differ by only one stereocenter, they are stereoisomers that are diastereomers (& epimers in this case).



QUESTIONS

Q5.9.1

What kind of isomers are the following pairs:

A – (*R*)-5-chlorohexene and 6-chlorohexene

B – (2*R*,3*R*)-dibromohexane and (2*R*,3*S*)-dibromohexane

SOLUTIONS

S5.9.1

A = Structural Isomers

B = Diastereomers

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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5.10: CHIRALITY AT NITROGEN, PHOSPHORUS, AND SULFUR

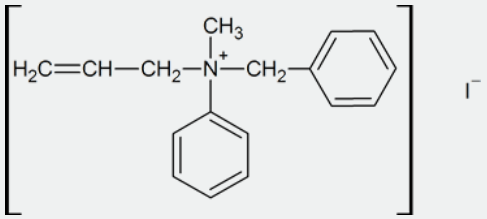
Objectives

After completing this section, you should be able to

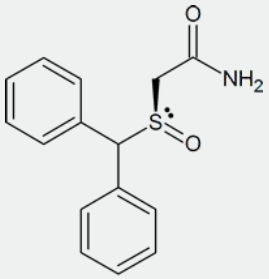
1. recognize that atoms other than carbon can be chiral centres.
2. explain why enantiomers of compounds such as ethylmethylamine cannot normally be isolated.

STUDY NOTES

The first example of a resolvable compound containing a chiral nitrogen atom was resolved by William Pope and Stanley Peachey in 1899. It had the structure shown below.



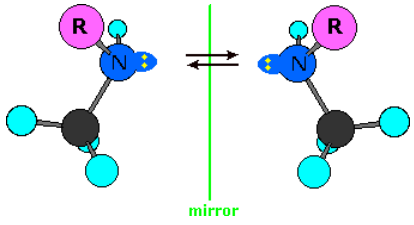
Chiral sulfoxides find application in certain drugs such as esomeprazole and armodafinil and are a good example of a stereogenic sulfur center.



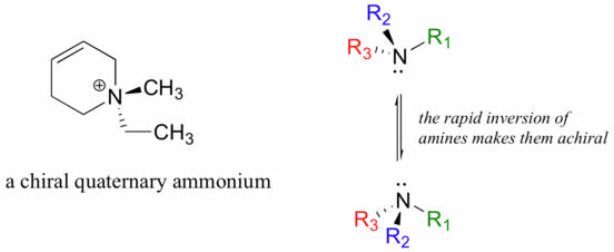
armodafinil

STEREOGENIC NITROGEN

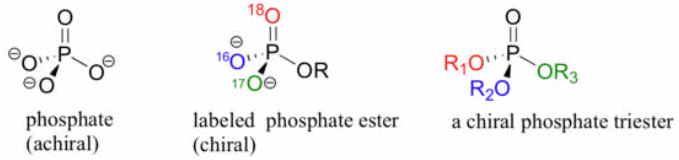
Single-bonded nitrogen is pyramidal in shape, with the non-bonding electron pair pointing to the unoccupied corner of a tetrahedral region. Since the nitrogen in these compounds is bonded to three different groups, its configuration is chiral. The non-identical mirror-image configurations are illustrated in the following diagram (the remainder of the molecule is represented by R, and the electron pair is colored yellow). If these configurations were stable, there would be four additional stereoisomers of ephedrine and pseudoephedrine. However, pyramidal nitrogen is normally not configurationally stable. It rapidly inverts its configuration (equilibrium arrows) by passing through a planar, sp^2-hybridized transition state, leading to a mixture of interconverting R and S configurations. If the nitrogen atom were the only chiral center in the molecule, a 50:50 (racemic) mixture of R and S configurations would exist at equilibrium. If other chiral centers are present, as in the ephedrin isomers, a mixture of diastereomers will result. The take-home message is that nitrogen does not contribute to isolable stereoisomers.



Asymmetric quaternary ammonium groups are also chiral. Amines, however, are not chiral, because they rapidly invert, or turn ‘inside out’, at room temperature.



The phosphorus center of phosphate ions and organic phosphate esters is also tetrahedral, and thus potentially a stereocenter. In order to investigate the stereochemistry of reactions at the phosphate center, ^{17}O and ^{18}O isotopes of oxygen (the 'normal' isotope is ^{16}O) can be incorporated to create chiral phosphate groups. Phosphate triesters are chiral if the all four substituent groups are different (including the carbonyl oxygen).



CONTRIBUTORS AND ATTRIBUTIONS

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- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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5.11: PROCHIRALITY

Objectives

After completing this section, you should be able to

1. identify a compound as being prochiral.
2. identify the *Re* and *Si* faces of prochiral sp^2 centre.
3. identify atoms (or groups of atoms) as *pro-R* or *pro-S* on a prochiral sp^3 centre.

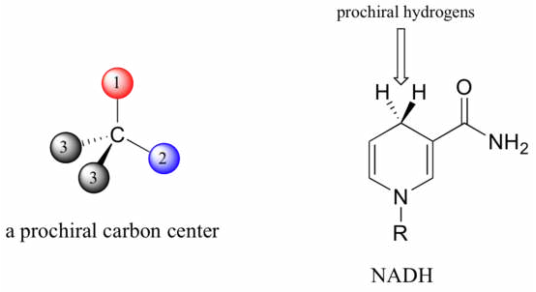
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- prochiral
- *pro-R*
- *pro-S*
- *Re*
- *Si*

PROCHIRAL SUBSTITUENTS ON TETRAHEDRAL CARBONS

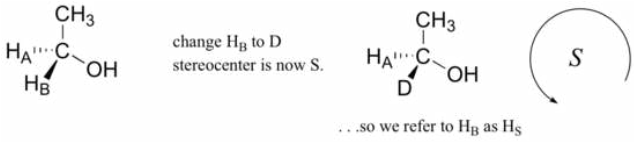
When a tetrahedral carbon can be converted to a chiral center by changing only one of its attached groups, it is referred to as a '**prochiral**' center. The actual example shown below is the reduced form of a molecule called nicotinamide adenine dinucleotide (NADH), an important participant in many biochemical oxidation/reduction reactions (section 16.4A).



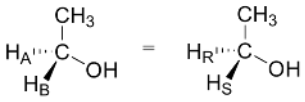
Note that if, in a thought experiment, we changed either one of the indicated hydrogens on NADH to a deuterium (the ^{2}H isotope of hydrogen), the carbon would become a chiral center. Prochirality is an important concept in biological chemistry, because enzymes can distinguish between the two 'identical' groups bound to a prochiral carbon center due to the fact that *they occupy different regions in three-dimensional space*. For example in the following reaction, which is a key step in the oxidation of fatty acids, it is specifically H_A and H_D that are lost, while H_B and H_C remain in the resulting conjugated alkene.



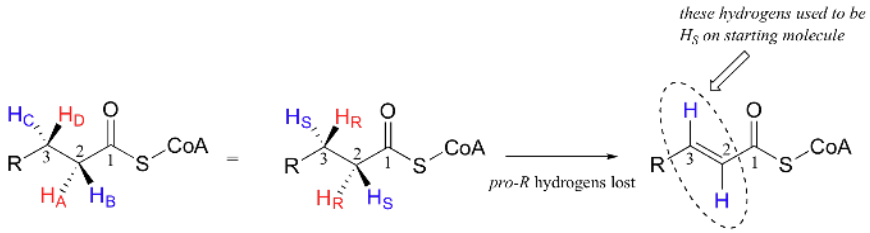
The prochiral hydrogens on $C_2$and C_3 of the fatty acid can be designated according to a variation on the *R/S* system. For the sake of clarity, we'll look at a much simpler molecule (ethanol) to explain this system.



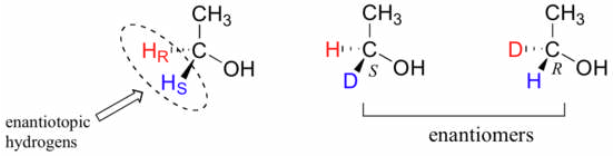
To name the two prochiral hydrogens on ethanol, we again need to engage in a thought experiment. If we, in our imagination, were to arbitrarily change H_B to a deuterium, the molecule would now be chiral and the stereocenter would have the *S* configuration (D has a higher priority than H). For this reason, we can refer to H_B as the *pro-S* hydrogen of ethanol, and label it H_S. Conversely, if we change H_A to D and leave H_B as a hydrogen, the configuration of the molecule becomes *R*, so we can refer to H_A as the *pro-R* hydrogen of ethanol, and label it H_R.



Looking back at our fatty acid example, we see that it is specifically the *pro-R* hydrogens on carbons 2 and 3 that are lost in the reaction.

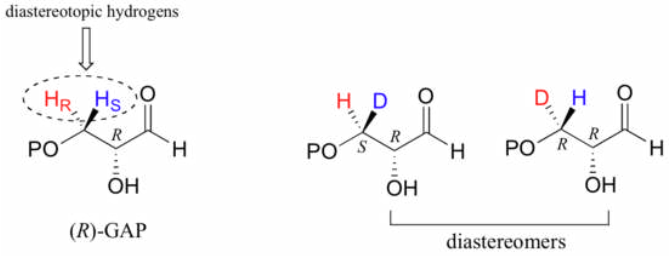


Prochiral hydrogens can be designated either enantiotopic or diastereotopic. If either H_R or H_S on ethanol were replaced by a deuterium, the two resulting molecules would be enantiomers (because there are no other stereocenters)



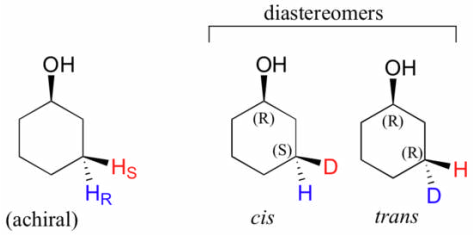
Thus, these two hydrogens are referred to as **enantiotopic**.

In glyceraldehyde-3-phosphate (GAP), however, we see something different:

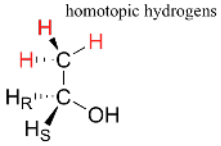


If either H_R or H_S is replaced by a deuterium, the two resulting molecules will be diastereomers - thus, in this molecule, H_R and H_S are referred to as **diastereotopic** hydrogens. The importance of the distinction between enantiotopic and diastereotopic groups will become apparent when we learn about the analytical technique called nuclear magnetic resonance.

Two hydrogens on the same carbon of a substituted ring structure can be diastereotopic - we determine this by carrying out the same thought experiment as discussed above. In the example below, the diastereotopic hydrogens indicated are either on the same side or on the opposite side of the ring relative to the hydroxyl group.



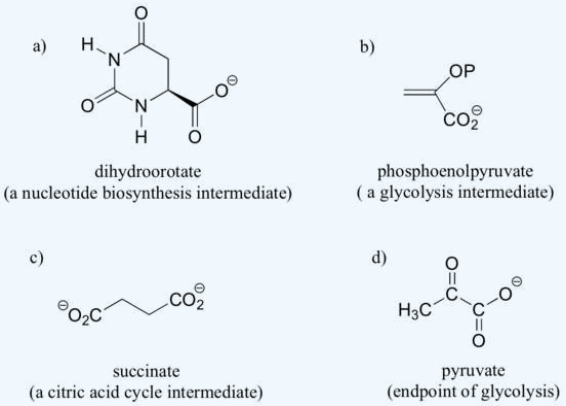
Finally, hydrogens that are completely identical and can be designated neither enantiotopic nor diastereotopic are called **homotopic**. If a homotopic hydrogen is replaced by deuterium, a chiral center is *not* created. The three hydrogen atoms on the methyl (CH_3) group of ethanol (and on *any* methyl group) are homotopic.



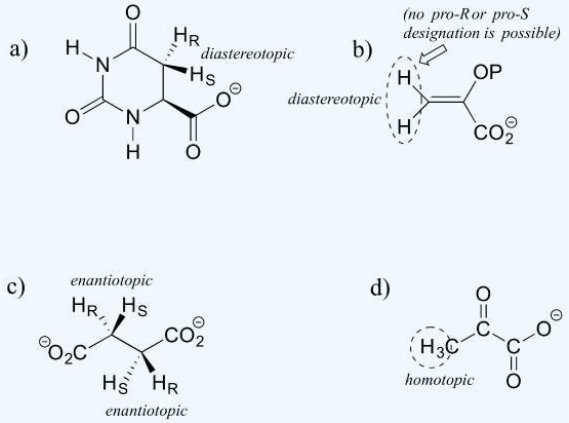
Even to an enzyme, all three of these hydrogens will look the same.

EXAMPLE 5.11.1

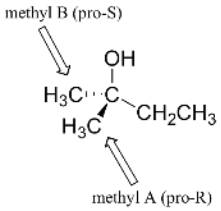
Identify in the molecules below all pairs/groups of hydrogens that are homotopic, enantiotopic, or diastereotopic. When appropriate, label prochiral hydrogens as H_R or H_S.



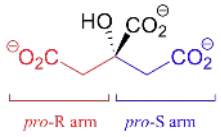
Answer



Groups other than hydrogens can be considered prochiral. The alcohol below has two prochiral methyl groups - methyl A is the *pro-R* methyl, and methyl B is *pro-S*. (How do we make these designations? Simple - just arbitrarily make methyl A higher priority than methyl B, and the compound now has the *R* configuration).

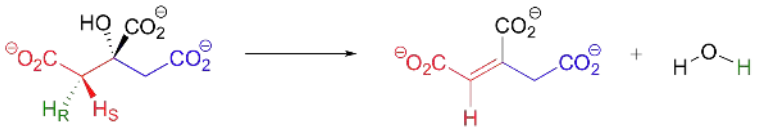


Citrate provides a more complex example. The central carbon is a prochiral center with two 'arms' that are identical except that one can be designated *pro-R* and the other *pro-S*.



citrate

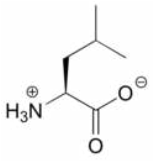
In a reaction of the citric acid cycle (Krebs cycle), a water molecule is specifically lost on the *pro-R* arm (we will study this reaction in section 14.1B).



Notice also that it is specifically the *pro-R* hydrogen on the *pro-R* arm of citrate that is lost - one more layer of stereoselectivity!

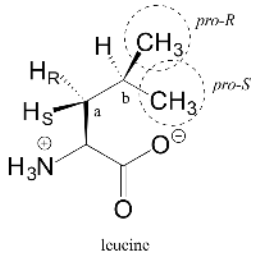
EXAMPLE 5.11.2

Assign *pro-R* and*pro-S* designations to all prochiral groups in the amino acid leucine. (*Hint*: there are two pairs of prochiral groups!). Are these prochiral groups diastereotopic or enantiotopic?



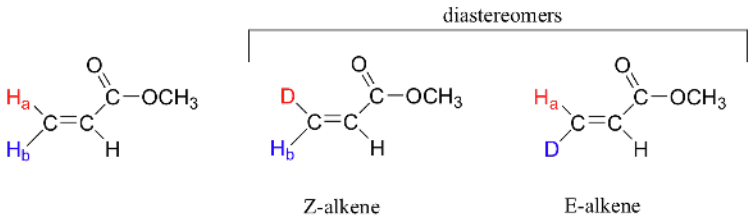
leucine

Answer



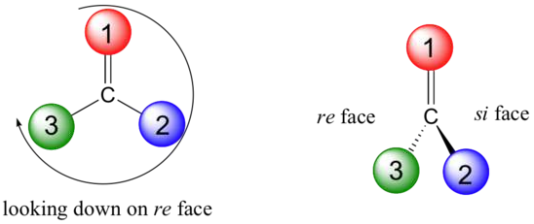
leucine

Although an alkene carbon bonded to two identical groups is *not* considered a prochiral center, these two groups *can* be diastereotopic. H_a and H_b on the alkene below, for example, are diastereotopic: if we change one, and then the other, of these hydrogens to deuterium, the resulting compounds are *E* and *Z* diastereomers.



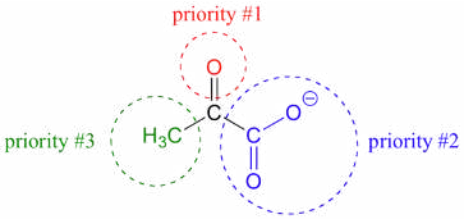
CARBONYL AND IMINE CARBONS AS PROCHIRAL CENTERS

Trigonal planar, sp^2-hybridized carbons are not, as we well know, chiral centers– but they are referred to as prochiral centers if they are bonded to three different substitutuents. As you might expect, we (and the enzymes that catalyze their reactions) can distinguish between the two planar 'faces' of a prochiral sp^2 - hybridized group. These faces are designated by the terms ***re*** and ***si***. To determine which is the *re* and which is the *si* face of a planar organic group, we simply use the same priority rankings that we are familiar with from the R/S system, and trace a circle: *re* is clockwise and *si* is counterclockwise.



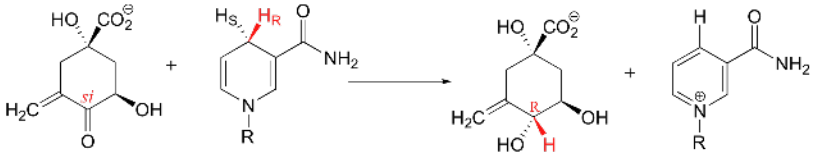
looking down on *re* face

Below, for example, we are looking down on the *re* face of the ketone group in pyruvate:



If we flipped the molecule over, we would be looking at the *si* face of the ketone group. Note that the carboxylate group does not have *re* and *si* faces, because two of the three substituents on that carbon are identical (when the two resonance forms of carboxylate are taken into account).

As we will see beginning in chapter 11, enzymes which catalyze reactions at carbonyl carbons act specifically from one side or the other.

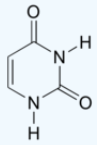


pro-R hydrogen is transferred to *si* face of ketone group

Notice that the 'hydrogenation' reaction above is specific not only in terms of which face of the carbonyl group is affected, but also in terms of which of the two diastereotopic hydrogens on NADH is transferred (we will study this type of reaction in more detail in section 16.4).

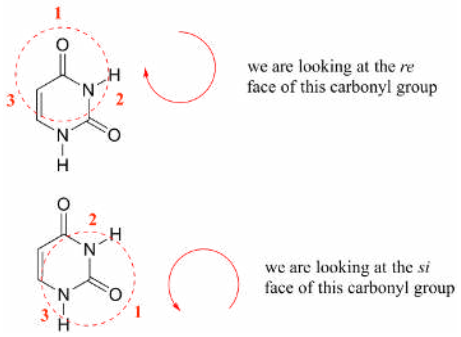
EXAMPLE 5.11.3

For each of the carbonyl groups in uracil, state whether we are looking at the *re* or the *si* face in the structural drawing below.



uracil

Answer



EXERCISES

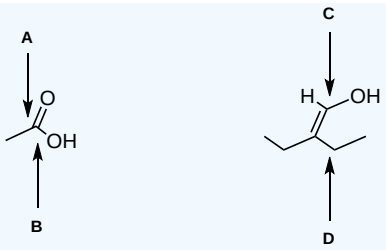
EXERCISE 5.11.1

a) State which of the following hydrogen atoms are *pro-R* or *pro-S*.



b) Identify which side is Re or Si.

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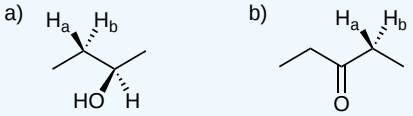
Answer

a) Left compound: H_a = *pro-S* and H_b = *pro-R*; Right compound: H_a = *pro-R* and H_b = *pro-S*

b) A – Re; B – Si; C – Re; D – Si\)

EXERCISE 5.11.2

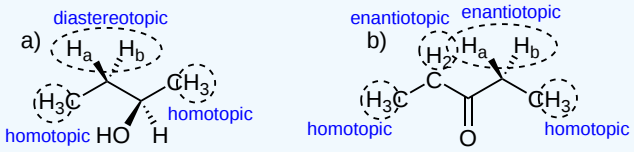
In the structures below, determine if the H's are homotopic, enantiotopic, or diastereotopic.



Answer

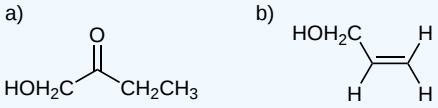
In a), the CH_2 is diastereotopic since there is another chiral center on the molecule. Both CH_3's are homotopic since replacing one of them doesn't create a chiral center.

IN b), the CH_2's are enantiotopic since it would create the only chiral center on the molecule. Both CH_3's are homotopic since replacing one of them doesn't create a chiral center.



EXERCISE 5.11.3

State whether you are looking down at the molecule from the re face or si face.



Answer

a. You are looking at the **si face**. The re face would be if you were facing the molecule from the back.

b. You are looking at the **re face**. The si face would be if you were facing the molecule from the back.

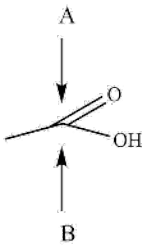
Q5.11.1

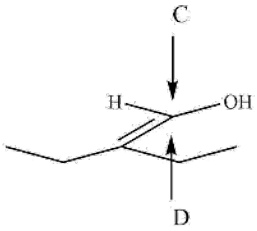
State which of the following hydrogen atoms are *pro-R* or *pro-S*.



Q5.11.2

Identify which side is Re or Si





Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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5.12: CHIRALITY IN NATURE AND CHIRAL ENVIRONMENTS

Objective

After completing this section, you should be able to explain how chiral molecules in nature can have such dramatically different biological properties.

SOME CHIRAL ORGANIC MOLECULES

There are a number of important biomolecules that could occur as enantiomers, including amino acids and sugars. In most cases, only one enantiomer occurs (although some fungi, for example, are able to produce mirror-image forms of these compounds). We will look later at some of these biomolecules, but first we will look at a compound that occurs naturally in both enantiomeric forms.

Carvone is a secondary metabolite. That means it is a naturally-occurring compound that is not directly connected to the very basic functions of a cell, such as self-replication or the production of energy. The role of secondary metabolites in nature is often difficult to determine. However, these compounds often play roles in self-defense, acting as deterrents against competitor species in a sort of small-scale chemical warfare scenario. They are also frequently used in communications; this role has been studied most extensively among insects, which use lots of compounds to send information to each other.

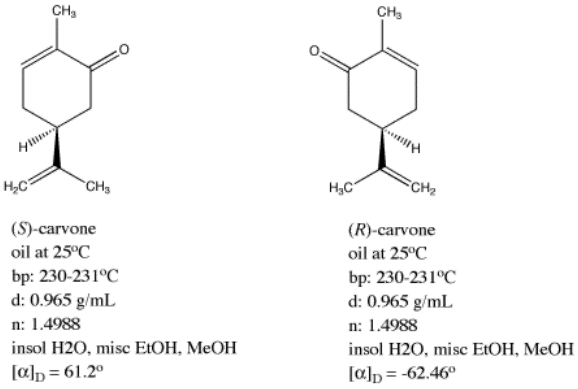


***Figure 5.12.1**: The two naturally-occurring enantiomers of carvone.*

Carvone is produced in two enantiomeric forms. One of these forms, called (-)-carvone, is found in mint leaves, and it is a principal contributor to the distinctive odor of mint. The other form, (+)-carvone, is found in caraway seeds. This form has a very different smell, and is typically used to flavor rye bread and other Eastern European foods.

Note that (+)-carvone is the same thing as (S)-carvone. The (+) designation is based on its positive optical rotation value, which is experimentally measured. The (S) designation is determined by the Cahn-Ingold-Prelog rules for designating stereochemistry, which deal with looking at the groups attached to a chiral center and assigning priority based on atomic number. However, carvone's chiral center actually has three carbons attached to it; they all have the same atomic number. We need a new rule to break the tie.

- If two substituent groups have the same atomic number, go one bond further to the next atom.
- If there is a difference among the second tier of atoms, stop.
- The group in which you have encountered a higher atomic number gets the highest priority.
- If there is not a clear difference, proceed one additional bond to the next set of atoms, and so on, until you find a difference.

In carvone, this decision tree works as follows:

- The chiral center is connected to a H, a C, a C and a C.
- The H is lowest priority.
- One C eventually leads to a C=O. However, at the second bond from the chiral center, this C is connected to a C and two H's.
- A second C is also part of the six-membered ring, but the C=O is farther away in this direction. At the second bond from the chiral center, this C is connected to a C and two H's, just like the first one.
- The third C is part of a little three-carbon group attached to the six-membered ring. At the second bond from the chiral center, it is connected to only one H and has two bonds to another C (this is counted as two bonds to C and one to H).
- Those first two carbon groups are identical so far.
- However, the third group is different; it has an extra bond to C, whereas the others have an extra bond to H. C has a higher atomic number than H, so this group has higher priority.

- The second-highest priority is the branch that reaches the oxygen at the third bond from the chiral center.

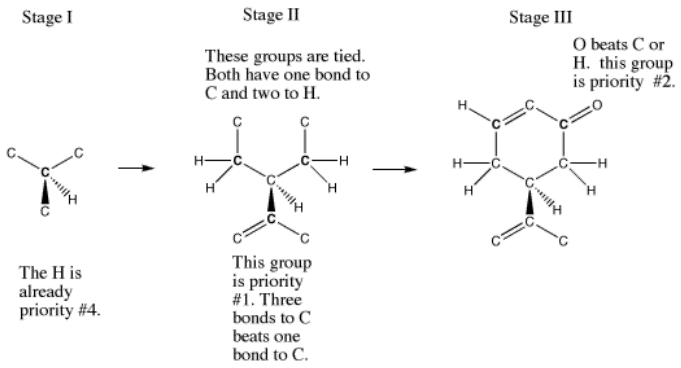


Figure 5.12.2: *Comparing atoms step-by-step to assign configuration.*

How different, exactly, are these two compounds, (+)- and (-)-carvone? Are they completely different isomers, with different physical properties? In most ways, the answer is no. These two compounds have the same appearance (colorless oil), the same boiling point (230 °C), the same refractive index (1.499) and specific gravity (0.965). However, they have optical rotations that are almost exactly opposite values.

- Two enantiomers have the same physical properties.
- Enantiomers have opposite optical rotations.

Clearly they have different biological properties; since they have slightly different odors, they must fit into slightly different nasal receptors, signaling to the brain whether the person next to you is chewing a stick of gum or a piece of rye bread. This different shape complimentarity is not surprising, just as it isn't surprising that a left hand only fits into a left handed baseball glove and not into a right handed one.

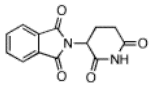


Figure 5.12.3*: Thalidomide.*

There are other reasons that we might concern ourselves with an understanding of enantiomers, apart from dietary and olfactory preferences. Perhaps the most dramatic example of the importance of enantiomers can be found in the case of thalidomide. Thalidomide was a drug commonly prescribed during the 1950's and 1960's in order to alleviate nausea and other symptoms of morning sickness. In fact, only one enantiomer of thalidomide had any therapeutic effect in this regard. The other enantiomer, apart from being therapeutically useless in this application, was subsequently found to be a teratogen, meaning it produces pronounced birth defects. This was obviously not a good thing to prescribe to pregnant women. Workers in the pharmaceutical industry are now much more aware of these kinds of consequences, although of course not all problems with drugs go undetected even through the extensive clinical trials required in the United States. Since the era of thalidomide, however, a tremendous amount of research in the field of synthetic organic chemistry has been devoted to methods of producing only one enantiomer of a useful compound and not the other. This effort probably represents the single biggest aim of synthetic organic chemistry through the last quarter century.

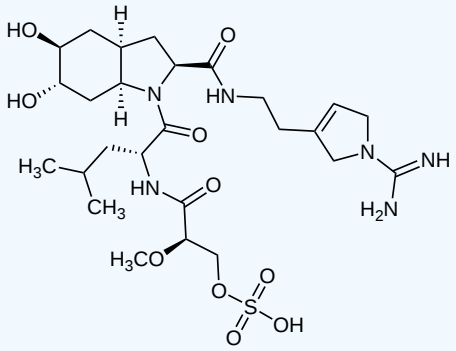
- Enantiomers may have very different biological properties.
- Obtaining enantiomerically pure compounds is very important in medicine and the pharmaceutical industry.

EXERCISE

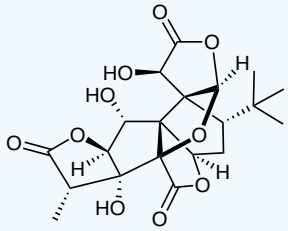
? EXERCISE 5.12.1

The following are three molecules found in nature. Please identify four chiral centers in each, mark them with asterisks, and identify each center as having a R or S configuration. Each molecule contains more than four chiral centers.

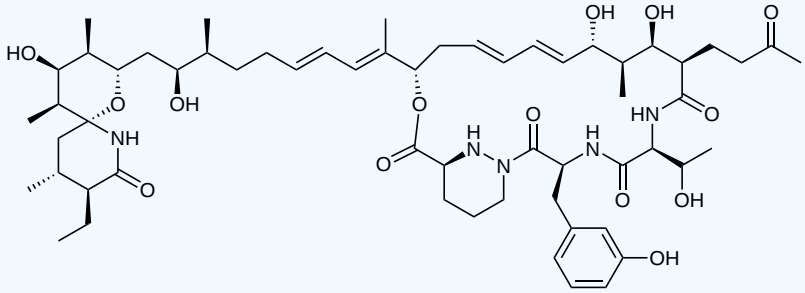
a) The following is the structure of dysinosin A, a potent thrombin inhibitor that consequently prevents blood clotting.



b) Ginkgolide B (below) is a secondary metabolite of the ginkgo tree, extracts of which are used in Chinese medicine.

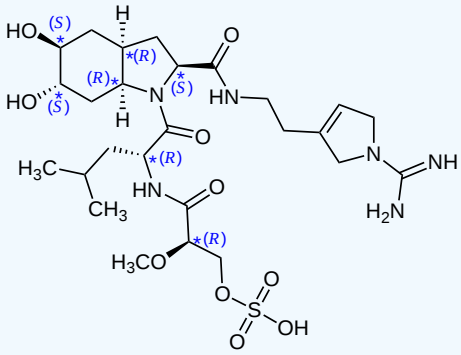


c) Sanglifehrin A, shown below, is produced by a bacteria that may be found in the soil of coffee plantations in Malawi. It is also a promising candidate for the treatment of organ transplant patients owing to its potent immuno-suppressant activity.



Answer

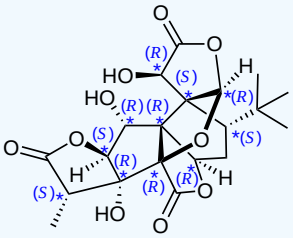
a)

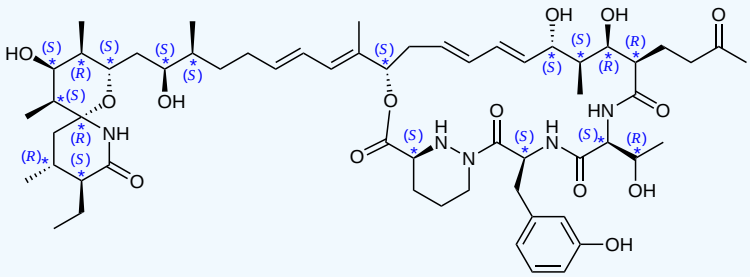


b)

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c)





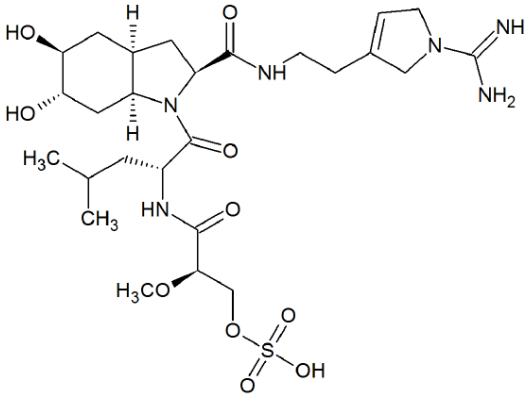
Q5.12.1

Draw the two enantiomeric forms of 2-butanol, $CH_3CH(OH)CH_2CH_3$. Label their configurations.

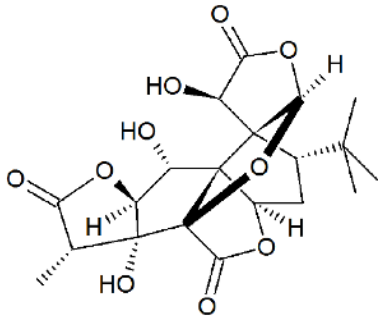
Q5.12.2

Sometimes, compounds have many chiral centers in them. For the following compounds, identify four chiral centers in each, mark them with asterisks, and identify each center as R or S configuration.

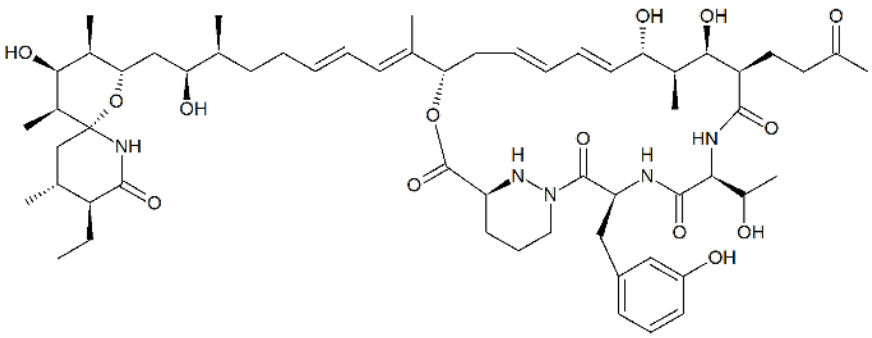
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Ginkgolide B (below) is a secondary metabolite of the ginkgo tree, extracts of which are used in Chinese medicine.



Sanglifehrin A, shown below, is produced by a bacteria that may be found in the soil of coffee plantations in Malawi. It is also a promising candidate for the treatment of organ transplant patients owing to its potent immuno-suppressant activity.



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John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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5.S: STEREOCHEMISTRY AT TETRAHEDRAL CENTERS (SUMMARY)

CONCEPTS & VOCABULARY

5.1: Enantiomers and the Tetrahedral Carbon

- Every molecule is either **chiral** (not superimposable on its mirror image) or **achiral** (superimposable on its mirror image).
- **Chiral** molecules do not have a plane of symmetry, while **achiral** molecules have one or more **planes of symmetry**.
- **Stereoisomers** vary by spatial arrangement of atoms but have the same atom connectivity.
- **Stereoisomers** that are mirror images of one another but are not superimposable are called **enantiomers**.

5.2: The Reason for Handedness in Molecules - Chirality

- A Tetrahedral carbon atom bonded to four different substituents is an **asymetric** carbon (also called a **stereocenter** or **chiral** carbon), which typically leads to a **chiral** molecule (meso compounds are the exception in section 5.7).

5.3: Optical Activity

- **Enantiomers** cause rotation of plane-polarized light in equal amounts in opposite directions. This is called **optical activity.** Clockwise rotation is called d**extrorotatory** (+) and counter-clockwise is called **levorotatory** (-).
- **Specific rotation** is the amount that a sample of a chemical rotates planne-polarized light. It can be used to calculate the purity of a mixture of **enantiomers** called the **enantiomeric excess**.
- **Resolution** is the separation of a mixture of **enatiomers**.
- **Racemates** are defined as a 50:50 mixture of **enantiomers**, resulting in a sample that is not **optically active**. The process of forming a **racemic** mixture is called **racemization**.

5.4: Pasteur's Discovery of Enantiomers

5.5: Sequence Rules for Specifying Configuration

- Use the CIP rules to determine the priority of each substituent attached to a **chiral** carbon to determine whether configuration is **R** or **S**. With the lowest priority group facing away from you, draw an arc connecting groups 1-2-3. If that arc is clockwise, the configuration is **R**. If counterclockwise, the configuration is **S**.

5.6: Diastereomers

- **Stereoisomers** that are not mirror images of one another are called **diastereomers**.
- **Diastereomers** have two or more **stereocenters**. The configurations of the **stereocenters** cannot be inverse of each other (example R,R and S,S) because that defines a pair of **enantiomers**.

5.7: Meso Compounds

- **Meso** compounds are **achiral** but have **chiral** centers. This is caused by having an internal **plane of symmetry** that allows the two molecules to be superimposable on one another and be **optically inactive**.

5.8: Racemic Mixtures and the Resolution of Enantiomers

- Each component of a **racemic** mixture rotates plane polarized light an equal amount in opposite directions, so there is no **optical activity**.
- **Racemic** mixtures can be separated into the component **enantiomers** by reaction with a **chiral** reagent, which will form **diastereomer** intermediates of the molecules which can then be separated. Following separation the **chiral** reagent is removed to yield the two pure **enantiomers**.

5.9: A Review of Isomerism

- There are several categories of **isomers** with the largest distinction between:
  - constitutional (structural) isomers that contain the same number of each atom but differ in connectivity
  - **stereoisomers** that have all the same atoms with the same connectivity, but only differ in how the atoms are arranged three dimensionally
- In addition to the **diastereomers** and **enantiomers** that have been discussed at length in this chapter, **stereoisomers** can also be:
  - cis/trans or E/Z isomers which differ by spatial arrangement around a double bond
  - conformational **isomers** (conformers) which occur due to free rotation of sigma bonds

5.10: Chirality at Nitrogen, Phosphorus, and Sulfur

- Nitrogen when bonded to three different atoms is **chiral**, however the lone pair of electrons moves freely between positions on the Nitrogen causing these molecules to become a **racemic** mixture.
- When bonded to four different atoms in quaternary ammonium salts, nitrogen atoms lead to **chiral** molecules.
- Organic phosphates with four different groups can also be **chiral**.

5.11: Prochirality

- When a carbon can be converted to a **chiral** center by changing only one of its attached groups, it is called **prochiral**.
- If a molecule has two hydrogens on the same atom and replacement of either one with deuterium would lead to **enantiomers**, the hydrogens are **enantiotopic**.
- Similarly if this replacement would lead to **diastereomer** molecules, the hydrogens are **diastereotopic**.
- If replacement of a hydrogen would not lead to a chiral center being created, they are termed **homotopic**.

5.12: Chirality in Nature and Chiral Environments

SKILLS TO MASTER

- Skill 5.1 Identify stereocenters in molecular structures.
- Skill 5.2 Identify whether two structures are identical (not meso), constitutional isomers, enantiomers, diastereomers or meso and identical.
- Skill 5.3 Explain how plane polarized light is used to show optical activity.
- Skill 5.4 Calculate specific rotation from experimental data.
- Skill 5.5 Calculate optical purity and enantiomeric excess from experimental data.
- Skill 5.6 Determine configuration of stereocenters as R or S.
- Skill 5.7 Draw the enantiomer and diastereomers of a given compound with one or more stereocenters.
- Skill 5.8 Identify planes of symmetry in meso compounds.
- Skill 5.9 Describe a process for separating a mixture of enantiomers.
- Skill 5.10 Explain why racemic mixtures are optically inactive.
- Skill 5.11 Explain the difference between constitutional and stereoisomers.
- Skill 5.12 Give an example of a chiral center that is not carbon.

MEMORIZATION TASKS

MT 5.1 Memorize the rules for determining R and S configuration.

MT 5.2 Memorize the types of isomers and how to identify them.

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- Dr. Kelly Matthews (Harrisburg Area Community College)

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CHAPTER OVERVIEW

6: AN OVERVIEW OF ORGANIC REACTIONS

LEARNING OBJECTIVES

After you have completed Chapter 6, you should be able to

1. fulfill the detailed objectives listed under each individual section.
2. identify the polarity pattern in the common functional groups, and explain the importance of being able to do so.
3. describe the essential differences between polar and radical reactions, and assign a given reaction to one of these two categories.
4. discuss how kinetic and thermodynamic factors determine the rate and extent of a chemical reaction.
5. use bond dissociation energies to calculate the $\Delta H°$ of simple reactions, and *vice versa*.
6. draw and interpret reaction energy diagrams.
7. define, and use in context, the new key terms.

This chapter is designed to provide a gentle introduction to the subject of reaction mechanisms. Two types of reactions are introduced—polar reactions and radical reactions.

The chapter briefly reviews a number of topics you should be familiar with, including rates and equilibria, elementary thermodynamics and bond dissociation energies. You must have a working knowledge of these topics to obtain a thorough understanding of organic reaction mechanisms. Reaction energy diagrams are used to illustrate the energy changes that take place during chemical reactions, and to emphasize the difference between a reaction intermediate and a transition state.

6.0: Prelude
6.1: Kinds of Organic Reactions
6.2: How Organic Reactions Occur - Mechanisms
6.3: Radical Reactions
6.4: Polar Reactions
6.5: An Example of a Polar Reaction - Addition of HBr to Ethylene
6.6: Using Curved Arrows in Polar Reaction Mechanisms
6.7: Describing a Reaction - Equilibria, Rates, and Energy Changes
6.8: Describing a Reaction - Bond Dissociation Energies
6.9: Describing a Reaction - Energy Diagrams and Transition States
6.10: Describing a Reaction - Intermediates
6.11: A Comparison between Biological Reactions and Laboratory Reactions
6.S: An Overview of Organic Reactions (Summary)

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6.0: Prelude

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6.1: KINDS OF ORGANIC REACTIONS

Objective

After completing this section, you should be able to list and describe the four important “kinds” of reactions that occur in organic chemistry.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- addition reaction
- elimination reaction
- rearrangement reaction
- substitution reaction

STUDY NOTES

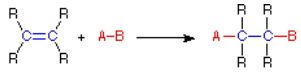
It is sufficient that you know the general form of each kind of reaction. However, given a chemical equation, you should be able to recognize which kind of reaction it involves.

If you scan any organic textbook you will encounter what appears to be a very large, often intimidating, number of reactions. These are the "tools" of a chemist, and to use these tools effectively, we must organize them in a sensible manner and look for patterns of reactivity that permit us make plausible predictions. Most of these reactions occur at special sites of reactivity known as functional groups, and these constitute one organizational scheme that helps us catalog and remember reactions.

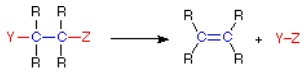
Ultimately, the best way to achieve proficiency in organic chemistry is to understand how reactions take place, and to recognize the various factors that influence their course.

First, we identify four broad classes of reactions based solely on the **structural change** occurring in the reactant molecules. This classification does not require knowledge or speculation concerning reaction paths or mechanisms. The four main reaction classes are additions, eliminations, substitutions, and rearrangements.

Addition Reaction



Elimination Reaction



Substitution Reaction



Rearrangement Reaction

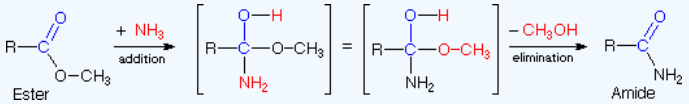


In an **addition** reaction the number of σ-bonds in the substrate molecule increases, usually at the expense of one or more π-bonds. The reverse is true of **elimination** reactions, *i.e.*the number of σ-bonds in the substrate decreases, and new π-bonds are often formed. **Substitution** reactions, as the name implies, are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change. A **rearrangement** reaction generates an isomer, and again the number of bonds normally does not change.

The examples illustrated above involve simple alkyl and alkene systems, but these reaction types are general for most functional groups, including those incorporating carbon-oxygen double bonds and carbon-nitrogen double and triple bonds. Some common reactions may actually be a combination of reaction types.

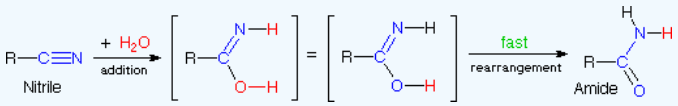
EXAMPLE 6.1.1: REACTION OF AN ESTER WITH AMMONIA

The reaction of an ester with ammonia to give an amide, as shown below, appears to be a substitution reaction (Y = CH_3O & Z = NH_2); however, it is actually two reactions, an addition followed by an elimination.



EXAMPLE 6.1.2: THE ADDITION OF WATER TO A NITRILE

The addition of water to a nitrile does not seem to fit any of the above reaction types, but it is simply a slow addition reaction followed by a rapid rearrangement, as shown in the following equation. Rapid rearrangements of this kind are called **tautomerizations**.



EXERCISE

EXERCISE 6.1.1

Classify each reaction as addition, elimination, substitution, or rearrangement.

A) $CH_3CH_2Br + LiOH \longrightarrow CH_3CH_2OH + LiBr$

B) $CH_3CH_2CH_2Cl \longrightarrow CH_3CH{=}CH_2 + HCl$

B) $CH_3CH{=}CH_2 + H_2 \longrightarrow CH_3CH_2CH_3$

Answer

A) Substitution

B) Elimination

C) Addition

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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6.2: HOW ORGANIC REACTIONS OCCUR - MECHANISMS

Objectives

After completing this section, you should be able to

1. explain the difference between heterolytic and homolytic bond breakage, and between heterogenic and homogenic bond formation.
2. state the two reaction types involved in symmetrical and unsymmetrical processes.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- heterogenic
- heterolytic
- homogenic
- homolytic
- polar reaction
- radical reaction
- reaction mechanism

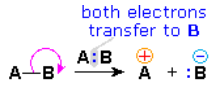
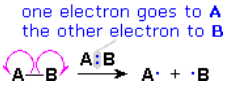
STUDY NOTES

Upon first reading first four key terms, it is easy to be puzzled. The ending of the word tells you whether a bond is being formed (-genic) or broken (-lytic), while the root of the word describes the nature of that formation or decomposition. So hetero (meaning different) reactions involve asymmetrical bond making (or breaking) and homo (meaning same) involve symmetrical processes.

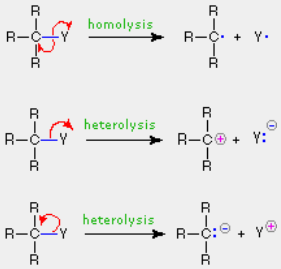
Because one pair of electrons constitutes a single bond, the unsymmetrical making or breaking of that bond in a hetero processes are described as polar reactions. Similarly, symmetrical homo processes of bond making and breaking are called radical reactions. Radicals (sometimes referred to as free radicals) are highly reactive neutral chemical species with one unpaired electron. In later sections we discuss radical and polar reactions in more detail.

THE ARROW NOTATION IN MECHANISMS

Since chemical reactions involve the breaking and making of bonds, a consideration of the movement of bonding (and non-bonding) valence shell electrons is essential to this understanding. It is now common practice to show the movement of electrons with curved arrows, and a sequence of equations depicting the consequences of such electron shifts is termed a **mechanism**. In general, two kinds of curved arrows are used in drawing mechanisms:

A full head on the arrow indicates the movement or shift of an electron pair:		
A partial head (fishhook) on the arrow indicates the shift of a single electron:		

The use of these symbols in bond-breaking and bond-making reactions is illustrated below. If a covalent single bond is broken so that one electron of the shared pair remains with each fragment, as in the first example, this bond-breaking is called **homolysis**. If the bond breaks with both electrons of the shared pair remaining with one fragment, as in the second and third examples, this is called **heterolysis**.

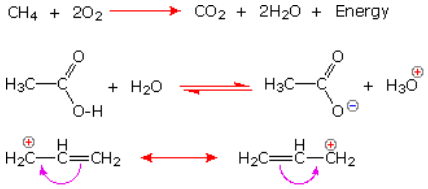
Bond-Breaking	Bond-Making
	

OTHER ARROW SYMBOLS

Chemists also use arrow symbols for other purposes, and it is essential to use them correctly.

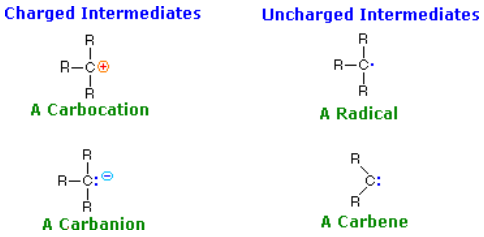
The Reaction Arrow	The Equilibrium Arrow	The Resonance Arrow
		

The following equations illustrate the proper use of these symbols:



REACTIVE INTERMEDIATES

The products of bond breaking, shown above, are not stable in the usual sense, and cannot be isolated for prolonged study. Such species are referred to as **reactive intermediates**, and are believed to be transient intermediates in many reactions. The general structures and names of four such intermediates are given below.



A pair of widely used terms, related to the Lewis acid-base notation, should also be introduced here.

- Electrophile: An electron deficient atom, ion or molecule that has an affinity for an electron pair, and will bond to a base or nucleophile.
- Nucleophile: An atom, ion or molecule that has an electron pair that may be donated in bonding to an electrophile (or Lewis acid).

Using these definitions, it is clear that carbocations (called carbonium ions in the older literature) are electrophiles and carbanions are nucleophiles. Carbenes have only a valence shell sextet of electrons and are therefore electron deficient. In this sense they are electrophiles, but the non-bonding electron pair also gives carbenes nucleophilic character. As a rule, the electrophilic character dominates carbene reactivity. Carbon radicals have only seven valence electrons, and may be considered electron deficient; however, they do not in general bond to nucleophilic electron pairs, so their chemistry exhibits unique differences from that of conventional electrophiles. Radical intermediates are often called **free radicals**.

The importance of electrophile / nucleophile terminology comes from the fact that many organic reactions involve at some stage the bonding of a nucleophile to an electrophile, a process that generally leads to a stable intermediate or product. Reactions of this kind are sometimes called **ionic reactions**, since ionic reactants or products are often involved. Some common examples of ionic reactions and their mechanisms may be examined below.

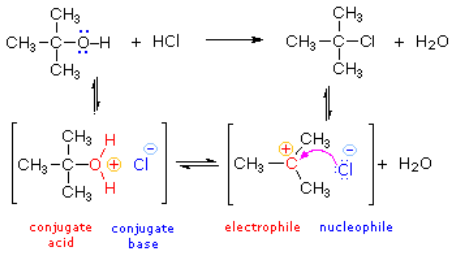
The shapes ideally assumed by these intermediates becomes important when considering the stereochemistry of reactions in which they play a role. A simple tetravalent compound like methane, CH_4, has a tetrahedral configuration. Carbocations have only three bonds to the charge bearing carbon, so it adopts a planar trigonal configuration. Carbanions are pyramidal in shape (tetrahedral if the electron pair is viewed as

a substituent), but these species invert rapidly at room temperature, passing through a higher energy planar form in which the electron pair occupies a p-orbital. Radicals are intermediate in configuration, the energy difference between pyramidal and planar forms being very small. Since three points determine a plane, the shape of carbenes must be planar; however, the valence electron distribution varies.

IONIC REACTIONS

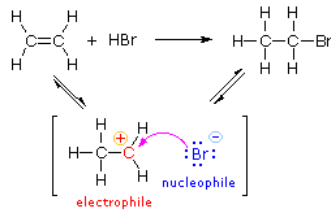
The principles and terms introduced in the previous sections can now be summarized and illustrated by the following three examples. Reactions such as these are called **ionic** or **polar** reactions, because they often involve charged species and the bonding together of **electrophiles and nucleophiles**. Ionic reactions normally take place in liquid solutions, where solvent molecules assist the formation of charged intermediates.

substitution



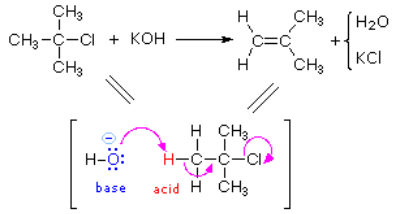
The substitution reaction shown on the left can be viewed as taking place in three steps. The first is an acid-base equilibrium, in which HCl protonates the oxygen atom of the alcohol. The resulting conjugate acid then loses water in a second step to give a carbocation intermediate. Finally, this electrophile combines with the chloride anion nucleophile to give the final product.

addition



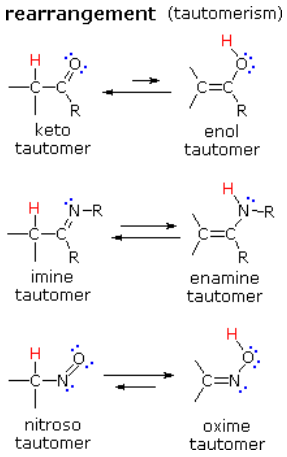
The addition reaction shown on the left can be viewed as taking place in two steps. The first step can again be considered an acid-base equilibrium, with the pi-electrons of the carbon-carbon double bond functioning as a base. The resulting conjugate acid is a carbocation, and this electrophile combines with the nucleophilic bromide anion.

elimination



The elimination reaction shown on the left takes place in one step. The bond breaking and making operations that take place in this step are described by the curved arrows.

The initial stage may also be viewed as an acid-base interaction, with hydroxide ion serving as the base and a hydrogen atom component of the alkyl chloride as an acid.



There are many kinds of molecular rearrangements. The examples shown on the left are from an important class called **tautomerization** or, more specifically, keto-enol tautomerization. Tautomers are rapidly interconverted constitutional isomers, usually distinguished by a different bonding location for a labile hydrogen atom (colored red here) and a differently located double bond. The equilibrium between tautomers is not only rapid under normal conditions, but it often strongly favors one of the isomers (acetone, for example, is 99.999% keto tautomer). Even in such one-sided equilibria, evidence for the presence of the minor tautomer comes from the chemical behavior of the compound. Tautomeric

equilibria are catalyzed by traces of acids or bases that are generally present in most chemical samples.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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6.3: RADICAL REACTIONS

Objectives

After completing this section, you should be able to

1. give an example of a radical substitution reaction.
2. identify the three steps (initiation, propagation and termination) that occur in a typical radical substitution reaction.
3. write out the steps involved in a simple radical substitution reaction, such as the chlorination of methane.
4. explain why the halogenation of an alkane is not a particularly useful method of preparing specific alkyl halides.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- chain reaction
- initiation step
- propagation step
- radical substitution
- termination step

STUDY NOTES

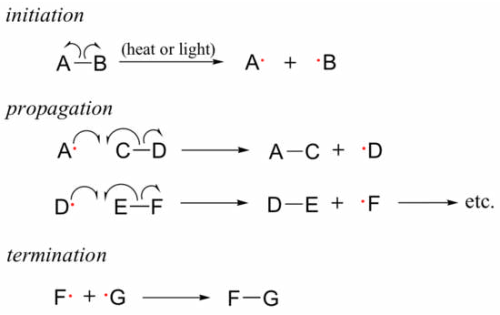
A *radical substitution reaction* is a reaction which occurs by a free radical mechanism and results in the substitution of one or more of the atoms or groups present in the substrate by different atoms or groups.

The *initiation step* in a radical chain reaction is the step in which a free radical is first produced. A *termination step* of a radical chain reaction is one in which two radicals react together in some way so that the chain can no longer be propagated.

While radical halogenation of very simple alkanes can be an effective synthetic strategy, it cannot be employed for larger more complex alkanes to yield specific alkyl halides, since the reactive nature of radicals always leads to mixtures of single- and multiple-halogenated products.

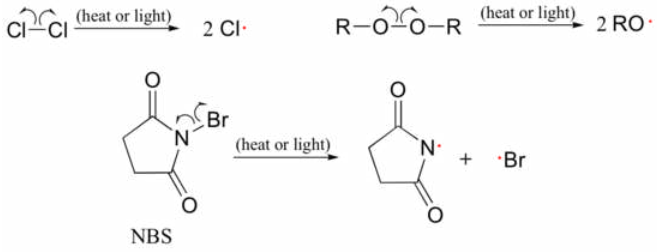
THE THREE PHASES OF RADICAL CHAIN REACTIONS

Because of their high reactivity, free radicals have the potential to be both extremely powerful chemical tools and extremely harmful contaminants. Much of the power of free radical species stems from the natural tendency of radical processes to occur in a chain reaction fashion. **Radical chain reactions** have three distinct phases: initiation, propagation, and termination.

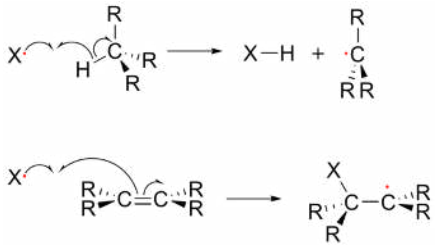


The **initiation phase** describes the step that initially creates a radical species. In most cases, this is a homolytic cleavage event, and takes place very rarely due to the high energy barriers involved. Often the influence of heat, UV radiation, or a metal-containing catalyst is necessary to overcome the energy barrier.

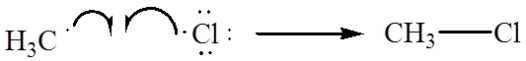
Molecular chlorine and bromine will both undergo homolytic cleavage to form radicals when subjected to heat or light. Other functional groups which also tend to form radicals when exposed to heat or light are chlorofluorocarbons, peroxides, and the halogenated amide N-bromosuccinimide (NBS).



The **propagation phase** describes the 'chain' part of chain reactions. Once a reactive free radical is generated, it can react with stable molecules to form new free radicals. These new free radicals go on to generate yet more free radicals, and so on. Propagation steps often involve hydrogen abstraction or addition of the radical to double bonds.



Chain termination occurs when two free radical species react with each other to form a stable, non-radical adduct. Although this is a very thermodynamically downhill event, it is also very rare due to the low concentration of radical species and the small likelihood of two radicals colliding with one another. In other words, the Gibbs free energy barrier is very high for this reaction, mostly due to entropic rather than enthalpic considerations. The active sites of enzymes, of course, can evolve to overcome this entropic barrier by positioning two radical intermediates adjacent to one another.

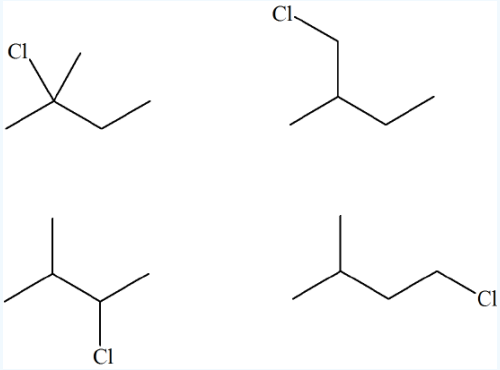


EXERCISES

? EXERCISE 6.3.1

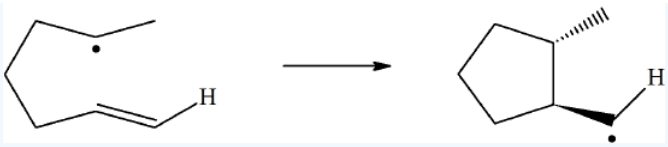
Radical chlorination of alkanes are not useful due to uncontrolled substitution. Draw the mono-substituted products of Cl_2 reacting with 2-methylbutane.

Answer



? EXERCISE 6.3.2

Propose a radical mechanism for the following reaction.



Answer



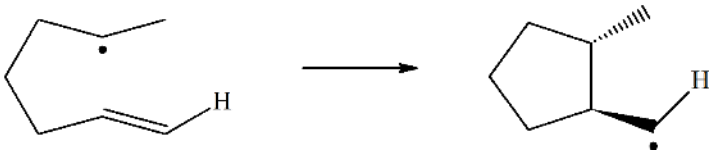
QUESTIONS

Q6.3.1

Radical chlorination of alkanes are not useful due to uncontrolled substitution. Draw the mono-substituted products of Cl_2 reacting with 2-methylbutane.

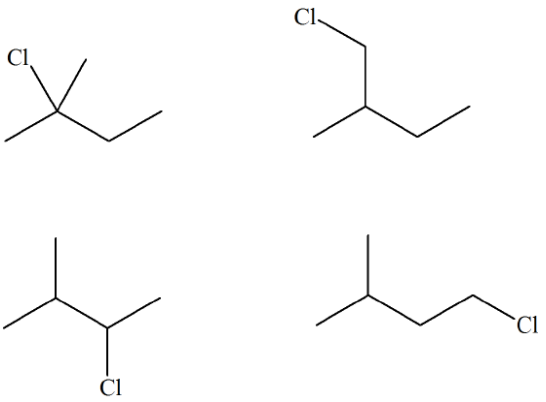
Q6.3.2

Propose a radical mechanism for the following reaction:

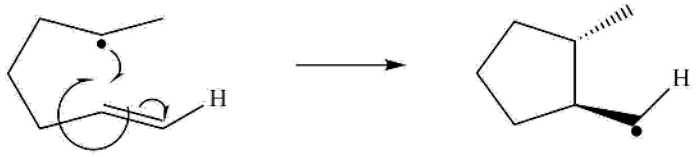


SOLUTIONS

S6.3.1



S6.3.2



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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6.4: POLAR REACTIONS

Objectives

After completing this section, you should be able to

1. identify the positive and negative ends of the bonds present in the common functional groups.
2. explain how bond polarity can be enhanced by the interaction of a functional group with a solvent, metal cation or acid.
3. explain how the polarizability of an atom can be an important factor in determining the reactivity of a bond.
4. describe the heterolytic bond-breaking process.
5. use curved (curly) arrows to indicate the movement of electron pairs during bond breakage and bond formation.
6. predict whether a given species (compound or ion) is likely to behave as a nucleophile or as an electrophile.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- electrophile
- nucleophile
- polar reaction
- polarizability

STUDY NOTES

You may wish to review Section 2.1 before you begin this section. The relative electronegativities of the elements shown in the periodic table should already be familiar. Remember that it is the relative electronegativities that are important, not the actual numerical values.

Make sure that you understand the polarity patterns of the common functional groups. Do not try to memorize these polarities; rather, concentrate on why they arise. You will encounter these group polarities so frequently that they will soon become "second nature" to you.

HALOGENS AND THE CHARACTER OF THE CARBON-HALOGEN BOND

With respect to electronegativity, halogens are more electronegative than carbons. This results in a carbon-halogen bond that is polarized. As shown in the image below, carbon atom has a partial positive charge, while the halogen has a partial negative charge.

The Polar C-X Bond



The following image shows the relationship between the halogens and electronegativity. Notice, as we move up the periodic table from iodine to fluorine, electronegativity increases.

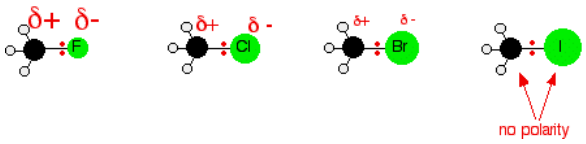
Electronegativity	I	<	Br	<	Cl	<	F

The following image shows the relationships between bond length, bond strength, and molecular size. As we progress down the periodic table from fluorine to iodine, molecular size increases. As a result, we also see an increase in bond length. Conversely, as molecular size increases and we get longer bonds, the strength of those bonds decreases.

Bond length	C-F	<	C-Cl	<	C-Br	<	C-I
Bond strength	C-I	<	C-Br	<	C-Cl	<	C-F
Molecular size	F	<	Cl	<	Br	<	I

THE INFLUENCE OF BOND POLARITY

Of the four halogens, fluorine is the most electronegative and iodine the least. That means that the electron pair in the carbon-fluorine bond will be dragged most towards the halogen end. Looking at the methyl halides as simple examples:



The electronegativities of carbon and iodine are equal and so there will be no separation of charge on the bond. One of the important set of reactions of alkyl halides involves replacing the halogen by something else - substitution reactions. These reactions involve either:

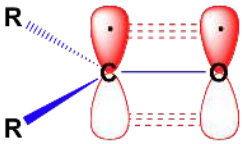
- the carbon-halogen bond breaking to give positive and negative ions. The ion with the positively charged carbon atom then reacts with something either fully or slightly negatively charged.
- something either fully or negatively charged attracted to the slightly positive carbon atom and pushing off the halogen atom.

You might have thought that either of these would be more effective in the case of the carbon-fluorine bond with the quite large amounts of positive and negative charge already present. But that's not so - quite the opposite is true! The thing that governs the reactivity is the strength of the bonds which have to be broken. If is difficult to break a carbon-fluorine bond, but easy to break a carbon-iodine one.

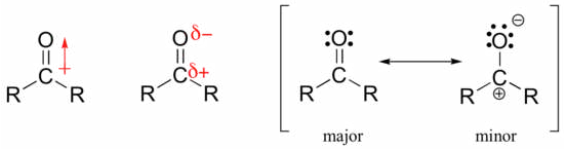
THE CARBONYL GROUP EDIT SECTION

C=O is prone to additions and nucleophillic attack because or carbon's positive charge and oxygen's negative charge. The resonance of the carbon partial positive charge allows the negative charge on the nucleophile to attack the Carbonyl group and become a part of the structure and a positive charge (usually a proton hydrogen) attacks the oxygen. Just a reminder, the nucleophile is a good acid therefore "likes protons" so it will attack the side with a positive charge.

Before we consider in detail the reactivity of aldehydes and ketones, we need to look back and remind ourselves of what the bonding picture looks like in a carbonyl. Carbonyl carbons are sp^2 hybridized, with the three sp^2 orbitals forming soverlaps with orbitals on the oxygen and on the two carbon or hydrogen atoms. These three bonds adopt trigonal planar geometry. The remaining unhybridized 2p orbital on the central carbonyl carbon is perpendicular to this plane, and forms a ‘side-by-side’ pbond with a 2p orbital on the oxygen.

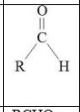
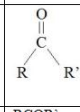
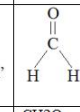
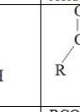
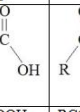
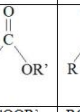
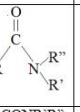
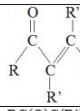
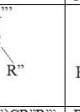


The carbon-oxygen double bond is polar: oxygen is more electronegative than carbon, so electron density is higher on the oxygen side of the bond and lower on the carbon side. Recall that bond polarity can be depicted with a dipole arrow, or by showing the oxygen as holding a partial negative charge and the carbonyl carbon a partial positive charge.



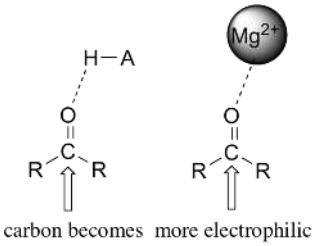
A third way to illustrate the carbon-oxygen dipole is to consider the two main resonance contributors of a carbonyl group: the major form, which is what you typically see drawn in Lewis structures, and a minor but very important contributor in which both electrons in the pbond are localized on the oxygen, giving it a full negative charge. The latter depiction shows the carbon with an empty 2p orbital and a full positive charge.

SOME CARBONYL COMPOUNDS EDIT SECTION

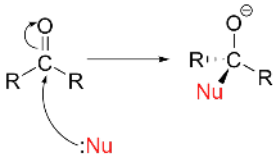
Compound	Aldehyde	Ketone	Formaldehyde	Carboxylic Acid	Ester	Amide	Enone	Acyl Halide	Acid Anhydride
Structure									
General Formula	RCHO	RCOR’	CH2O	RCOOH	RCOOR’	RCONR’R”	RC(O)C(R’)CR”R”’	RCOX	(RCO)2O

NUCLEOPHILIC ADDITION TO ALDEHYDES AND KETONES EDIT SECTION

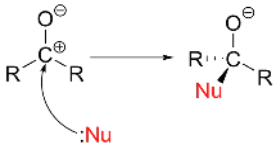
The result of carbonyl bond polarization, however it is depicted, is straightforward to predict. The carbon, because it is electron-poor, is an electrophile: it is a great target for attack by an electron-rich nucleophilic group. Because the oxygen end of the carbonyl double bond bears a partial negative charge, anything that can help to stabilize this charge by accepting some of the electron density will increase the bond's polarity and make the carbon more electrophilic. Very often a general acid group serves this purpose, donating a proton to the carbonyl oxygen.



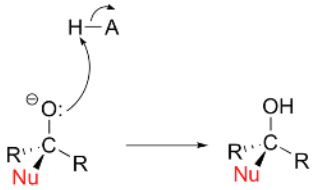
The same effect can also be achieved if a Lewis acid, such as a magnesium ion, is located near the carbonyl oxygen. Unlike the situation in a nucleophilic substitution reaction, when a nucleophile attacks an aldehyde or ketone carbon there is no leaving group – the incoming nucleophile simply 'pushes' the electrons in the pi bond up to the oxygen.



Alternatively, if you start with the minor resonance contributor, you can picture this as an attack by a nucleophile on a carbocation.



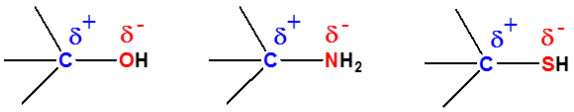
After the carbonyl is attacked by the nucleophile, the negatively charged oxygen has the capacity to act as a nucleophile. However, most commonly the oxygen acts instead as a base, abstracting a proton from a nearby acid group in the solvent or enzyme active site.



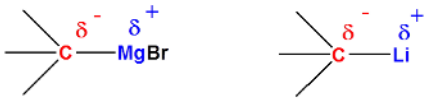
This very common type of reaction is called a **nucleophilic addition**. In many biologically relevant examples of nucleophilic addition to carbonyls, the nucleophile is an alcohol oxygen or an amine nitrogen, or occasionally a thiol sulfur. In one very important reaction type known as an aldol reaction, the nucleophile attacking the carbonyl is a resonance-stabilized carbanion. In this chapter, we will concentrate on reactions where the nucleophile is an oxygen or nitrogen.

1. Nucleophilic Addition to Aldehydes and Ketones
2. Nucleophilic Substitution of RCOZ (Z = Leaving Group)
3. General reaction
4. General mechanism

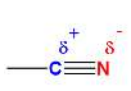
POLARITY PATTERNS IN OTHER COMMON FUNCTIONAL GROUPS

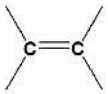


Alcohol **Amine** **Thiol**



Grignard Reagent **Alkyllithium**





Nitrile

Alkene
Symmetrical, Nonpolar

NUCLEOPHILE? EDIT SECTION

Nucleophilic functional groups are those which have electron-rich atoms able to donate a pair of electrons to form a new covalent bond. In both laboratory and biological organic chemistry, the most relevant nucleophilic atoms are oxygen, nitrogen, and sulfur, and the most common nucleophilic functional groups are water, alcohols, phenols, amines, thiols, and occasionally carboxylates.

More specifically in laboratory reactions, halide and azide (N_3^-) anions are commonly seen acting as nucleophiles.

Of course, carbons can also be nucleophiles - otherwise how could new carbon-carbon bonds be formed in the synthesis of large organic molecules like DNA or fatty acids? Enolate ions (section 7.5) are the most common carbon nucleophiles in biochemical reactions, while the cyanide ion (CN^-) is just one example of a carbon nucleophile commonly used in the laboratory. Reactions with carbon nucleophiles will be dealt with in chapters 13 and 14, however - in this chapter and the next, we will concentrate on non-carbon nucleophiles.

When thinking about nucleophiles, the first thing to recognize is that, for the most part, the same quality of 'electron-richness' that makes a something nucleophilic also makes it basic: *nucleophiles can be bases, and bases can be nucleophiles*. It should not be surprising, then, that most of the trends in basicity that we have already discussed also apply to nucleophilicity.

Neutral Nucleophiles

H_2O, NH_3, RNH_2, R_2NH, R_3N, ROH, RCOOH, RSH, and PR_3

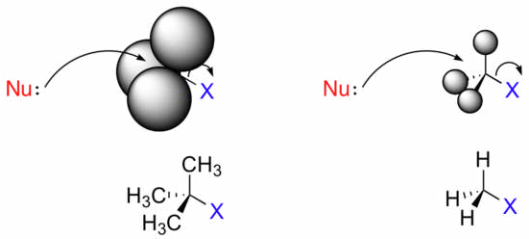
Charged Nucleophiles

RO^-, $^-NH_2$, $R\bar{N}H$, R_2N^-, HS^-, RS^-, RSe^-, Cl^-, Br^-, I^-, F^-, CN^-, ^-OH, RCO_2^-

ELECTROPHILES EDIT SECTION

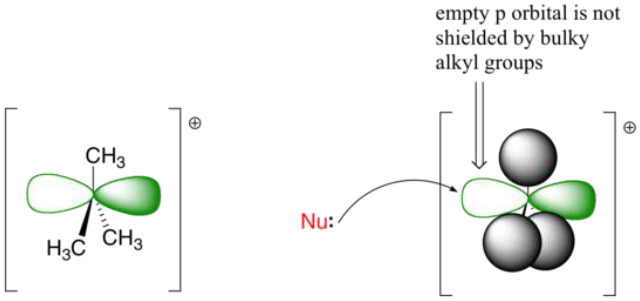
In the vast majority of the nucleophilic substitution reactions you will see in this and other organic chemistry texts, the electrophilic atom is a carbon which is bonded to an electronegative atom, usually oxygen, nitrogen, sulfur, or a halogen. The concept of electrophilicity is relatively simple: an electron-poor atom is an attractive target for something that is electron-rich, *i.e.* a nucleophile. However, we must also consider the effect of steric hindrance on electrophilicity. In addition, we must discuss how the nature of the electrophilic carbon, and more specifically the stability of a potential carbocationic intermediate, influences the S_N1 vs. S_N2 character of a nucleophilic substitution reaction. Edit section

Consider two hypothetical S_N2 reactions: one in which the electrophile is a methyl carbon and another in which it is tertiary carbon.



Because the three substituents on the methyl carbon electrophile are tiny hydrogens, the nucleophile has a relatively clear path for backside attack. However, backside attack on the tertiary carbon is blocked by the bulkier methyl groups. Once again, steric hindrance - this time caused by bulky groups attached to the electrophile rather than to the nucleophile - hinders the progress of an associative nucleophilic (S_N2) displacement.

The factors discussed in the above paragraph, however, do not prevent a sterically-hindered carbon from being a good electrophile - they only make it less likely to be attacked in a *concerted S_N2 reaction*. Nucleophilic substitution reactions in which the electrophilic carbon is sterically hindered are more likely to occur by a two-step, dissociative (S_N1) mechanism. This makes perfect sense from a geometric point of view: the limitations imposed by sterics are significant mainly in an S_N2 displacement, when the electrophile being attacked is a sp^3-hybridized tetrahedral carbon with its relatively 'tight' angles of 109.4º. Remember that in an S_N1 mechanism, the nucleophile attacks an sp^2-hybridized carbocation intermediate, which has trigonal planar geometry with 'open' 120 angles.

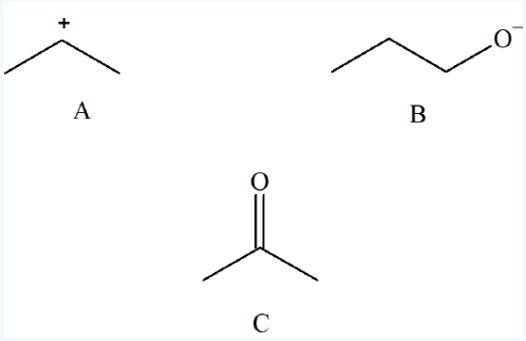


With this open geometry, the empty p orbital of the electrophilic carbocation is no longer significantly shielded from the approaching nucleophile by the bulky alkyl groups. A carbocation is a very potent electrophile, and the nucleophilic step occurs very rapidly compared to the first (ionization) step.

EXERCISE

? EXERCISE 6.4.1

Label the following either an electrophile or a nucleophile.



Answer

A = Electrophile

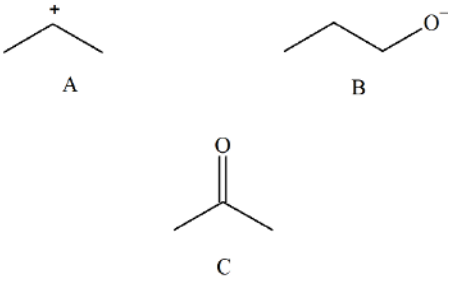
B = Nucleophile

C = Nucleophile

QUESTIONS

Q6.4.1

Label the following either an electrophile or a nucleophile.



SOLUTIONS

S6.4.1

A = Electrophile

B = Nucleophile

C = Both (carbonyl carbon is electrophile and oxygen is nucleophile)

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

6.4: Polar Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

6.5: AN EXAMPLE OF A POLAR REACTION - ADDITION OF HBR TO ETHYLENE

Objectives

After completing this section, you should be able to

1. give an example of a simple polar reaction (e.g., a electrophilic addition).
2. identify the electrophile and nucleophile in a simple polar reaction.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- electrophilic addition
- carbocation

STUDY NOTES

The curved arrows introduced in this section are used throughout the course to indicate the movement of electron pairs. It takes practice for the beginning student to feel comfortable using these arrows. Remember that the head of the arrow indicates where the electron pair moves to; its tail shows where the electron pair comes from. (Chemists often refer to the use of curved arrows as “electron pushing.")

This page looks at the reaction of the carbon-carbon double bond in alkenes such as ethene with hydrogen halides such as hydrogen chloride and hydrogen bromide. Symmetrical alkenes (like ethene or but-2-ene) are dealt with first. These are alkenes where identical groups are attached to each end of the carbon-carbon double bond.

ADDITION TO SYMMETRICAL ALKENES

All alkenes undergo addition reactions with the hydrogen halides. A hydrogen atom joins to one of the carbon atoms originally in the double bond, and a halogen atom to the other. For example, with ethene and hydrogen chloride, you get chloroethane:

$$CH_2{=}CH_2 + HCl \longrightarrow CH_3{-}CH_2Cl$$

With but-2-ene you get 2-chlorobutane:

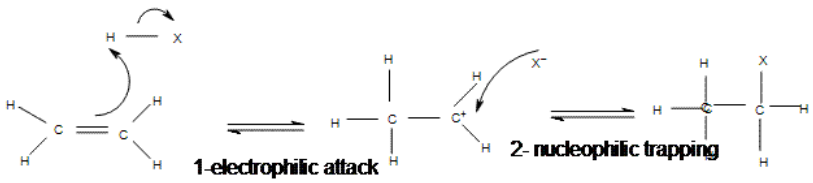
$$CH_3{-}CH{=}CH{-}CH_3 + HCl \longrightarrow CH_3{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3$$

What happens if you add the hydrogen to the carbon atom at the right-hand end of the double bond, and the chlorine to the left-hand end? You would still have the same product. The chlorine would be on a carbon atom next to the end of the chain - you would simply have drawn the molecule flipped over in space. That would be different of the alkene was unsymmetrical - that's why we have to look at them separately.

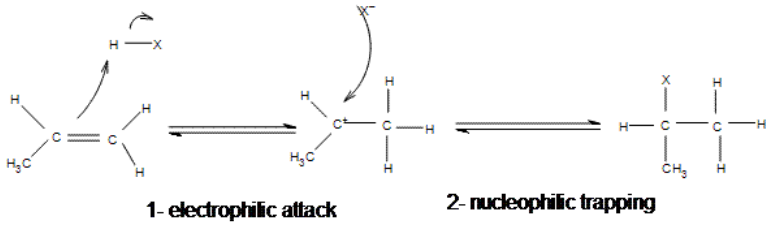
MECHANISM

The addition of hydrogen halides is one of the easiest electrophilic addition reactions because it uses the simplest electrophile: the proton. Hydrogen halides provide both a electrophile (proton) and a nucleophile (halide). First, the electrophile will attack the double bond and take up a set of pi electrons, attaching it to the molecule (1). This is basically the reverse of the last step in the E1 reaction (deprotonation step). The resulting molecule will have a single carbon-carbon bond with a positive charge on one of them (carbocation). The next step is when the nucleophile (halide) bonds to the carbocation, producing a new molecule with both the original hydrogen and halide attached to the organic reactant (2). The second step will only occur if a good nucleophile is used.

Mechanism of Electrophilic Addition of Hydrogen Halide to Ethene



Mechanism of Electrophilic Addition of Hydrogen Halide to Propene



All of the halides (HBr, HCl, HI, HF) can participate in this reaction and add on in the same manner. Although different halides do have different rates of reaction, due to the H-X bond getting weaker as X gets larger (poor overlap of orbitals)s.

REACTION RATES

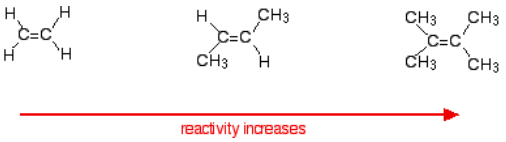
Variation of rates when you change the halogen

Reaction rates increase in the order HF - HCl - HBr - HI. Hydrogen fluoride reacts much more slowly than the other three, and is normally ignored in talking about these reactions. When the hydrogen halides react with alkenes, the hydrogen-halogen bond has to be broken. The bond strength falls as you go from HF to HI, and the hydrogen-fluorine bond is particularly strong. Because it is difficult to break the bond between the hydrogen and the fluorine, the addition of HF is bound to be slow.

Variation of rates when you change the alkene

This applies to unsymmetrical alkenes as well as to symmetrical ones. For simplicity the examples given below are all symmetrical ones- but they don't have to be. Reaction rates increase as the alkene gets more complicated - in the sense of the number of alkyl groups (such as methyl groups) attached to the carbon atoms at either end of the double bond.

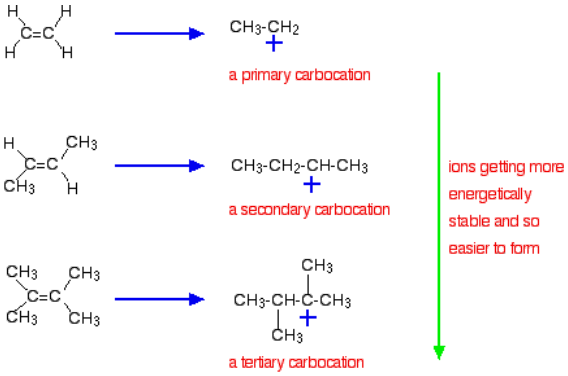
For example:



There are two ways of looking at the reasons for this - both of which need you to know about the mechanism for the reactions.

Alkenes react because the electrons in the pi bond attract things with any degree of positive charge. Anything which increases the electron density around the double bond will help this. Alkyl groups have a tendency to "push" electrons away from themselves towards the double bond. The more alkyl groups you have, the more negative the area around the double bonds becomes.

The more negatively charged that region becomes, the more it will attract molecules like hydrogen chloride. The more important reason, though, lies in the stability of the intermediate ion formed during the reaction. The three examples given above produce these carbocations (carbonium ions) at the half-way stage of the reaction:



The stability of the intermediate ions governs the activation energy for the reaction. As you go towards the more complicated alkenes, the activation energy for the reaction falls. That means that the reactions become faster.

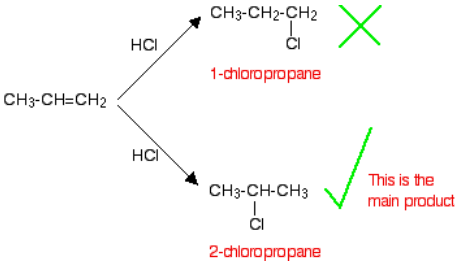
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ADDITION TO UNSYMMETRICAL ALKENES

In terms of reaction conditions and the factors affecting the rates of the reaction, there is no difference whatsoever between these alkenes and the symmetrical ones described above. The problem comes with the orientation of the addition - in other words, which way around the hydrogen and the halogen add across the double bond.

Orientation of addition

If HCl adds to an unsymmetrical alkene like propene, there are two possible ways it could add. However, in practice, there is only one major product.



This is in line with Markovnikov's Rule which says:

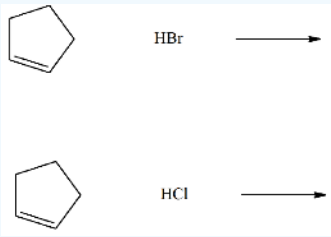
> When a compound HX is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already.

In this case, the hydrogen becomes attached to the CH_2 group, because the CH_2 group has more hydrogens than the CH group. Notice that only the hydrogens directly attached to the carbon atoms at either end of the double bond count. The ones in the CH_3 group are totally irrelevant.

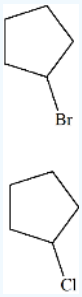
EXERCISES

? EXERCISE 6.5.1

Predict the product of the following reactions.

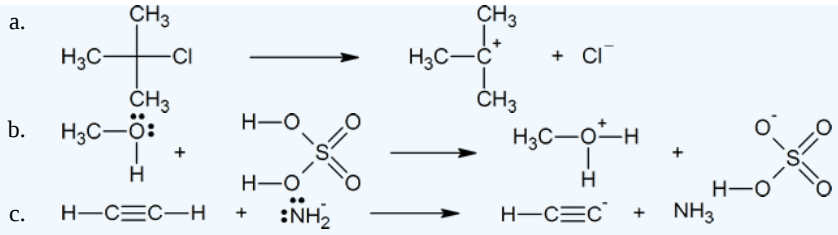


Answer

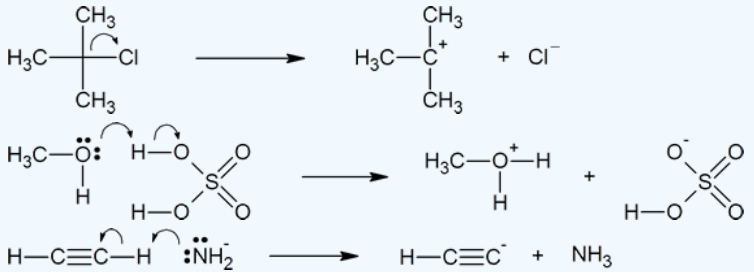


? EXERCISE 6.5.2

1. Supply the missing curved arrows in the equations given below.



Answer



QUESTIONS

Q6.5.1

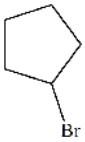
Predict the product of the following reactions:





SOLUTIONS

S6.5.1





CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

6.5: An Example of a Polar Reaction - Addition of HBr to Ethylene is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

6.6: USING CURVED ARROWS IN POLAR REACTION MECHANISMS

Objective

After completing this section, you should be able to use curved (curly) arrows, in conjunction with a chemical equation, to show the movement of electron pairs in a simple polar reaction, such as electrophilic addition.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- electrophilic
- nucleophilic

PUSHING ELECTRONS AND CURLY ARROWS

Understanding the location of electrons and being able to draw the curly arrows that depict the mechanisms by which the reactions occur is one of the most critical tools for learning organic chemistry since they allow you to understand what controls reactions, and how reactions proceed.

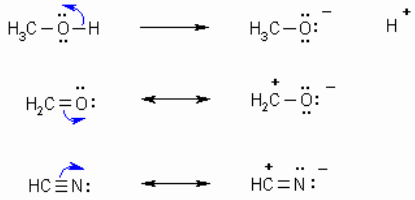
Before you can do this you need to understand that **a bond is due to a pair of electrons between atoms**.

When asked to draw a MECHANISM, curly arrows should be used to show ALL the BONDING changes that occur.

A few simple lessons

LESSON 1

If we remove the pair of electrons in a bond, then we BREAK that bond. This is true for single and mutliple bonds as shown below:

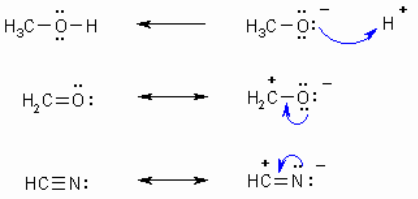


Notice that since the starting materials were NEUTRAL the products were also NEUTRAL.

In general terms, the SUM of the CHARGES on the starting materials MUST equal the SUM of the CHARGES on the products since we have the SAME NUMBER OF ELECTRONS.

The first example is a REACTION since we broke a sigma bond. In the second two examples, we moved pi electrons into lone pairs. This is RESONANCE.

If we move electrons between two atoms then we MAKE a new bond:



We ALWAYS show the electrons moving from ELECTRON RICH to ELECTRON POOR

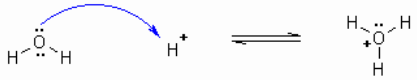
Lesson 2



This is a simple acid / base reaction, showing the formation of the hydronium ion produced when hydrogen chloride is dissolved in water. It is useful to analyse the bond changes that are occuring. Water is functioning as a BASE and hydrogen chloride as an ACID. Consider the reaction in discrete steps. Formation of a PROTON by the ACID which requires breaking the H-Cl bond which we do by taking the electrons OUT of the bond:



Next, reaction of the BASE with the PROTON to make a new O-H bond. This requires that we put electrons BETWEEN the atoms that are to be BONDED:



However, we should consider this reaction as a single process, the BASE abstracting the PROTON from the ACID:



Notice that in each of these diagrams, the overall CHARGE of the reactents EQUALS that of the products.

We can also draw the curly arrows for the reverse reaction:



This shows the formation of the new H-Cl bond by taking electrons from the electron rich chloride ion and using them to make a bond to the H, and breaking the H-O bond by taking electrons out of the bond and giving them to the electron poor oxygen atom. Notice that the CHARGES BALANCE !

Lesson 3

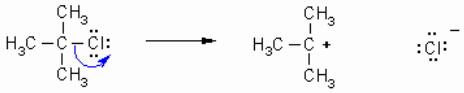
In this section we will look at the curly arrows for some NUCLEOPHILIC SUBSTITUTION reactions.

Overall the processes involved are similar to those for the ACID / BASE reactions we described above.

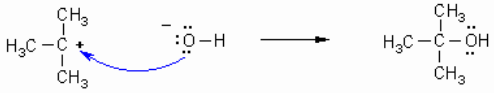
Overall in a nucleophilic substitution, a nucleophile (Nu) becomes bonded toa C and a leaving group (LG) is displaced. In bonding terms this means we must MAKE a Nu to C bond and BREAK a C to LG bond.



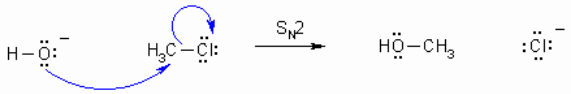
Lets consider the stepwise S_N1 reaction, for example the reaction of tBuCl with HO-. First we must remove the electrons from the C-Cl bond to break it:



Since we take electrons AWAY from C it becomes the +ve carbocation and since we give them to Cl it becomes -ve chloride. In the second step the electron rich Nu donates electrons to form a new C-O bond with the C+



In an S_N2 process, the bond making and breaking occur simultaneously. Below we see the Nu donating electrons to form a new C-O bond and the C-Cl bond breaking by removing the electrons and giving them to the Cl. By making the bond changes simultaneously we avoid violating the octet rule at C.



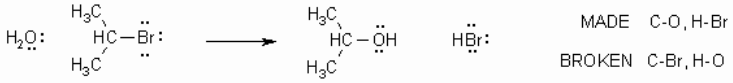
Notice that in ALL steps the CHARGES of the starting materials BALANCE those of the products.

Lesson 4

In this section we will be looking at another substitution reaction, but a little more involved. Lets consider the S_N2 reaction of isopropyl bromide with water:



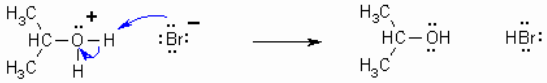
First we should draw in the lone pairs. Once we have done that we should work out which bonds have been made and which have been broken.



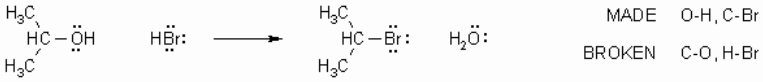
The curly arrows we draw must account for ALL of these bonding changes. Since we are dealing with an S_N2 process the Nu must attack as the LG is displaced:



Notice that these 2 curly arrows only show forming the C-O bond and breaking C-Br bond and that overall the CHARGES BALANCE. Note that since the neutral O in water gave away electrons to form the new C-O bond it becomes positive in the intermediate formed. To complete the reatcion we need to show making the H-Br bond and breaking an O-H bond. Notice that the CHARGES BALANCE !



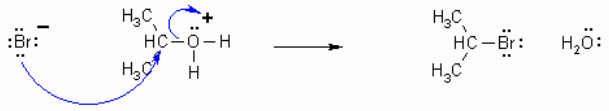
Now for the mechanism of the reverse reaction, i.e. the reaction of isopropanol with hydrogen bromide to give isopropyl bromide:



This mechanism must occur via the same pathway as the previous example (Law of Microscopic Reversibility). However, we should be able to deduce what happens without knowing that ! First we know that HBr is a strong acid and therefore we should expect it to protonate a base. The most basic sites in the whole system are the lone pairs on the O. SInce the lone pairs are electron rich, the arrows start there towards the proton:



The final part of the sequence is to make the bromide attack, donating electrons to form the new C-Br bond and have the leaving group, H_2O, break away taking the electrons from the C-O bond to neutralise the positive charge on the O. Notice how the electrons flow from electron rich (negative) to electron poor (positive).



QUESTION: Do the charges still balance in each step ?

CURLY ARROW SUMMARY

- Curly arrows flow from electron rich to electron poor.
- Therefore they start from lone pairs or bonds.

- The charges in any particular step should always be balanced.
- Remember to obey the rules of valence (*eg*. octet rule for C,N,O,F *etc*.)
- If electrons are taken out of a bond, then that bond is broken.
- If electrons are placed between two atoms then it implies a bond is being made.

EXERCISES

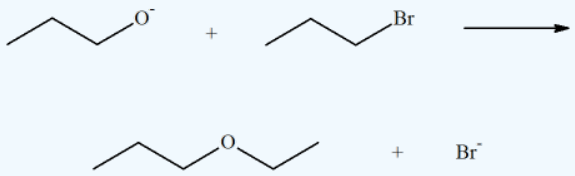
? EXERCISE 6.6.1

Draw arrows for the following reactions.

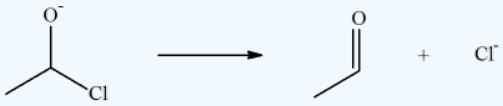
A)



B)

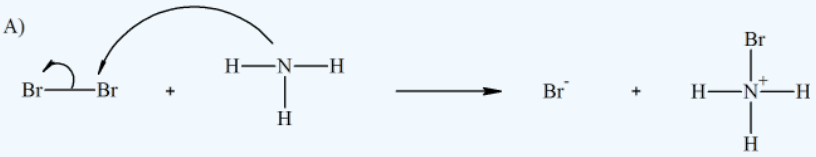


C)

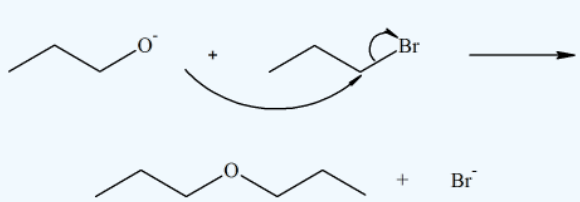


Answer

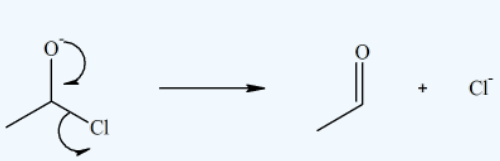
A)



B)



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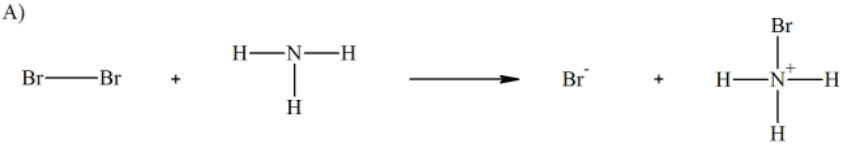
QUESTIONS

Q6.6.1

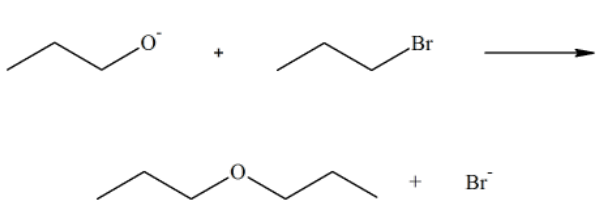
Draw curved arrows to indicate mechanisms for the following reactions:

https://chem.libretexts.org/@go/page/67113

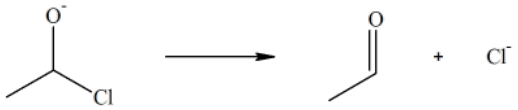
A)



B)



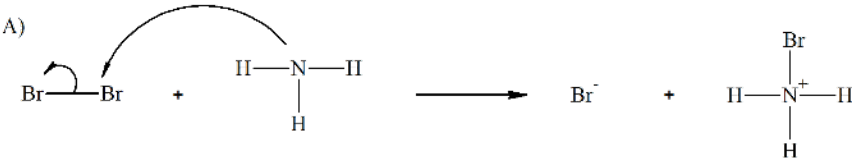
C)



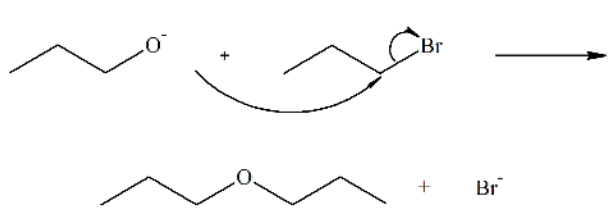
SOLUTIONS

S6.6.1

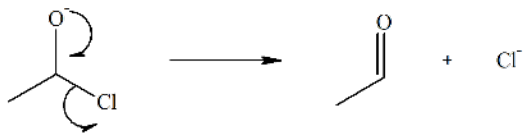
A)



B)



C)



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Ian Hunt, Department of Chemistry, University of Calgary
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

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6.7: DESCRIBING A REACTION - EQUILIBRIA, RATES, AND ENERGY CHANGES

Objectives

After completing this section, you should be able to

1. write the equilibrium constant expression for a given reaction.
2. assess, qualitatively, how far a reaction will proceed in a given direction, given the value of K_{eq}.
3. explain the difference between rate and equilibrium.
4. state the relationship between $\Delta G°$ and K_{eq}, and use this relationship to determine the value of either of the two variables, given the other.
5. state the relationship between Gibbs free-energy, enthalpy and entropy, and use the relationship to calculate any one of $\Delta G°$, $\Delta H°$ and $\Delta S°$, given the other two.
6. make a qualitative assessment of whether $\Delta S°$ for a given process is expected to be positive or negative.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- exergonic
- endergonic
- exothermic
- endothermic
- enthalpy change (heat of reaction), $\Delta H°$
- entropy change, $\Delta S°$
- reaction mechanism
- standard Gibbs free-energy change, $\Delta G°$

STUDY NOTES

Throughout this course you will be paying a great deal of attention to the mechanisms of the reactions that you study. Some students see this as a laborious task of little practical use. However, you will find that a knowledge of reaction mechanisms can help reduce the number of reactions to memorize, provide a connecting link between apparently unrelated reactions, and enable someone with a basic knowledge of organic chemistry to deduce how a previously unseen reaction might proceed. The investigation of reaction mechanisms is a popular research area for organic chemists.

EQUILIBRIUM CONSTANT

For the hypothetical chemical reaction:

$$aA + bB \rightleftharpoons cC + dD \tag{6.7.1}$$

the equilibrium constant is defined as:

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{6.7.2}$$

The notation [A] signifies the molar concentration of species A. An alternative expression for the equilibrium constant involves partial pressures:

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b} \tag{6.7.3}$$

Note that the expression for the equilibrium constant includes only solutes and gases; pure solids and liquids do not appear in the expression. For example, the equilibrium expression for the reaction

$$CaH_2(s) + 2H_2O(g) \rightleftharpoons Ca(OH)_2(s) + 2H_2(g) \tag{6.7.4}$$

is the following:

$$K_C = \frac{[H_2]^2}{[H_2O]^2} \tag{6.7.5}$$

Observe that the gas-phase species H_2O and H_2 appear in the expression but the solids CaH_2 and $Ca(OH)_2$ do not appear.

The equilibrium constant is most readily determined by allowing a reaction to reach equilibrium, measuring the concentrations of the various solution-phase or gas-phase reactants and products, and substituting these values into the Law of Mass Action.

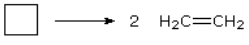
FREE ENERGY

The interaction between enthalpy and entropy changes in chemical reactions is best observed by studying their influence on the equilibrium constants of reversible reactions. To this end a new thermodynamic function called **Free Energy** (or Gibbs Free Energy), symbol **ΔG**, is defined as shown in the first equation below. Two things should be apparent from this equation. First, in cases where the entropy change is small, ΔG ≅ ΔH. Second, the importance of ΔS in determining ΔG increases with increasing temperature.

$\Delta G^o = \Delta H^o - T\Delta S^o$ T = temperature in ºK

The free energy function provides improved insight into the thermodynamic driving forces that influence reactions. A negative ΔG^o is characteristic of an **exergonic reaction**, one which is thermodynamically favorable and often spontaneous, as is the melting of ice at 1 ºC. Likewise a positive ΔG^o is characteristic of an **endergonic reaction**, one which requires an input of energy from the surroundings.

For an example of the relationship of free energy to enthalpy consider the decomposition of cyclobutane to ethene, shown in the following equation. The standard state for all the compounds is gaseous.



This reaction is endothermic, but the increase in number of molecules from one (reactants) to two (products) results in a large positive ΔS^o. At 25 ºC (298 ºK), ΔG^o = 19 kcal/mol – 298(43.6) cal/mole = 19 – 13 kcal/mole = +6 kcal/mole. Thus, the entropy change opposes the enthalpy change, but is not sufficient to change the sign of the resulting free energy change, which is endergonic. Indeed, cyclobutane is perfectly stable when kept at room temperature.

Because the entropy contribution increases with temperature, this energetically unfavorable transformation can be made favorable by raising the temperature. At 200 ºC (473 ºK), ΔG^o = 19 kcal/mol – 473(43.6) cal/mole = 19 – 20.6 kcal/mole = –1.6 kcal/mole. This is now an **exergonic reaction**, and the thermal cracking of cyclobutane to ethene is known to occur at higher temperatures.

$\Delta G^o = -RT \ln K = -2.303RT \log K$ R = 1.987 cal/ ºK mole T = temperature in ºK K = equilibrium constant

A second equation, shown above, is important because it demonstrates the fundamental relationship of ΔG^o to the equilibrium constant, K. Because of the negative logarithmic relationship between these variables, a negative ΔG^o generates a K>1, whereas a positive ΔG^o generates a K<1. When ΔG^o = 0, K = 1. Furthermore, small changes in ΔG^o produce large changes in K. A change of 1.4 kcal/mole in ΔG^o changes K by approximately a factor of 10. This interrelationship may be explored with the calculator on the right. Entering free energies outside the range -8 to 8 kcal/mole or equilibrium constants outside the range 10^{-6} to 900,000 will trigger an alert, indicating the large imbalance such numbers imply.

EXERCISES

? EXERCISE 6.7.1

At 155°C, the equilibrium constant, K_{eq}, for the reaction

$\ce{\sf{CH3CO2H + CH3CH2OH <=> CH3CO2CH2CH3 + H2O}}$

has a value of 4.0. Calculate $\Delta G°$ for this reaction at 155 °C.

Answer

$\Delta G° = -RT \ln K_{eq}$

$= -(8.314\ J \cdot K^{-1} \cdot mol^{-1})(428\ K) \ln(4.0)$

$= -(8.314\ J \cdot K^{-1} \cdot mol^{-1})(428\ K)(1.386)$

$= -4.9 \times 10^3\ J \cdot mol^{-1}$

$= -4.9\ kJ \cdot mol^{-1}$

EXERCISE 6.7.2

Acetylene (C_2H_2) can be converted into benzene (C_6H_6) according to the equation:

$\ce{\sf{3H-C#C-H (g) <=> C6H6 (l)}}$

At 25 °C, $\Delta G°$ for this reaction is −503 kJ and $\Delta H°$ is −631 kJ. Determine $\Delta S°$ and indicate whether the size of $\Delta S°$ agrees with what you would have predicted simply by looking at the chemical equation.

Answer

The entropy change is negative, as one would expect from looking at the chemical equation, since three moles of reactants yield one mole of product; that is, the system becomes much more “ordered” as it goes from reactants to products.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Jim Clark (Chemguide.co.uk)

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6.8: DESCRIBING A REACTION - BOND DISSOCIATION ENERGIES

Objectives

After completing this section, you should be able to

1. predict the value of $\Delta H°$ for a gas-phase reaction, given the necessary bond dissociation energy data.
2. predict the dissociation energy of a particular bond, given $\Delta H°$ for a reaction involving the bond and any other necessary bond dissociation energy data.
3. outline the limitations of using bond dissociation energies to predict whether or not a given reaction will occur.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- bond dissociation energy
- solvation

STUDY NOTES

The idea of calculating the standard enthalpy of a reaction from the appropriate bond dissociation energy data should be familiar to you from your first-year chemistry course.

Solvation is the interaction between solvent molecules and the ions or molecules dissolved in that solvent.

The homolytic bond dissociation energy is the amount of energy needed to break apart one mole of covalently bonded gases into a pair of radicals. The SI units used to describe bond energy are kiloJoules per mole of bonds (kJ/Mol). It indicates how strongly the atoms are bonded to each other.

INTRODUCTION

Breaking a covalent bond between two partners, A-B, can occur either heterolytically, where the shared pair of electron goes with one partner or another

$$A - B \rightarrow A^+ + B:^-$$

or

$$A - B \rightarrow A:^- + B^+$$

or homolytically, where one electron stays with each partner.

$$A - B \rightarrow A^\bullet + B^\bullet$$

The products of homolytic cleavage are radicals and the energy that is required to break the bond homolytically is called the *Bond Dissociation Energy* (BDE) and is a measure of the strength of the bond.

CALCULATION OF THE BDE

The BDE for a molecule A-B is calculated as the difference in the enthalpies of formation of the products and reactants for homolysis

$$BDE = \Delta_f H(A^\bullet) + \Delta_f H(B^\bullet) - \Delta_f H(A - B)$$

Officially, the IUPAC definition of bond dissociation energy refers to the energy change that occurs at 0 K, and the symbol is D_o. However, it is commonly referred to as BDE, the bond dissociation energy, and it is generally used, albeit imprecisely, interchangeably with the bond dissociation *enthalpy*, which generally refers to the enthalpy change at room temperature (298K). Although there are technically differences between BDEs at 0 K and 298 K, those difference are not large and generally do not affect interpretations of chemical processes.

BOND BREAKAGE/FORMATION

Bond dissociation energy (or enthalpy) is a state function and consequently does not depend on the path by which it occurs. Therefore, the specific mechanism in how a bond breaks or is formed does not affect the BDE. Bond dissociation energies are useful in assessing the energetics of chemical processes. For chemical reactions, combining bond dissociation energies for bonds formed and bonds broken in a chemical reaction using Hess's Law can be used to estimate reaction enthalpies.

EXAMPLE 6.8.1: CHLORINATION OF METHANE

Consider the chlorination of methane

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

the overall reaction thermochemistry can be calculated exactly by combining the BDEs for the bonds broken and bonds formed

$CH_4 \rightarrow CH_3\bullet + H\bullet$ BDE(CH_3-H)

$Cl_2 \rightarrow 2Cl\bullet$ BDE(Cl_2)\]

$H\bullet + Cl\bullet \rightarrow HCl$ -BDE(HCl)

$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$ -BDE(CH_3-Cl)

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$\Delta H = BDE(R-H) + BDE(Cl_2) - BDE(HCl) - BDE(CH_3 - Cl)$$

Because reaction enthalpy is a state function, it does not matter what reactions are combined to make up the overall process using Hess's Law. However, BDEs are convenient to use because they are readily available.

Alternatively, BDEs can be used to assess individual steps of a mechanism. For example, an important step in free radical chlorination of alkanes is the abstraction of hydrogen from the alkane to form a free radical.

$$RH + Cl\bullet \rightarrow R\bullet + HCl$$

The energy change for this step is equal to the difference in the BDEs in RH and HCl

$$\Delta H = BDE(R-H) - BDE(HCl)$$

This relationship shows that the hydrogen abstraction step is more favorable when BDE(R-H) is smaller. The difference in energies accounts for the selectivity in the halogenation of hydrocarbons with different types of C-H bonds.

Table 6.8.1: Representative C-H BDEs in Organic Molecules

R-H	D_o, kJ/mol	D_{298}, kJ/mol	R-H	D_o, kJ/mol	D_{298}, kJ/mol
CH_3-H	432.7±0.1	439.3±0.4	H_2C=CH-H	456.7±2.7	463.2±2.9
CH_3CH_2-H		423.0±1.7	C_6H_5-H	465.8±1.9	472.4±2.5
$(CH_3)_2$CH-H		412.5±1.7	HCCH	551.2±0.1	557.8±0.3
$(CH_3)_3$C-H		403.8±1.7			
			H_2C=CHCH_2-H		371.5±1.7
HC(O)-H		368.6±0.8	$C_6H_5CH_2$-H		375.3±2.5
CH_3C(O)-H		374.0±1.2			

TRENDS IN C-H BDES

It is important to remember that C-H BDEs refer to the energy it takes to break the bond, and is the difference in energy between the reactants and the products. Therefore, it is not appropriate to interpret BDEs solely in terms of the "stability of the radical products" as is often done.

Analysis of the BDEs shown in the table above shows that there are some systematic trends:

1. **BDEs vary with hybridization:** Bonds with sp^3 hybridized carbons are weakest and bonds with sp hybridized carbons are much stronger. The vinyl and phenyl C-H bonds are similar, reflecting their sp^2 hybridization. The correlation with hybridization can be

viewed as a reflection of the C-H bond lengths. Longer bonds formed with sp^3 orbitals are consequently weaker. Shorter bonds formed with orbitals that have more s-character are similarly stronger.

2. **C-H BDEs vary with substitution:** Among sp^3 hybridized systems, methane has the strongest C-H bond. C-H bonds on primary carbons are stronger than those on secondary carbons, which are stronger than those on tertiary carbons.

INTERPRETATION OF C-H BDES FOR SP^3 HYBRIDIZED CARBONS

The interpretation of the BDEs in saturated molecules has been subject of recent controversy. As indicated above, the variation in BDEs with substitution has traditionally been interpreted as reflecting the stabilities of the alkyl radicals, with the assessment that more highly substituted radicals are more stable, as with carbocations. Although this is a popular explanation, it fails to account fo the fact the bonds to groups other than H do not show the same types of variation.

R	BDE(R-CH_3)	BDE(R-Cl)	BDE(R-Br)	BDE(R-OH)
CH_3-	377.0±0.4	350.2±0.4	301.7±1.3	385.3±0.4
CH_3CH_2-	372.4±1.7	354.8±2.1	302.9±2.5	393.3±1.7
$(CH_3)_2CH$-	370.7±1.7	356.5±2.1	309.2±2.9	399.6±1.7
$(CH_3)_3C$-	366.1±1.7	355.2±2.9	303.8±2.5	400.8±1.7

Therefore, although C-CH_3 bonds get weaker with more substitution, the effect is not nearly as large as that observed with C-H bonds. The strengths of C-Cl and C-Br bonds are not affected by substitution, despite the fact that the same radicals are formed as when breaking C-H bonds, and the C-OH bonds in alcohols actually *increase* with more substitution.

Gronert has proposed that the variation in BDEs is alternately explained as resulting from destabilization of the reactants due to steric repulsion of the substituents, which is released in the nearly planar radicals.[1] Considering that BDEs reflect the relative energies of reactants and products, either explanation can account for the trend in BDEs.

Another factor that needs to be considered is the electronegativity. The Pauling definition of electronegativity says that the bond dissociation energy between unequal partners is going to be dependent on the difference in electrongativities, according to the expression

$$D_o(A-B) = \frac{D_o(A-A) + D_o(B-B)}{2} + (X_A - X_B)^2$$

where X_A and X_B are the electronegativities and the bond energies are in eV. Therefore, the variation in BDEs can be interpreted as reflecting variation in the electronegativities of the different types of alkyl fragments.

There is likely some merit in all three interpretations. Since Gronert's original publication of his alternate explanation, there have been many desperate attempts to defend the radical stability explanation.

REFERENCES

1. Gronert, S. *J. Org. Chem.* **2006**, *13*, 1209

FURTHER READING

MasterOrganicChemistry

Bond Strengths And Radical Stability

EXERCISES

? EXERCISE \PageIndex1

Given that $\Delta H°$ for the reaction

$$CH_4(g) + 4\,F_2(g) \longrightarrow CF_4(g) + 4\,HF(g)$$

is −1936 kJ, use the following data to calculate the average bond energy of the C−F bonds in CF_4.

Bond	Average Bond Energy
C–H	413 kJ · mol^{-1}
F–F	155 kJ · mol^{-1}
H–F	567 kJ · mol^{-1}

Answer

Bonds broken:

$$4 \text{ mol C–H bonds} \times \frac{(413\text{ kJ})}{(1\text{ mol})} = 1652\text{ kJ}$$

$$4 \text{ mol F–F bonds} \times \frac{(155\text{ kJ})}{(1\text{ mol})} = 620\text{ kJ}$$

Bonds formed:

$$4 \text{ mol CF bonds} \times \frac{(x\text{ kJ})}{(1\text{ mol})} = 4x\text{ kJ}$$

(where x = the average energy of one mole of C–F bonds in CF_4, expressed in kJ)

$$4 \text{ mol H–F bonds} \times \frac{(567\text{ kJ})}{(1\text{ mol})} = 2268\text{ kJ}$$

$$\begin{aligned}\Delta H^\circ &= \Delta H^\circ(\text{bonds broken}) - \Delta H^\circ(\text{bonds formed})\\ &= (1652\text{ kJ} + 620\text{ kJ}) - (4x + 2268\text{ kJ})\\ &= 1652\text{ kJ} + 620\text{ kJ} - 4x - 2268\text{ kJ}\\ &= -1936\text{ kJ}\end{aligned}$$

EXERCISE \PageIndex2

1. Calculate ΔH° for the reactions given below. [Access bond energy tables via left-hand blue column Resources > Reference Tables > Reference Tables > Thermodynamic Tables > T3: Bond Energies]
   a. $CH_3CH_2OCH_3 + HI \longrightarrow CH_3CH_2OH + CH_3I$
   b. $CH_3Cl + NH_3 \longrightarrow CH_3NH_2 + HCl$

Answer

a. $CH_3CH_2OCH_3 + HI \longrightarrow CH_3CH_2OH + CH_3I$

Reactant bonds broken	D	Product bonds formed	D
$CH_3CH_2O–CH_3$	339 kJ/mol	$CH_3CH_2O–H$	438 kJ/mol
H–I	298 kJ/mol	$CH_3–I$	238 kJ/mol
	637 kJ/mol		676 kJ/mol

$$\begin{aligned}\Delta H^\circ &= D_{\text{bonds broken}} + D_{\text{bonds formed}}\\ &= 637\text{ kJ/mol} - 676\text{ kJ/mol}\\ &= -39\text{ kJ/mol}\end{aligned}$$

b. $CH_3Cl + NH_3 \longrightarrow CH_3NH_2 + HCl$

Reactant bonds broken	D	Product bonds formed	D
$CH_3–Cl$	356 kJ/mol	$CH_3–NH_2$	364 kJ/mol
$NH_2–H$	450 kJ/mol	H–Cl	432 kJ/mol
	806 kJ/mol		796 kJ/mol

$$\begin{aligned}\Delta H^\circ &= D_{\text{bonds broken}} + D_{\text{bonds formed}}\\ &= 806\text{ kJ/mol} - 796\text{ kJ/mol}\\ &= +10\text{ kJ/mol}\end{aligned}$$

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Prof. Paul G. Wenthold (Purdue University)

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6.9: DESCRIBING A REACTION - ENERGY DIAGRAMS AND TRANSITION STATES

Objectives

After completing this section, you should be able to

1. sketch the reaction energy diagram for a single-step reaction, given some indication of whether the reaction is fast or slow, exothermic or endothermic.
2. interpret the reaction energy diagram for a single-step process (e.g., use the diagram to decide whether the reaction is exothermic or endothermic).
3. suggest possible transition-state structures for simple one-step processes.
4. assess the likelihood of a reaction occurring at room temperature, given the value of the activation energy $\Delta G^{\ddagger}$.

KEY TERMS

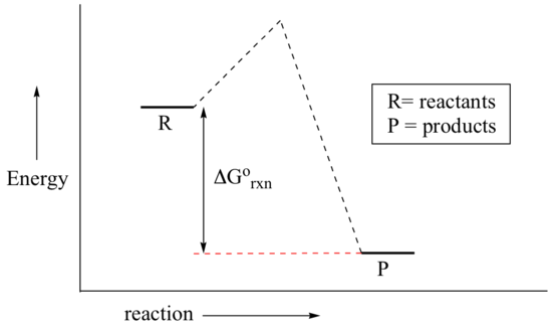
Make certain that you can define, and use in context, the key terms below.

- activation energy, $\Delta G^{\ddagger}$
- reaction energy diagram
- transition state

STUDY NOTES

You may have been taught to use the term “activated complex” rather than “transition state,” as the two are often used interchangeably. Similarly, the activation energy of a reaction is often represented by the symbol E_{act} or E_a.

You may recall from general chemistry that it is often convenient to describe chemical reactions with energy diagrams. In an energy diagram, the vertical axis represents the overall energy of the reactants, while the horizontal axis is the ‘reaction coordinate’, tracing from left to right the progress of the reaction from starting compounds to final products. The energy diagram for a typical one-step reaction might look like this:



Despite its apparent simplicity, this energy diagram conveys some very important ideas about the thermodynamics and kinetics of the reaction. Recall that when we talk about the **thermodynamics** of a reaction, we are concerned with the difference in energy between reactants and products, and whether a reaction is ‘downhill’ (exergonic, energy releasing) or ‘uphill (endergonic, energy absorbing). When we talk about **kinetics**, on the other hand, we are concerned with the *rate* of the reaction, regardless of whether it is uphill or downhill thermodynamically.

First, let’s review what this energy diagram tells us about the thermodynamics of the reaction illustrated by the energy diagram above. The energy level of the products is *lower* than that of the reactants. This tells us that the change in standard Gibbs Free Energy for the reaction (ΔG°_{rnx}) is negative. In other words, the reaction is exergonic, or ‘downhill’. Recall that the ΔG°_{rnx} term encapsulates both ΔH°_{rnx}, the change in enthalpy (heat) and ΔS°_{rnx} , the change in entropy (disorder):

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{6.9.1}$$

where T is the absolute temperature in Kelvin. For chemical processes where the entropy change is small (~0), the enthalpy change is essentially the same as the change in Gibbs Free Energy. Energy diagrams for these processes will often plot the enthalpy (H) instead of

Free Energy for simplicity.

The standard Gibbs Free Energy change for a reaction can be related to the reaction's equilibrium constant (\(K_{eq}_) by a simple equation:

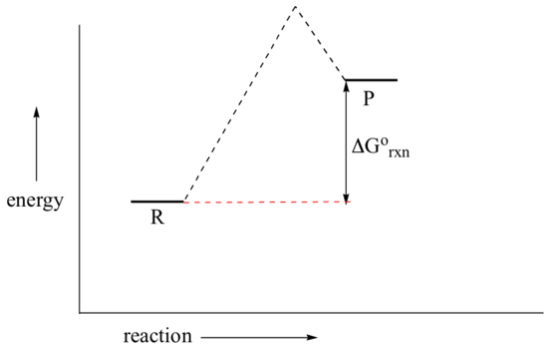
$$\Delta G^\circ = -RT \ln K_{eq} \tag{6.9.2}$$

where:

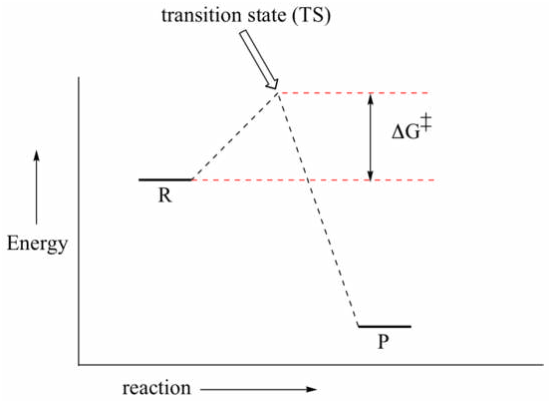
- K_{eq} = [product] / [reactant] at equilibrium
- R = 8.314 J×K^{-1}×mol^{-1} *or* 1.987 cal× K^{-1}×mol^{-1}
- T = temperature in Kelvin (K)

If you do the math, you see that a negative value for ΔG°_{rnx} (an exergonic reaction) corresponds - as it should by intuition - to K_{eq} being greater than 1, an equilibrium constant which favors product formation.

In a hypothetical endergonic (energy-absorbing) reaction the products would have a higher energy than reactants and thus ΔG°_{rnx} would be positive and K_{eq} would be less than 1, favoring reactants.

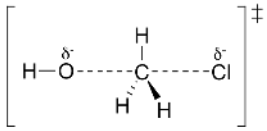


Now, let's move to kinetics. Look again at the energy diagram for exergonic reaction: although it is 'downhill' overall, it isn't a straight downhill run.



First, an 'energy barrier' must be overcome to get to the product side. The height of this energy barrier, you may recall, is called the '**activation energy**' ($\Delta G^\ddagger$). The activation energy is what determines the kinetics of a reaction: the higher the energy hill, the slower the reaction. At the very top of the energy barrier, the reaction is at its **transition state** (TS), which is the point at which the bonds are in the process of breaking and forming. The transition state is an '**activated complex**': a transient and dynamic state that, unlike more stable species, does not have any definable lifetime. It may help to imagine a transition state as being analogous to the exact moment that a baseball is struck by a bat. Transition states are drawn with dotted lines representing bonds that are in the process of breaking or forming, and the drawing is often enclosed by brackets. Here is a picture of a likely transition state for a substitution reaction between hydroxide and chloromethane:

$$CH_3Cl + HO^- \rightarrow CH_3OH + Cl^- \tag{6.9.3}$$



This reaction involves a collision between *two* molecules: for this reason, we say that it has **second order kinetics**. The **rate expression** for this type of reaction is:

$$\text{rate} = k[\text{reactant 1}][\text{reactant 2}]$$

. . . which tells us that the rate of the reaction depends on the **rate constant** k as well as on the concentration of *both* reactants. The rate constant can be determined experimentally by measuring the rate of the reaction with different starting reactant concentrations. The rate constant depends on the activation energy, of course, but also on temperature: a higher temperature means a higher k and a faster reaction, all else being equal. This should make intuitive sense: when there is more heat energy in the system, more of the reactant molecules are able to get over the energy barrier.

Here is one more interesting and useful expression. Consider a simple reaction where the reactants are A and B, and the product is AB (this is referred to as a **condensation reaction**, because two molecules are coming together, or condensing). If we know the rate constant k for the forward reaction and the rate constant $k_{reverse}$ for the reverse reaction (where AB splits apart into A and B), we can simply take the quotient to find our equilibrium constant $\boldsymbol{K_{eq}}$:

$$A + B \rightleftharpoons AB \qquad K_{eq} = \frac{[AB]}{[A]\,[B]} = \frac{k_{forward}}{k_{reverse}}$$

This too should make some intuitive sense; if the forward rate constant is higher than the reverse rate constant, equilibrium should lie towards products.

EXERCISE

? EXERCISE 6.9.1

Which reaction is faster, $\Delta G^{\ddagger}$ = +55 kJ/mol or $\Delta G^{\ddagger}$ = +75 kJ/mol?

Answer

The +55 kJ/mol reaction is the faster reaction

QUESTIONS

Q6.9.1

Which reaction is faster, $\Delta G^{\ddagger}$ = + 55 kJ/mol or $\Delta G^{\ddagger}$ = + 75 kJ/mol?

SOLUTIONS

S6.9.1

The + 55 kJ/mol reaction is the faster reaction.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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6.10: DESCRIBING A REACTION - INTERMEDIATES

Objectives

After completing this section, you should be able to

1. explain the difference between a transition state and an intermediate.
2. draw a reaction energy diagram for a given multistep process.
3. interpret the reaction energy diagram of a multistep process (e.g., determine which of the steps is rate-determining).

KEY TERMS

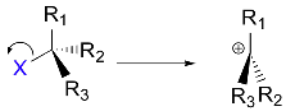
Make certain that you can define, and use in context, the key term below.

- reaction intermediate

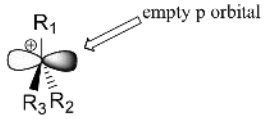
STUDY NOTES

Each step in a multistep reaction has its own activation energy. The overall activation energy is the difference in energy between the reactants and the transition state of the slowest (rate-determining) step. The rate-determining step, that is, the one that controls the overall rate of reaction, is the step with the highest activation energy.

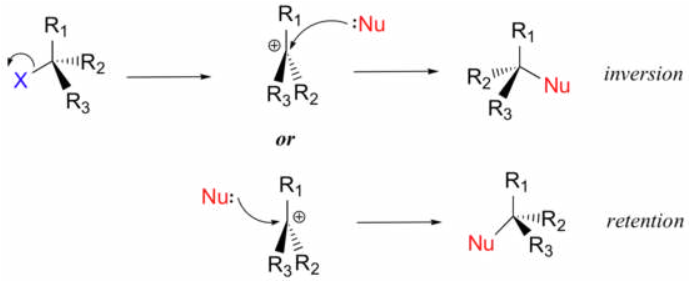
A second model for a nucleophilic substitution reaction is called the '**dissociative**', or '**S_N1**' mechanism: in this picture, the C-X bond breaks *first*, before the nucleophile approaches:



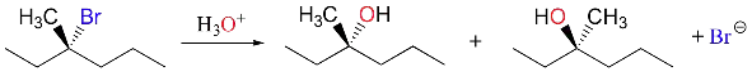
This results in the formation of a carbocation: because the central carbon has only three bonds, it bears a formal charge of +1. Recall that a carbocation should be pictured as sp^2 hybridized, with trigonal planar geometry. Perpendicular to the plane formed by the three sp^2 hybrid orbitals is an empty, unhybridized *p* orbital.



In the second step of this two-step reaction, the nucleophile attacks the empty, 'electron hungry' *p* orbital of the carbocation to form a new bond and return the carbon to tetrahedral geometry.



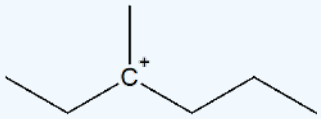
We saw that S_N2 reactions result specifically in inversion of stereochemistry at the electrophilic carbon center. What about the stereochemical outcome of S_N1 reactions? In the model S_N1 reaction shown above, the leaving group dissociates completely from the vicinity of the reaction before the nucleophile begins its attack. Because the leaving group is no longer in the picture, the nucleophile is free to attack from either side of the planar, sp^2-hybridized carbocation electrophile. This means that about half the time the product has the same stereochemical configuration as the starting material (retention of configuration), and about half the time the stereochemistry has been inverted. In other words, *racemization* has occurred at the carbon center. As an example, the tertiary alkyl bromide below would be expected to form a racemic mix of *R* and *S* alcohols after an S_N1 reaction with water as the incoming nucleophile.



EXERCISE 6.10.1

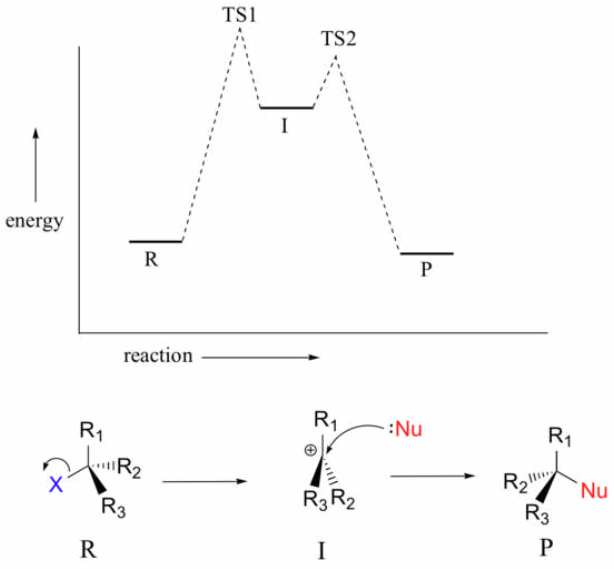
Draw the structure of the intermediate in the two-step nucleophilic substitution reaction above.

Answer



S_N1 intermediate (sp^2)

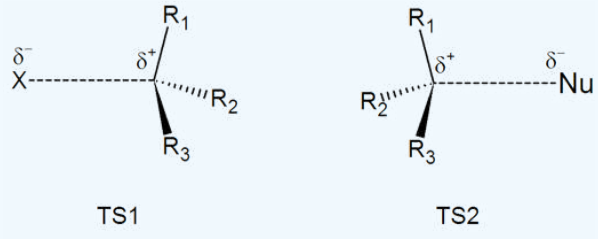
The S_N1 reaction we see an example of a reaction intermediate, a very important concept in the study of organic reaction mechanisms that was introduced earlier in the module on organic reactivity Recall that many important organic reactions do not occur in a single step; rather, they are the sum of two or more discreet bond-forming / bond-breaking steps, and involve transient intermediate species that go on to react very quickly. In the S_N1 reaction, the carbocation species is a reaction intermediate. A potential energy diagram for an S_N1 reaction shows that the carbocation intermediate can be visualized as a kind of valley in the path of the reaction, higher in energy than both the reactant and product but lower in energy than the two transition states.



EXERCISE 6.10.2

Draw structures representing TS1 and TS2 in the reaction above. Use the solid/dash wedge convention to show three dimensions.

Answer

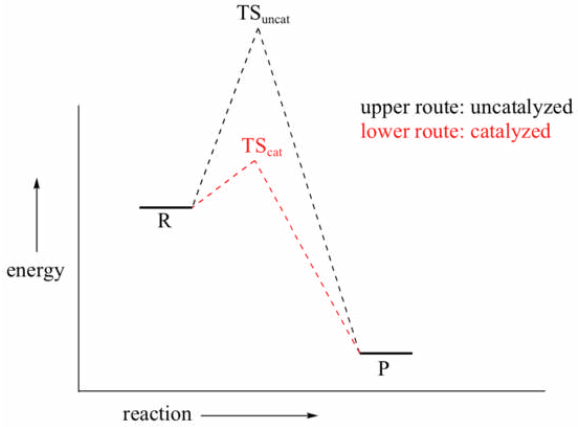


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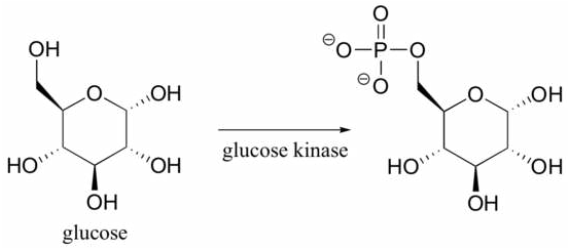
Recall that the first step of the reaction above, in which two charged species are formed from a neutral molecule, is much the slower of the two steps, and is therefore rate-determining. This is illustrated by the energy diagram, where the activation energy for the first step is higher than that for the second step. Also recall that an S_N1 reaction has *first order* kinetics, because the rate determining step involves one molecule splitting apart, not two molecules colliding

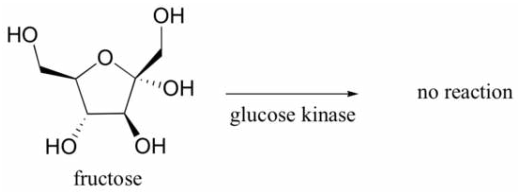
We come now to the subject of catalysis. Our hypothetical bowl of sugar (from section 6.2) is still stubbornly refusing to turn into carbon dioxide and water, even though by doing so it would reach a much more stable energy state. There are, in fact, two ways that we could speed up the process so as to avoid waiting several millennia for the reaction to reach completion. We could supply enough energy, in the form of heat from a flame, to push some of the sugar molecules over the high energy hill. Heat would be released from the resulting exothermic reaction, and this energy would push more molecules over their energy hills, and so on - the sugar would literally burn up.

A second way to make the reaction go faster is to employ a **catalyst**. You probably already know that a catalyst is an agent that causes a chemical reaction to go faster by lowering its activation energy.



How might you catalyze the conversion of sugar to carbon dioxide and water? It's not too hard – just eat the sugar, and let your digestive enzymes go to work catalyzing the many biochemical reactions involved in breaking it down. Enzymes are proteins, and are very effective catalysts. 'Very effective' in this context means very specific, and very fast. Most enzymes are very selective with respect to reactant molecules: they have evolved over millions of years to catalyze their specific reactions. An enzyme that attaches a phosphate group to glucose, for example, will not do anything at all to fructose (the details of these reactions are discussed in section 10.2B).





Glucose kinase is able to find and recognize glucose out of all of the other molecules floating around in the 'chemical soup' of a cell. A different enzyme, fructokinase, specifically catalyzes the phosphorylation of fructose.

We have already learned (section 3.9) that enzymes are very specific in terms of the stereochemistry of the reactions that they catalyze . Enzymes are also highly **regiospecific**, acting at only one specific part of a molecule. Notice that in the glucose kinase reaction above only one of the alcohol groups is phosphorylated.

Finally, enzymes are capable of truly amazing rate acceleration. Typical enzymes will speed up a reaction by anywhere from a million to a billion times, and the most efficient enzyme currently known to scientists is believed to accelerate its reaction by a factor of about 10^{17} (see

Chemical and Engineering News, March 13, 2000, p. 42 for an interesting discussion about this enzyme, orotidine monophosphate decarboxylase).

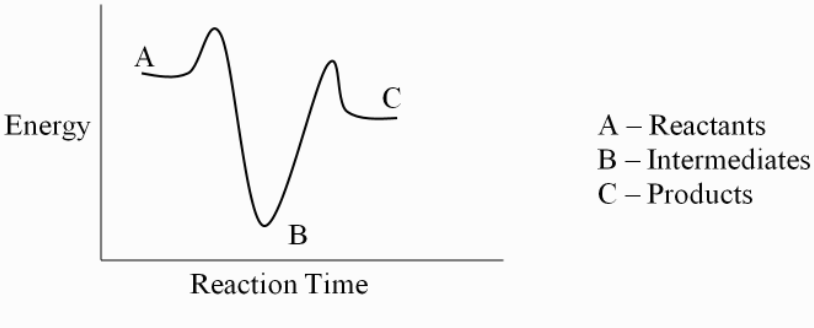
We will now begin an exploration of some of the basic ideas about how enzymes accomplish these amazing feats of catalysis, and these ideas will be revisited often throughout the rest of the text as we consider various examples of enzyme-catalyzed organic reactions. But in order to begin to understand how enzymes work, we will first need to learn (or review, as the case may be) a little bit about protein structure.

EXERCISE

? EXERCISE 6.10.3

Draw an energy diagram with a exergonic first step and an endergonic second step. Label the diagram.

Answer



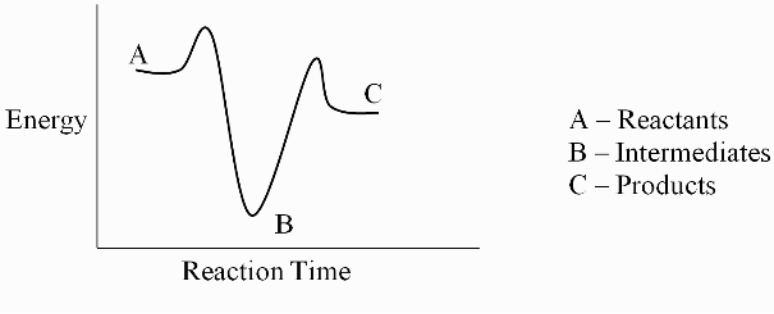
QUESTIONS

Q6.10.1

Draw an energy diagram with a exergonic first step and an endergonic second step. Label the diagram.

SOLUTIONS

S6.10.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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6.11: A COMPARISON BETWEEN BIOLOGICAL REACTIONS AND LABORATORY REACTIONS

Objectives

- No objectives have been identified for this section

KEY TERMS

Make certain that you can define, and use in context, the key term below.

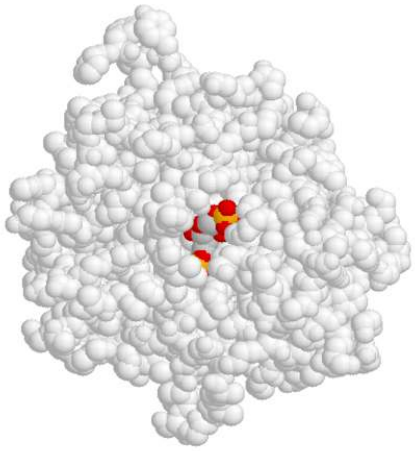
- enzyme

STUDY NOTES

This section is a brief (but perhaps interesting) overview of some of the key differences between reactions performed in the lab and those in living systems. At this point, do not concern yourself with memorizing large biological molecules and reactions.

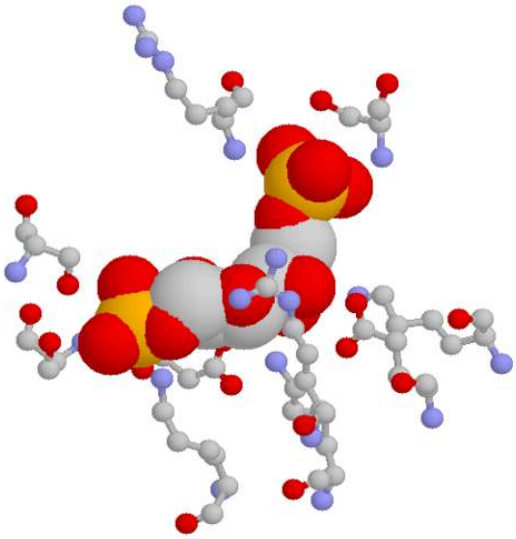
THE ACTIVE SITE

A critical element in the three-dimensional structure of any enzyme is the presence of an '**active site'**, which is a pocket, usually located in the interior of the protein, that serves as a docking point for the enzyme's **substrate**(s) ('substrate' is the term that biochemists use for a reactant molecule in an enzyme-catalyzed reaction). It is inside the active site pocket that enzymatic catalysis occurs. Shown below is an image of the glycolytic enzyme fructose-1,6-bisphosphate aldolase, with its substrate bound inside the active site pocket.

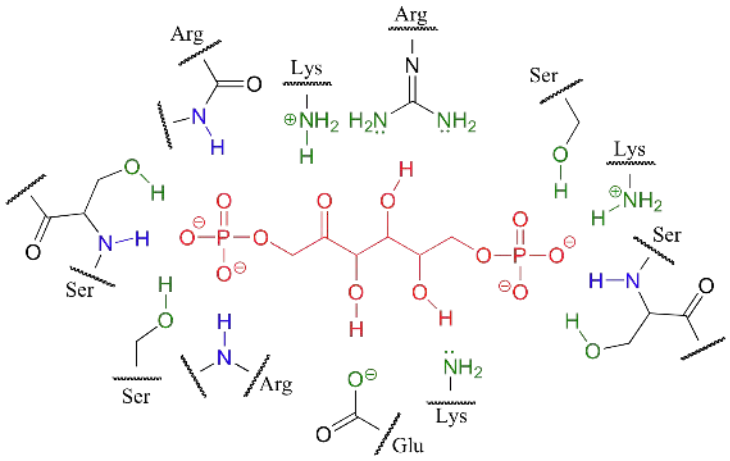


When the substrate binds to the active site, a large number of noncovalent interactions form with the amino acid residues that line the active site. The shape of the active site, and the enzyme-substrate interactions that form as a result of substrate binding, are *specific to the substrate-enzyme pair*: the active site has evolved to 'fit' one particular substrate and to catalyze one particular reaction. Other molecules do not fit in this active site nearly so well as fructose 1,6-bisphosphate.

Here are two close-up views of the same active site pocket, showing some of the specific hydrogen-bonding interactions between the substrate and active site amino acids. The first image below is a three-dimensional rendering directly from the crystal structure data. The substrate is shown in 'space-filling' style, while the active site amino acids are shown in the 'ball and stick' style. Hydrogens are not shown. The color scheme is grey for carbon, red for oxygen, blue for nitrogen, and orange for phosphorus.



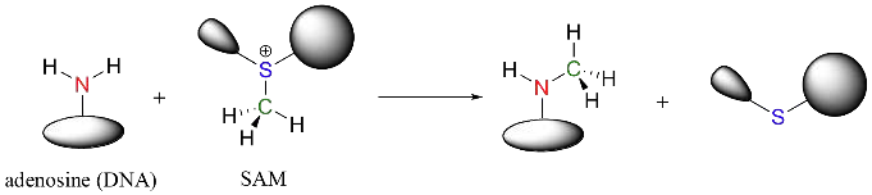
Below is a two-dimensional picture of the substrate (colored red) surrounded by hydrogen-bonding active site amino acids. Notice that both main chain and side chain groups contribute to hydrogen bonding: in this figure, main chain H-bonding groups are colored blue, and side chain H-bonding groups are colored green.



Looking at the last three images should give you some appreciation for the specific manner in which a substrate fits inside its active site.

TRANSITION STATE STABILIZATION

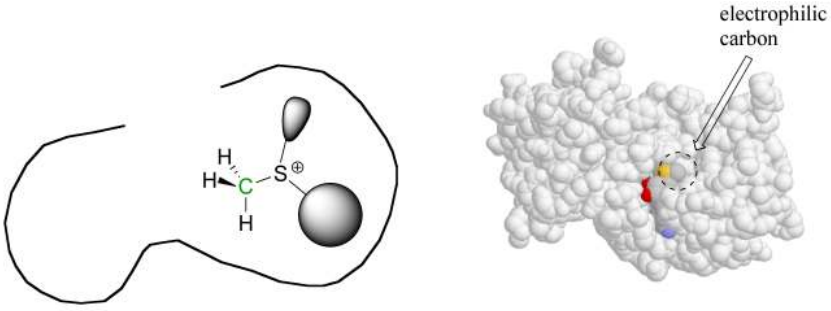
One of the most important ways that an enzyme catalyzes any given reaction is through entropy reduction: by bringing order to a disordered situation (remember that entropy is a component of Gibbs Free Energy, and thus a component of the activation energy). Let's turn again to our previous example (from section 6.1C) of a biochemical nucleophilic substitution reaction, the methylation of adenosine in DNA. The reaction is shown below with non-reactive sections of the molecules depicted by variously shaped 'bubbles' for the sake of simplicity.



In order for this reaction to occur, the two substrates (reactants) must come into contact in precisely the right way. If they are both floating around free in solution, the likelihood of this occurring is very small – the entropy of the system is simply too high. In other words, this reaction takes place *very* slowly without the help of a catalyst.

Here's where the enzyme's active site pocket comes into play. It is lined with various functional groups from the amino acid main and side chains, and has a very specific three-dimensional architecture that has evolved to bind to both of the substrates. If the SAM molecule, for

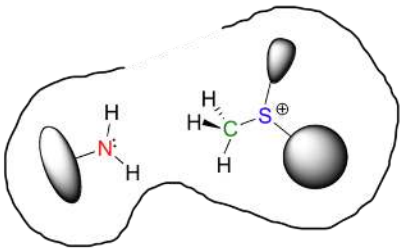
example, diffuses into the active site, it can replace its (favorable) interactions with the surrounding water molecules with (even more favorable) new interactions with the functional groups lining the active site.



SAM bound in active site

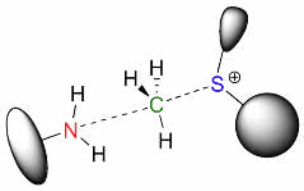
In a sense, SAM is moving from one solvent (water) to another 'solvent' (the active site), where many new energetically favorable interactions are possible. Remember: these new contacts between SAM and the active site groups are *highly specific* to SAM and SAM alone – no other molecule can 'fit' so well in this precise active site environment, and thus no other molecule will be likely to give up its contacts to water and bind to the active site.

The second substrate also has a specific spot reserved in the active site. (Because in this case the second substrate is a small segment of a long DNA molecule, the DNA-binding region of the active site is more of a 'groove' than a 'pocket').



So now we have both substrates bound in the active site. But they are not just bound in any random orientation – they are specifically positioned relative to one another so that the nucleophilic nitrogen is held very close to the electrophilic carbon, with a free path of attack. What used to be a very disordered situation – two reactants diffusing freely in solution – is now a very highly ordered situation, with everything set up for the reaction to proceed. This is what is meant by entropy reduction: the entropic component of the energy barrier has been lowered.

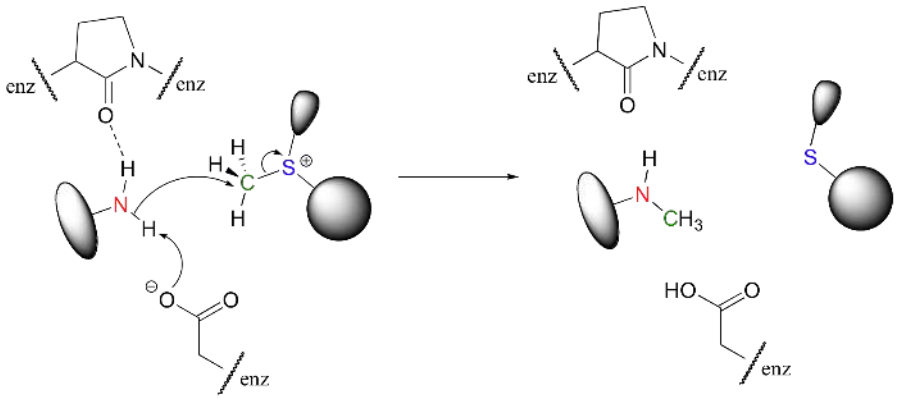
Looking a bit deeper, though, it is not really the noncovalent interaction between enzyme and *substrate* that are responsible for catalysis. Remember: all catalysts, enzymes included, accelerate reactions by lowering the energy of the *transition state*. With this in mind, it should make sense that the primary job of an enzyme is to maximize favorable interactions with the transition state, *not* with the starting substrates. This does not imply that enzyme-substrate interactions are not strong, rather that enzyme-TS interactions are far *stronger*, often by several orders of magnitude. Think about it this way: if an enzyme were to bind to (and stabilize) its substrate(s) more tightly than it bound to (and stabilized) the transition state, it would actually *slow down* the reaction, because it would be *increasing* the energy difference between starting state and transition state. ***The enzyme has evolved to maximize favorable noncovalent interactions to the transition state***: in our example, this is the state in which the nucleophilic nitrogen is already beginning to attack the electrophilic carbon, and the carbon-sulfur bond has already begun to break.



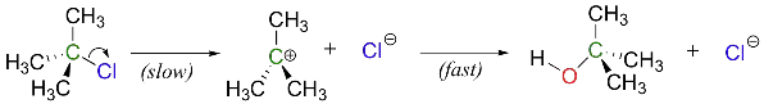
enzyme binds best to the
transition state

In many enzymatic reactions, certain active site amino acid residues contribute to catalysis by *increasing the reactivity of the substrates*. Often, the catalytic role is that of acid and/or base. In our DNA methylation example, the nucleophilic nitrogen is deprotonated by a nearby

aspartate side chain as it begins its nucleophilic attack on the methyl group of SAM. We will study nucleophilicity in greater detail in chapter 8, but it should make intuitive sense that deprotonating the amine increases the electron density of the nitrogen, making it *more nucleophilic*. Notice also in the figure below that the main chain carbonyl of an active site proline forms a hydrogen bond with the amine, which also has the effect of increasing the nitrogen's electron density and thus its nucleophilicity (*Nucleic Acids Res.* **2000**, *28*, 3950).

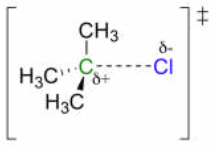


How does our picture of enzyme catalysis apply to multi-step reaction mechanisms? Although the two-step nucleophilic substitution reaction between *tert*-butyl chloride and hydroxide (section 6.1C) is not a biologically relevant process, let's pretend just for the sake of illustration that there is a hypothetical enzyme that catalyzes this reaction.



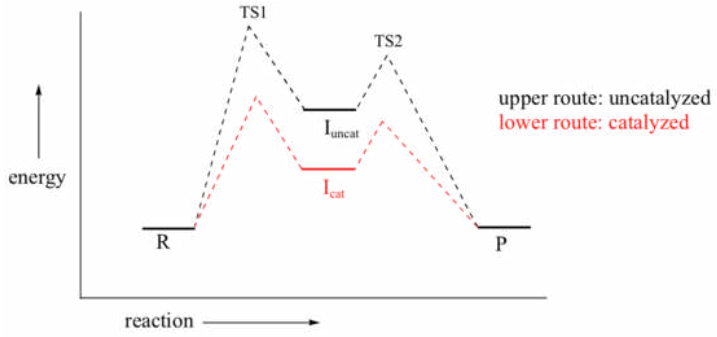
The same basic principles apply here: the enzyme binds best to the transition state. But therein lies the problem: there are two transition states! To which TS does the enzyme maximize its contacts?

Recall that the first step – the loss of the chloride leaving group to form the carbocation intermediate – is the slower, rate-limiting step. It is this step that our hypothetical enzyme needs to accelerate if it wants to accelerate the overall reaction, and it is thus the energy of TS1 that needs to be lowered.



enzyme maximizes interactions with TS1

By Hammond's postulate, we also know that the intermediate I is a close approximation of TS1. So the enzyme, by stabilizing the intermediate, will also stabilize TS1 (as well as TS2) and thereby accelerate the reaction.



If you read scientific papers about enzyme mechanisms, you will often see researchers discussing how an enzyme stabilizes a reaction intermediate. By virtue of Hammond's postulate, they are, at the same time, talking about how the enzyme lowers the energy of the transition state.

An additional note: although we have in this section been referring to SAM as a 'substrate' of the DNA methylation reaction, it is also often referred to as a **coenzyme**, or **cofactor**. These terms are used to describe small (relative to protein and DNA) biological organic molecules

that bind specifically in the active site of an enzyme and help the enzyme to do its job. In the case of SAM, the job is methyl group donation. In addition to SAM, we will see many other examples of coenzymes in the coming chapters, a number of which - like ATP (adenosine triphosphate), coenzyme A, thiamine, and flavin - you have probably heard of before. The full structures of some common coenzymes are shown in table 6 in the tables section.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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6.S: AN OVERVIEW OF ORGANIC REACTIONS (SUMMARY)

CONCEPTS & VOCABULARY

6.1: Kinds of Organic Reactions

- **Addition** reactions increase the number of sigma bonds in a molecule.
- **Elimination** reactions reduce the number of sigma bonds in a molecule.
- **Substitution** reactions incorporate replacement of an atom or group with another.
- **Rearrangement** reactions cause a molecule to be converted to a constitutional isomer without gaining or losing any atoms.

6.2: How Organic Reactions Occur: Mechanisms

- A reaction **mechanism** describes movement of electrons by using curved arrows to show bonds that are breaking and forming.
- **Homolysis** occurs when a bond breaks with each atom keeping one electron.
- **Heterolysis** occurs when a bond breaks and both electrons remain with one of the atoms.
- Some reactions occur in more than one step with a **reactive intermediate** formed briefly on the way to the new product.
- **Reactive intermediates** can be charged species such as carbocations and carbanions or uncharged species such as **radicals**.
- In organic chemistry Lewis acids are more often referred to as **electrophiles**, having an affinity for an electron pair.
- In organic chemistry Lewis bases are more often referred to as **nucleophiles**, having an electron pair that is available to bond to an **electrophile**.
- **Ionic** reactions involve charged species.
- **Polar** reactions involve bonds with unequally shared electrons.

6.3: Radical Reactions

- **Radical chain reactions** have three distinct phases: initiation, propagation and termination.
  - Initiation causes radicals to be created from non-radical species.
  - During the Propagation phase, radicals react with stable molecules to form new radicals.
  - Termination occurs when two radicals react together to form a stable molecule.

6.4: Polar Reactions

- Carbon when bonded to a halogen, oxygen, nitrogen, sulfur, or metal has a partial positive charge. This allows these carbons to react with many **nucleophiles**.
- For carbonyl groups bond polarity is reinforced by resonance making the carbon even more positive than in other molecules. This makes carbonyl groups prone to addition and substitution reactions with **nucleophiles**.
- **Nucleophiles** have electron rich atoms that are able to donate a pair of electrons.
- In nucleophilic substitution reactions, the **electrophile** is typically carbon bonded to a more electronegative atom.

6.5: An Example of a Polar Reaction: Addition of HBr to Ethylene

- Alkene addition reaction with HBr occurs through the pi bond reacting as a nucleophile and abstracting a proton from the acid. This creates a carbocation intermediate which reacts with the bromide ion to form the final product.
- Reaction rates for this alkene addition reaction increase with larger halogens and more substituted alkenes.
- Markovnikov's Rule states that addition reactions of unsymmetrical alkenes yield the more substituted product.

6.6: Using Curved Arrows in Polar Reaction Mechanisms

- Curved arrows in mechanism drawings always represent electrons moving, starting at either a bond or lone pair of electrons.
- Electrons flow from electron rich to electron poor.

6.7: Describing a Reaction: Equilibria, Rates, and Energy Changes

- **Exergonic reactions** have a negative free energy meaning they are thermodynamically favorable and give off energy.
- **Endergonic reactions** have a positive free energy and require energy from the surroundings to occur.

6.8: Describing a Reaction: Bond Dissociation Energies

- **Bond dissociation energy** for a molecule is the difference in enthalpy of formation (**homolytic**) for the products and reactants.
- **Bond dissociation energies** are independent of path of reaction, so they do not give direct information on mechanisms. However, they can be used to evaluate the results of individual steps of a mechanism.
- **Bond dissociation energies** show that sigma bonds formed with sp hybridized carbon are stronger than sp^2 which are stronger than bonds formed with sp^3 carbons.

- **Bond dissociation energies** show that carbon-hydrogen bonds on primary carbons are stronger than secondary, which are stronger than tertiary.

6.9: Describing a Reaction: Energy Diagrams and Transition States

- **Reaction coordinate** diagrams are a special type of energy diagram that has the reaction coordinate (or reaction progress) on the x-axis.
- **Thermodynamics** of a reaction is conveyed on a reaction coordinate diagram by the difference in energy between the reactants and products.
- **Activation energy** is the energy barrier to a reaction occurring.
- A **transition state** is the highest energy point during the process of bonds forming and breaking in a reaction step.
- **Kinetics** of a reaction is conveyed on a **reaction coordinate** diagram by the difference in energy between the reactants and transition state.
- A r**ate expression** relates rate to the **rate constant** and concentration of reactants.

6.10: Describing a Reaction: Intermediates

- A **reaction intermediate** is a short-lived species that goes on to react in a subsequent reaction step.
- **Reaction intermediates** appear as a local minimum (or valley) on a reaction coordinate diagram.
- **Catalysts** cause reaction rates to increase by lowing activation energy.

6.11: A Comparison between Biological Reactions and Laboratory Reactions

- An enzyme **active site** is the location where the enzyme interacts with its **substrate** and where **catalysis** occurs.
- **Substrates** are reactant molecules in enzymatic reactions.

SKILLS TO MASTER

- Skill 6.1 Identify organic reactions by type (addition, elimination, substitution, rearrangement).
- SKil 6.2 Draw homolytic and heterolytic bond breaking as part of reaction mechanisms.
- Skill 6.3 Identify radical and ionic reactions.
- Skill 6.4 Identify and write out steps in a typical radical substitution reaction (initiation, propagation, termination).
- Skill 6.5 Identify polarity of bonds in organic molecules.
- Skill 6.6 Use curved arrows to indicate movement of electrons in resonance and reaction mechanisms.
- Skill 6.7 Predict whether a chemical species will act as an electrophile or nucleophile.
- Skill 6.8 Write an equilibrium expression for a reaction.
- Skill 6.9 Determine the direction of a reaction based on the equilibrium constant.
- Skill 6.10 Explain how rate and equilibrium are related to $\Delta G°$ and K_{eq}.
- Skill 6.11 Calculate bond dissociation energy given enthalpies of formation for reactants and products.
- Skill 6.12 Describe order of bond strength based on bond dissociation energy.
- Skill 6.13 Explain activation energy, kinetics, thermodynamics and transition states based on energy diagrams (reaction coordinate diagrams).
- Skill 6.14 Predict possible transition state structures for single reaction steps.
- Skill 6.15 Differentiate between transition states and intermediates.
- Skill 6.16 Draw a reaction coordinate diagram for a given multi-step process.
- Skill 6.17 Interpret a reaction coordinate diagram for a multi-step process.
- Skill 6.18 Briefly explain how enzymes catalyze reactions.

MEMORIZATION TASKS

MT 6.1 Memorize that arrows in reaction mechanisms always define movement of electrons.

MT 6.2 Memorize the relative electronegativities of common atoms (necessary for determining polarity of bonds).

MT 6.3 Memorize the equations that relate equilibrium, free energy, enthalpy and entropy.

$\Delta G^o = -RT\ln K$

$\Delta G^o = \Delta H^o - T\Delta S^o$

CONTRIBUTORS

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CHAPTER OVERVIEW

7: ALKENES- STRUCTURE AND REACTIVITY

LEARNING OBJECTIVES

After you have completed Chapter 7, you should be able to

1. fulfill all of the detailed objectives listed under each individual section.
2. describe the importance of alkenes to the chemical industry.
3. use the concept of “degree of unsaturation” in determining chemical structures.
4. describe the electronic structure and geometry of alkenes.
5. describe the factors that influence alkene stability, and determine the relative stability of a number of given alkenes.
6. write the IUPAC name of a given alkene, and draw the structure of any alkene, given its IUPAC name.
7. determine whether a given alkene has an *E* configuration or a *Z* configuration.
8. explain why alkenes are more reactive than alkanes.
9. describe the reaction between an alkene and a hydrogen halide, and explain why one product is formed rather than another. Base your explanation on the concepts of carbocation stability and the Hammond postulate.
10. define, and use in context, the key terms introduced in this chapter.

This, the first of two chapters devoted to the chemistry of alkenes, describes how certain alkenes occur naturally, then shows the industrial importance of ethylene and propylene (the simplest members of the alkene family). The electronic structure of alkenes is reviewed, and their nomenclature discussed in detail. After dealing with the question of cis-trans isomerism in alkenes, Chapter 7 introduces the reactivity of the carbon-carbon double bond. The chapter then focuses on one specific reaction—the addition of hydrogen halides to alkenes—to raise a number of important concepts, including carbocation stability and the Hammond postulate.

7.0: Introduction
7.1: Industrial Preparation and Use of Alkenes
7.2: Calculating Degree of Unsaturation
7.3: Naming Alkenes
7.4: Cis-Trans Isomerism in Alkenes
7.5: Sequence Rules - The E,Z Designation
7.6: Stability of Alkenes
7.7: Electrophilic Addition Reactions of Alkenes
7.8: Orientation of Electrophilic Additions - Markovnikov's Rule
7.9: Carbocation Structure and Stability
7.10: The Hammond Postulate
7.11: Evidence for the Mechanism of Electrophilic Additions- Carbocation Rearrangements
7.S: Alkenes - Structure and Reactivity (Summary)

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7.0: INTRODUCTION

Objective

After completing this section, you should be able to give an example of a naturally occurring compound that contains at least one double bond.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- olefin

STUDY NOTES

Alkenes are a class of hydrocarbons (i.e., containing only carbon and hydrogen). They are unsaturated compounds with at least one carbon-to-carbon double bond. The double bond makes Alkenes more reactive than alkanes. Olefin is another term used to describe alkenes.

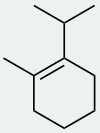
The graphic (structure 7-0) shows three alkenes. The more complex alkene is commonly known as 1-methene, but its full proper IUPAC name is 1-methyl-2-(1-methylethyl)-cyclohexene.



ethene



1,3-cyclopentadiene



1-menthene
(peppermint fragrance)

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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7.1: INDUSTRIAL PREPARATION AND USE OF ALKENES

OBJECTIVES

After completing this section, you should be able to

1. discuss the industrial importance of ethylene (ethene) and propylene (propene).
2. describe, briefly, the industrial process known as thermal cracking.

STUDY NOTES

Among the most important and most abundant organic chemicals produced worldwide are the two simple alkenes, ethylene and propylene. They are used as the starting materials to synthesize numerous valuable compounds.

Produced from ethylene (ethene)

Chemical	Uses
ethanol	solvent; constituent of cleaning preparations; in synthesis of esters
acetaldehyde	slug killer, in the form of methaldehyde $(CH_3CHO)_4$
acetic acid	manufacture of vinyl acetate polymers, ethyl acetate solvent and cellulose acetate polymers
ethylene oxide	“cellosolves” (industrial solvents)
ethylene glycol	anti-freeze; production of DacronOR
ethylene dichloride	solvent; production of vinyl chloride
vinyl chloride	manufacture of poly (vinyl chloride)—PVC
vinyl acetate	manufacture of poly (vinyl acetate) used in paint emulsions, plywood adhesives and textiles
polyethylene	“plastic” bags; toys; packaging

Produced from propylene (propene)

Chemical	Uses
isopropyl alcohol	rubbing alcohol; cosmetics; synthesis of acetone
propylene oxide	manufacture of polyurethanes; polyesters
cumene	industrial preparation of phenol and acetone
polypropylene	molded articles (e.g., kitchenware); fibres for indoor-outdoor carpeting

CATALYTIC CRACKING TO PRODUCE PROPYLENE

Cracking is the name given to breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst (thermal cracking), or at lower temperatures and pressures in the presence of a catalyst (catalytic cracking).

In the case of catalytic cracking, the source of the large hydrocarbon molecules is usually the gas oil fraction of crude oil (petroleum). Useful "straight run" products, such as gasoline, kerosene, diesel, butane and propane are separated from the crude oil mixture in the Atmospheric Distillation Unit (at atmospheric pressure). These "straight run" products only account for 30-50% of the crude oil, depending on its origin, the balance is in the form of atmospheric residue, typically boiling above about ~350°C/650°F. Atmospheric residue is typically routed to the Vacuum Distillation unit for separation into gas oil (usually termed vacuum gas oil, or VGO for short) and vacuum residue; via distillation at reduced pressure. VGO is the principle feed used in the Fluid Catalytic Cracking (FCC) process, though many FCC units also co-feed some portion of lower cost atmospheric residue too, typically 10-20% depending operational constraints.

The FCC unit employs a sophisticated powdered catalyst to lower the activation energy of cracking and thereby drive the cracking process. The particle size and density of the powder are set such that the catalyst powder is fluidizable - the powder behaves like a fluid when aerated. This allows the catalyst to form fluidized beds

and be transported between the FCC reactor and regenerator with ease. FCC catalyst are considered to have two catalytically active parts: (a) the "zeolite", and (b) what is termed the "matrix".

The zeolite (referred to as Zeolite-Y) is a rare-earth stabilized synthetic form of a rare naturally occurring aluminosilicate mineral called faujasite. Ultrastabilization of Zeolite-Y (USY) further improves its hydrothermal stability; the final rare earth / ultrastable form of the zeolite is denoted RE-USY for short. RE-USY is a solid acid, with acidity equivalent to ~90% sulphuric acid. It is also highly crystalline and has a very regular micropore structure with mean pore mouth diameters in the range of diesel molecules - hence it behaves as a molecular sieve. Acid sites within the crystalline micropores very selectively crack diesel range molecules to gasoline and some light olefins (propene and butenes).

However, VGO consists of molecules that are bigger than diesel, too large to access the zeolite micropores. The catalyst "matrix" is designed to include a high surface area mesoporous alumina which has acid sites situated in larger pores that are able to pre-crack VGO molecules into the diesel range - in order to feed the zeolite so to speak. Optimization of FCC yields between gasoline and diesel can be achieved by adjusting the catalyst zeolite-to-matrix ratio. The main role of the FCC unit has until recently been the production of gasoline.

Propene is a very important product for polypropylene production and today 30-35% of the worlds propene monomer is made in the FCC process. Use of a co-catalysts called an "FCC Additive" is required to shift product selectivity towards propene in the FCC. FCC Additives are specially designed catalysts in separate particles that look much like the main FCC catalyst particles and can be added in any chosen proportion to achieve the desired selectivity shifts. Typically such Additives are so effective that they are only required as a minor part of the overall catalyst powder mixture in conventional FCC units (e.g. up to ~25%). An FCC Additive designed to maximize propene is very similar in concept to the main FCC catalyst above, its main active component is also a zeolite. However, in this case the zeolite has smaller crystalline micropores that will selectively admit gasoline range molecules for selectve cracking to propene and mixed butenes. This zeolite is usually called ZSM-5 for historical reasons (though more strictly it's scientific name is MFI - "Mobil Five"). Use of ZSM-5 Additives allows the FCC to double it's propene yield.

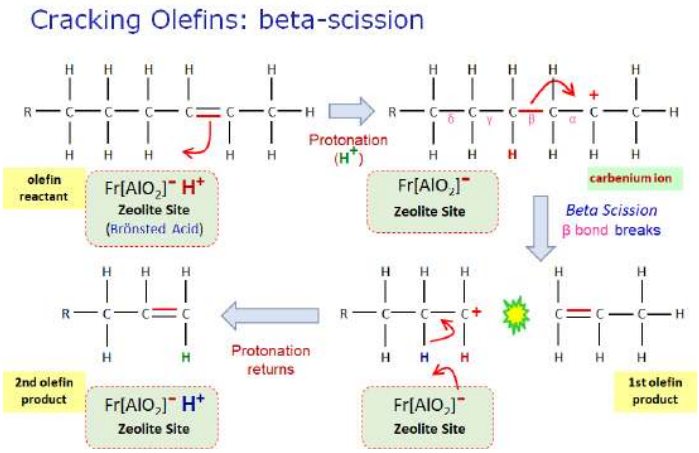
Ethene is not a catalytic product in the FCC, a small amount is formed via thermal cracking reactions which are considered undesirable in the FCC because they are non-selective and limit operations by increasing coke and light gas make. Every effort is made in the design and operation of an FCC unit to minimize thermal cracking because coke drives up the regenerator temperature and increases its air demand, while light gases are more difficult to compress in the product recovery section and limit product recovery. Ethene is a very minor product in the FCC that is not generally economically worth recovering.

The FCC process itself consists three main sections, the: (a) riser (reactor), (b) disengager, and (c) regenerator. Pre-heated liquid feed (typically at ~200°C/400°F) is injected into the lower section of the riser through feed nozzles that atomize the feed into tiny droplets (~50 micron droplets). The droplets contact hot freshly regenerated catalyst (typically at ~735°C/1350°F) where they vaporize and quench the mix zone temperature (typically to about ~570°C/1060°F). Volumetric expansion carries catalyst particles and feed vapours up the riser together, feed vapours diffuse into the catalyst (and FCC Additive) pores and crack. Cracking is endothermic, so the temperature continues to decrease until it reaches the top of the riser (typically at ~535°C/1000°F). Catalyst and product vapours are then disengaged using cyclones, the vapours leave the disengager to go to product separation and recovery section. A small amount of coke (~1 wt%) builds up on the catalyst during the reaction cycle, the disengaged catalyst is passed to the regenerator to burn off the coke and prepare the catalyst for the next cycle. The heat produced via combustion of coke on catalyst heats up the catalyst. The FCC is operated in heat-balance, where the heat of coke combustion provides the energy required to vaporize and crack the feed.

This is an example of heterogeneous catalysis - the catalyst is in a different phase (solid) from the reactants (vapours).

There are a complex combination of a number of catalyzed reactions taking place in the FCC unit. The initial step is formation of carbenium ions, either via protonation at Bronsted acid sites, or hydride abstraction at Lewis acid sites on the solid catalyst . Once formed carbenium ions undergo a number of reactions in parallel: beta-scission (cracking), isomerization (skeletal rearrangements), hydrogen transfer, and others. The relative rates of these reactions are optimized by adjusting operating conditions and catalyst design.

Bellow is a schematic of the beta-scission mechanism for an olefin (alkene): note the key steps: (1) initiation: carbenium ion formation via protonation from a Bronsted acid site within a zeolite, (2) propagation: beta-bond cleavage - the negatively charged electrons in the beta bond are attracted to the positive charge on the cabenium ion, (3) termination: the carbenium ion intermediate returns a proton to the zeolite site to complete the catalytic cycle.



Propene is an important material for making plastics and producing other organic chemicals, polypropylene is made by polymerization of propene monomers into long polymeric chains.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
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7.2: CALCULATING DEGREE OF UNSATURATION

OBJECTIVES

After completing this section, you should be able to

1. determine the degree of unsaturation of an organic compound, given its molecular formula, and hence determine the number of double bonds, triple bonds and rings present in the compound.
2. draw all the possible isomers that correspond to a given molecular formula containing only carbon (up to a maximum of six atoms) and hydrogen.
3. draw a specified number of isomers that correspond to a given molecular formula containing carbon, hydrogen, and possibly other elements, such as oxygen, nitrogen and the halogens.

KEY TERMS

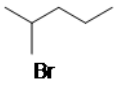
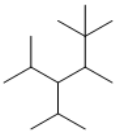
Make certain that you can define, and use in context, the key terms below.

- degree of unsaturation
- saturated
- unsaturated

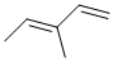
There are many ways one can go about determining the structure of an unknown organic molecule. Although, nuclear magnetic resonance (NMR) and infrared radiation (IR) are the primary ways of determining molecular structures, calculating the degrees of unsaturation is useful information since knowing the degrees of unsaturation make it easier for one to figure out the molecular structure; it helps one double-check the number of π bonds and/or cyclic rings.

SATURATED AND UNSATURATED MOLECULES

In the lab, saturation may be thought of as the point when a solution cannot dissolve anymore of a substance added to it. In terms of degrees of unsaturation, a molecule only containing single bonds with no rings is considered saturated.

$CH_3CH_2CH_3$   1-methyoxypentane

Unlike saturated molecules, unsaturated molecules contain double bond(s), triple bond(s) and/or ring(s).

$CH_3CH{=}CHCH_3$    3-chloro-5-octyne

CALCULATING THE DEGREE OF UNSATURATION (DOU)

If the molecular formula is given, plug in the numbers into this formula:

$$DoU = \frac{2C + 2 + N - X - H}{2} \tag{7.2.1}$$

- C is the number of carbons
- N is the number of nitrogens
- X is the number of halogens (F, Cl, Br, I)
- H is the number of hydrogens

As stated before, a saturated molecule contains only single bonds and no rings. Another way of interpreting this is that a saturated molecule has the maximum number of hydrogen atoms possible to be an acyclic alkane. Thus, the number of hydrogens can be represented by 2C+2, which is the general molecular representation of an alkane. As an example, for the molecular formula C_3H_4 the number of actual hydrogens needed for the compound to be saturated is 8 *[2C+2=(2x3)+2=8]*. The compound needs 4 more hydrogens in order to be fully saturated *(expected number of hydrogens-observed number of hydrogens=8-4=4)*. Degrees of unsaturation is equal to 2, or half the number of hydrogens the molecule needs to be classified as saturated. Hence, the DoB formula divides by 2. The formula subtracts the number of X's because a halogen (X) replaces a hydrogen in a compound. For instance, in chloroethane, C_2H_5Cl, there is one less hydrogen compared to ethane, C_2H_6.

For a compound to be saturated, there is one more hydrogen in a molecule when nitrogen is present. Therefore, we add the number of nitrogens (N). This can be seen with C_3H_9N compared to C_3H_8. Oxygen and sulfur are not included in the formula because saturation is unaffected by these elements. As seen in alcohols, the same number of hydrogens in ethanol, C_2H_5OH, matches the number of hydrogens in ethane, C_2H_6.

The following chart illustrates the possible combinations of the number of double bond(s), triple bond(s), and/or ring(s) for a given degree of unsaturation. Each row corresponds to a different combination.

- One degree of unsaturation is equivalent to 1 ring or 1 double bond (1 π bond).
- Two degrees of unsaturation is equivalent to 2 double bonds, 1 ring and 1 double bond, 2 rings, or 1 triple bond (2 π bonds).

DoU	Possible combinations of rings/ bonds		
	# of rings	# of double bonds	# of triple bonds
1	1	0	0
	0	1	0
2	2	0	0
	0	2	0
	0	0	1
	1	1	0

Remember, the degrees of unsaturation only gives the sum of double bonds, triple bonds and/or rings. For instance, a degree of unsaturation of 3 can contain 3 rings, 2 rings+1 double bond, 1 ring+2 double bonds, 1 ring+1 triple bond, 1 double bond+1 triple bond, *or* 3 double bonds.

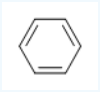
EXAMPLE 7.2.1: BENZENE

What is the Degree of Unsaturation for Benzene?

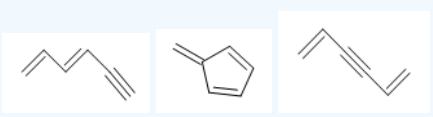
Solution

The molecular formula for benzene is C_6H_6. Thus,

DoU= 4, where C=6, N=0,X=0, and H=6. 1 DoB can equal 1 ring or 1 double bond. This corresponds to benzene containing 1 ring and 3 double bonds.



However, when given the molecular formula C_6H_6, benzene is only one of many possible structures (isomers). The following structures all have DoB of 4 and have the same molecular formula as benzene.



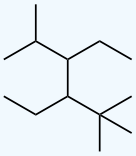
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1. Vollhardt, K. P.C. & Shore, N. (2007). *Organic Chemistry* (5thEd.). New York: W. H. Freeman. (473-474)
2. Shore, N. (2007). *Study Guide and Solutions Manual for Organic Chemistry* (5th Ed.). New York: W.H. Freeman. (201)

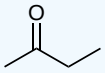
EXERCISES

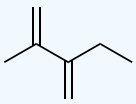
EXERCISE 7.2.1

How many degrees of unsaturation do the following compounds have?

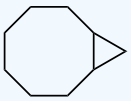
a) 

b) $CH_3CH_2CH{=}CHCF_3$

c) 

d) 

e) 3-chloro-5-octyne

f) 

Answer

a) 0

b) 1

c) 1

d) 2

e) 2

f) 2

EXERCISE 7.2.2

Determine whether the following molecules are saturated or unsaturated.

Answer

a) **unsaturated** (*Even though the rings only contain single bonds, rings are considered unsaturated.)*

b) **unsaturated**

c) **saturated**

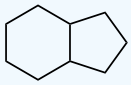
d) **unsaturated**

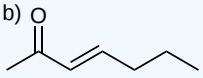
e) **unsaturated**

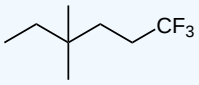
f) **saturated**

EXERCISE 7.2.3

Determine the degrees of unsaturation for each of the following compounds.

a) 

b) 

c) 

d) $C_{10}H_6N_4$

e) $C_5H_{10}O$

f) $C_6H_{12}F_2$

Answer

If the molecular structure is given, the easiest way to solve is to count the number of double bonds, triple bonds and/or rings. However, you can also determine the molecular formula and solve for the degrees of unsaturation by using the formula.

a) **2** (2 rings)

b) **2** *(one double bond and the double bond from the carbonyl)*

c) **0** (no double bonds or rings)

d) **10 (2(10) + 2 + 4 - 0 - 6)/2 = 10**

e) **1 (2(5) + 2 + 0 - 0 - 10)/2 = 1**

f) **0 (2(6) + 2 + 0 - 2 - 12)/2 = 0**

? EXERCISE 7.2.4

Calculate the degrees of unsaturation for the following molecular formulas:

a) C_9H_{20} b) C_7H_8 c) C_5H_7Cl d) $C_9H_9NO_4$

Answer

Use the formula to solve (O not involved in the formula)

(a.) **0 (2(9) + 2 - 20)/2 = 0**

(b.) **4 (2(7) + 2 - 8)/2 = 4**

(c.) **2 (2(5) + 2 - 1 -7)/2 = 2**

(d.) **6 (2(9) + 1 - 7)/2 = 6**

QUESTIONS

Q7.2.1

Calculate degrees of unsaturation (DoU) for the following, and propose a structure for each.

A – C_5H_8

B – C_4H_4

Q7.2.1

Calculate the degree of unsaturation (DoU) for the following molecules

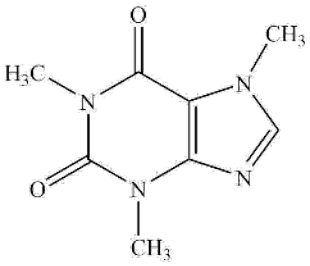
A – C_5H_5N

B – $C_5H_5NO_2$

C – C_5H_5Br

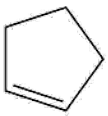
Q7.2.3

The following molecule is caffeine ($C_8H_{10}N_4O_2$), determine the degrees of unsaturation (DoU).



SOLUTIONS

S7.2.1



A)
2 DoU
1 ring, 1 double bond



B)
3 DoU
1 ring, 2 double bonds

S7.2.2

A = 4, B = 4, C = 3

S7.2.3

6 DoU

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Kim Quach (UCD)

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7.3: NAMING ALKENES

OBJECTIVES

After completing this section, you should be able to

1. provide the correct IUPAC name for an acyclic or cyclic alkene, given its Kekulé, condensed or shorthand structure.
2. draw the Kekulé, condensed or shorthand structure of an alkene (cyclic or acyclic), given its IUPAC name.
3. give the IUPAC equivalent of the following trivial names: ethylene, propylene, isobutylene and isoprene.
4. draw the structure of a vinyl (ethenyl) and allyl (2-propenyl) group, and use these names in alkene nomenclature.

STUDY NOTES

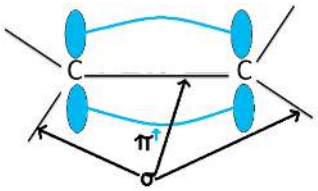
This course uses IUPAC nomenclature; therefore, you need not usually memorize a large number of trivial names. However, you will encounter some trivial names so frequently in books and articles that they soon become familiar.

An alkene that can exhibit geometric isomerism has not been properly named unless its name specifies whether the double bond (or bonds) is (or are) cis or trans. The most effective way of giving this information is discussed, and more details of cis and trans follow in Section 7.4.

Alkenes contain carbon-carbon double bonds and are unsaturated hydrocarbons with the molecular formula is C_nH_{2n}. This is also the same molecular formula as cycloalkanes. Alkenes are named by dropping the -ane ending of the parent and adding -ene.

INTRODUCTION

The parent structure is the longest chain containing both carbon atoms of the double bond. The two carbon atoms of a double bond and the four atoms attached to them lie in a plane, with bond angles of approximately 120° A double bond consists of one sigma bond formed by overlap of sp^2 hybrid orbitals and one pi bond formed by overlap of parallel 2 p orbitals



THE BASIC RULES

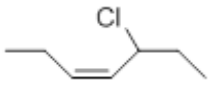
For straight chain alkenes, it is the same basic rules as nomenclature of alkanes except change the suffix to "-ene."

i. Find the Longest Carbon Chain that Contains the Carbon Carbon double bond. If you have two ties for longest Carbon chain, and both chains contain a Carbon Carbon double bond, then identify the most substituted chain.

ii. Give the lowest possible number to the Carbon Carbon double bond.
   - Do not need to number cycloalkenes because it is understood that the double bond is in the one position.
   - Alkenes that have the same molecular formula but the location of the doble bonds are different means they are constitutional isomers.
   - Functional Groups with higher priority:

iii. Add substituents and their position to the alkene as prefixes. Of course remember to give the lowest numbers possible. And remember to name them in alphabetical order when writting them.

iv. Next is identifying stereoisomers. when there are only two non hydrogen attachments to the alkene then use cis and trans to name the molecule.



In this diagram this is a cis conformation. It has both the substituents going upward. This molecule would be called (cis) 5-chloro-3-heptene.)

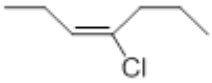
Trans would look like this

v. On the other hand if there are 3 or 4 non-hydrogen different atoms attached to the alkene then use the E, Z system.

E (entgegen) means the higher priority groups are opposite one another relative to the double bond.

Z (zusammen) means the higher priority groups are on the same side relative to the double bond.

(You could think of Z as Zame Zide to help memorize it.)



In this example it is E-4-chloro-3-heptene. It is E because the Chlorine and the CH_2CH_3 are the two higher priorities and they are on opposite sides.

vi. A hydroxyl group gets precedence over th double bond. Therefore alkenes containing alchol groups are called alkenols. And the prefix becomes --enol. And this means that now the alcohol gets lowest priority over the alkene.

vii. Lastly remember that alkene substituents are called alkenyl. Suffix --enyl.

Here is a chart containing the systemic name for the first twenty straight chain alkenes.

Table 7.3.1: systemic name for the first twenty straight chain alkenes.

Name	Molecular formula
Ethene	C_2H_4
Propene	C_3H_6
Butene	C_4H_8
Pentene	C_5H_{10}
Hexene	C_6H_{12}
Heptene	C_7H_{14}
Octene	C_8H_{16}
Nonene	C_9H_{18}
Decene	$C_{10}H_{20}$
Undecene	$C_{11}H_{22}$
Dodecene	$C_{12}H_{24}$
Tridecene	$C_{13}H_{26}$
Tetradecene	$C_{14}H_{28}$
Pentadecene	$C_{15}H_{30}$
Hexadecene	$C_{16}H_{32}$
Heptadecene	$C_{17}H_{34}$
Octadecene	$C_{18}H_{36}$
Nonadecene	$C_{19}H_{38}$
Eicosene	$C_{20}H_{40}$

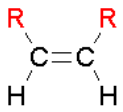
Did you notice how there is no methene? Because it is impossible for a Carbon to have a double bond with nothing.

GEOMETRIC ISOMERS

Double bonds can exist as geometric isomers and these isomers are designated by using either the cis / trans designation or the modern E / Z designation.

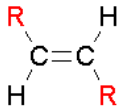
CIS ISOMERS

.The two largest groups are on the same side of the double bond.



TRANS ISOMERS

...The two largest groups are on opposite sides of the double bond.



E/Z NOMENCLATURE

E = entgegan ("trans") Z = zusamen ("cis")

Priority of groups is based on the atomic mass of attached atoms (not the size of the group). An atom attached by a multiple bond is counted once for each bond.

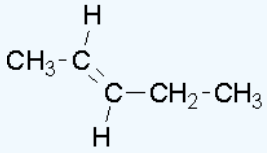
fluorine atom > isopropyl group > n-hexyl group

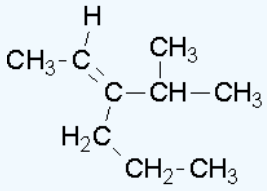
deuterium atom > hydrogen atom

$$-CH_2-CH=CH_2 > -CH_2CH_2CH_3$$

EXAMPLE 7.3.1

Try to name the following compounds using both conventions...





Answer

Structure 1: (*trans)* 2-pentene or (*E*) 2-pentene

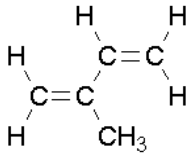
Structure 2: cis and trans convention cannot be used there are more than two non hydrogen attachments to the alkene

(*E*) 3-isopropyl-2-hexene or (*E*) 3-(1-methylethyl)-2-hexene

COMMON NAMES

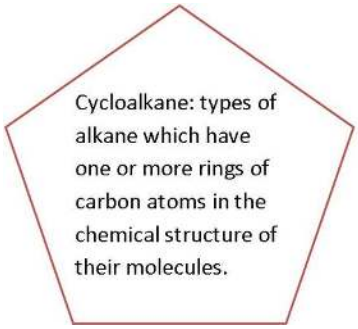
Remove the -ane suffix and add -ylene. There are a couple of unique ones like ethenyl's common name is vinyl and 2-propenyl's common name is allyl. That you should know are...

- vinyl substituent $H_2C=CH-$
- allyl substituent $H_2C=CH-CH_2-$
- allene molecule $H_2C=C=CH_2$
- isoprene



ENDOCYCLIC ALKENES

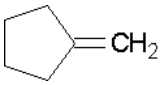
Endocyclic double bonds have both carbons in the ring and exocyclic double bonds have only one carbon as part of the ring.



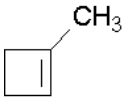
Cyclopentene is an example of an endocyclic double bond.



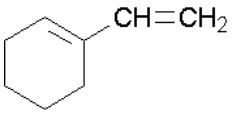
Methylenecylopentane is an example of an exocyclic double bond.



Name the following compounds...



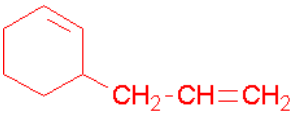
1-methylcyclobut-1-ene



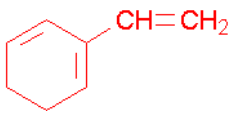
1-ethenylcyclohex-1-ene, the methyl group places the double bond. A common name would be 1-vinylcyclohexene.

Try to draw structures for the following compounds...

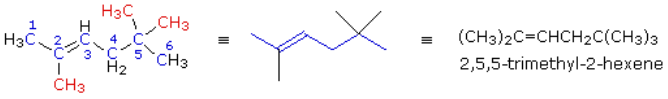
- 3-(2-propenyl)-cyclohexa-1-ene

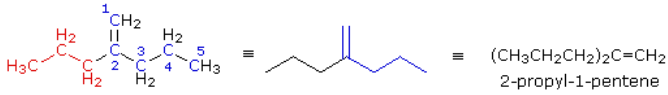


- 2-ethyl-cyclohexa-1,3-diene



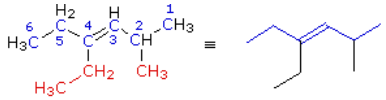
EXAMPLES

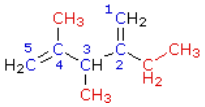
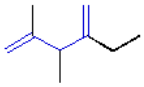
(1) 

(2) 

Both these compounds have double bonds, making them alkenes. In example (1) the longest chain consists of six carbons, so the root name of this compound will be hexene. Three methyl substituents (colored red) are present. Numbering the six-carbon chain begins at the end nearest the double bond (the left end), so the methyl groups are located on carbons 2 & 5. The IUPAC name is therefore: 2,5,5-trimethyl-2-hexene.

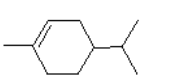
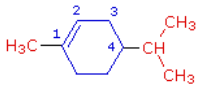
In example (2) the longest chain incorporating both carbon atoms of the double bond has a length of five. There is a seven-carbon chain, but it contains only one of the double bond carbon atoms. Consequently, the root name of this compound will be pentene. There is a propyl substituent on the inside double bond carbon atom (#2), so the IUPAC name is: 2-propyl-1-pentene.

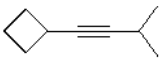
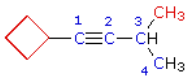
(3)  ≡ ≡ $(CH_3CH_2)_2C{=}CHCH(CH_3)_2$
4-ethyl-2-methyl-3-hexene

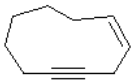
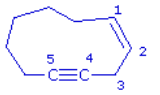
(4)  ≡  ≡ $CH_2{=}C(CH_3)CH(CH_3)C(C_2H_5){=}CH_2$
2-ethyl-3,4-dimethyl-1,4-pentadiene

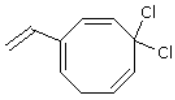
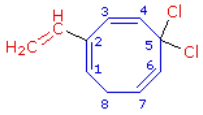
The double bond in example (3) is located in the center of a six-carbon chain. The double bond would therefore have a locator number of 3 regardless of the end chosen to begin numbering. The right hand end is selected because it gives the lowest first-substituent number (2 for the methyl as compared with 3 for the ethyl if numbering were started from the left). The IUPAC name is assigned as shown.

Example (4) is a diene (two double bonds). Both double bonds must be contained in the longest chain, which is therefore five- rather than six-carbons in length. The second and fourth carbons of this 1,4-pentadiene are both substituted, so the numbering begins at the end nearest the alphabetically first-cited substituent (the ethyl group).

(5)  ≡ 
4-isopropyl-1-methylcyclohexene

(6)  ≡ 
1-cyclobutyl-3-methyl-1-butyne

(7)  ≡ 
1-cyclodecen-4-yne

(8)  ≡ 
5,5-dichloro-2-vinyl-1,3,6-cyclooctatriene

These examples include rings of carbon atoms as well as some carbon-carbon triple bonds. Example (6) is best named as an alkyne bearing a cyclobutyl substituent. Example (7) is simply a ten-membered ring containing both a double and a triple bond. The double bond is cited first in the IUPAC name, so numbering begins with those two carbons in the direction that gives the triple bond carbons the lowest locator numbers. Because of the linear geometry of a triple bond, a-ten membered ring is the smallest ring in which this functional group is easily accommodated. Example (8) is a cyclooctatriene (three double bonds in an eight-membered ring). The numbering must begin with one of the end carbons of the conjugated diene moiety (adjacent double bonds), because in this way the double bond carbon atoms are assigned the smallest possible locator numbers (1, 2, 3, 4, 6 & 7). Of the two ways in which this can be done, we choose the one that gives the vinyl substituent the lower number.

OUTSIDE LINKS

- http://www.vanderbilt.edu/AnS/Chemis...0a/alkenes.pdf

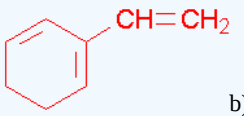
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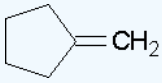
1. Vollhardt, Peter, and Neil E. Schore. Organic Chemistry: Structure and Function. 5th Edition. New York: W. H. Freeman & Company, 2007.

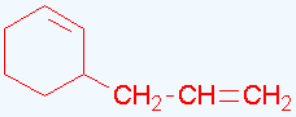
EXERCISES

EXERCISE 7.3.1

Name the following compounds using common fragment names.

a) 

b) 

C) 

Answer

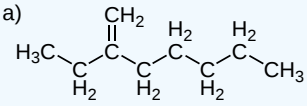
a) 2-Vinyl-1,3-cyclohexadiene

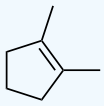
b) Methylenecylopentane

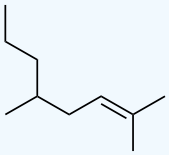
c) 3-Allylcyclohexene

EXERCISE 7.3.2

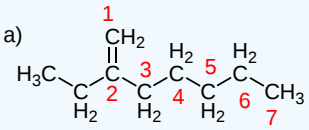
Name the following alkenes.

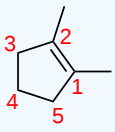
a) 

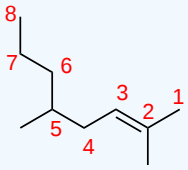
b) 

c) 

Answer

a) 

b) 

c) 

a) 2-ethylhept-1-ene or 2-ethyl-1-heptene

b) 1,2-dimethylcyclopent-1-ene

c) 2,5-dimethyloct-2-ene or 2,5-dimethyl-1-octene

EXERCISE 7.3.3

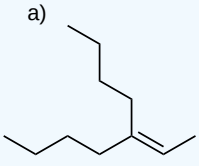
Draw structures for the following compounds from the given names.

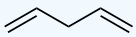
a. 3-butylhept-2-ene (3-butyl-2-heptene)

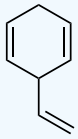
b. 1,4-pentadiene (penta-1,4-diene)

c. 3-vinyl-1,4-cyclohexadiene (3-ethylcyclohexa-1,4-diene)

Answer

a) 

b) 

c) 

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- S. Devarajan (UCD)
- Prof. Steven Farmer (Sonoma State University)

Richard Banks (Boise State University)

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7.4: CIS-TRANS ISOMERISM IN ALKENES

OBJECTIVES

After completing this section, you should be able to

1. discuss the formation of carbon-carbon double bonds using the concept of sp^2 hybridization.
2. describe the geometry of compounds containing carbon-carbon double bonds.
3. compare the molecular parameters (bond lengths, strengths and angles) of a typical alkene with those of a typical alkane.
4. explain why free rotation is not possible about a carbon-carbon double bond.
5. explain why the lack of free rotation about a carbon-carbon double bond results in the occurrence of cis-trans isomerism in certain alkenes.
6. decide whether or not cis-trans isomerism is possible for a given alkene, and where such isomerism is possible, draw the Kekulé structure of each isomer.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- cis-trans stereoisomers

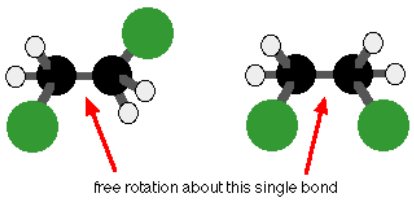
STUDY NOTES

Your previous studies in chemistry may have prepared you to discuss the nature of a carbon-carbon double bond. If not, you should review Section 1.8 of this course before beginning the present section. It is particularly important that you make molecular models of some simple alkenes to gain insight into the geometry of these compounds.

Geometric isomerism (also known as cis-trans isomerism or E-Z isomerism) is a form of stereoisomerism. Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. That excludes any different arrangements which are simply due to the molecule rotating as a whole, or rotating about particular bonds. Where the atoms making up the various isomers are joined up in a different order, this is known as structural isomerism. Structural isomerism is **not** a form of stereoisomerism, and is dealt with elsewhere. In stereoisomerism, the atoms making up the isomers are joined up in the same order, but still manage to have a different spatial arrangement. Geometric isomerism is one form of stereoisomerism.

GEOMETRIC (CIS / TRANS) ISOMERISM

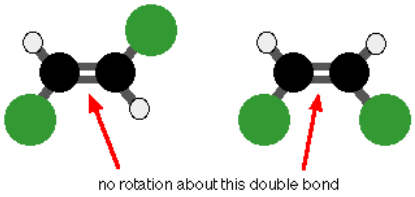
These isomers occur where you have restricted rotation somewhere in a molecule. At an introductory level in organic chemistry, examples usually just involve the carbon-carbon double bond - and that's what this page will concentrate on. Think about what happens in molecules where there is **un**restricted rotation about carbon bonds - in other words where the carbon-carbon bonds are all single. The next diagram shows two possible configurations of 1,2-dichloroethane.



These two models represent exactly the same molecule. You can get from one to the other just by twisting around the carbon-carbon single bond. These molecules are *not* isomers. If you draw a structural formula instead of using models, you have to bear in mind the possibility of this free rotation about single bonds. You must accept that these two structures represent the same molecule:



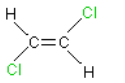
But what happens if you have a carbon-carbon double bond - as in 1,2-dichloroethene?



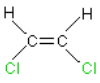
These two molecules are not the same. The carbon-carbon double bond won't rotate and so you would have to take the models to pieces in order to convert one structure into the other one. That is a simple test for isomers. If you have to take a model to pieces to convert it into another one, then you've got isomers. If you merely have to twist it a bit, then you haven't!

Drawing structural formulae for the last pair of models gives two possible isomers:

1. In one, the two chlorine atoms are locked on opposite sides of the double bond. This is known as the **trans** isomer. (trans : from latin meaning "across" - as in transatlantic).
2. In the other, the two chlorine atoms are locked on the same side of the double bond. This is know as the **cis** isomer. (cis : from latin meaning "on this side")

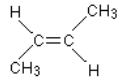


trans-1,2-dichloroethene

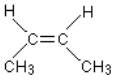


cis-1,2-dichloroethene

The most likely example of geometric isomerism you will meet at an introductory level is but-2-ene. In one case, the CH_3 groups are on opposite sides of the double bond, and in the other case they are on the same side.



trans-but-2-ene



cis-but-2-ene

THE IMPORTANCE OF DRAWING GEOMETRIC ISOMERS PROPERLY

It's very easy to miss geometric isomers in exams if you take short-cuts in drawing the structural formulae. For example, it is very tempting to draw but-2-ene as

$$CH_3CH{=}CHCH_3$$

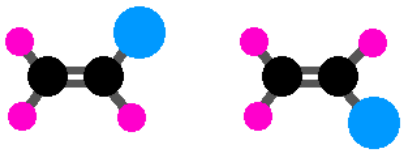
If you write it like this, you will almost certainly miss the fact that there are geometric isomers. If there is even the slightest hint in a question that isomers might be involved, always draw compounds containing carbon-carbon double bonds showing the correct bond angles (120°) around the carbon atoms at the ends of the bond. In other words, use the format shown in the last diagrams above.

HOW TO RECOGNIZE THE POSSIBILITY OF GEOMETRIC ISOMERISM

You obviously need to have restricted rotation somewhere in the molecule. Compounds containing a carbon-carbon double bond have this restricted rotation. (Other sorts of compounds may have restricted rotation as well, but we are concentrating on the case you are most likely to meet when you first come across geometric isomers.) If you have a carbon-carbon double bond, you need to think carefully about the possibility of geometric isomers.

What needs to be attached to the carbon-carbon double bond?

Think about this case:



Although we've swapped the right-hand groups around, these are still the same molecule. To get from one to the other, all you would have to do is to turn the whole model over. You won't have geometric isomers if there are two groups the same on one end of the bond - in this case, the two pink groups on the left-hand end. So there must be two different groups on the left-hand carbon and two different groups on the right-hand one. The cases we've been exploring earlier are like this:



But you could make things even more different and still have geometric isomers:



Here, the blue and green groups are either on the same side of the bond or the opposite side. Or you could go the whole hog and make everything different. You still get geometric isomers, but by now the words cis and trans are meaningless. This is where the more sophisticated E-Z notation comes in.



? WORKED EXAMPLE 7.4.1

Are the following molecules *cis-trans* isomers?



Answer

Although the two molecules *are seemingly* different propenes, these two structures are not really different from each other. Because the one of the double-bond carbons is attached to two identical groups (Hydrogens) it is incapable of forming *cis-trans* isomers. The interchange of two substituens seen here does not create a new isomer. If either molecule were flipped over top to bottom, the two would you would look identical.

SUMMARY

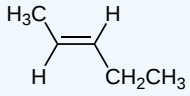
To get geometric isomers you must have:

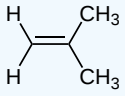
- restricted rotation (often involving a carbon-carbon double bond for introductory purposes);
- two different groups on the left-hand end of the bond and two different groups on the right-hand end. It doesn't matter whether the left-hand groups are the same as the right-hand ones or not.

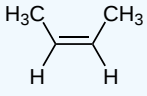
EXERCISES

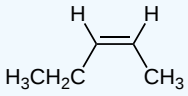
? EXERCISE 7.4.1

Classify each compound as a *cis* isomer, a *trans* isomer, or neither.

a)


b)


c)


d)


Answer

a) trans isomer

b) neither

c) cis isomer

d) cis isomer

EXERCISE 7.4.2

Which of the following compounds could exist as cis/trans isomers? Draw (& label) both of the isomers for the ones that can.

a) $CH_3CH{=}CHCH_3$

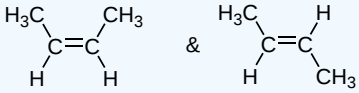
b) $(CH_3)_2C{=}CHCH_3$

c) $H_2C{=}CHCH_3$

d) $CH_3CH_2CH{=}CHBr$

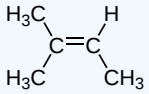
Answer

a)



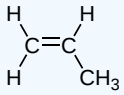
cis isomer & trans isomer

b)



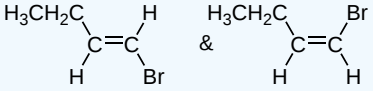
no cis/trans isomers

c)



no cis/trans isomers

d)



trans isomer & cis isomer

EXERCISE 7.4.3

Draw (& label) the cis and trans isomer for each of the following compound names. If no cis/trans isomerism is possible, write none.

a. 3-hexene

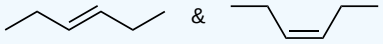
b. 1-hexene

c. 4-methylpent-2-ene (4-methyl-2-pentene)

d. 1,1-dibromobut-2-ene (1,1-dibromo-2-butene)

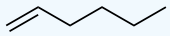
Answer

a)



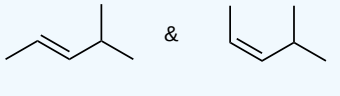
trans isomer & cis isomer

b)



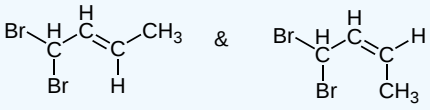
no cis/trans isomers

c)



trans isomer & cis isomer

d)

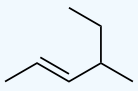


trans isomer & cis isomer

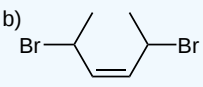
EXERCISE 7.4.4

Name the following compounds using cis/trans nomenclature

a)



b)



Answer

a) *trans*-4-methylhex-2-ene (*trans*-4-methyl-2-hexene)

b) *cis*-2,5-dibromohex-3-ene (*cis*-2,5-dibromo-3-hexene)

QUESTIONS

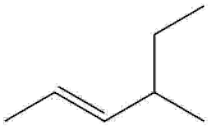
Q7.4.1

Which of the following can have *cis/trans* isomers? Draw their isomers.

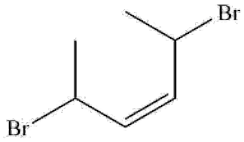
$(CH_3CH_2)CH=CH_2$, $(CH_3CH_2)_2C=CHCH_3$, $(CH_3CH_2)CH=CHCH_3$

Q7.4.2

Name the following compounds, with *cis/trans* nomenclature.



A

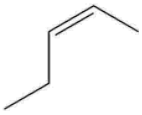


B

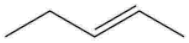
SOLUTIONS

S7.4.1

The last compound in the list can be a *cis/trans* isomer.



cis



trans

S7.4.2

A – *trans*-4-methyl-2-hexene

B – *cis*-2,5-dibromo-3-hexene

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Jim Clark (Chemguide.co.uk)

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7.5: SEQUENCE RULES - THE E,Z DESIGNATION

OBJECTIVES

After completing this section, you should be able to

1. illustrate, by means of a suitable example, the limitations of the terms cis and trans in naming isomeric alkenes.
2. use the *E*,*Z* designation to describe the geometry of a given alkene structure.
3. incorporate the *E*,*Z* designation into the IUPAC name of a given alkene.
4. draw the correct Kekulé, condensed or shorthand structure of an alkene, given its *E*,*Z* designation plus other necessary information (e.g., molecular formula, IUPAC name).

KEY TERMS

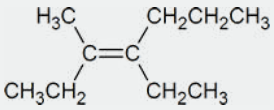
Make certain that you can define, and use in context, the key term below.

- sequence rules (Cahn-Ingold-Prelog rules)

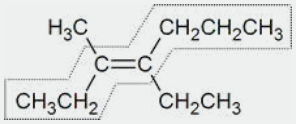
STUDY NOTES

The limitations of the cis-trans system are illustrated in the examples given below.

1. From your study of the IUPAC system, you should be able to identify this compound as 4-ethyl-3-methyl-3-heptene, but is it cis or trans?

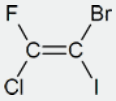


At first you might say cis, because it appears that two ethyl groups appear on the same side of the double bond. However, the correct answer is trans. The rule is that the designation cis or trans must correspond to the configuration of the *longest* carbon chain. Tracing out the seven-carbon chain in the compound shown above, you change sides as you pass through the double bond:

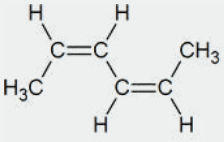


So, the full name for this compound is 4-ethyl-3methyl-*trans*-3-heptene.

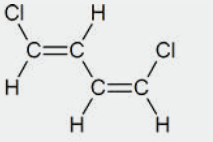
2. The cis-trans system breaks down completely in a compound such as that shown below. The *E*,*Z* system, which is the subject of this section, is designed to accommodate such situations.



In cases where two or more double bonds are present, you must be prepared to assign an *E* or *Z* designation to each of the double bonds. For example:



(2*Z*,4*Z*)-2,4-hexadiene



(1*E*,3*Z*)-1,4-dichloro-1,3-butadiene

Another use for these sequence rules will be part of the discussion of optical isomerism in Section 9.5.

E/Z NOMENCLATURE

The traditional system for naming the geometric isomers of an alkene, in which the same groups are arranged differently, is to name them as cis or trans. However, it is easy to find examples where the cis-trans system is not easily applied. IUPAC has a more complete system for

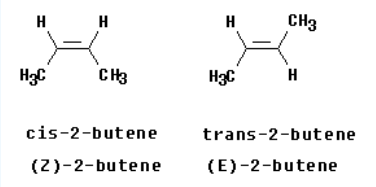
naming alkene isomers. The R-S system is based on a set of "priority rules", which allow you to rank any groups. The rigorous IUPAC system for naming alkene isomers, called the E-Z system, is based on the same priority rules.

NOTE

The priority rules are often called the Cahn-Ingold-Prelog (CIP) rules, after the chemists who developed the system

The general strategy of the E-Z system is to analyze the two groups at each end of the double bond. At each end, rank the two groups, using the CIP priority rules, discussed in Ch 15. Then, see whether the higher priority group at one end of the double bond and the higher priority group at the other end of the double bond are on the **same** side (Z, from German zusammen = together) or on **opposite** sides (E, from German entgegen = opposite) of the double bond.

EXAMPLE 7.5.1: BUTENE



The Figure above shows the two isomers of 2-butene. You should recognize them as cis and trans. Let's analyze them to see whether they are E or Z. Start with the left hand structure (the cis isomer). On C2 (the left end of the double bond), the two atoms attached to the double bond are C and H. By the CIP priority rules, C is higher priority than H (higher atomic number). Now look at C3 (the right end of the double bond). Similarly, the atoms are C and H, with C being higher priority. We see that the higher priority group is "down" at C2 and "down" at C3. Since the two priority groups are both on the **same** side of the double bond ("down", in this case), they are zusammen = together. Therefore, this is (Z)-2-butene.

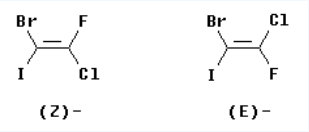
Now look at the right hand structure (the trans isomer). In this case, the priority group is "down" on the left end of the double bond and "up" on the right end of the double bond. Since the two priority groups are on **opposite** sides of the double bond, they are entgegen = opposite. Therefore, this is (E)-2-butene.

E,Z WILL WORK -- EVEN WHEN CIS,TRANS FAILS

In simple cases, such as 2-butene, Z corresponds to cis and E to trans. However, that is **not** a rule. This section and the following one illustrate some idiosyncrasies that happen when you try to compare the two systems. The real advantage of the E-Z system is that it will always work. In contrast, the cis-trans system breaks down with many ambiguous cases.

EXAMPLE 7.5.2

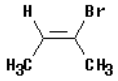
The following figure shows two isomers of an alkene with four different groups on the double bond, 1-bromo-2-chloro-2-fluoro-1-iodoethene.



It should be apparent that the two structures shown are distinct chemicals. However, it is impossible to name them as cis or trans. On the other hand, the E-Z system works fine... Consider the left hand structure. On C1 (the left end of the double bond), the two atoms attached to the double bond are Br and I. By the CIP priority rules, I is higher priority than Br (higher atomic number). Now look at C2. The atoms are Cl and F, with Cl being higher priority. We see that the higher priority group is "down" at C1 and "down" at C2. Since the two priority groups are both on the **same** side of the double bond ("down", in this case), they are zusammen = together. Therefore, this is the (Z) isomer. Similarly, the right hand structure is (E).

E,Z WILL WORK, BUT MAY NOT AGREE WITH CIS,TRANS

Consider the molecule shown at the left.



This is 2-bromo-2-butene -- ignoring the geometric isomerism for now. Cis or trans? This molecule is clearly cis. The two methyl groups are on the same side. More rigorously, the "parent chain" is cis.

E or Z? There is a methyl at each end of the double bond. On the left, the methyl is the high priority group -- because the other group is -H. On the right, the methyl is the low priority group -- because the other group is -Br. That is, the high priority groups are -CH_3 (left) and -Br (right). Thus the two priority groups are on opposite sides = entgegen = E.

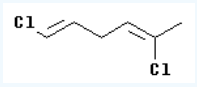
NOTE

This example should convince you that cis and Z are not synonyms. Cis/trans and E,Z are determined by distinct criteria. There may seem to be a simple correspondence, but it is not a rule. Be sure to determine cis,trans or E,Z separately, as needed.

MULTIPLE DOUBLE BONDS

If the compound contains more than one double bond, then each one is analyzed and declared to be E or Z.

EXAMPLE 7.5.3

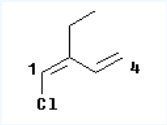


The configuration at the left hand double bond is E; at the right hand double bond it is Z. Thus this compound is (1E,4Z)-1,5-dichloro-1,4-hexadiene.

THE DOUBLE-BOND RULE IN DETERMINING PRIORITIES

EXAMPLE 7.5.4

Consider the compound below

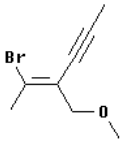


This is 1-chloro-2-ethyl-1,3-butadiene -- ignoring, for the moment, the geometric isomerism. There is no geometric isomerism at the second double bond, at 3-4, because it has 2 H at its far end.

What about the first double bond, at 1-2? On the left hand end, there is H and Cl; Cl is higher priority (by atomic number). On the right hand end, there is -CH_2-CH_3 (an ethyl group) and -CH=CH_2 (a vinyl or ethenyl group). Both of these groups have C as the first atom, so we have a tie so far and must look further. What is attached to this first C? For the ethyl group, the first C is attached to C, H, and H. For the ethenyl group, the first C is attached to a C twice, so we count it twice; therefore that C is attached to C, C, H. CCH is higher than CHH; therefore, the ethenyl group is higher priority. Since the priority groups, Cl and ethenyl, are on the same side of the double bond, this is the Z-isomer; the compound is (Z)-1-chloro-2-ethyl-1,3-butadiene.

THE "FIRST POINT OF DIFFERENCE" RULE

Which is higher priority, by the CIP rules: a C with an O and 2 H attached to it or a C with three C? The first C has one atom of high priority but also two atoms of low priority. How do these "balance out"? Answering this requires a clear understanding of how the ranking is done. The simple answer is that the first point of difference is what matters; the O wins.



To illustrate this, consider the molecule at the left. Is the double bond here E or Z? At the left end of the double bond, Br > C. But the right end of the double bond requires a careful analysis.

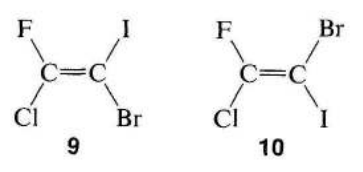
At the right hand end, the first atom attached to the double bond is a C at each position. A tie, so we look at what is attached to this first C. For the upper C, it is CCC (since the triple bond counts three times). For the lower C, it is OHH -- listed in order from high priority atom to low. OHH is higher priority than CCC, because of the first atom in the list. That is, the O of the lower group beats the C of the upper group. In other words, the O is the highest priority atom of any in this comparison; thus the O "wins".

Therefore, the high priority groups are "up" on the left end (the -Br) and "down" on the right end (the $-CH_2-O-CH_3$). This means that the isomer shown is opposite = entgegen = E. And what is the name? The "name" is (E)-2-Bromo-3-(methoxymethyl)hex-2-en-4-yne.

EXAMPLE 7.5.5

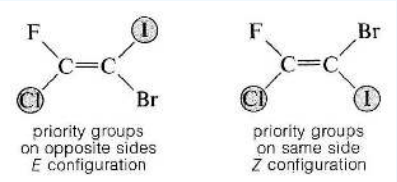
A common method for preparing oxygen is the

The configuration about double bonds is undoubtedly best specified by the cis-trans notation when there is no ambiguity involved. Unfortunately, many compounds cannot be described adequately by the cis-trans system. Consider, for example, configurational isomers of 1 -fluoro- 1 -chloro-2- bromo-2-iodo-ethene, 9 and 10. There is no obvious way in which the cis-trans system can be used:

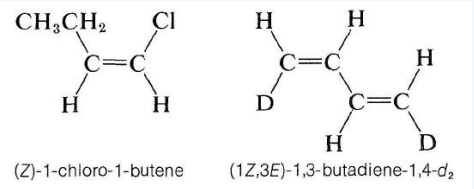


A system that is easy to use and which is based on the sequence rules already described for the R,S system works as follows:

1. An order of precedence is established for the two atoms or groups attached to each end of the double bond according to the sequence rules of Section 19-6. When these rules are applied to 1-fluoro- 1-chloro-2-bromo-2- iodoethene, the priority sequence is:
   - at carbon atom 1, C1 > F
   - at carbon atom 2, I > Br
2. Examination of the two configurations shows that the two priority groups- one on each end- are either on the same side of the double bond or on opposite sides:



The Z isomer is designated as the isomer in which the top priority groups are on the same side (Z is taken from the German word zusammen- together). The E isomer has these groups on opposite sides (E, German for entgegen across). Two further examples show how the nomenclature is used:



EXERCISES

EXERCISE 7.5.1

Which of the following sets has a higher ranking?

a. $-CH_3$ or $-CH_2Br$
b. -Br or -Cl

c. -CH=CH_2 or -CH=O

Answer

a) -CH_2Br

b) -Br

c) -CH=O

EXERCISE 7.5.2

Place the following sets of substituents in each group in order of lowest priority (1st) to highest priority (4th)

a. -$CH(CH_3)_2$, -CH_2CH_3, -$C(CH_3)_3$, -CH_3

b. -NH_2, -F, -Br, -CH_3

c. -SH, -NH_2, -F, -H

Answer

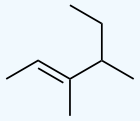
a) (lowest priority) -CH_3 < -CH_2CH_3 < -$CH(CH_3)_2$ < -$C(CH_3)_3$ (highest priority)

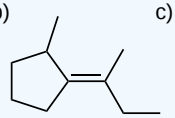
b) (lowest priority) -CH_3 < -NH_2 < -F < -Br (highest priority)

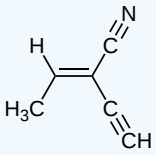
c) (lowest priority) -H < -NH_2 < -F < -SH (highest priority)

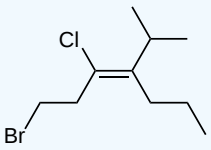
EXERCISE 7.5.3

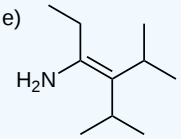
Label the following alkenes as E, Z, or neither.

a) 

b) 

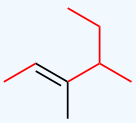
c) 

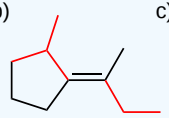
d) 

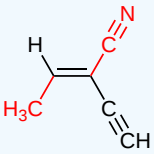
e) 

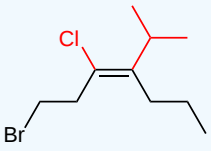
Answer

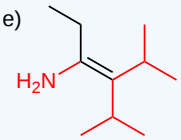
The higher priority group is highlighted in red.

a) 

b) 

c) 

d) 

e) 

a) E

b) E

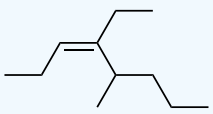
c) E

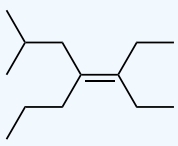
d) Z

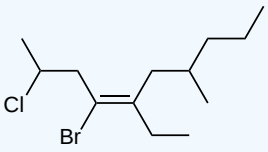
e) neither (both isopropyls on the right have the same priority)

EXERCISE 7.5.4

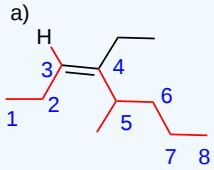
Name the following alkenes.

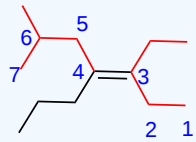
a) 

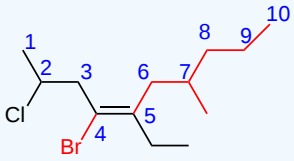
b) 

c) 

Answer

a) 

b) 

c) 

The higher priority group is highlighted in red.

a. (Z)-4-ethyl-5-methyloct-3-ene or (Z)-4-ethyl-5-methyl-3-octene
b. 3-ethyl-6-methyl-4-propylhept-3-ene or 3-ethyl-6-methyl-4-propyl-3-heptene
c. (E)-4-bromo-2-chloro-5-ethyl-7-methyldec-4-ene or (E)-4-bromo-2-chloro-5-ethyl-7-methyl-4-decene

QUESTIONS

Q7.5.1

Order the following in increasing priority.

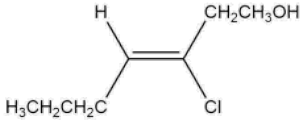
A) –H, –Cl, –OH

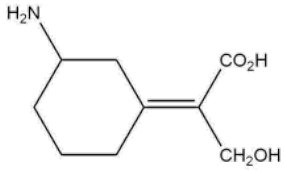
B) –CH_3, –CH_2OH, –CH_2CH_3

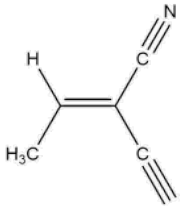
C) –C≡CH, –CH=CH_2, –CH=O

Q7.5.2

Label the following as *E* or *Z* conformations.

A) 

B) 

C) 

SOLUTIONS

S7.5.1

A) –H < –OH < –Cl (highest priority)

B) –CH_3 < –CH_2CH_3 < –CH_2OH (highest priority)

C) –CH=CH_2 < –C≡CH < –CH=O (highest priority)

S7.5.2

A – *Z*

B – *Z*

C – *E*

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

>Robert Bruner (http://bbruner.org)

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

7.5: Sequence Rules - The E,Z Designation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

7.6: STABILITY OF ALKENES

OBJECTIVES

After completing this section, you should be able to

1. explain why cis alkenes are generally less stable than their trans isomers.
2. explain that catalytic reduction of a cis alkene produces the same alkane as the catalytic reduction of the trans isomer.
3. explain how heats of hydrogenation ($\Delta H°_{hydrog}$) can be used to show that cis alkenes are less stable than their trans isomers, and discuss, briefly, the limitations of this approach.
4. arrange a series of alkenes in order of increasing or decreasing stability.
5. describe, briefly, two of the hypotheses proposed to explain why alkene stability increases with increased substitution. [**Note:** This problem is a typical example of those instances in science where there is probably no single "correct" explanation for an observed phenomenon.]

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- catalytic hydrogenation
- heat of hydrogenation, ($\Delta H°_{hydrog}$)
- hyperconjugation

STUDY NOTES

The two alkenes, *cis* $CH_3CH{=}CHCH_3$ and $(CH_3)_2C{=}CH_2$ have similar heats of hydrogenation (−120 kJ/mol and −119 kJ/mol, respectively), and are therefore of similar stability. However, they are both less stable than *trans* $CH_3CH{=}CHCH_3$ (−116 kJ/mol).

You may wonder why an sp^2 -sp^3 bond is stronger than an sp^3-sp^3 bond. Bond strength depends on the efficiency with which orbitals can overlap. In general, *s* orbitals overlap more efficiently than do *p* orbitals; therefore, the *s*-*s* bond in the hydrogen molecule is stronger than the *p*-*p* bond in fluorine. In hybrid orbitals, the greater the *s* character of the orbital, the more efficiently it can overlap: an sp^2 orbital, which has a 33% *s* character, can overlap more effectively than an sp^3 orbital, with only 25% *s* character.

Alkene hydrogenation is the syn-addition of hydrogen to an alkene, saturating the bond. The alkene reacts with hydrogen gas in the presence of a metal catalyst which allows the reaction to occur quickly. The energy released in this process, called the heat of hydrogenation, indicates the relative stability of the double bond in the molecule (see Catalytic Hydrogenation).

INTRODUCTION

The reaction begins with H_2 gas and an alkene (a carbon-carbon double bond). The pi bond in the alkene acts as a nucleophile; the two electrons in it form a sigma bond with one of the hydrogen atoms in H_2. With the pi bond broken, the other carbon (the one that did not newly receive a hydrogen) is left with a positive formal charge. This is the carbocation intermediate. The remaining (unreacted) hydrogen is now a hydride anion, as it was left with two electrons previously in the H-H sigma bond. Next, the electrons of the negatively charged hydride ion form a bond with the positively charged carbon. This reaction is exothermic. It will occur, but it is very slow without a catalyst.

THE CATALYST

A catalyst increases the reaction rate by lowering the activation energy of the reaction. Although the catalyst is not consumed in the reaction, it is required to accelerate the reaction sufficiently to be observed in a reasonable amount of time. Catalysts commonly used in alkene hydrogenation are: platinum, palladium, and nickel. The metal catalyst acts as a surface on which the reaction takes place. This increases the rate by putting the reactants in close proximity to each other, facilitating interactions between them. With this catalyst present, the sigma bond of H_2 breaks, and the two hydrogen atoms instead bind to the metal (see #2 in the figure below). The π bond of the alkene weakens as it also interacts with the metal (see #3 below).

Since both the reactants are bound to the metal catalyst, the hydrogen atoms can easily add, one at a time, to the previously double-bonded carbons (see #4 and #5 below). The position of both of the reactants bound to the catalyst makes it so the hydrogen atoms are only exposed to one side of the alkene. This explains why the hydrogen atoms add to same side of the molecule, called syn-addition.

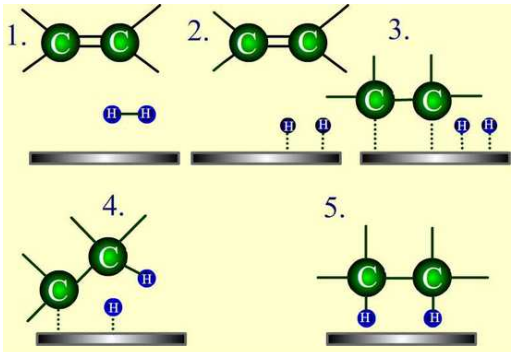
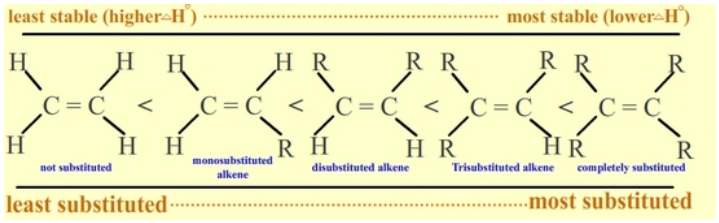


Figure 7.6.1: *Hydrogenation takes place in the presence of a metal catalyst.*

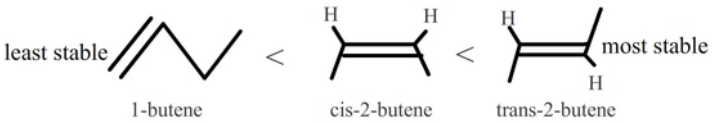
> NOTE
>
> The catalyst remains intact and unchanged throughout the reaction.

HEATS OF HYDROGENATION

The stability of alkene can be determined by measuring the amount of energy associated with the hydrogenation of the molecule. Since the double bond is breaking in this reaction, the energy released in hydrogenation is proportional to the energy in the double bond of the molecule. This is a useful tool because heats of hydrogenation can be measured very accurately. The ΔH^o is usually around -30 kcal/mol for alkenes. Stability is simply a measure of energy. Lower energy molecules are more stable than higher energy molecules. More substituted alkenes are more stable than less substituted ones due to hyperconjugation. They have a lower heat of hydrogenation. The following illustrates stability of alkenes with various substituents:



In disubstituted alkenes, trans isomers are more stable than cis isomers due to steric hindrance. Also, internal alkenes are more stable than terminal ones. See the following isomers of butene:



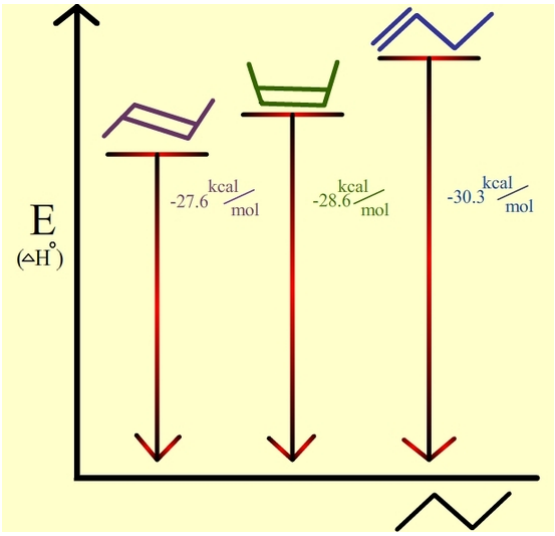


Figure 7.6.3: *Trans-2-butene is the most stable because it has the lowest heat of hydrogenation.*

NOTE

In cycloalkenes smaller than cyclooctene, the cis isomers are more stable than the trans as a result of ring strain.

OUTSIDE LINKS

- Helpful Information: http://www.wou.edu/las/physci/ch334/...ure/lect16.htm
- Hydrogenation Wikipedia page: http://en.Wikipedia.org/wiki/Hydrogenation
- More professional animation: http://www.jbpub.com/organic-online/movies/cathyd.htm

REFERENCES

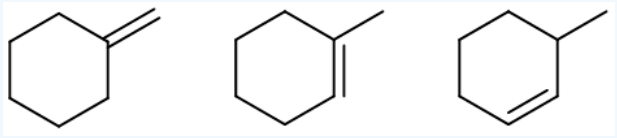
1. Fox, Marye Anne, and James K. Whitesell. Organic Chemistry. 3rd ed. Sudbury, MA: Janes and Bartlett Publishers, 2004.
2. Hanson, James R. Functional Group Chemistry. Bristol, UK: The Royal Society of Chemistry, 2001.
3. Streitwieser, Andrew Jr., and Clayton H. Heathcock. Introduction to Organic Chemistry. 2nd ed. New York, NY: Macmillan Publishing Co., Inc., 1981.
4. Vollhardt, Peter C., and Neil E. Schore. Organic Chemistry: Structure and Function. 5th ed. New York, NY: W.H. Freeman and Company, 2007.
5. Zlatkis, Albert, Eberhard Breitmaier, and Gunther Jung. A Concise Introduction to Organic Chemistry. New York: McGraw-Hill Book Company, 1973.

EXERCISES

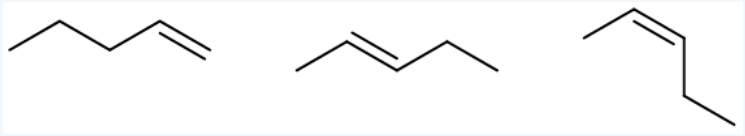
EXERCISE \PageIndex1

1) Of the three following isomers which would be expected to be the most stable?

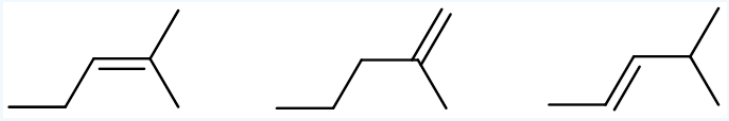
a)



b)



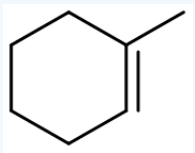
c)



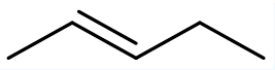
Answer

1)

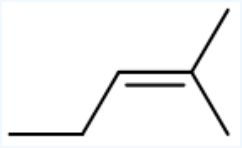
a)



b)

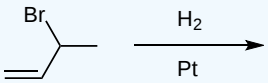


c)



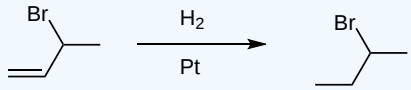
EXERCISE \PageIndex2

3-Bromobut-1-ene reacts with hydrogen gas in the presence of a platinum catalyst. What is the name of the product?



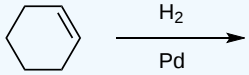
Answer

2-Bromobutane (numbering changes when alkene is no longer present)



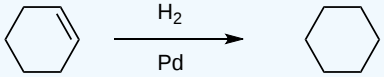
EXERCISE \PageIndex3

Cyclohexene reacts with hydrogen gas in the presence of a palladium catalyst. What is the name of the product?



Answer

Cyclohexane



EXERCISE \PageIndex4

What is the stereochemistry (syn or anti addition) of an alkene hydrogenation reaction?

Answer

Syn-addition

EXERCISE \PageIndex5

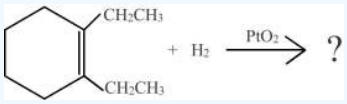
When looking at their heats of hydrogenation, is the cis or the trans isomer generally more stable?

Answer

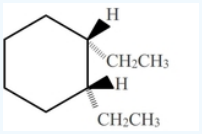
Trans

? EXERCISE \PageIndex1

Show the product for the following



Answer

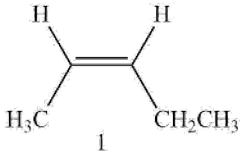


QUESTIONS

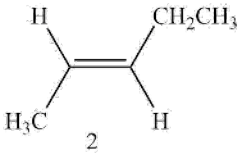
Q7.6.1

Which is the more stable alkene in each pair?

A)

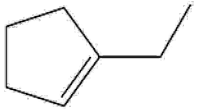


1

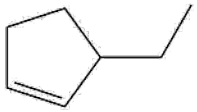


2

B)



1



2

SOLUTIONS

S7.6.1

A – 2

B – 1

CONTRIBUTORS AND ATTRIBUTIONS

- Anna Manis (UCD)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

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7.7: ELECTROPHILIC ADDITION REACTIONS OF ALKENES

OBJECTIVES

After completing this section, you should be able to

1. explain the term “electrophilic addition reaction,” using the reaction of a protic acid, HX, with an alkene as an example.
2. write the mechanism for the reaction of a protic acid, HX, with an alkene.
3. sketch a reaction energy diagram for the electrophilic addition of an acid, HX, to an alkene.

KEY TERMS

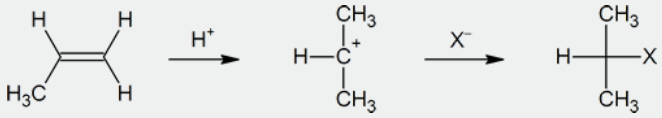
Make certain that you can define, and use in context, the key terms below.

- carbocation (carbonium ion)
- electrophilic addition reaction

STUDY NOTES

An *electrophilic addition reaction* is a reaction in which a substrate is initially attacked by an electrophile, and the overall result is the addition of one or more relatively simple molecules across a multiple bond.

The mechanism for the addition of hydrogen halide to propene shown in the reading is quite detailed. Normally, an organic chemist would write this mechanism as follows:



However, the more detailed mechanism shown in the reading does allow you to see the exact fate of all the electrons involved in the reaction.

In your previous chemistry course, you were probably taught the importance of balancing chemical equations. It may come as a surprise to you that organic chemists usually do not balance their equations, and often represent reactions using a format which is quite different from the carefully written, balanced equations encountered in general chemistry courses. In fact, organic chemists are rarely interested in the inorganic products of their reactions; furthermore, most organic reactions are non-quantitative in nature.

In many of the reactions in this course, the percentage yield is indicated beneath the products: you are not expected to memorize these figures. The question of yield is very important in organic chemistry, where two, five, ten or even twenty reactions may be needed to synthesize a desired product. For example, if a chemist wishes to prepare compound D by the following reaction sequence:

$$A \rightarrow B \rightarrow C \rightarrow D$$

and each of the individual steps gives only a 50% yield, one mole of A would give only

$$1 \text{ mol} \times \frac{50\%}{100\%} \times \frac{50\%}{100\%} \times \frac{50\%}{100\%} = 0.125 \text{ mol of D}$$

You will gain first-hand experience of such situations in the laboratory component of this course.

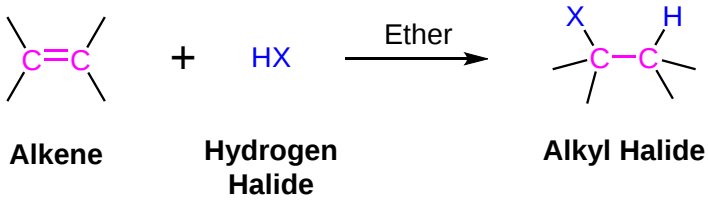
INTRODUCTION

One of the most important reactions for alkenes is called electrophilic addition. In this chapter several variations of the electrophilic addition reaction will be discussed. Each case will have aspects common among all electrophilic addition. In this section, the electrophilic addition reaction will be discussed in general to provide a better understanding of subsequent alkene reactions.

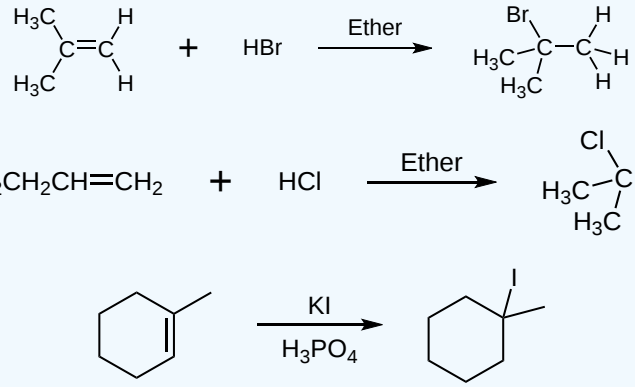
As discussed in Section 6-5, the double bond in alkenes is electron rich due to the prescience of 4 electrons instead of the two in a single bond. Also, the pi electrons are positioned above and below the double bond making them more accessibly for reactions. Overall, double bonds can easily donate lone pair electrons to act like a nucleophile (nucleus-loving, electron rich, a Lewis acid). During an electrophilic addition reactions double bonds donate lone pair electrons to an electrophile (Electron-loving, electron poor, a Lewis base). There are many types of electrophilic addition, but this section will focus on the addition of hydrogen halides (HX). Many of the basic ideas discussed will aplicable to subsequent electrophilic addition reactions.

GENERAL REACTION

Overall during this reaction the pi bond of the alkene is broken to form two single, sigma bonds. As shown in the reaction mechanism, one of these sigma bonds is connected to the H and the other to the X of the hydrogen halide. This reaction works well with HBr and HCl. HI can also but used but is is usually generated during the reaction by reacting potassium iodidie (KI) with phosphoric acid (H_3PO_4).



EXAMPLE \PageIndex1



ADDITION TO SYMMETRICAL ALKENES

What happens?

All alkenes undergo addition reactions with the hydrogen halides. A hydrogen atom joins to one of the carbon atoms originally in the double bond, and a halogen atom to the other.

For example, with ethene and hydrogen chloride, you get chloroethane:



With but-2-ene you get 2-chlorobutane:



What happens if you add the hydrogen to the carbon atom at the right-hand end of the double bond, and the chlorine to the left-hand end? You would still have the same product.

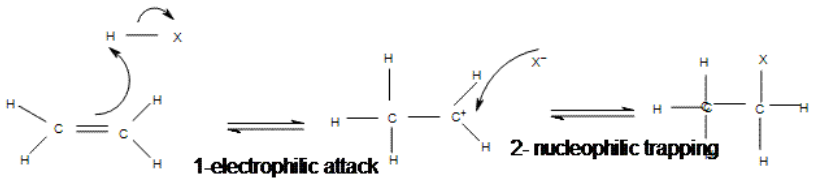
The chlorine would be on a carbon atom next to the end of the chain - you would simply have drawn the molecule flipped over in space.

That would be different of the alkene was unsymmetrical - that's why we have to look at them separately.

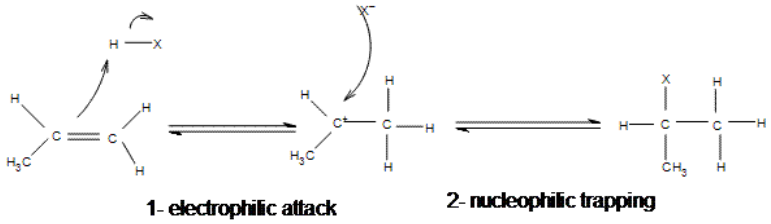
MECHANISM

The addition of hydrogen halides is one of the easiest electrophilic addition reactions because it uses the simplest electrophile: the proton. Hydrogen halides provide both a electrophile (proton) and a nucleophile (halide). First, the electrophile will attack the double bond and take up a set of electrons, attaching it to the molecule (1). This is basically the reverse of the last step in the E1 reaction (deprotonation step). The resulting molecule will have a single carbon- carbon bond with a positive charge on one of them (carbocation). The next step is when the nucleophile (halide) bonds to the carbocation, producing a new molecule with both the original hydrogen and halide attached to the organic reactant (2). The second step will only occur if a good nucleophile is used.

Mechanism of Electrophilic Addition of Hydrogen Halide to Ethene



Mechanism of Electrophilic Addition of Hydrogen Halide to Propene



All of the halides (HBr, HCl, HI, HF) can participate in this reaction and add on in the same manner. Although different halides do have different rates of reaction, due to the H-X bond getting weaker as X gets larger (poor overlap of orbitals)s.

REACTION RATES

Variation of rates when you change the halogen

Reaction rates increase in the order HF - HCl - HBr - HI. Hydrogen fluoride reacts much more slowly than the other three, and is normally ignored in talking about these reactions.

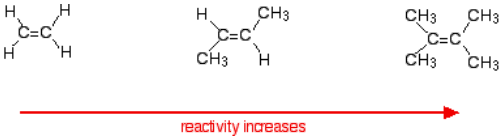
When the hydrogen halides react with alkenes, the hydrogen-halogen bond has to be broken. The bond strength falls as you go from HF to HI, and the hydrogen-fluorine bond is particularly strong. Because it is difficult to break the bond between the hydrogen and the fluorine, the addition of HF is bound to be slow.

Variation of rates when you change the alkene

This applies to unsymmetrical alkenes as well as to symmetrical ones. For simplicity the examples given below are all symmetrical ones- but they don't have to be.

Reaction rates increase as the alkene gets more complicated - in the sense of the number of alkyl groups (such as methyl groups) attached to the carbon atoms at either end of the double bond.

For example:



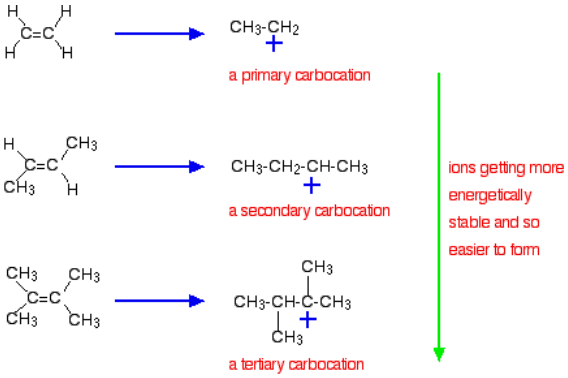
There are two ways of looking at the reasons for this - both of which need you to know about the mechanism for the reactions.

Alkenes react because the electrons in the pi bond attract things with any degree of positive charge. Anything which increases the electron density around the double bond will help this.

Alkyl groups have a tendency to "push" electrons away from themselves towards the double bond. The more alkyl groups you have, the more negative the area around the double bonds becomes.

The more negatively charged that region becomes, the more it will attract molecules like hydrogen chloride.

The more important reason, though, lies in the stability of the intermediate ion formed during the reaction. The three examples given above produce these carbocations (carbonium ions) at the half-way stage of the reaction:



The stability of the intermediate ions governs the activation energy for the reaction. As you go towards the more complicated alkenes, the activation energy for the reaction falls. That means that the reactions become faster.

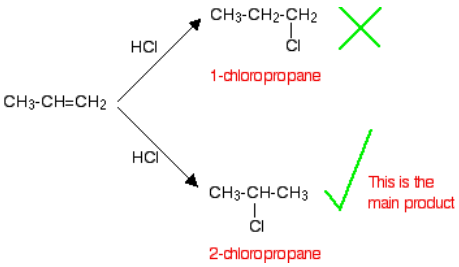
Addition to unsymmetrical alkenes

What happens?

In terms of reaction conditions and the factors affecting the rates of the reaction, there is no difference whatsoever between these alkenes and the symmetrical ones described above. The problem comes with the orientation of the addition - in other words, which way around the hydrogen and the halogen add across the double bond.

Orientation of addition

If HCl adds to an unsymmetrical alkene like propene, there are two possible ways it could add. However, in practice, there is only one major product.



This is in line with Markovnikov's Rule which says:

> When a compound HX is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already.

In this case, the hydrogen becomes attached to the CH_2 group, because the CH_2 group has more hydrogens than the CH group.

Notice that only the hydrogens directly attached to the carbon atoms at either end of the double bond count. The ones in the CH_3 group are totally irrelevant.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

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7.8: ORIENTATION OF ELECTROPHILIC ADDITIONS - MARKOVNIKOV'S RULE

Objectives

After completing this section, you should be able to

1. use Markovnikov's rule to predict the product formed when a protic acid, HX, reacts with an alkene.
2. identify the protic acid, HX, and the alkene that must be reacted together to produce a given alkyl halide. [**Note:** Special conditions are needed if an alkyl iodide is to be produced.]
3. distinguish among primary, secondary and tertiary carbocations.

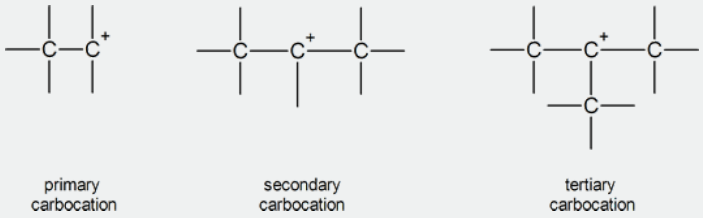
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- Markovnikov's rule
- regioselective (regiospecific)

STUDY NOTES

Recall the definitions of primary, secondary and tertiary hydrogen atoms given in Section 3.3. It follows that a "primary carbocation" is a carbocation in which the carbon atom carrying the positive charge is bonded to only one other carbon atom, a "secondary carbocation" is one in which the carbon atom carrying the positive charge is bonded to two other carbon atoms, and so on.



This page looks at the reaction of the carbon-carbon double bond in alkenes such as ethene with hydrogen halides such as hydrogen chloride and hydrogen bromide. Symmetrical alkenes (like ethene or but-2-ene) are dealt with first. These are alkenes where identical groups are attached to each end of the carbon-carbon double bond.

ADDITION TO SYMMETRICAL ALKENES

All alkenes undergo addition reactions with the hydrogen halides. A hydrogen atom joins to one of the carbon atoms originally in the double bond, and a halogen atom to the other. For example, with ethene and hydrogen chloride, you get chloroethane:

$$CH_2{=}CH_2 + HCl \rightarrow CH_3{-}CH_2Cl \tag{7.8.1}$$

With but-2-ene you get 2-chlorobutane:



What happens if you add the hydrogen to the carbon atom at the right-hand end of the double bond, and the chlorine to the left-hand end? You would still have the same product. The chlorine would be on a carbon atom next to the end of the chain - you would simply have drawn the molecule flipped over in space. That would be different of the alkene was unsymmetrical - that's why we have to look at them separately.

MECHANISM

The addition of hydrogen halides is one of the easiest electrophilic addition reactions because it uses the simplest electrophile: the proton. Hydrogen halides provide both a electrophile (proton) and a nucleophile (halide). First, the electrophile will attack the double bond and take up a set of π electrons, attaching it to the molecule (1). This is basically the reverse of the last step in the E1 reaction (deprotonation step). The resulting molecule will have a single carbon-carbon bond with a positive charge on one of them (carbocation). The next step is when the nucleophile (halide) bonds to the carbocation, producing a new molecule with both the original hydrogen and halide attached to the organic reactant (2). The second step will only occur if a good nucleophile is used.

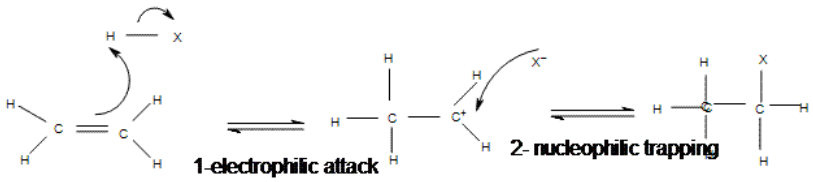


Figure 7.8.1: *Mechanism of Electrophilic Addition of Hydrogen Halide to Ethene*

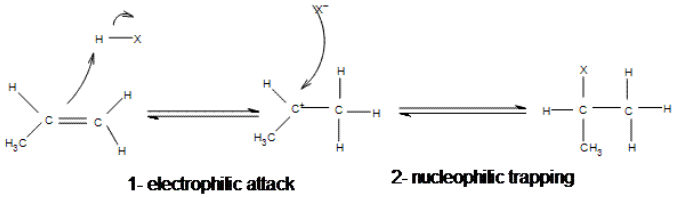


Figure 7.8.2: *Mechanism of Electrophilic Addition of Hydrogen Halide to Propene*

All of the halides (HBr, HCl, HI, HF) can participate in this reaction and add on in the same manner. Although different halides do have different rates of reaction, due to the H-X bond getting weaker as X gets larger (poor overlap of orbitals)s.

REACTION RATES

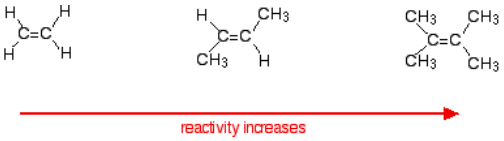
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VARIATION OF RATES WHEN YOU CHANGE THE ALKENE

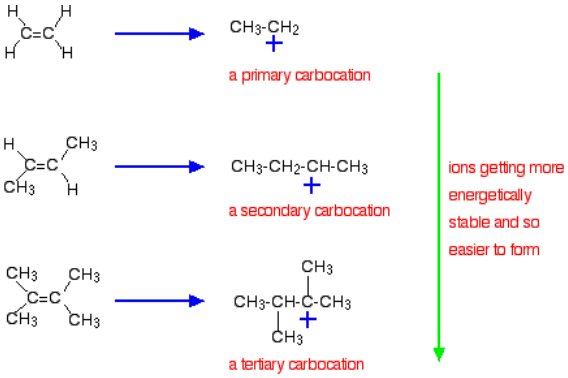
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For example:



There are two ways of looking at the reasons for this - both of which need you to know about the mechanism for the reactions. Alkenes react because the electrons in the pi bond attract things with any degree of positive charge. Anything which increases the electron density around the double bond will help this.

Alkyl groups have a tendency to "push" electrons away from themselves towards the double bond. The more alkyl groups you have, the more negative the area around the double bonds becomes. The more negatively charged that region becomes, the more it will attract molecules like hydrogen chloride. The more important reason, though, lies in the stability of the intermediate ion formed during the reaction. The three examples given above produce these carbocations (carbonium ions) at the half-way stage of the reaction:



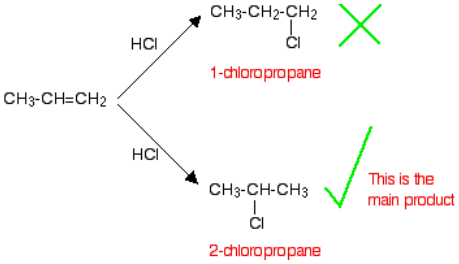
The stability of the intermediate ions governs the activation energy for the reaction. As you go towards the more complicated alkenes, the activation energy for the reaction falls. That means that the reactions become faster.

ADDITION TO UNSYMMETRICAL ALKENES

In terms of reaction conditions and the factors affecting the rates of the reaction, there is no difference whatsoever between these alkenes and the symmetrical ones described above. The problem comes with the orientation of the addition - in other words, which way around the hydrogen and the halogen add across the double bond.

ORIENTATION OF ADDITION

If HCl adds to an unsymmetrical alkene like propene, there are two possible ways it could add. However, in practice, there is only one major product.



This is in line with Markovnikov's Rule which says:

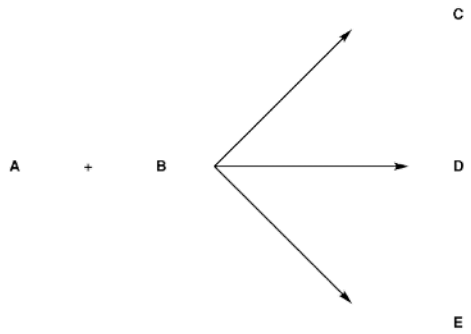
> When a compound HX is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already.

In this case, the hydrogen becomes attached to the CH_2 group, because the CH_2 group has more hydrogens than the CH group. Notice that only the hydrogens directly attached to the carbon atoms at either end of the double bond count. The ones in the CH_3 group are totally irrelevant.

REGIOSELECTIVE

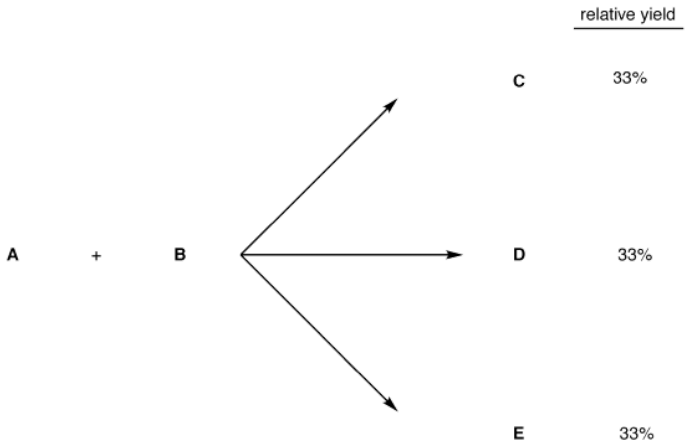
If more than one reaction could occur between a set of reactants under the same conditions giving products that are constitutional isomers and if one product forms in greater amounts than the others, the overall reaction is said to be regioselective.

Say three reactions could occur between the hypothetical reactants **A** and **B** under the same conditions giving the constitutionally isomeric products **C**, **D**, and **E**.



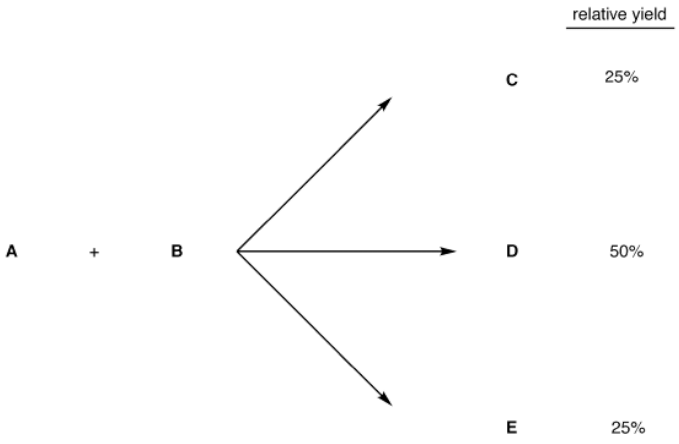
There are two possibilities:

1. The three products form in equal amounts, i.e., of the total product 33% is **C**, another 33% **D**, the remaining 33% **E**. (These percentages are called relative yields of the products.)



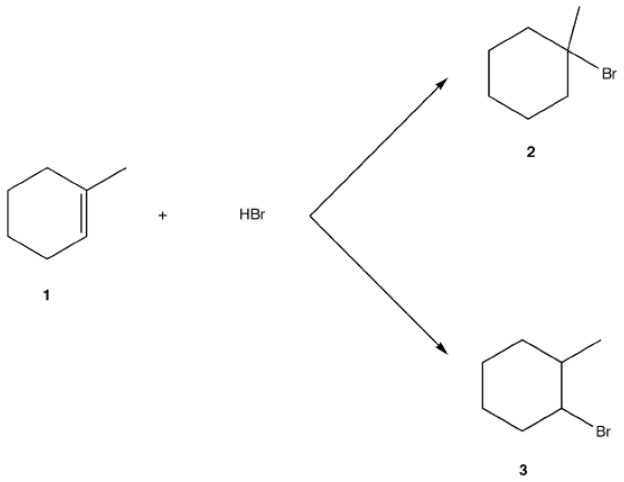
If this is what is observed, the overall reaction between **A** and **B** is not regioselective.

2. One product forms in greater amounts than the others. Say, for example, the relative yields of **C**, **D**, and **E** are 25%, 50%, and 25%, respectively.



If this is what is observed, the overall reaction between **A** and **B** is regioselective.

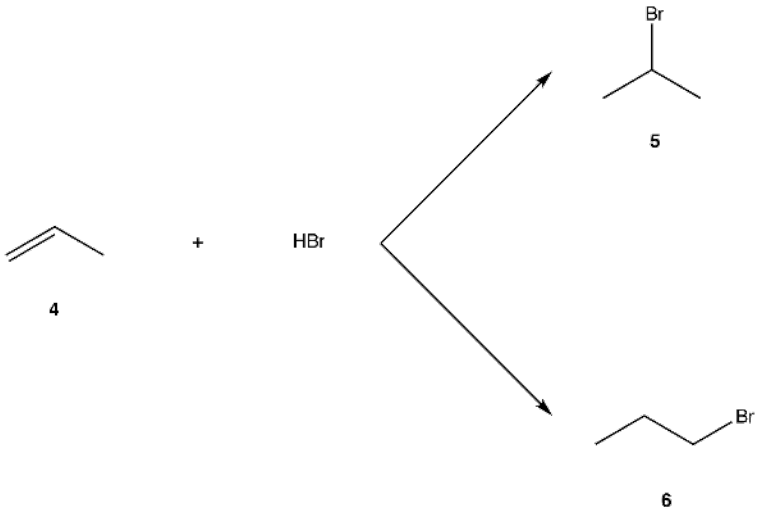
eg:



Experimentally, **2** is the major product; **3** is the minor product. Thus, the overall reaction between **1** and HBr is regioselective toward **2**.

If more than one reaction could occur between a set of reactants under the same conditions giving products that are constitutional isomers and if only one product is observed, the overall reaction is said to be 100% regioselective or regiospecific.

eg:

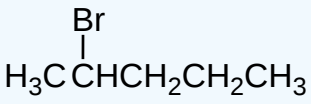


The only observed product is **5**. (Relative yields of **5** and **6** are 100% and 0%, respectively.) Thus the overall reaction between **4** and HBr is regiospecific toward **5**.

Regiospecificity is merely the limiting case of regioselectivity. All regiospecific reactions are regioselective, but not all regioselective reactions are regiospecific.

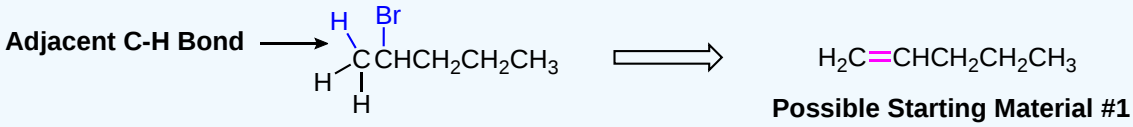
? WORKED EXAMPLE 7.8.1

What alkene would be required to make the following 2-bromopentane using an electrophilic addition?

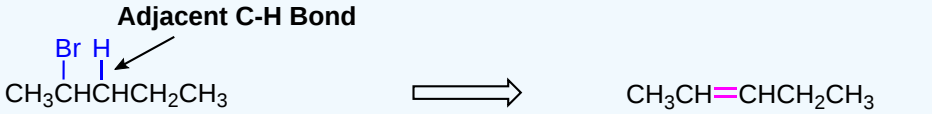


Answer

Analysis: Possible starting materials can be made by first removing the C-Br bond and an adjacent C-H bond. Then connecting the two carbons with a double bond. Because there are two different locations where an adjacent C-H bond can be removed there will be two possible starting material.

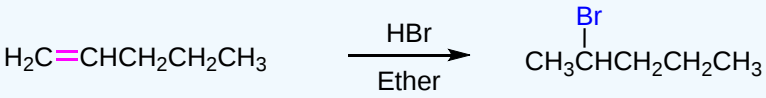


Possible Starting Material #1

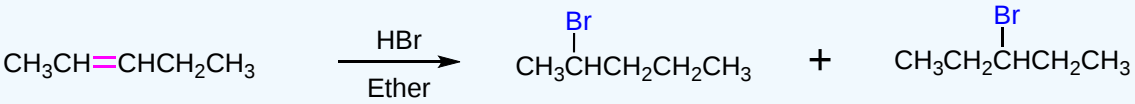


Possible Starting Material #2

Solution: When comparing the the possible starting materials, #1 will follow Markovnikov's rule and produce 2-bromopentane as the sole product. Starting material #2 is symmertrically alkyl substituted, so Markovnikov's rule does not apply. A mixture of 2-bromopentane and 3-bromopentane would be produced. Between the two possible starting material #1 would be preferred because only one product is produced.



Possible Starting Material #1 **2-Bromopentane**

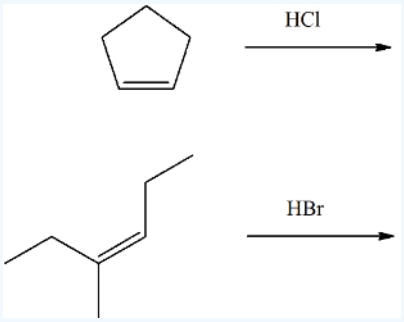


Possible Starting Material #2 **2-Bromopentane** **2-Bromopentane**

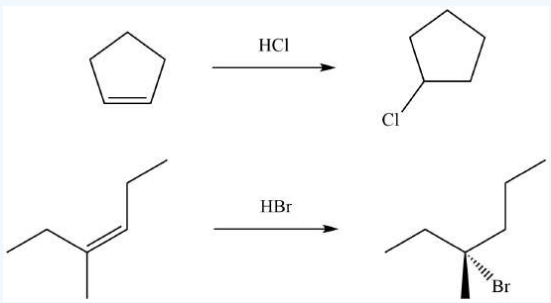
EXERCISES

? EXERCISE 7.8.1

Predict the product(s) for the following reactions:

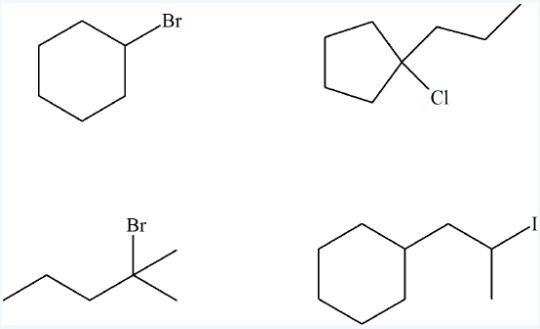


Answer

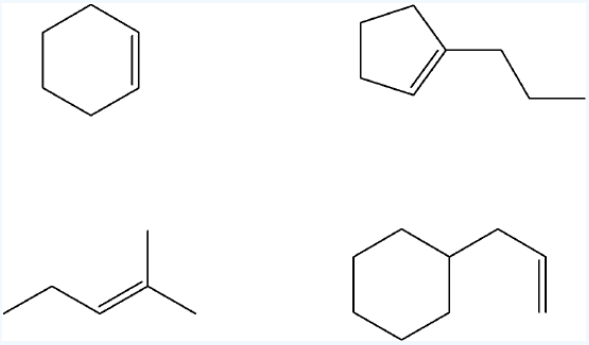


EXERCISE 7.8.2

In each case, suggest an alkene that would give the product shown.

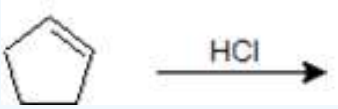


Answer

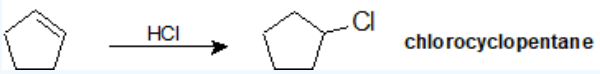


EXERCISE 7.8.3

Give the IUPAC name for the product of the following reaction.



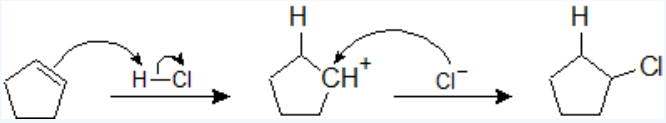
Answer



EXERCISE 7.8.4

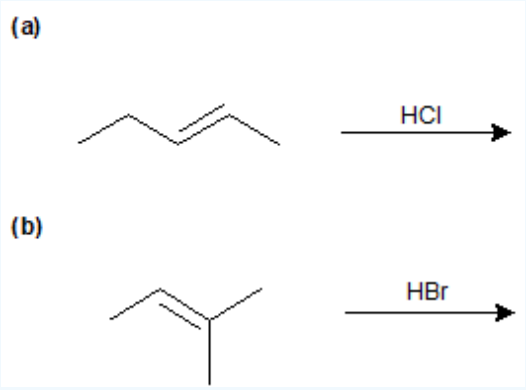
Draw the reaction mechanism of the previous problem

Answer

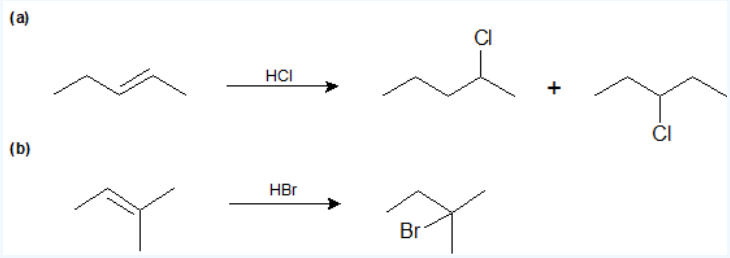


EXERCISE 7.8.5

Identify the products of the following reactions.



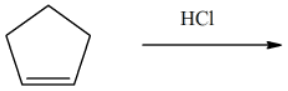
Answer

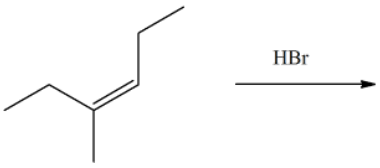


QUESTIONS

Q7.8.1

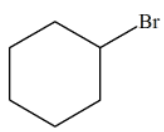
Predict the product(s) for the following reactions:

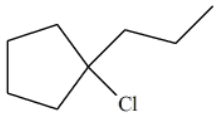


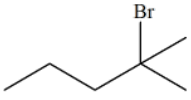


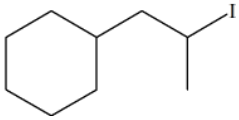
Q7.8.2

In each case, suggest an alkene that would give the product shown.



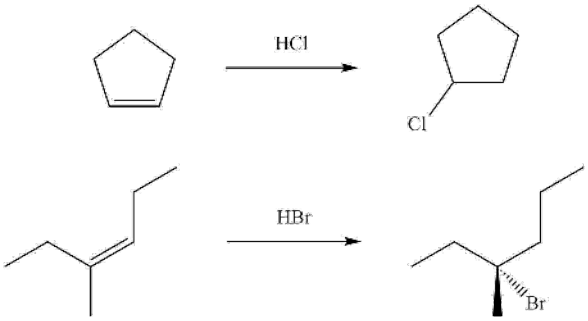




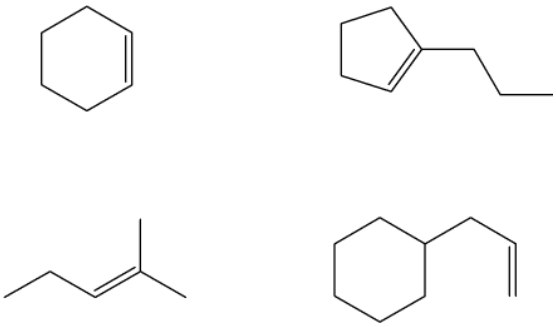


SOLUTIONS

S7.8.1



S7.8.2



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Jim Clark (Chemguide.co.uk)
- Gamini Gunawardena from the OChemPal site (Utah Valley University)

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7.9: CARBOCATION STRUCTURE AND STABILITY

OBJECTIVES

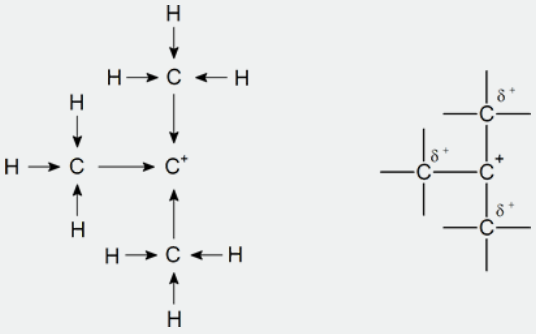
After completing this section, you should be able to

1. describe the geometry of a given carbocation.
2. arrange a given series of carbocations in order of increasing or decreasing stability.
3. explain the relative stability of methyl, primary, secondary and tertiary carbocations in terms of hyperconjugation and inductive effects.

STUDY NOTES

Although hyperconjugation can be used to explain the relative stabilities of carbocations, this explanation is certainly not the only one, and is by no means universally accepted. A more common explanation, involving the concept of an inductive effect, is given below.

It is a general principle in chemistry that the more a charge is dispersed, the more stable is the species carrying the charge. Put simply, a species in which a positive charge is shared between two atoms would be more stable than a similar species in which the charge is borne wholly by a single atom. In a tertiary carbocation, the positively charged carbon atom attracts the bonding electrons in the three carbon-carbon sigma (σ) bonds, and thus creates slight positive charges on the carbon atoms of the three surrounding alkyl groups (and, indeed, on the hydrogen atoms attached to them). Chemists sometimes use an arrow to represent this inductive release:



Note: These diagrams do not reflect the geometry of the carbocation. The overall charge on the carbocation remains unchanged, but some of the charge is now carried by the alkyl groups attached to the central carbon atom; that is, the charge has been dispersed.

In the tertiary carbocation shown above, the three alkyl groups help to stabilize the positive charge. In a secondary carbocation, only two alkyl groups would be available for this purpose, while a primary carbocation has only one alkyl group available. Thus the observed order of stability for carbocations is as follows:

tertiary > secondary > primary > methyl.

STABILITY OF CARBOCATION INTERMEDIATES

We know that the rate-limiting step of an S_N1 reaction is the first step - formation of the this carbocation intermediate. The rate of this step – and therefore, the rate of the overall substitution reaction – depends on the activation energy for the process in which the bond between the carbon and the leaving group breaks and a carbocation forms. According to Hammond's postulate (section 6.2B), the more stable the carbocation intermediate is, the faster this first bond-breaking step will occur. In other words, the likelihood of a nucleophilic substitution reaction proceeding by a dissociative (S_N1) mechanism depends to a large degree on the stability of the carbocation intermediate that forms.

The critical question now becomes, *what stabilizes a carbocation?*

So if it takes an electron *withdrawing* group to stabilize a negative charge, what will stabilize a positive charge? An electron *donating* group!

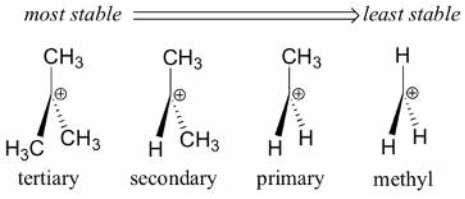


Electron Donating Group: stabilizes a carbocation

Electron Withdrawing Group: *de*stabilizes a carbocation

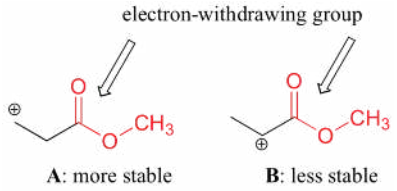
A positively charged species such as a carbocation is very electron-poor, and thus anything which donates electron density to the center of electron poverty will help to stabilize it. Conversely, a carbocation will be *destabilized* by an electron withdrawing group.

Alkyl groups – methyl, ethyl, and the like – are weak electron donating groups, and thus stabilize nearby carbocations. What this means is that, in general, *more substituted carbocations are more stable*: a tert-butyl carbocation, for example, is more stable than an isopropyl carbocation. Primary carbocations are highly unstable and not often observed as reaction intermediates; methyl carbocations are even less stable.



Alkyl groups are electron donating and carbocation-stabilizing because the electrons around the neighboring carbons are drawn towards the nearby positive charge, thus slightly reducing the electron poverty of the positively-charged carbon.

It is not accurate to say, however, that carbocations with higher substitution are *always* more stable than those with less substitution. Just as electron-donating groups can stabilize a carbocation, electron-withdrawing groups act to destabilize carbocations. Carbonyl groups are electron-withdrawing by inductive effects, due to the polarity of the C=O double bond. It is possible to demonstrate in the laboratory (see section 16.1D) that carbocation A below is more stable than carbocation B, even though A is a primary carbocation and B is secondary.

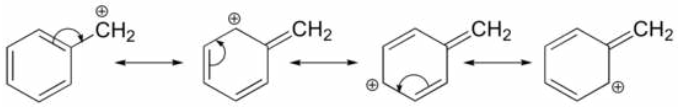


The difference in stability can be explained by considering the electron-withdrawing inductive effect of the ester carbonyl. Recall that inductive effects - whether electron-withdrawing or donating - are relayed through covalent bonds and that the strength of the effect decreases rapidly as the number of intermediary bonds increases. In other words, the effect decreases with distance. In species B the positive charge is closer to the carbonyl group, thus the destabilizing electron-withdrawing effect is stronger than it is in species A.

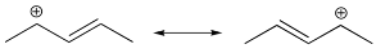
NOTE

In the next chapter we will see how the carbocation-destabilizing effect of electron-withdrawing fluorine substituents can be used in experiments designed to address the question of whether a biochemical nucleophilic substitution reaction is S_N1 or S_N2.

Stabilization of a carbocation can also occur through resonance effects, and as we have already discussed in the acid-base chapter, resonance effects as a rule are more powerful than inductive effects. Consider the simple case of a **benzylic** carbocation:



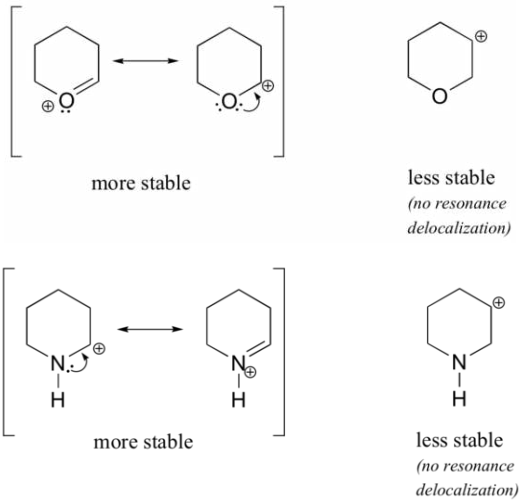
This carbocation is comparatively stable. In this case, electron donation is a resonance effect. Three additional resonance structures can be drawn for this carbocation in which the positive charge is located on one of three aromatic carbons. The positive charge is not isolated on the benzylic carbon, rather it is delocalized around the aromatic structure: this delocalization of charge results in significant stabilization. As a result, benzylic and **allylic** carbocations (where the positively charged carbon is conjugated to one or more non-aromatic double bonds) are significantly more stable than even tertiary alkyl carbocations.



an allylic carbocation

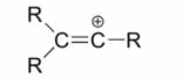
Because heteroatoms such as oxygen and nitrogen are more electronegative than carbon, you might expect that they would by definition be electron withdrawing groups that destabilize carbocations. In fact, the opposite is often true: if the oxygen or nitrogen atom is in the correct position, the overall effect is carbocation stabilization. This is due to the fact that although these heteroatoms are electron *withdrawing* groups by induction, they are electron *donating* groups by resonance, and it is this resonance effect which is more powerful. (We previously

encountered this same idea when considering the relative acidity and basicity of phenols and aromatic amines in section 7.4). Consider the two pairs of carbocation species below:



In the more stable carbocations, the heteroatom acts as an electron donating group by resonance: in effect, the lone pair on the heteroatom is available to delocalize the positive charge. In the less stable carbocations the positively-charged carbon is more than one bond away from the heteroatom, and thus no resonance effects are possible. In fact, in these carbocation species the heteroatoms actually *destabilize* the positive charge, because they are electron withdrawing by induction.

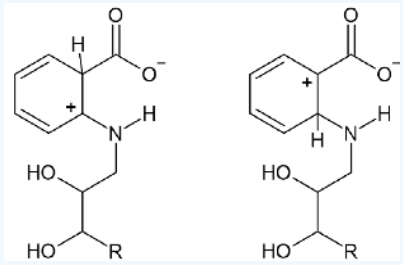
Finally, **vinylic** carbocations, in which the positive charge resides on a double-bonded carbon, are very unstable and thus unlikely to form as intermediates in any reaction.



a vinylic carbocation
(very unstable)

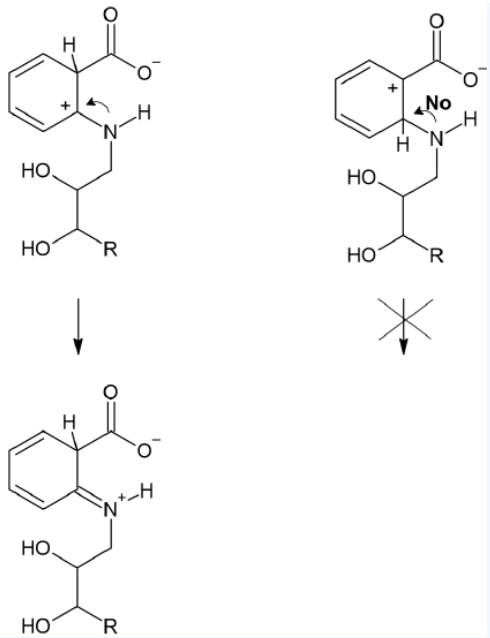
EXAMPLE 7.9.1

In which of the structures below is the carbocation expected to be more stable? Explain.

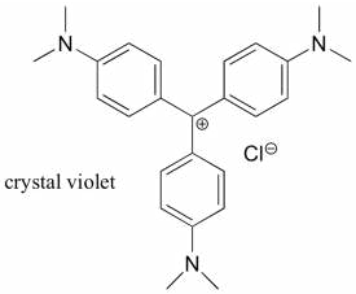


Answer

In the carbocation on the left, the positive charge is located in a position relative to the nitrogen such that the lone pair of electrons on the nitrogen can be donated to fill the empty orbital. This is not possible for the carbocation species on the right.



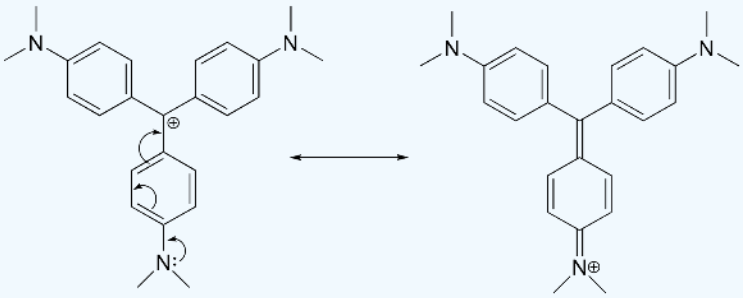
For the most part, carbocations are very high-energy, transient intermediate species in organic reactions. However, there are some unusual examples of very stable carbocations that take the form of organic salts. Crystal violet is the common name for the chloride salt of the carbocation whose structure is shown below. Notice the structural possibilities for extensive resonance delocalization of the positive charge, and the presence of three electron-donating amine groups.



EXAMPLE 7.9.2

Draw a resonance structure of the crystal violet cation in which the positive charge is delocalized to one of the nitrogen atoms.

Answer

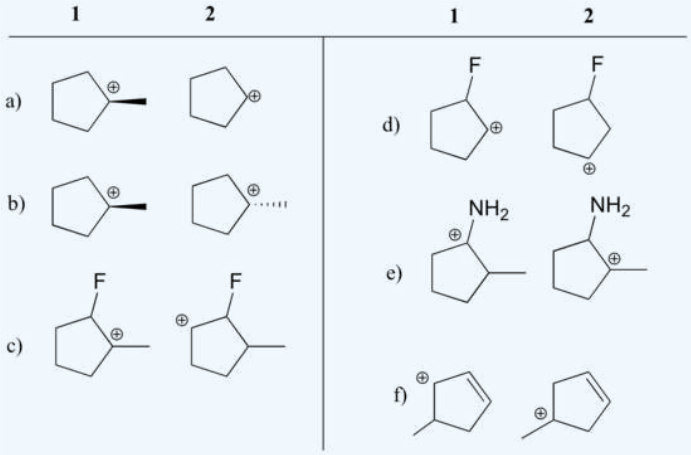


When considering the possibility that a nucleophilic substitution reaction proceeds *via* an S_N1 pathway, it is critical to evaluate the stability of the hypothetical carbocation intermediate. If this intermediate is not sufficiently stable, an S_N1 mechanism must be considered unlikely, and the reaction probably proceeds by an S_N2 mechanism. In the next chapter we will see several examples of biologically important S_N1

reactions in which the positively charged intermediate is stabilized by inductive and resonance effects inherent in its own molecular structure.

EXAMPLE 7.9.3

State which carbocation in each pair below is more stable, or if they are expected to be approximately equal. Explain your reasoning.



Answer

a) 1 (tertiary vs. secondary carbocation)

b) equal

c) 1 (tertiary vs. secondary carbocation)

d) 2 (positive charge is further from electron-withdrawing fluorine)

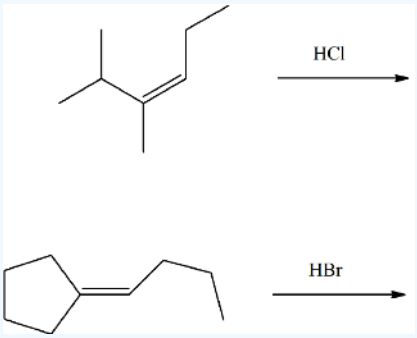
e) 1 (lone pair on nitrogen can donate electrons by resonance)

f) 1 (allylic carbocation – positive charge can be delocalized to a second carbon)

EXERCISE

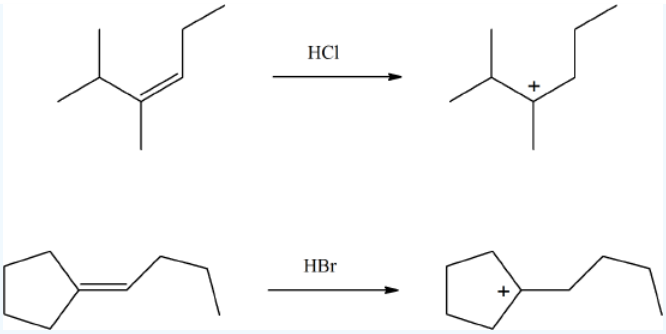
EXERCISE 7.9.1

Draw the cationic intermediates that are seen in the following reactions.



Answer

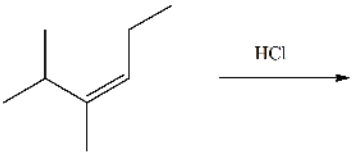
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QUESTIONS

Q7.9.1

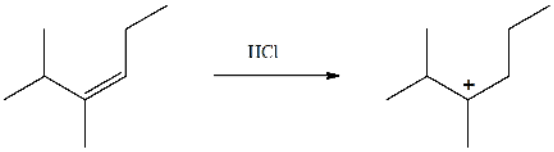
Draw the cationic intermediates that are seen in the following reactions:

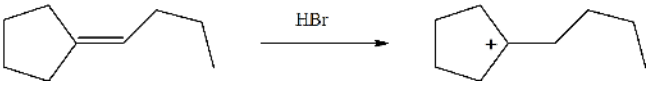




SOLUTIONS

S7.9.1





CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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7.10: THE HAMMOND POSTULATE

OBJECTIVE

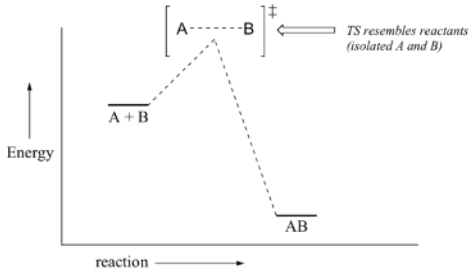
After completing this section, you should be able to use the Hammond postulate to explain the formation of the most stable carbocation during the addition of a protic acid, HX, to an alkene.

KEY TERMS

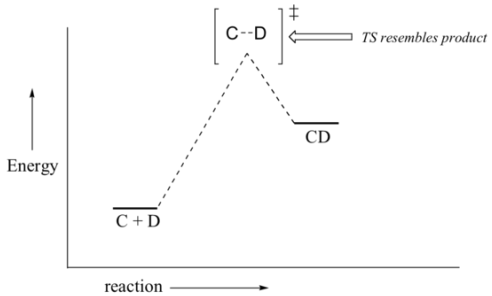
Make certain that you can define, and use in context, the key term below.

- Hammond postulate

Now, back to transition states. Chemists are often very interested in trying to learn about what the transition state for a given reaction looks like, but addressing this question requires an indirect approach because the transition state itself cannot be observed. In order to gain some insight into what a particular transition state looks like, chemists often invoke the **Hammond postulate**, which states that *a transition state resembles the structure of the nearest stable species*. For an exergonic reaction, therefore, the transition state resembles the reactants more than it does the products.



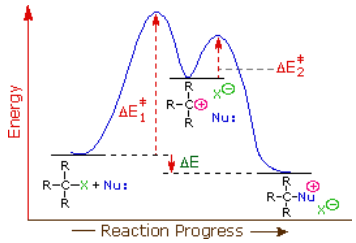
If we consider a hypothetical exergonic reaction between compounds A and B to form AB, the distance between A and B would be relatively large at the transition state, resembling the starting state where A and B are two isolated species. In the hypothetical endergonic reaction between C and D to form CD, however, the bond formation process would be much further along at the TS point, resembling the product.



The Hammond Postulate is a very simplistic idea, which relies on an assumption that potential energy surfaces are parabolic. Although such an assumption is not rigorously true, it is fairly reliable and allows chemists to make energetic arguments about transition states by employing arguments about the stability of a related species. Since the formation of a reactive intermediate is very reliably **endergonic**, arguments about the stability of reactive intermediates can serve as proxy arguments about transition state stability.

THE HAMMOND POSTULATE AND THE S_N1 REACTION

the Hammond postulate suggests that the activation energy of the rate-determining first step will be inversely proportional to the stability of the carbocation intermediate. The stability of carbocations was discussed earlier, and a qualitative relationship is given below:



Carbocation Stability	$CH_3^{(+)} < CH_3CH_2^{(+)} < (CH_3)_2CH^{(+)} \approx \underset{CH_2^{(+)}}{CH_2{=}CH\text{-}} < C_6H_5CH_2^{(+)} \approx (CH_3)_3C^{(+)}$

Consequently, we expect that 3º-alkyl halides will be more reactive than their 2º and 1º-counterparts in reactions that follow an S_N1 mechanism. This is opposite to the reactivity order observed for the S_N2 mechanism. Allylic and benzylic halides are exceptionally reactive by either mechanism.

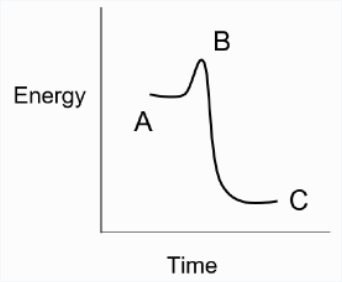
EXERCISE

? EXERCISE 7.10.1

Consider the second step in the electrophilic addition of HBr to an alkene. Is this step exergonic or endergonic and does the transition state resemble the product or the reactant (cation)? Draw out an energy diagram of this step reaction.

Answer

As shown, the second step going from intermediate cation (A) to final product (C) it is exergonic. The transition state (B) resembles more the reactant (intermediate cation - A).



QUESTIONS

Q7.10.1

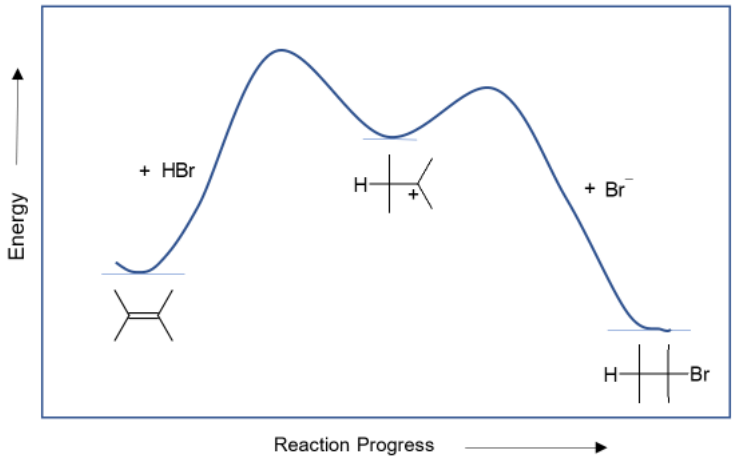
Consider the second step in the electrophilic addition of HBr to an alkene. Is this step exergonic or endergonic and does the transition state represent the product or the reactant (cation)? Draw out an energy diagram of this step reaction.

SOLUTIONS

S7.10.1

Exergonic and the transition state (second step) represents the reactant (cation).

As shown to go from intermediate cation to final product the step is exergonic.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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7.11: EVIDENCE FOR THE MECHANISM OF ELECTROPHILIC ADDITIONS- CARBOCATION REARRANGEMENTS

OBJECTIVE

After completing this section, you should be able to explain the “unusual” products formed in certain reactions in terms of the rearrangement of an intermediate carbocation.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- alkyl shift
- hydride shift

STUDY NOTES

Whenever possible, carbocations will rearrange from a less stable isomer to a more stable isomer. This rearrangement can be achieved by either a hydride shift, where a hydrogen atom migrates from one carbon atom to the next, taking a pair of electrons with it; or an alkyl shift, in which an alkyl group undergoes a similar migration, again taking a bonding pair of electrons with it. These migrations usually occur between neighbouring carbon atoms, and hence are termed 1,2-hydride shifts or 1,2-alkyl shifts.

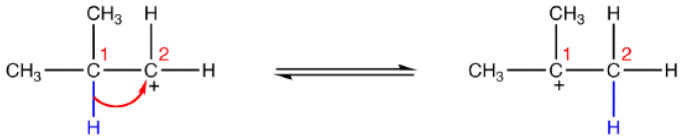
[A hydride ion consists of a proton and two electrons, that is, $[H:]^-$. Hydride ions exist in compounds such as sodium hydride, NaH, and calcium hydride, CaH_2.]

An electrophilic reaction such as HX with an alkene will often yield more than one product. This is strong evidence that the mechanism includes intermediate rearrangement steps of the cation.

1,2-HYDRIDE SHIFT

A 1,2-hydride shift is a carbocation rearrangement in which a hydrogen atom in a carbocation migrates to the carbon atom bearing the formal charge of +1 (carbon 2) from an adjacent carbon (carbon 1).

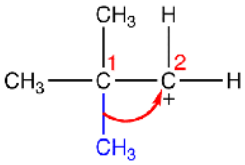
eg:



see also 1,2-aryl shift

1,2-ALKYL SHIFT

A 1,2-alkyl shift is a carbocation rearrangement in which an alkyl group migrates to the carbon atom bearing the formal charge of +1 (carbon 2) from an adjacent carbon atom (carbon 1), e.g.



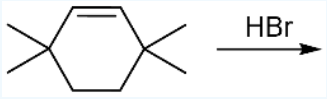
see also 1,2-aryl shift, hydride shift, alkyl shift

EXERCISES

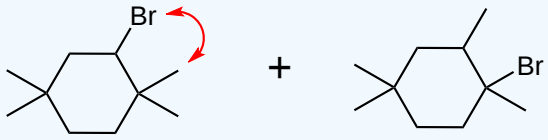
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EXERCISE 7.11.1

Draw the expectred produts of the following reaction.



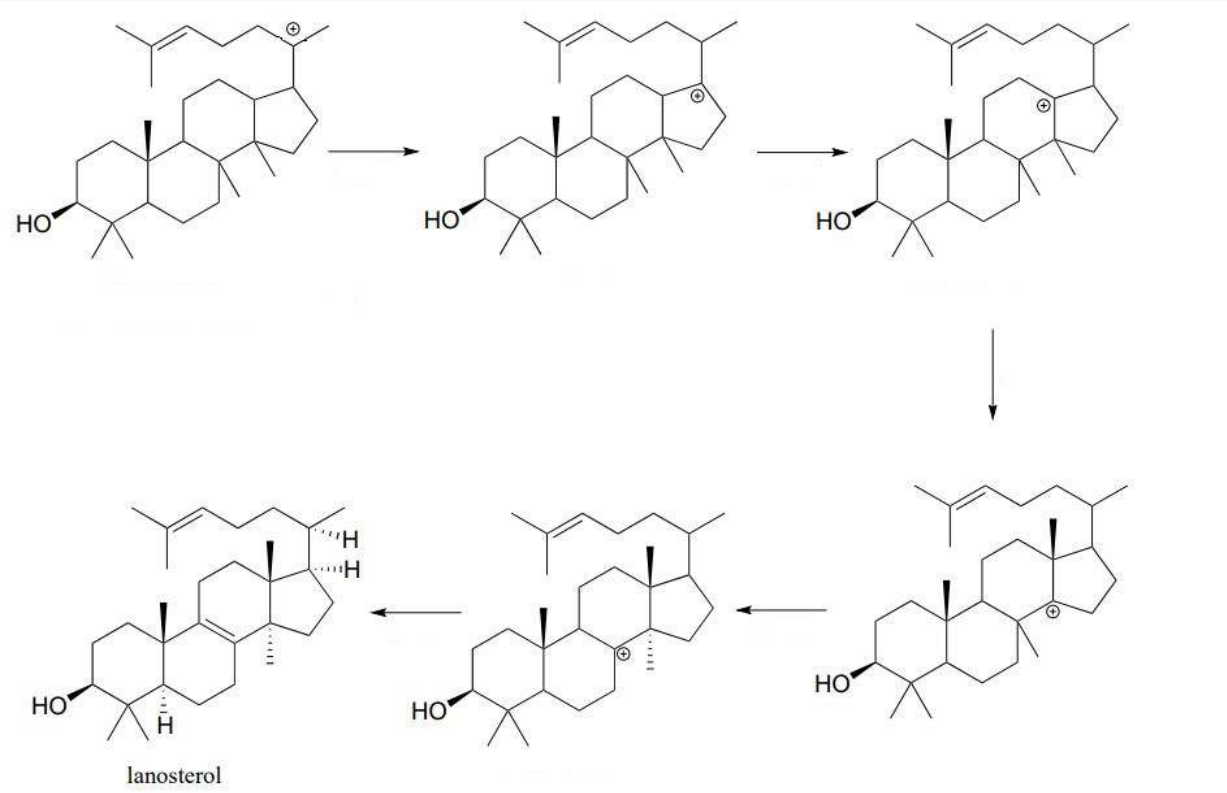
Answer



Electrophilic Addition Product **Alkyl Shift Product**

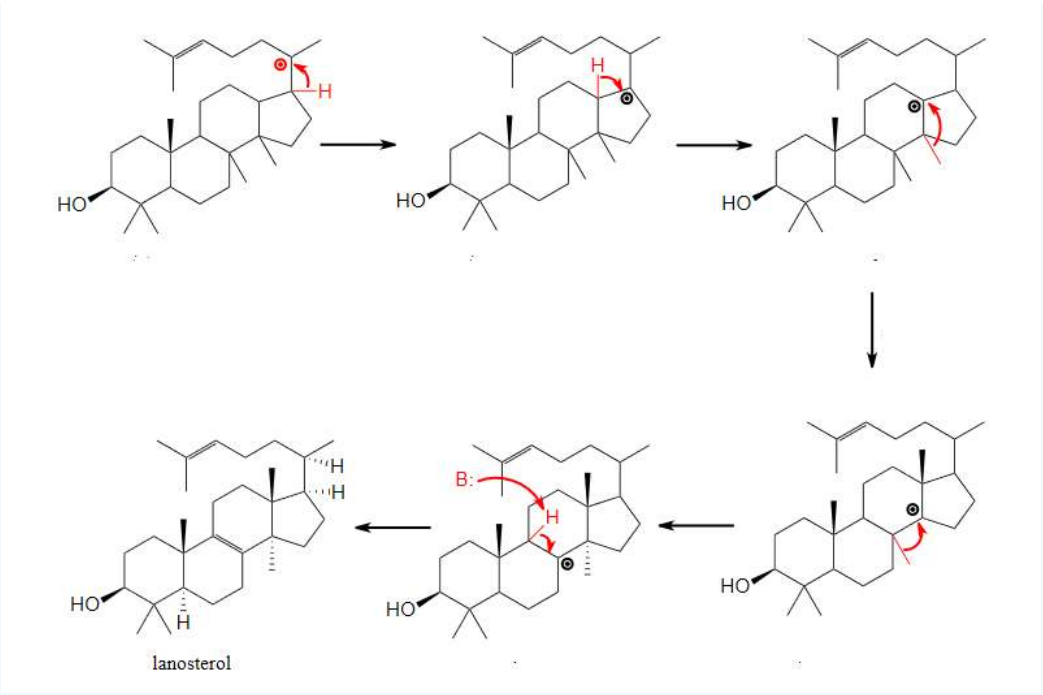
EXERCISE 7.11.2

The second phase of the cyclase reaction mechanism involves multiple rearrangement steps and a deprotonation. Please supply the missing mechanistic arrows.



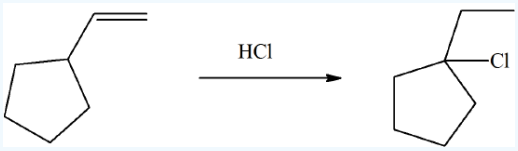
lanosterol

Answer

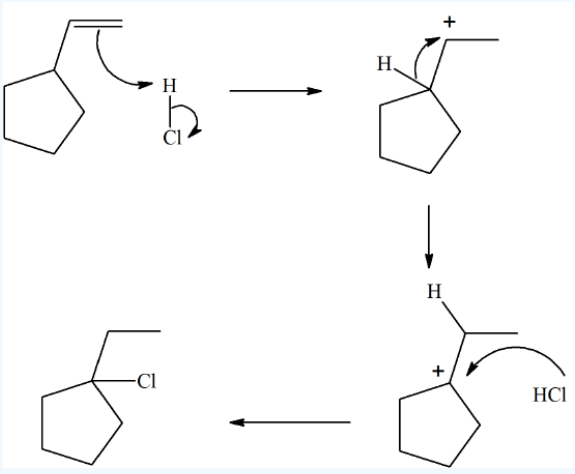


EXERCISE 7.11.3

The following reaction shows a rearrangement within the mechanism. Propose a mechanism that shows this.

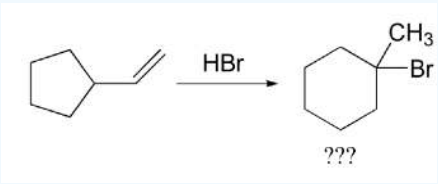


Answer



EXERCISE 7.11.4

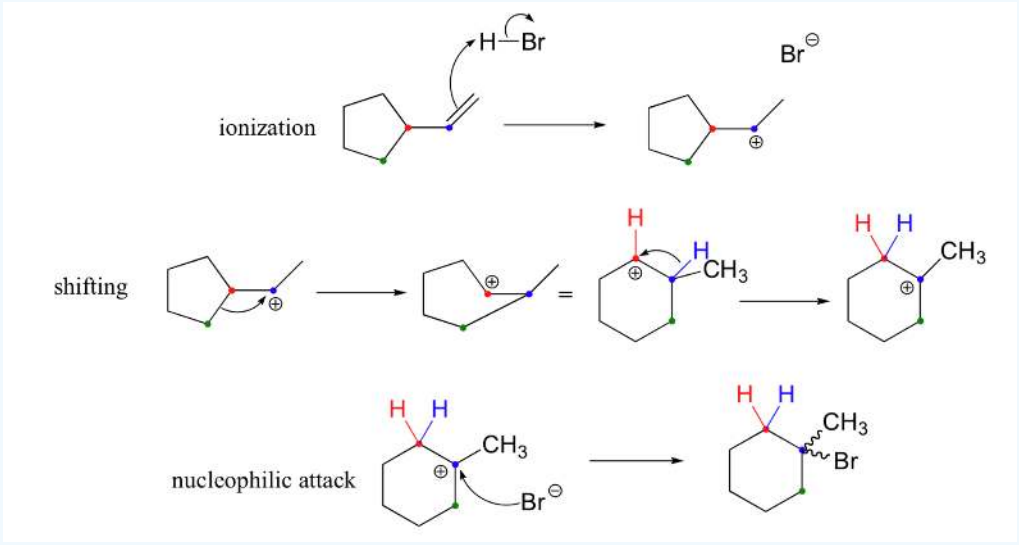
Propose a mechanism for the following reaction. It involves an electrophilic addition and the shift of a C-C and a C-H bond.



Answer

In most examples of carbocation rearrangements that you are likely to encounter, the shifting species is a hydride or methyl group. However, pretty much any alkyl group is capable of shifting. Sometimes, the entire side of a ring will shift over in a ring-expanding rearrangement.

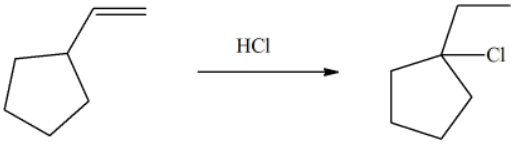
The first 1,2-alkyl shift is driven by the expansion of a five-membered ring to a six-membered ring, which has slightly less ring strain. A hydride shift then converts a secondary carbocation to a tertiary carbocation, which is the electrophile ultimately attacked by the bromide nucleophile.



QUESTIONS

Q7.11.1

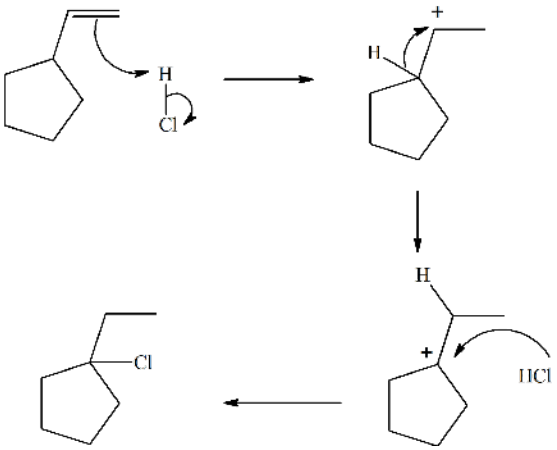
The following reaction shows a rearrangement within the mechanism. Propose a mechanism that shows this.



SOLUTIONS

S7.11.1

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CONTRIBUTORS

- Gamini Gunawardena from the OChemPal site (Utah Valley University)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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7.S: ALKENES - STRUCTURE AND REACTIVITY (SUMMARY)

CONCEPTS & VOCABULARY

7.1 Industrial Preparation and Use of Alkenes

- Breaking up of large hydrocarbon molecules into smaller, useful molecules is called cracking.

7.2 Calculating Degree of Unsaturation

- Saturated molecules contain only single bonds and no rings.
- Saturated hydrocarbons have the formula C_nH_{2n+2}, where n can be any integer.
- Degrees of unsaturation account for the total number of rings and pi bonds in a molecule.
- Each degree of unsaturation reduces the number of hydrogens in the molecule by 2.

7.3 Naming Alkenes

- When the two largest groups are on the same side of the double bond (top or bottom) they are called cis or *Z*.
- When the two largest groups are on opposite sides of the double bond (top or bottom) they are called trans or *E*.
- Endocyclic double bonds occur when there is a pi bond within a ring.

7.4 Cis-Trans Isomerism in Alkenes

7.5 Alkene Stereochemistry and the E, Z Designation

- *E* and *Z* are less limited than cis and trans in naming.
- *E* and *Z* configurations use the same priority rules as R and S (CIP rules).

7.6 Stability of Alkenes

- Relative stability of alkenes can be measured by using heats of hydrogenation upon reduction to the related alkane.
- More substituted alkenes are more stable than less substituted.
- Alkenes with the largest groups trans are more stable than cis.

7.7 Electrophilic Addition Reactions of Alkenes

- In electrophilic addition reactions, the pi bond of the alkene acts as the nucleophile.
- Electrophilic addition reactions occur faster with larger hydrogen halides as well as more substituted alkenes.

7.8 Orientation of Electrophilic Additions: Markovnikov's Rule

- The more substituted carbocation intermediate forms during electrophilic addition reactions, since more substituted carbocations are more stable. This is known as Markovnikov's rule.

7.9 Carbocation Structure and Stability

- Molecules or ions that can disperse (delocalize) charge are more stable than structures with charge localized on a single atom.
- Due to inductive stabilization, carbocation stability follows the order:

tertiary > secondary > primary > methyl

- Electron donating groups stabilize carbocations.
- Electron withdrawing groups destabilize carbocations.
- Resonance effects can stabilize a carbocation (some examples include benzylic and allylic carbocations).
- Vinylic carbocations are unstable and are unlikely to form.

7.10 The Hammond Postulate

- The Hammond Postulate states that transition state structure most resembles the nearest stable species.
- Based on the Hammond Postulate, transition states for exothermic reaction steps resemble reactants, while endergonic step transition states resemble products.

7.11 Evidence for the Mechanism of Electrophilic Additions: Carbocation Rearrangements

- Carbocations will rearrange from less stable to more stable isomers through hydride shifts or alkyl shifts.

SKILLS TO MASTER

- Skill 7.1 Calculate degree of unsaturation for organic molecular formulae.

- Skill 7.2 Draw isomers from a molecular formula.
- Skill 7.3 Name alkenes following IUPAC rules, including configuration (*E*, *Z*).
- Skill 7.4 Draw structures from IUPAC name.
- Skill 7.5 Describe bonding in alkenes including bond length, strength, angle and restricted rotation.
- Skill 7.6 Explain stability of alkenes.
- Skill 7.7 Rank alkenes in order of stability.
- Skill 7.8 Draw mechanism for electrophilic addition of HX to alkenes, including regiochemistry.
- Skill 7.9 Explain stability of carbocations.
- Skill 7.10 Explain transition states related to the Hammond Postulate.
- Skill 7.11 Explain products formed by carbocation rearrangements.

MEMORIZATION TASKS

MT 7.1 Memorize formula for saturated hydrocarbons C_nH_{2n+2}.

MT 7.2 Memorize basic IUPAC naming rules.

MT 7.3 Memorize relative stability of alkenes.

MT 7.4 Memorize relative stability of carbocations.

CONTRIBUTORS

- Layne Morsch (University of Illinois Springfield)

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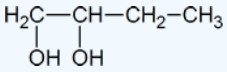
CHAPTER OVERVIEW

8: ALKENES- REACTIONS AND SYNTHESIS

LEARNING OBJECTIVES

After you have completed Chapter 8, you should be able to

1. fulfill all of the detailed objectives listed under each section.
2. design a relatively simple, multistep synthesis using the reactions introduced in this chapter, given the structure, name, or both, of the starting material and product. For example, show how you would convert 1-bromobutane to



3. deduce the structures of a number of compounds involved in a certain reaction sequence, given sufficient information. In other words, solve so-called road-map problems.
4. define, and use in context, the key terms introduced in this chapter.

As you have seen, addition reactions dominate the chemistry of alkenes. This chapter shows how a variety of reagents can add to alkenes; how hydrogen bromide can be made to add to alkenes in a non-Markovnikov manner; and how alkene molecules can be cleaved into easily identifiable parts. First, you will examine the preparation of alkenes by elimination reactions.

8.0: Prelude
8.1: Preparation of Alkenes- A Preview of Elimination Reactions
8.2: Halogenation of Alkenes - Addition of X_2
8.3: Halohydrins from Alkenes - Addition of HOX
8.4: Hydration of Alkenes - Addition of H_2O by Oxymercuration
8.5: Hydration of Alkenes - Addition of H_2O by Hydroboration
8.6: Reduction of Alkenes - Hydrogenation
8.7: Oxidation of Alkenes - Epoxidation and Hydroxylation
8.8: Oxidation of Alkenes - Cleavage to Carbonyl Compounds
8.9: Addition of Carbenes to Alkenes - Cyclopropane Synthesis
8.10: Radical Additions to Alkenes - Chain-Growth Polymers
8.11: Biological Additions of Radicals to Alkenes
8.12: Stereochemistry of Reactions - Addition of H_2O to an Achiral Alkene
8.13: Stereochemistry of Reactions - Addition of H_2O to a Chiral Alkene
8.S: Alkenes - Reactions and Synthesis (Summary)

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8.1: PREPARATION OF ALKENES- A PREVIEW OF ELIMINATION REACTIONS

Objectives

After completing this section, you should be able to

1. explain the relationship between an addition reaction and an elimination reaction.
2. write an equation to describe the dehydrohalogenation of an alkyl halide.
3. identify the reagents required to bring about dehydrohalogenation of an alkyl halide.
4. write an equation to represent the dehydration of an alcohol.
5. identify the reagents required to dehydrate a given alcohol.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- dehydration
- dehydrohalogenation
- elimination reaction

STUDY NOTES

An *elimination reaction* is a reaction in which two or more atoms, one of which is usually hydrogen, are removed from adjacent atoms in the reactant, resulting in the formation of a multiple bond.

The relationship between addition reactions and elimination reactions is shown in Figure 8.1, below.

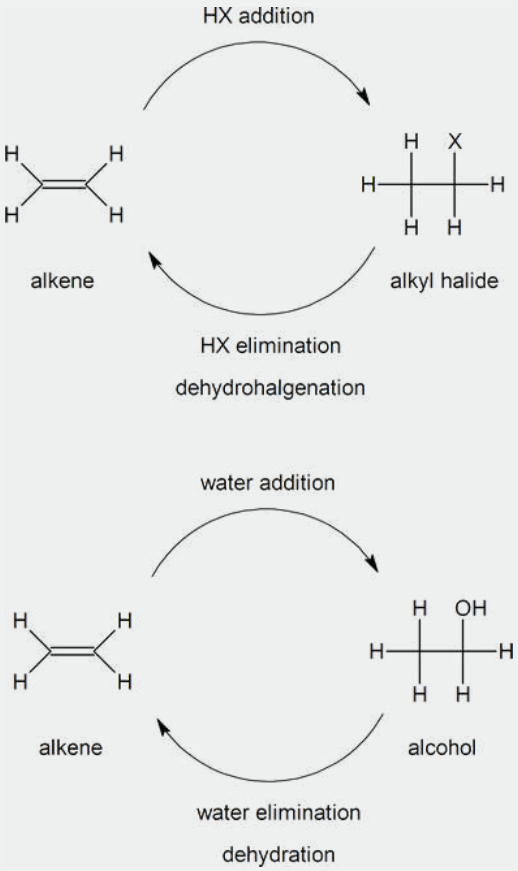
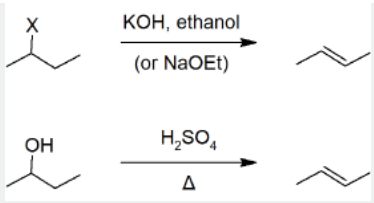


Figure 8.1: *Relationship of addition and elimination reactions*

Alkenes can be readily prepared from the alkylhalide (X = Cl, Br, I) or the alcohol.

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ELECTROPHILIC ADDITION

Alkenes are found throughout nature. They form the basis of many natural products, such as terpenes, which play a variety of roles in the lives of plants and insects. The C=C bonds of alkenes are very different from the C=O bonds that are also common in nature. The C=C bonds of alkenes are electron-rich and nucleophilic, in contrast to the electron-poor C=O bonds of carbohydrates, fatty acids and proteins. That difference plays a role in how terpenes form in nature.

Alkenes, or olefins, are also a major product of the petroleum industry. Reactions of alkenes form the basis for a significant porion of our manufacturing economy. Commonly used plastics such as polyethylene, polypropylene and polystyrene are all formed through the reactions of alkenes. These materials continue to find use in our society because of their valuable properties, such as high strength, flexibility and low weight.

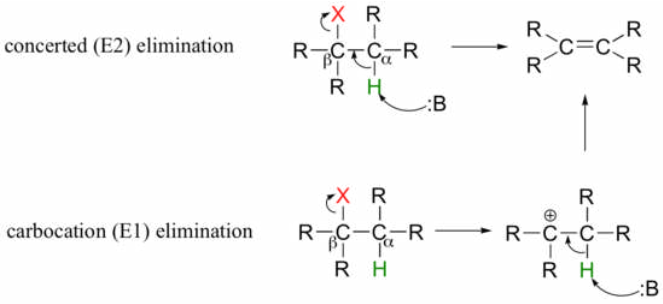
Alkenes undergo addition reactions like carbonyls do. Often, they add a proton to one end of the double bond and another group to the other end. These reactions happen in slightly different ways, however.

Alkenes are reactive because they have a high-lying pair of π-bonding electrons. These electrons are loosely held, being high in energy compared to σ-bonds. The fact that they are not located between the carbon nuclei, but are found above and below the plane of the double bond, also makes these electrons more accessible.

Alkenes can donate their electrons to strong electrophiles other than protons, too. Sometimes their reactivity pattern is a little different than the simple addition across the double bond, but that straightforward pattern is what we will focus on in this chapter.

ELIMINATION REACTIONS

So far in this chapter, we have seen several examples of carbanion-intermediate (E1cb) beta-elimination reactions, in which the first step was proton abstraction at a carbon positioned ato an electron-withdrawing carbonyl or imine. Elimination reactions are also possible at positions that are isolated from carbonyls or any other electron-withdrawing groups. This type of elimination can be described by two model mechanisms: it can occur in a single concerted step (proton abstraction at C_α occurring at the same time as C_β-X bond cleavage), or in two steps (C_β-X bond cleavage occurring first to form a carbocation intermediate, which is then 'quenched' by proton abstraction at the alpha-carbon).



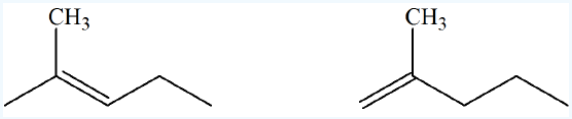
These mechanisms, termed E2 and E1, respectively, are important in laboratory organic chemistry, but are less common in biological chemistry. As explained below, which mechanism actually occurs in a laboratory reaction will depend on the identity of the R groups (ie., whether the alkyl halide is primary, secondary, tertiary, etc.) as well as on the characteristics of the base.

EXERCISES

EXERCISE 8.1.1

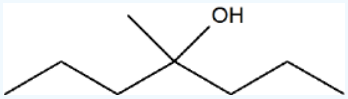
In elimination reactions there tends to have a mixture of products. What are the two possible alkene products for the reaction of 2-bromo-2-methylpentane with NaOH?

Answer

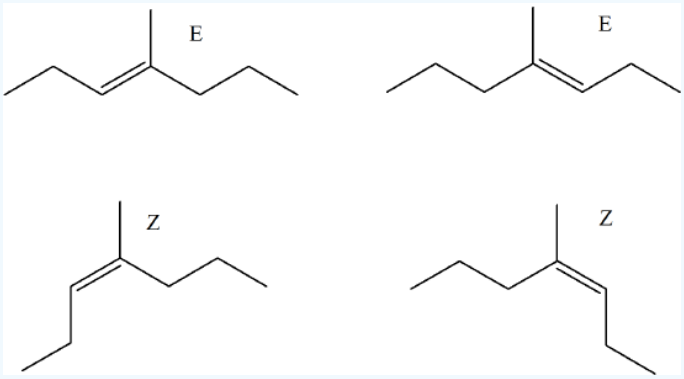


EXERCISE 8.1.2

Predict the *E/Z* isomers for the following molecule when reacted with H_2SO_4.



Answer



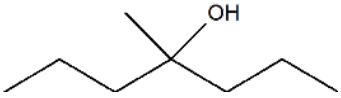
QUESTIONS

Q8.1.1

In elimination reactions there tends to have a mixture of products. What are the two possible alkene products for the reaction of 2-bromo-2-methylpentane with NaOH?

Q8.1.2

Predict the *E/Z* isomers for the following molecule when reacted with H_2SO_4.

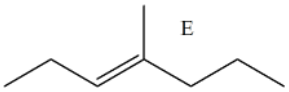


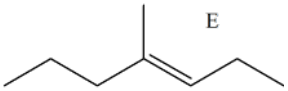
SOLUTIONS

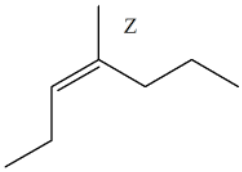
S8.1.1

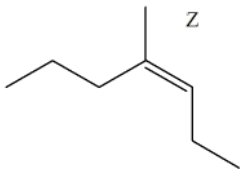


S8.1.2









CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

8.1: Preparation of Alkenes- A Preview of Elimination Reactions is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.2: HALOGENATION OF ALKENES - ADDITION OF X_2

Objectives

After completing this section, you should be able to

1. write the equation for the reaction of chlorine or bromine with a given alkene.
2. identify the conditions under which an addition reaction occurs between an alkene and chlorine or bromine.
3. draw the structure of the product formed when a given alkene undergoes an addition reaction with chlorine or bromine.
4. write the mechanism for the addition reaction that occurs between an alkene and chlorine or bromine, and account for the stereochemistry of the product.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- anti stereochemistry
- bromonium ion

STUDY NOTES

In the laboratory you will test a number of compounds for the presence of a carbon-carbon double bond. A common test is the decolourization of a reddish-brown bromine solution by an alkene.

The two-step mechanism shown in the LibreText pages gives you an idea of how the reaction between an alkene and a halogen occurs. Note the formation of the bridged bromonium ion intermediate and the anti stereochemistry of the final product because the two bromine atoms come from opposite faces of the double bond.

Additional evidence in support of the bromonium ion mechanism comes from the results obtained when an alkene (such as cyclopentene) reacts with bromine in the presence of sodium chloride (see Figure 8.2: Reaction of an alkene with bromine in the presence of sodium chloride, below).

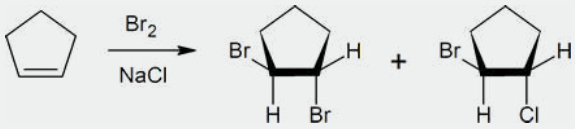


Figure 8.2: *Reaction of an alkene with bromine in the presence of sodium chloride*

Once formed, the bromonium ion is susceptible to attack by two nucleophiles—chloride ion and bromide ion—and, in fact, a mixture of two products (both produced by anti attack) is formed.

Halogens can act as electrophiles to attack a double bond in alkene. Double bond represents a region of electron density and therefore functions as a nucleophile. How is it possible for a halogen to obtain positive charge to be an electrophile?

INTRODUCTION

As halogen molecule, for example Br_2, approaches a double bond of the alkene, electrons in the double bond repel electrons in bromine molecule causing polarization of the halogen bond. This creates a dipolar moment in the halogen molecule bond. Heterolytic bond cleavage occurs and one of the halogens obtains positive charge and reacts as an electrophile. The reaction of the addition is not regioselective but stereoselective.Stereochemistry of this addition can be explained by the mechanism of the reaction.In the first step electrophilic halogen with a positive charge approaches the double carbon bond and 2 p orbitals of the halogen, bond with two carbon atoms and create a cyclic ion with a halogen as the intermediate step. In the second step, halogen with the negative charge attacks any of the two carbons in the cyclic ion from the back side of the cycle as in the S_N2 reaction. Therefore stereochemistry of the product is **vicinial dihalides through anti** addition.

$$\mathbf{R_2C{=}CR_2 + X_2 \rightarrow R_2CX{-}CR_2X} \tag{8.2.1}$$

Halogens that are commonly used in this type of the reaction are: ***Br*** and ***Cl***. In thermodynamical terms ***I*** is too slow for this reaction because of the size of its atom, and ***F*** is too vigorous and explosive. Solvents that are used for this type of electrophilic halogenation are inert (e.g., CCl_4) can be used in this reaction.

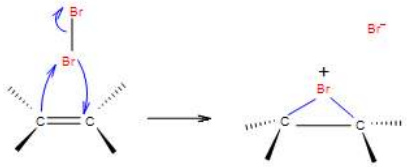
Because halogen with negative charge can attack any carbon from the opposite side of the cycle it creates a mixture of steric products.Optically inactive starting material produce optically inactive achiral products (meso) or a racemic mixture.

ELECTROPHILIC ADDITION MECHANISM CONSISTS OF TWO STEPS.

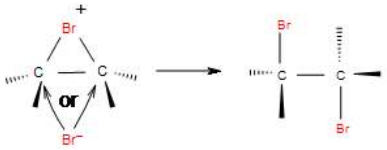
Before constructing the mechanism let us summarize conditions for this reaction. We will use Br_2 in our example for halogenation of ethylene.

Nucleophile	Double bond in alkene
Electrophile	Br_2, Cl_2
Regiochemistry	not relevant
Stereochemistry	**ANTI**

Step 1: In the first step of the addition the Br-Br bond polarizes, heterolytic cleavage occurs and Br with the positive charge forms a intermediate cycle with the double bond.



Step 2: In the second step, bromide anion attacks any carbon of the bridged bromonium ion from the back side of the cycle. Cycle opens up and two halogens are in the position **anti**.



SUMMARY

Hallogens can act as electrophiles due to polarizability of their covalent bond.Addition of halogens is stereospecific and produces vicinial dihalides with anti addition.Cis starting material will give mixture of enantiomers and trans produces a meso compound.

REFERENCES

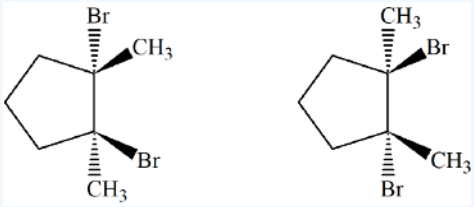
1. Vollhard,K.Peter C., and Neil E.Schore.Organic Chemistry:Structure and Function.New Yourk: W.H.Freeman and Company 2007
2. Chemestry-A Europian Journal 9 (2003) :1036-1044

EXERCISES

? EXERCISE 8.2.1

Predict the product of 1,2-dimethylcyclpentene reacting with Br_2 with proper stereochemistry.

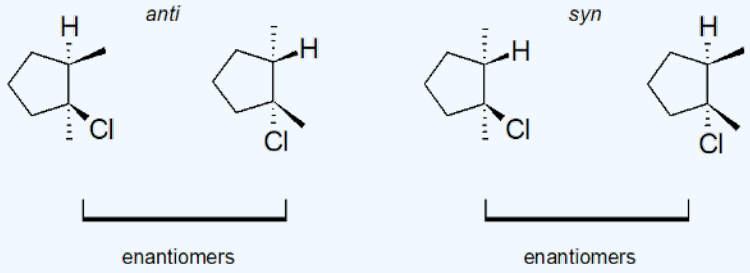
Answer



EXERCISE 8.2.2

Predict the 4 products for 1,2-dimethylcyclpentene reacting with HCl (Section 7.8), give the proper stereochemistry. What is the relationship between the products?

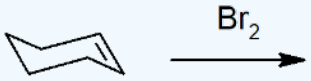
Answer



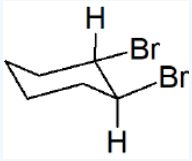
In each case HCl, can add on opposite sides of the double bond (*anti*) on different carbons or on the same side of the double bond (*syn*) on different carbons. In each case (*anti* or *syn* stereochemsitry) the pairs formed are enantiomers of each other.

EXERCISE 8.2.3

Predict the product and give the proper stereochemistry.



Answer



QUESTIONS

Q8.2.1

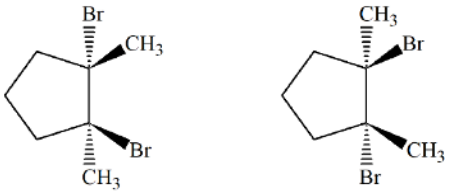
Predict the products for 1,2-dimethylcyclopentene reacting with Br_2 with proper stereochemistry.

Q8.2.2

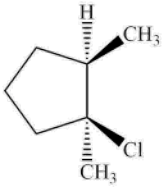
Predict the products for 1,2-dimethylcyclpentene reacting with HCl, give the proper stereochemistry. What is the relationship between the two products?

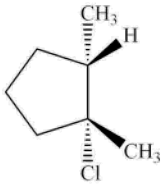
SOLUTIONS

S8.2.1



S8.2.2





These compounds are enantiomers.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Jim Clark (Chemguide.co.uk)

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8.3: HALOHYDRINS FROM ALKENES - ADDITION OF HOX

Objectives

After completing this section, you should be able to

1. write the equation for the formation of a halohydrin from an alkene.
2. write the mechanism for the formation of a halohydrin from an alkene and a mixture of halogen and water.
3. predict the mechanism of the addition reaction that occurs between a given reagent and an alkene, basing your prediction on mechanisms you have studied in this chapter.
4. identify the alkene, the reagents, or both, that should be used to produce a given halohydrin by an addition reaction.
5. identify N-bromosuccinimide in aqueous dimethyl sulfoxide as an alternative source of bromine for producing bromohydrins.

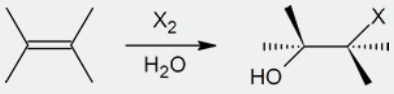
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- bromohydrin
- halohydrin

STUDY NOTES

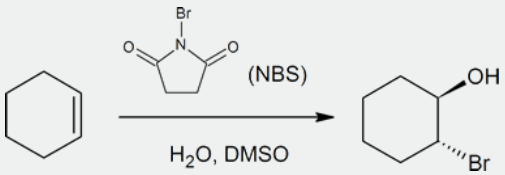
Bromohydrin and chlorohydrin are examples of halohydrins (where X = Br or Cl).



alkene halohydrin

Chemists often abbreviate the names of frequently used chemicals: DMSO for dimethyl sulfoxide, NBS for N-bromosuccinimide, etc. You should already be familiar with some similar examples from everyday life: DDT for dichlorodiphenyltrichloroethane, PCB for polychlorinated biphenyl, and ASA for acetylsalicylic acid (aspirin). You can see how someone with a limited knowledge of chemistry could misinterpret the abbreviation NBS—it is not a compound containing nitrogen, boron and sulfur!

NBS can serve as a less dangerous and easier to handle replacement for Br_2 in the formation of bromohydrins.



The proton is not the only electrophilic species that initiates addition reactions to the double bond of alkenes. Lewis acids like the halogens, boron hydrides and certain transition metal ions are able to bond to the alkene pi-electrons, and the resulting complexes rearrange or are attacked by nucleophiles to give addition products.The electrophilic character of the halogens is well known. Chlorine (Cl_2) and bromine(Br_2) react selectively with the double bond of alkenes, and these reactions are what we will focus on. Fluorine adds uncontrollably with alkenes,and the addition of iodine is unfavorable, so these are not useful preparative methods.

The addition of chlorine and bromine to alkenes, as shown below, proceeds by an initial electrophilic attack on the pi-electrons of the double bond. Dihalo-compounds in which the halogens are bound to adjacent carbons are called vicinal, from the Latin *vicinalis*, meaning neighboring.

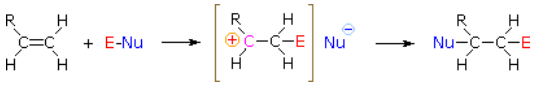
$$R_2C{=}CR_2 + X_2 \longrightarrow R_2CX\text{-}CR_2X$$

Other halogen-containing reagents which add to double bonds include hypohalous acids, HOX, and sulfenyl chlorides, RSCl. These reagents are unsymmetrical, so their addition to unsymmetrical double bonds may in principle take place in two ways. In practice, these addition reactions are regioselective, with one of the two possible constitutionally isomeric products being favored. The electrophilic moieties for these HOBr and C_6H_5SCl reagents are Br and C_6H_5S, respectively.

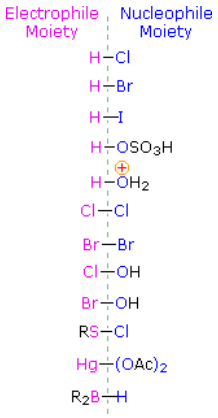
$(CH_3)_2C{=}CH_2 + HOBr \longrightarrow (CH_3)_2COH\text{-}CH_2Br$

$(CH_3)_2C{=}CH_2 + C_6H_5SCl \longrightarrow (CH_3)_2CCl\text{-}CH_2SC_6H_5$

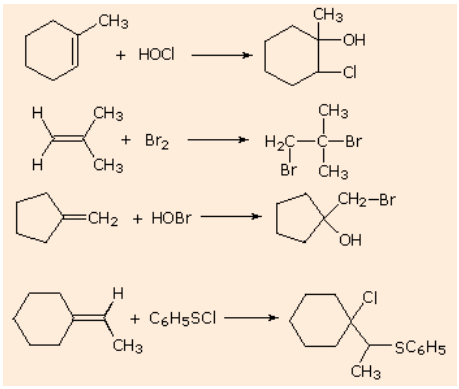
The regioselectivity of the above reactions may be explained by the same mechanism we used to rationalize the Markovnikov rule. Thus, bonding of an electrophilic species to the double bond of an alkene should result in preferential formation of the more stable (more highly substituted) carbocation, and this intermediate should then combine rapidly with a nucleophilic species to produce the addition product.



To apply this mechanism we need to determine the electrophilic moiety in each of the reagents. By using electronegativity differences we can dissect common addition reagents into electrophilic and nucleophilic moieties, a**s shown on the right**. In the case of hypochlorous and hypobromous acids (HOX), these weak Brønsted acids (pKa's ca. 8) do not react as proton donors; and since oxygen is more electronegative than chlorine or bromine, the electrophile will be a halide cation. The nucleophilic species that bonds to the intermediate carbocation is then hydroxide ion, or more likely water (the usual solvent for these reagents), and the products are called halohydrins. Sulfenyl chlorides add in the opposite manner because the electrophile is a sulfur cation, RS(+), whereas the nucleophilic moiety is chloride anion (chlorine is more electronegative than sulfur).



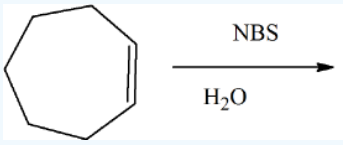
Below are some examples illustrating the addition of various electrophilic halogen reagents to alkene groups. Notice the specific regiochemistry of the products, as explained above.



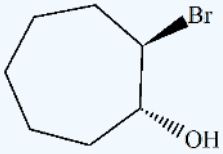
EXERCISES

? EXERCISE 8.3.1

Predict the product of the following reaction.



Answer



EXERCISE 8.3.2

When butene is treated with NBS in the presence of water, the product shows that the bromine is on the least substituted carbon, is this Markovnikov or anti-Markovnikov?

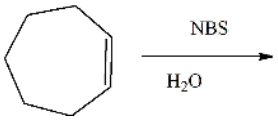
Answer

Since the bromine is the first addition to the alkene, this addition would be an anti-Markovnikov addition.

QUESTIONS

Q8.3.1

Predict the product of the following reaction:

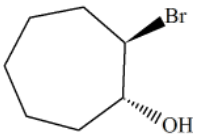


Q8.3.2

When butene is treated with NBS in the presence of water, the product shows that the bromine is on the least substituted carbon, is this Markovnikov or anti-Markovnikov?

SOLUTIONS

S8.3.1



S8.3.2

Since the bromine is the first addition to the alkene, this addition would be an anti-Markovnikov addition.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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8.4: HYDRATION OF ALKENES - ADDITION OF H_2O BY OXYMERCURATION

Objectives

After completing this section, you should be able to

1. write an equation for the hydration of an alkene with sulfuric acid.
2. write an equation for the formation of an alcohol from an alkene by the oxymercuration-demercuration process.
3. identify the alkene, the reagents, or both, that should be used to produce a given alcohol by the oxymercuration-demercuration process.
4. write the mechanism for the reaction of an alkene with mercury(II) acetate in aqueous tetrahydrofuran (THF).

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

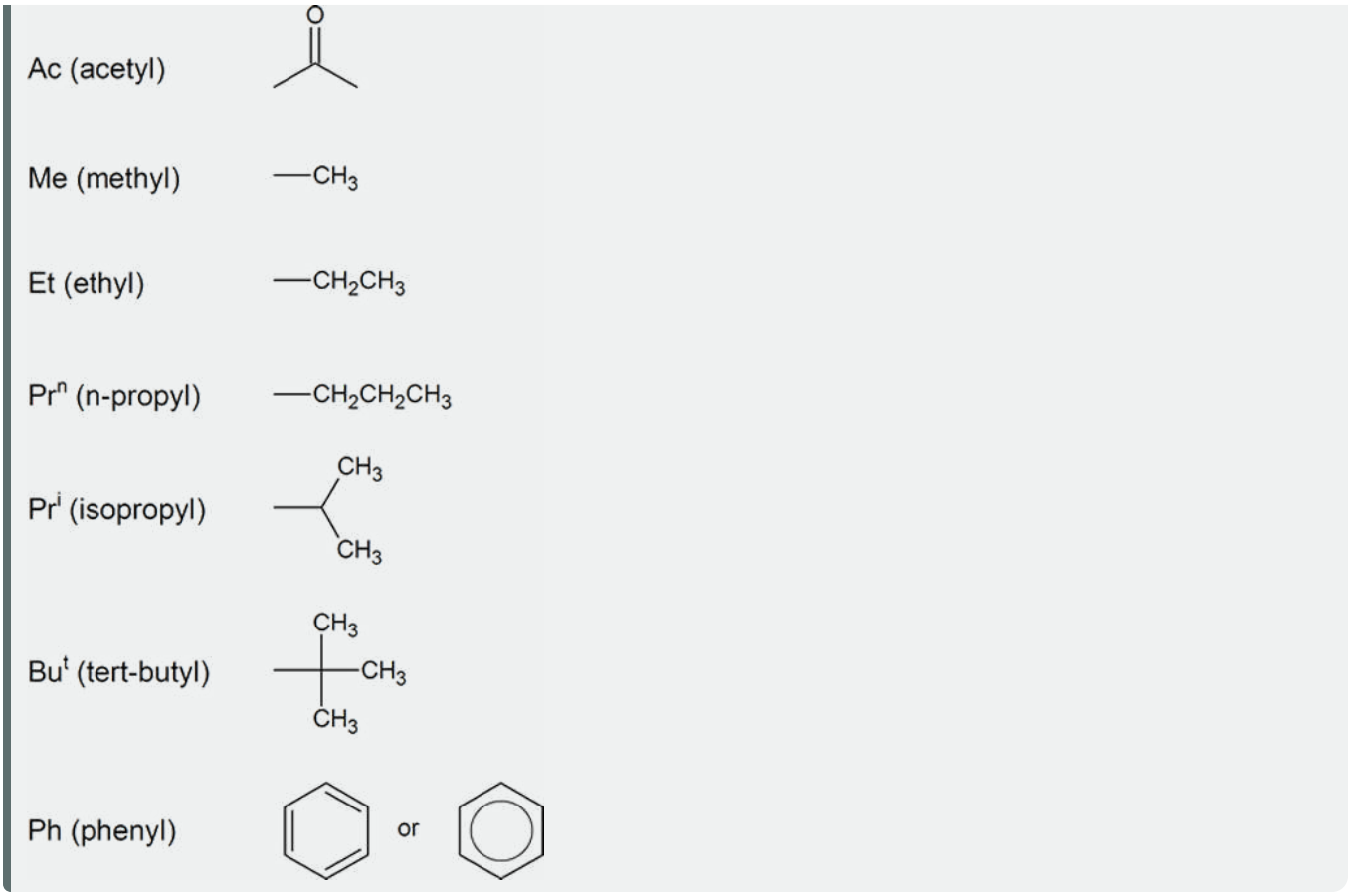
- hydration
- oxymercuration

STUDY NOTES

Oxymercuration is the reaction of an alkene with mercury(II) acetate in aqueous THF, followed by reduction with sodium borohydride. The final product is an alcohol.

It is important that you recognize the similarity between the mechanisms of bromination and oxymercuration. Recognizing these similarities helps you to reduce the amount of factual material that you need to remember.

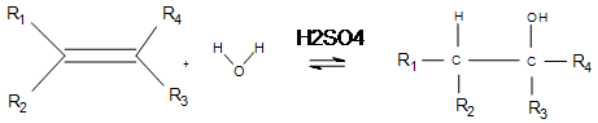
Mercuric acetate, or mercury(II) acetate, to give it the preferred IUPAC name, is written as $Hg(OAc)_2$; by comparing this formula with the formula $Hg(O_2CCH_3)_2$, you can equate Ac with $OCCH_3$. In fact, Ac is an abbreviation used for the acetyl group with the structure shown below as are other similar abbreviations that you will encounter.



Electrophilic hydration is the act of adding electrophilic hydrogen from a non-nucleophilic strong acid (a reusable catalyst, examples of which include sulfuric and phosphoric acid) and applying appropriate temperatures to break the alkene's double bond. After a carbocation is formed, water bonds with the carbocation to form a 1º, 2º, or 3º alcohol on the alkane.

WHAT IS ELECTROPHILIC HYDRATION?

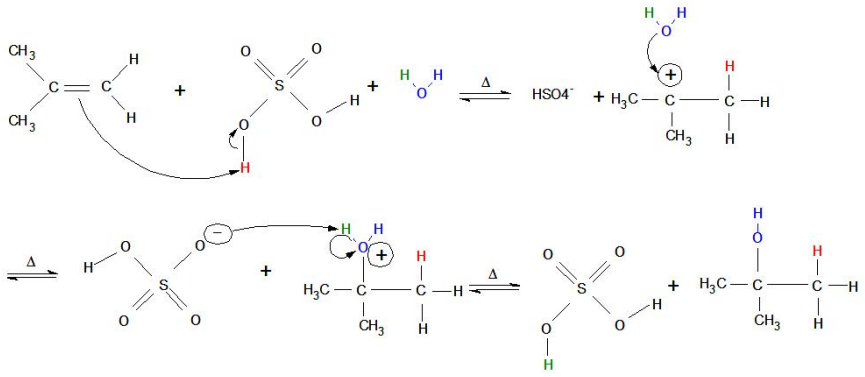
Electrophilic hydration is the reverse dehydration of alcohols and has practical application in making alcohols for fuels and reagents for other reactions. The basic reaction under certain temperatures (given below) is the following:



The phrase "electrophilic" literally means "electron loving" (whereas "nucleophilic" means "nucleus loving"). Electrophilic hydrogen is essentially a proton: a hydrogen atom stripped of its electrons. Electrophilic hydrogen is commonly used to help break double bonds or restore catalysts (see S_N2 for more details).

HOW DOES ELECTROPHILIC HYDRATION WORK?

MECHANISM FOR 3º ALCOHOL (1º AND 2º MECHANISMS ARE SIMILAR):



TEMPERATURES FOR TYPES OF ALCOHOL SYNTHESIS

Heat is used to catalyze electrophilic hydration; because the reaction is in equilibrium with the dehydration of an alcohol, which requires higher temperatures to form an alkene, lower temperatures are required to form an alcohol. *The exact temperatures used are highly variable and depend on the product being formed.*

- Primary Alcohol: Less than 170ºC
- Secondary Alcohol: Less than 100ºC
- Tertiary Alcohol: Less than 25ºC

BUT...WHY DOES ELECTROPHILIC HYDRATION WORK?

- An alkene placed in an aqueous non-nucleophilic strong acid immediately "reaches out" with its double bond and attacks one of the acid's hydrogen atoms (meanwhile, the bond between oxygen and hydrogen performs heterolytic cleavage toward the oxygen—in other words, both electrons from the oxygen/hydrogen single bond move onto the oxygen atom).
- A carbocation is formed on the original alkene (now alkane) in the more-substituted position, where the oxygen end of water attacks with its 4 non-bonded valence electrons (oxygen has 6 total valence electrons because it is found in Group 6 on the periodic table and the second row down: two electrons in a 2s-orbital and four in 2p-orbitals. Oxygen donates one valence electron to each bond it forms, leaving four 4 non-bonded valence electrons).
- After the blue oxygen atom forms its third bond with the more-substituted carbon, it develops a positive charge (3 bonds and 2 valence electrons give the blue oxygen atom a formal charge of +1).
- The bond between the green hydrogen and the blue oxygen undergoes heterolytic cleavage, and both the electrons from the bond move onto the blue oxygen. The now negatively-charged strong acid picks up the green electrophilic hydrogen.
- Now that the reaction is complete, the non-nucleophilic strong acid is regenerated as a catalyst and an alcohol forms on the most substituted carbon of the current alkane. At lower temperatures, more alcohol product can be formed.

WHAT IS REGIOCHEMISTRY AND HOW DOES IT APPLY?

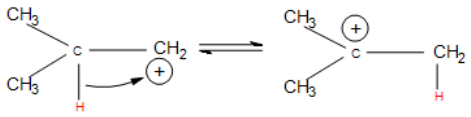
Regiochemistry deals with where the substituent bonds on the product. **Zaitsev**'s and **Markovnikov**'s rules address regiochemistry, but Zaitsev's rule applies when synthesizing an alkene while Markovnikov's rule describes where the substituent bonds onto the product. In the case of electrophilic hydration, Markovnikov's rule is the only rule that *directly* applies. See the following for an in-depth explanation of regiochemistry Markovnikov explanation: Radical Additions--Anti-Markovnikov Product Formation

In the mechanism for a 3º alcohol shown above, the red H is added to the least-substituted carbon connected to the nucleophilic double bonds (it has less carbons attached to it). This means that the carbocation forms on the 3º carbon, causing it to be highly stabilized by *hyperconjugation*—electrons in nearby sigma (single) bonds help fill the empty p-orbital of the carbocation, which lessens the positive charge. More substitution on a carbon means more sigma bonds are available to "help out" (by using overlap) with the positive charge, which creates greater *carbocation stability*. In other words, **carbocations form on the most substituted carbon** connected to the double bond. Carbocations are also stabilized by resonance, but resonance is not a large factor in this case because any carbon-carbon double bonds are used to initiate the reaction, and other double bonded molecules can cause a completely different reaction.

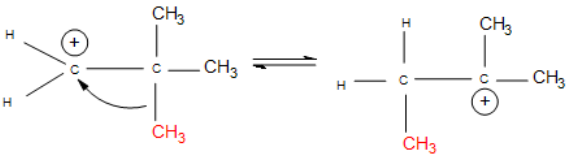
If the carbocation does originally form on the less substituted part of the alkene, carbocation rearrangements occur to form more substituted products:

- **Hydride shifts:** a hydrogen atom bonded to a carbon atom next to the carbocation leaves that carbon to bond with the carbocation (after the hydrogen has taken both electrons from the single bond, it is known as a hydride). This changes the once neighboring carbon to a

carbocation, and the former carbocation becomes a neighboring carbon atom.



- **Alkyl shifts:** if no hydrogen atoms are available for a hydride shift, an entire methyl group performs the same shift.

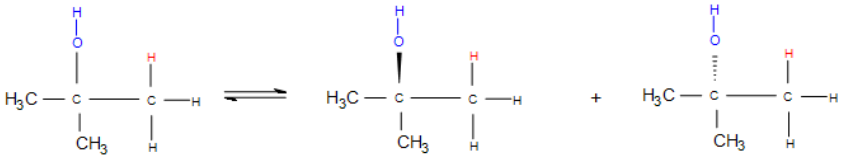


The nucleophile attacks the positive charge formed on the most substituted carbon connected to the double bond, because the nucleophile is seeking that positive charge. In the mechanism for a 3º alcohol shown above, water is the nucleophile. When the green H is removed from the water molecule, the alcohol attached to the most substituted carbon. Hence, **electrophilic hydration follows Markovnikov's rule.**

WHAT IS STEREOCHEMISTRY AND HOW DOES IT APPLY?

Stereochemistry deals with how the substituent bonds on the product directionally. Dashes and wedges denote stereochemistry by showing whether the molecule or atom is going into or out of the plane of the board. Whenever the bond is a simple single straight line, the molecule that is bonded is equally likely to be found going into the plane of the board as it is out of the plane of the board. This indicates that **the product is a racemic mixture**.

Electrophilic hydration adopts a stereochemistry wherein the substituent is equally likely to bond pointing into the plane of the board as it is pointing out of the plane of the board. The 3º alcohol product could look like either of the following products:



Note: Whenever a straight line is used along with dashes and wedges on the same molecule, it could be denoting that the straight line bond is in the same plane as the board. Practice with a molecular model kit and attempting the practice problems at the end can help eliminate any ambiguity.

IS THIS A REVERSIBLE SYNTHESIS?

Electrophilic hydration is reversible because an alkene in water is in equilibrium with the alcohol product. To sway the equilibrium one way or another, the temperature or the concentration of the non-nucleophilic strong acid can be changed. For example:

- Less sulfuric or phosphoric acid and an excess of water help synthesize more alcohol product.
- Lower temperatures help synthesize more alcohol product.

IS THERE A BETTER WAY TO ADD WATER TO SYNTHESIZE AN ALCOHOL FROM AN ALKENE?

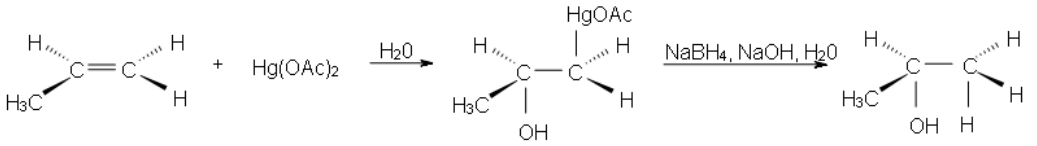
A more efficient pathway does exist: see Oxymercuration - Demercuration: A Special Electrophilic Addition. Oxymercuration does not allow for rearrangements, but it does require the use of mercury, which is highly toxic. Detractions for using electrophilic hydration to make alcohols include:

- Allowing for carbocation rearrangements
- Poor yields due to the reactants and products being in equilibrium
- Allowing for product mixtures (such as an (R)-enantiomer and an (S)-enantiomer)
- Using sulfuric or phosphoric acid

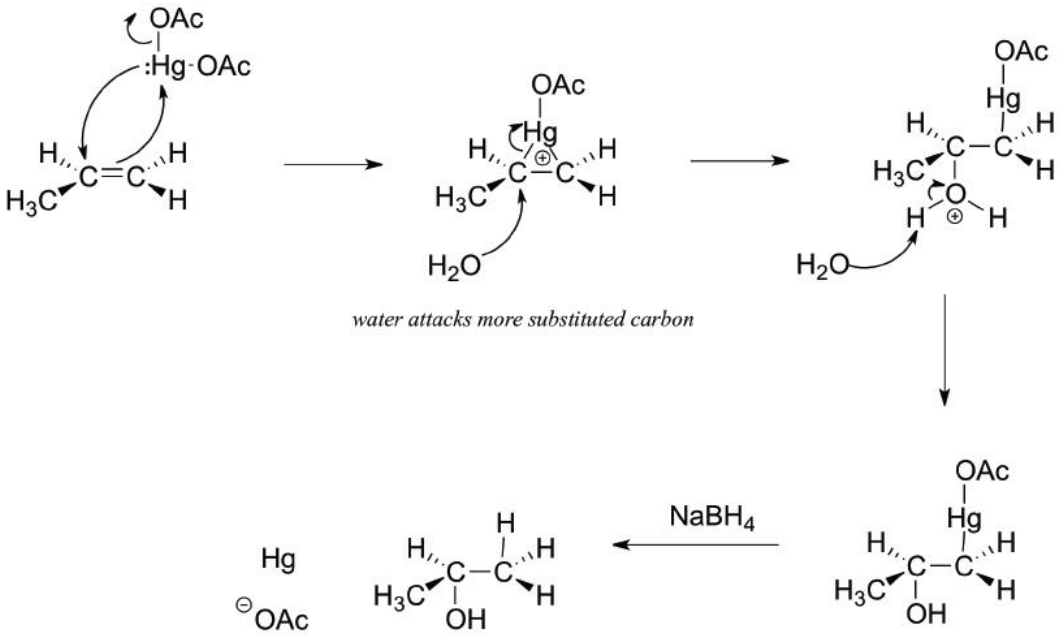
Oxymercuration is a special electrophilic addition. It is anti-stereospecific and regioselective. Regioselectivity is a process in which the substituents choses one direction it prefers to be attached to over all the other possible directions. The good thing about this reaction is that there are no carbocation rearrangement due to stabilization of the reactive intermediate. Similar stabilization is also seen in bromination addition to alkenes.

INTRODUCTION

Carbocation rearrangement is a process in which the carbocation intermediate can form a more stable ion. With carbocation rearrangement, the reaction would not be able to hydrate quickly under mild conditions and be produced in high yields. This reaction is very fast and proceeds with 90% yield.



This reaction involves a mercury acting as a reagent attacking the alkene double bond to form a *Mercurinium Ion Bridge*. A water molecule will then attack the most substituted carbon to open the mercurium ion bridge, followed by proton transfer to solvent water molecule.



The organomercury intermediate is then reduced by sodium borohydride - the mechanism for this final step is beyond the scope of our discussion here. Notice that overall, the oxymercuration - demercuration mechanism follows Markovnikov's Regioselectivity with the OH group is attached to the most substituted carbon and the H is attach to the least substituted carbon. The reaction is useful, however, because strong acids are not required, and carbocation rearrangements are avoided because no discreet carbocation intermediate forms.

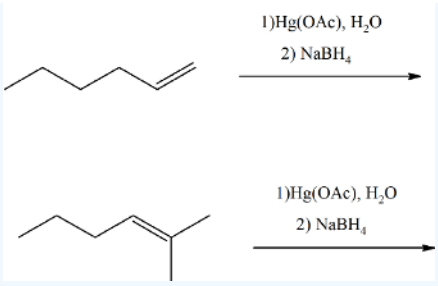
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1. Vollhardt, K. Peter C. Organic chemistry structure and function. New York: W.H. Freeman, 2007.
2. Smith, Michael B., and Jerry March. March's Advanced Organic Chemistry Reactions, Mechanisms, and Structure (March's Advanced Organic Chemistry). New York: Wiley-Interscience, 2007 2007.
3. Roderic P. Quirk , Robert E. Lea, Reductive demercuration of hex-5-enyl-1-mercuric bromide by metal hydrides. Rearrangement, isotope effects, and mechanism, *J. Am. Chem. Soc.*, 1976, 98 (19), pp 5973–5978.

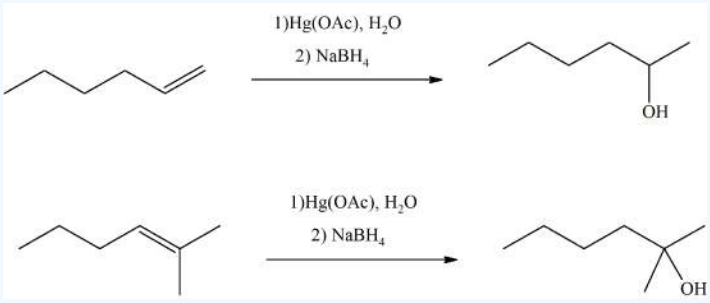
EXERCISES

? EXERCISE 8.4.1

Predict the products of these oxymercuration reactions.

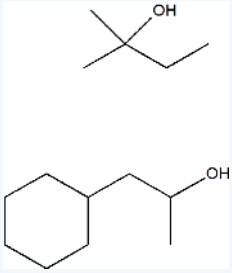


Answer

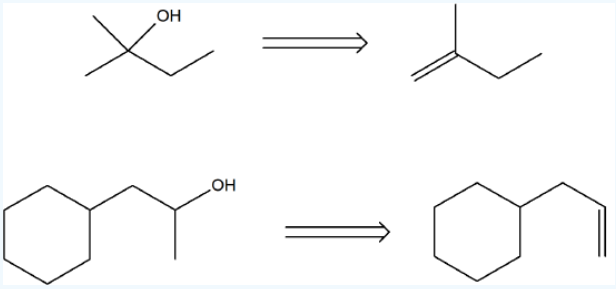


EXERCISE 8.4.2

Propose the alkene that was the reactant for these products of oxymercuration.



Answer

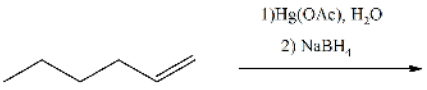


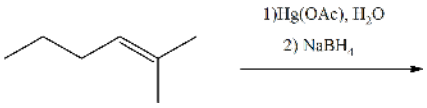
QUESTIONS

Q8.4.1

In each case, predict the product(s) of these reactants of oxymercuration.

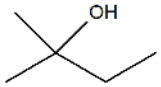
https://chem.libretexts.org/@go/page/67139

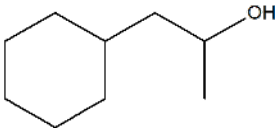




Q8.4.2

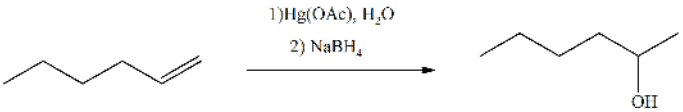
Propose the alkene that was the reactant for each of these products of oxymercuration.

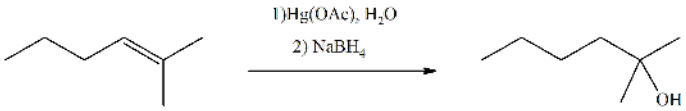




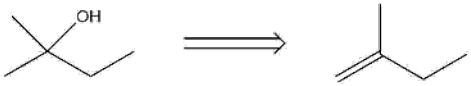
SOLUTIONS

S8.4.1





S8.4.2





CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Lance Peery (UCD), Duyen Dao-Tran
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)
- Prof. Steven Farmer (Sonoma State University)

8.4: Hydration of Alkenes - Addition of H_2O by Oxymercuration is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.5: HYDRATION OF ALKENES - ADDITION OF H_2O BY HYDROBORATION

Objectives

After completing this section, you should be able to

1. identify hydroboration (followed by oxidation) as a method for bringing about the (apparently) non-Markovnikov addition of water to an alkene.
2. write an equation for the formation of a trialkylborane from an alkene and borane.
3. write an equation for the oxidation of a trialkylborane to an alcohol.
4. draw the structure of the alcohol produced by the hydroboration, and subsequent oxidation, of a given alkene.
5. determine whether a given alcohol should be prepared by oxymercuration-demercuration or by hydroboration-oxidation, and identify the alkene and reagents required to carry out such a synthesis.
6. write the detailed mechanism for the addition of borane to an alkene, and explain the stereochemistry and regiochemistry of the reaction.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- hydroboration

STUDY NOTES

The two most important factors influencing organic reactions are polar (or electronic) effects and steric effects.

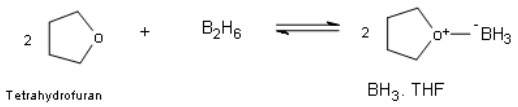
Hydroboration-Oxidation is a two step pathway used to produce alcohols. The reaction proceeds in an Anti-Markovnikov manner, where the hydrogen (from BH_3 or BHR_2) attaches to the more substituted carbon and the boron attaches to the least substituted carbon in the alkene bouble bond. Furthermore, the borane acts as a lewis acid by accepting two electrons in its empty p orbital from an alkene that is electron rich. This process allows boron to have an electron octet. A very interesting characteristic of this process is that it does not require any activation by a catalyst. The Hydroboration mechanism has the elements of both hydrogenation and electrophilic addition and it is a stereospecific (***syn addition),*** meaning that the hydroboration takes place on the same face of the double bond, this leads ***cis*** stereochemistry.

INTRODUCTION EDIT SECTION

Hydroboration-oxidation of alkenes has been a very valuable laboratory method for the stereoselectivity and regioselectivity of alkenes. An Additional feature of this reaction is that it occurs without rearrangement.

THE BORANE COMPLEX EDIT SECTION

First off it is very imporatnt to understand little bit about the structure and the properties of the borane molecule. Borane exists naturally as a very toxic gas and it exists as dimer of the general formula B_2H_6 (diborane). Additionally, the dimer B_2H_6ignites spontaneously in air. Borane is commercially available in ether and tetrahydrofuran (THF), in these solutions the borane can exist as a lewis acid-base complex, which allows boron to have an electron octet.



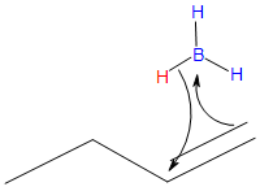
Tetrahydrofuran (THF)

BH_3. THF

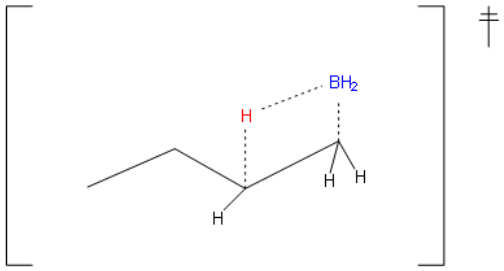
THE MECHANISM

STEP #1

- Part #1: Hydroboration of the alkene. In this first step the addittion of the borane to the alkene is initiated and prceeds as a concerted reaction because bond breaking and bond formation occurs at the same time. This part consists of the vacant 2p orbital of the boron electrophile pairing with the electron pair of the ? bondof the nucleophile.

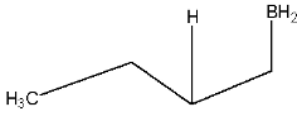


Transition state



*** Note that a carbocation is not formed. Therefore, no rearrangement takes place.**

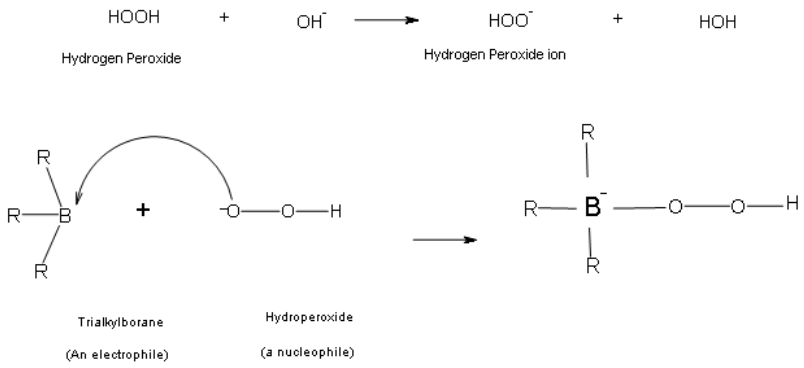
- Part #2: The Anti Markovnikov addition of Boron. The boron adds to the less substituted carbon of the alkene, which then places the hydrogen on the more substituted carbon. Both, the boron and the hydrogen add simultaneously on the same face of the double bond (syn addition).



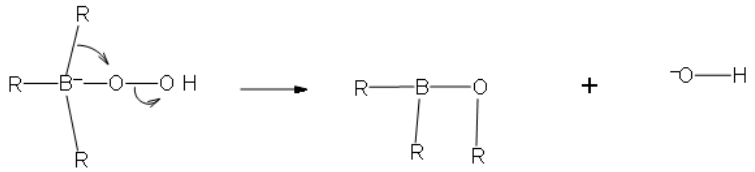
OXIDATION OF THE TRIALKYLBORANE BY HYDROGEN PEROXIDE EDIT SECTION

STEP #2

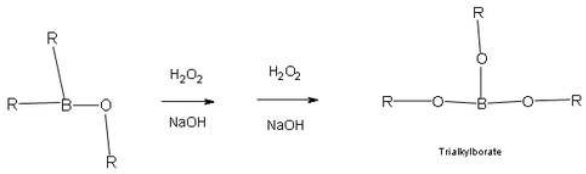
- Part #1: the first part of this mechanism deals with the donation of a pair of electrons from the hydrogen peroxide ion. the hydrogen peroxide is the nucleophile in this reaction because it is the electron donor to the newly formed trialkylborane that resulted from hydroboration.



- Part 2: In this second part of the mechanism, a rearrangement of an R group with its pair of bonding electrons to an adjacent oxygen results in the removal of a hydroxide ion.



Two more of these reactions with hydroperoxide will occur in order give a trialkylborate



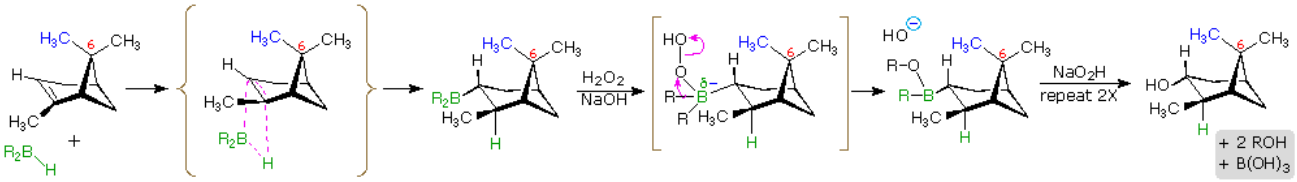
- Part 3: This is the final part of the Oxidation process. In this part the trialkylborate reacts with aqueous NaOH to give the alcohol and sodium borate.



If you need additional visuals to aid you in understanding the mechanism, click on the outside links provided here that will take you to other pages and media that are very helpful as well.

STEREOCHEMISTRY OF HYDROBORATION

The hydroboration reaction is among the few simple addition reactions that proceed cleanly in a *syn* fashion. As noted above, this is a single-step reaction. Since the bonding of the double bond carbons to boron and hydrogen is concerted, it follows that the geometry of this addition must be syn. Furthermore, rearrangements are unlikely inasmuch as a discrete carbocation intermediate is never formed. These features are illustrated for the hydroboration of α-pinene.



Since the hydroboration procedure is most commonly used to hydrate alkenes in an anti-Markovnikov fashion, we also need to know the stereoselectivity of the second oxidation reaction, which substitutes a hydroxyl group for the boron atom. Independent study has shown this reaction takes place with retention of configuration so the overall addition of water is also syn.

The hydroboration of α-pinene also provides a nice example of steric hindrance control in a chemical reaction. In the less complex alkenes used in earlier examples the plane of the double bond was often a plane of symmetry, and addition reagents could approach with equal ease from either side. In this case, one of the methyl groups bonded to C-6 (colored blue in the equation) covers one face of the double bond, blocking any approach from that side. All reagents that add to this double bond must therefore approach from the side opposite this methyl.

OUTSIDE LINKS EDIT SECTION

- http://en.Wikipedia.org/wiki/Hydroboration-oxidation
- bcs.whfreeman.com/vollhardtschore4e/cat_010/ch12/12010-03.htm
- http://www.chemhelper.com/hydroboration.html
- www.cartage.org.lb/en/themes/...roboration.htm
- http://www.organic-chemistry.org/nam...oboration.shtm

REFERENCES EDIT SECTION

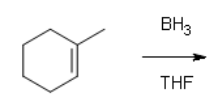
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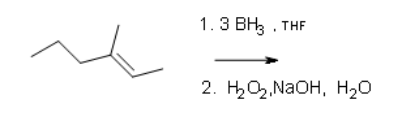
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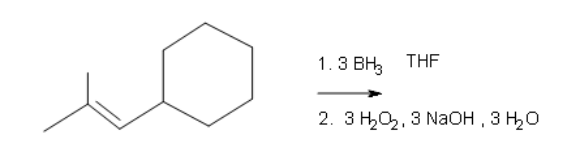
EXERCISES

? EXERCISE 8.5.1

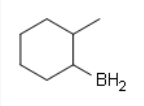
What is the product of the following reactions?

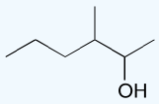


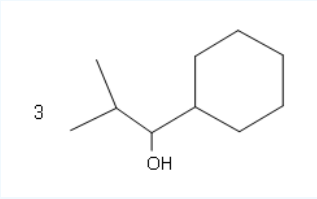




Answer



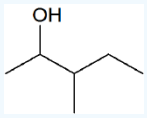




? EXERCISE 8.5.2

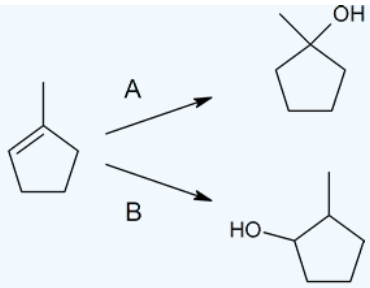
Draw the structural formula for the alcohol that result from hydroboration-oxidation of (*E*)-3-methyl-2-pentene.

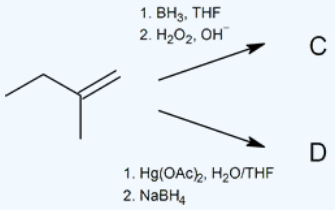
Answer



? EXERCISE 8.5.3

Write out the reagents or products (A–D) shown in the following reaction schemes.

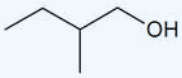


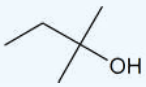


Answer

A
1. $Hg(OAc)_2$, H_2O/THF
2. $NaBH_4$

B
1. BH_3, THF
2. H_2O_2, OH^-

C 

D 

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

8.5: Hydration of Alkenes - Addition of H_2O by Hydroboration is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.6: REDUCTION OF ALKENES - HYDROGENATION

Objectives

After completing this section, you should be able to

1. write an equation for the catalytic hydrogenation of an alkene.
2. identify the product obtained from the hydrogenation of a given alkene.
3. identify the alkene, the reagents, or both, required to prepare a given alkane by catalytic hydrogenation.
4. describe the mechanism of the catalytic hydrogenation of alkenes.
5. explain the difference between a heterogeneous reaction and a homogeneous reaction.
6. recognize that other types of compounds containing multiple bonds, such as ketones, esters, nitriles and aromatic compounds, do not react with hydrogen under the conditions used to hydrogenate alkenes.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- Adams' catalyst
- hydrogenation

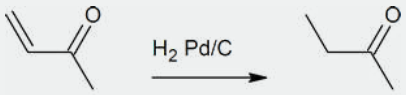
STUDY NOTES

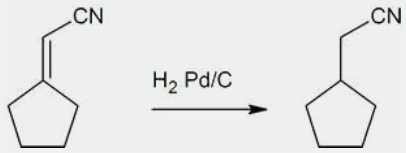
Chemical reactions that are heterogeneous have reactants that are in at least two different phases (e.g. gas with a solid), whereas homogeneous reactions occur in a single phase (e.g. gas with another gas).

Some confusion may arise from the description of the catalyst used in the reaction between alkenes and hydrogen. Three metals—nickel, platinum and palladium—are commonly used, but a chemist cannot simply place a piece of one of these metals in a mixture of the alkene and hydrogen and get a reaction. Each metal catalyst must be prepared in a special way:

- nickel is usually used in a finely divided form called "Raney nickel." It is prepared by reacting a Ni-Al alloy with NaOH.
- palladium is obtained commercially "supported" on an inert substance, such as charcoal, (Pd/C). The alkene is usually dissolved in ethanol when Pd/C is used as the catalyst.
- platinum is used as PtO_2, Adams' catalyst, although it is actually platinum metal that is the catalyst. The hydrogen used to add to the carbon-carbon double bond also reduces the platinum(IV) oxide to finely divided platinum metal. Ethanol or acetic acid is used as the solvent for the alkene.

Other types of compounds containing multiple bonds, such as ketones, esters, and nitriles, do not react with hydrogen under the conditions used to hydrogenate alkenes. The examples below show reduction of an alkene, but the ketone and nitrile groups present remain intact and are not reduced.

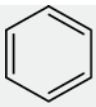




Aromatic rings are also not reduced under the conditions used to reduce alkenes, although these rings appear to contain three carbon-carbon double bonds. As you will see later, aromatic rings do not really contain any double bonds, and many chemists prefer to represent the benzene ring as a hexagon with a circle inside it

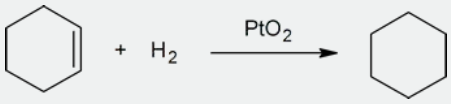


rather than as a hexagon with three alternating double bonds.

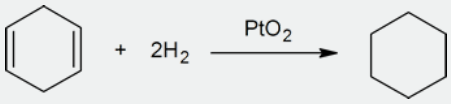


The representation of the benzene ring will be discussed further in Section 15.2.

The reaction between carbon-carbon double bonds and hydrogen provides a method of determining the number of double bonds present in a compound. For example, one mole of cyclohexene reacts with one mole of hydrogen to produce one mole of cyclohexane:



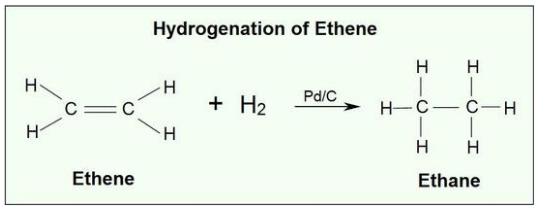
but one mole of 1,4-cyclohexadiene reacts with two moles of hydrogen to form one mole of cyclohexane:

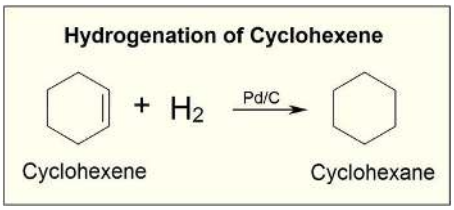


A chemist would say that cyclohexene reacts with one equivalent of hydrogen, and 1,4-cyclohexadiene reacts with two equivalents of hydrogen. If you take a known amount of an unknown, unsaturated hydrocarbon and determine how much hydrogen it will absorb, you can readily determine the number of double bonds present in the hydrocarbon (see question 2, below).

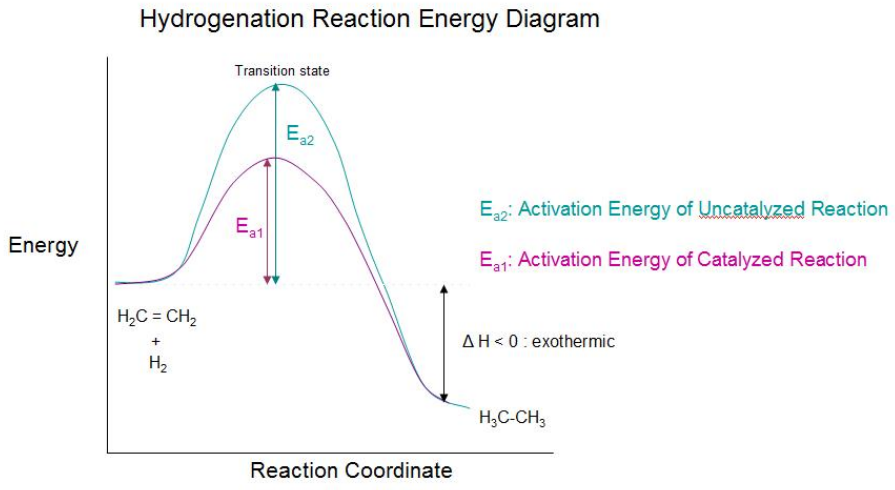
Addition of hydrogen to a carbon-carbon double bond is called hydrogenation. The overall effect of such an addition is the reductive removal of the double bond functional group. Regioselectivity is not an issue, since the same group (a hydrogen atom) is bonded to each of the double bond carbons. The simplest source of two hydrogen atoms is molecular hydrogen (H_2), but mixing alkenes with hydrogen does not result in any discernible reaction. Although the overall hydrogenation reaction is exothermic, a high activation energy prevents it from taking place under normal conditions. This restriction may be circumvented by the use of a catalyst, as shown in the following diagram.

An example of an alkene addition reaction is a process called hydrogenation.In a hydrogenation reaction, two hydrogen atoms are added across the double bond of an alkene, resulting in a saturated alkane. Hydrogenation of a double bond is a thermodynamically favorable reaction because it forms a more stable (lower energy) product. In other words, the energy of the product is lower than the energy of the reactant; thus it is exothermic (heat is released). The heat released is called the heat of hydrogenation, which is an indicator of a molecule's stability.





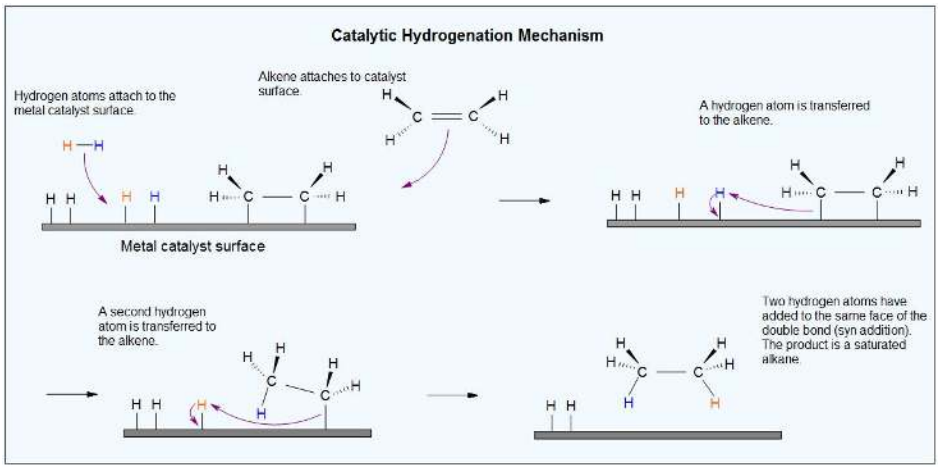
Catalysts are substances that changes the rate (velocity) of a chemical reaction without being consumed or appearing as part of the product. Catalysts act by lowering the activation energy of reactions, but they do not change the relative potential energy of the reactants and products. Finely divided metals, such as platinum, palladium and nickel, are among the most widely used hydrogenation catalysts. Catalytic hydrogenation takes place in at least two stages, as depicted in the diagram. First, the alkene must be adsorbed on the surface of the catalyst along with some of the hydrogen. Next, two hydrogens shift from the metal surface to the carbons of the double bond, and the resulting saturated hydrocarbon, which is more weakly adsorbed, leaves the catalyst surface. The exact nature and timing of the last events is not well understood.



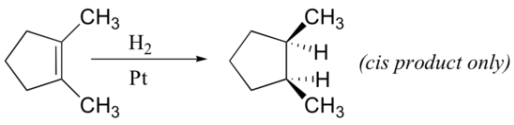
A catalyst lowers the activation energy needed for the reacting molecules to reach the transition state. The addition of a catalyst enables the hydrogenation reaction to occur, that otherwise, would not.

As shown in the energy diagram, the hydrogenation of alkenes is exothermic, and heat is released corresponding to the ΔE (colored green) in the diagram. This heat of reaction can be used to evaluate the thermodynamic stability of alkenes having different numbers of alkyl substituents on the double bond. For example, the following table lists the heats of hydrogenation for three C_5H_{10} alkenes which give the same alkane product (2-methylbutane). Since a large heat of reaction indicates a high energy reactant, these heats are inversely proportional to the stabilities of the alkene isomers. To a rough approximation, we see that each alkyl substituent on a double bond stabilizes this functional group by a bit more than 1 kcal/mole.

Alkene Isomer	$(CH_3)_2CHCH=CH_2$ 3-methyl-1-butene	$CH_2=C(CH_3)CH_2CH_3$ 2-methyl-1-butene	$(CH_3)_2C=CHCH_3$ 2-methyl-2-butene
Heat of Reaction (ΔH°)	–30.3 kcal/mole	–28.5 kcal/mole	–26.9 kcal/mole



From the mechanism shown here we would expect the addition of hydrogen to occur with syn-stereoselectivity. This is often true, but the hydrogenation catalysts may also cause isomerization of the double bond prior to hydrogen addition, in which case stereoselectivity may be uncertain.

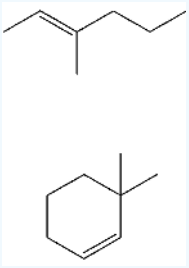


(cis product only)

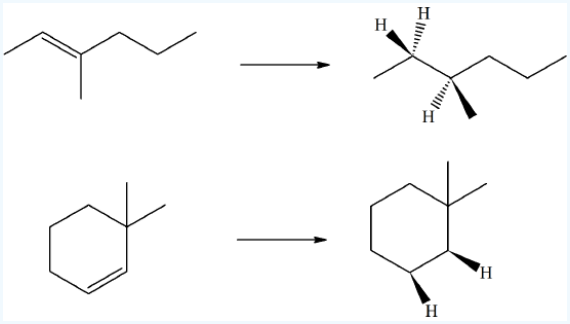
EXERCISES

EXERCISE \PageIndex1

Predict the products if the following alkenes were reacted with catalytic hydrogen.



Answer



EXERCISE 8.6.2

1. In the reaction

$$H_2C{=}CH_2 \quad + \quad H_2 \quad \xrightarrow{PtO_2} \quad H_3C{-}CH_3$$

   a. 0.500 mol of ethene reacts with _____ mol of hydrogen. Thus a chemist might say that ethene reacts with one _____ of hydrogen.
   b. ethene is being _____; while _____ is being oxidized.
   c. the oxidation number of carbon in ethene is _____; in ethane it is _____.

Answer

   a. 0.500 mol of ethene reacts with 0.500 mol of hydrogen. Thus a chemist might say that ethene reacts with one equivalent of hydrogen.
   b. ethene is being reduced; while hydrogen is being oxidized.
   c. the oxidation number of carbon in ethene is −2; in ethane it is −3.

EXERCISE 8.6.3

When 1.000 g of a certain triglyceride (fat) is treated with hydrogen gas in the presence of Adams' catalyst, it is found that the volume of hydrogen gas consumed at 99.8 kPa and 25.0°C is 162 mL. A separate experiment indicates that the molar mass of the fat is 914 g mol^{-1}. How many carbon-carbon double bonds does the compound contain?

Answer

Amount of hydrogen consumed

$= n\,\text{mol}$

$= \dfrac{PV}{RT} \qquad ^{-1} \cdot K^{-1} \times 298\,K = 6.53 \times 10^{-3}\ \text{mol}\ H_2$

$= \dfrac{99.8\,kPa \times 0.162\,L}{8.31\,kPa \cdot mol}$

Amount of fat used

$= \dfrac{(1.000\,g) \times (1\,mol)}{(914\,g)}$

$= 1.09 \times 10$ Unknown node type: sup Unknown node type: sup mol fat

Ratio of moles of hydrogen consumed to moles of fat

$= 6.53 \times 10$ Unknown node type: sup Unknown node type: sup $: 1.09 \times 10$ Unknown node type: sup Unknown node type: sup

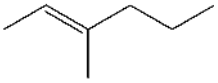
$= 6:1$

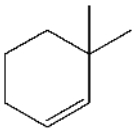
Thus, the fat contains six carbon-carbon double bonds per molecule.

QUESTIONS

Q8.6.1

Predict the products if the following alkenes were reacted with catalytic hydrogen.

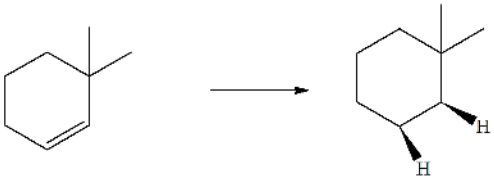




SOLUTIONS

S8.6.1





CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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8.7: OXIDATION OF ALKENES - EPOXIDATION AND HYDROXYLATION

Objectives

After completing this section, you should be able to

1. write the equation for the epoxidation of an alkene using meta-chloroperoxybenzoic acid.
2. identify the alkene, reagents, or both, that must be used to prepare a given epoxide.
3. write the equation for the hydroxylation of an alkene using osmium tetroxide, and draw the structure of the cyclic intermediate.
4. draw the structure of the diol formed from the reaction of a given alkene with osmium tetroxide.
5. identify the alkene, the reagents, or both, that must be used to prepare a given 1,2-diol.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- diol
- glycol
- hydroxylation

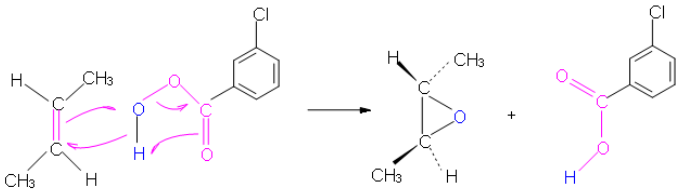
Oxacyclopropane rings, also called epoxide rings, are useful reagents that may be opened by further reaction to form anti vicinal diols. One way to synthesize oxacyclopropane rings is through the reaction of an alkene with peroxycarboxylic acid.

OXACYCLOPROPANE SYNTHESIS BY PEROXYCARBOXYLIC ACID

Oxacyclopropane synthesis by peroxycarboxylic acid requires an alkene and a peroxycarboxylic acid as well as an appropriate solvent. The peroxycarboxylic acid has the unique property of having an electropositive oxygen atom on the COOH group. The reaction is initiated by the electrophilic oxygen atom reacting with the nucleophilic carbon-carbon double bond. The mechanism involves a concerted reaction with a four-part, circular transition state. The result is that the originally electropositive oxygen atom ends up in the oxacyclopropane ring and the COOH group becomes COH.

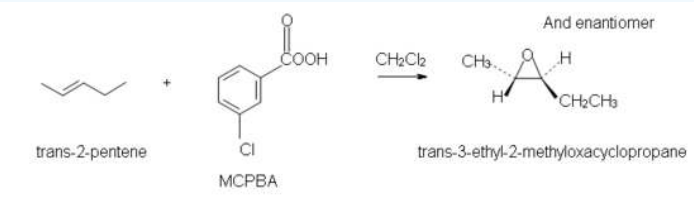
MECHANISM

Peroxycarboxylic acids are generally unstable. An exception is meta-chloroperoxybenzoic acid, shown in the mechanism above. Often abbreviated MCPBA, it is a stable crystalline solid. Consequently, MCPBA is popular for laboratory use. However, MCPBA can be explosive under some conditions.



Peroxycarboxylic acids are sometimes replaced in industrial applications by monoperphthalic acid, or the monoperoxyphthalate ion bound to magnesium, which gives magnesium monoperoxyphthalate (MMPP). In either case, a nonaqueous solvent such as chloroform, ether, acetone, or dioxane is used. This is because in an aqueous medium with any acid or base catalyst present, the epoxide ring is hydrolyzed to form a vicinal diol, a molecule with two OH groups on neighboring carbons. (For more explanation of how this reaction leads to vicinal diols, see below.) However, in a nonaqueous solvent, the hydrolysis is prevented and the epoxide ring can be isolated as the product. Reaction yields from this reaction are usually about 75%. The reaction rate is affected by the nature of the alkene, with more nucleophilic double bonds resulting in faster reactions.

EXAMPLE 8.7.1

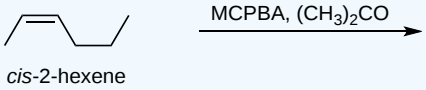


Since the transfer of oxygen is to the same side of the double bond, the resulting oxacyclopropane ring will have the same stereochemistry as the starting alkene. A good way to think of this is that the alkene is rotated so that some constituents are coming forward and some are behind. Then, the oxygen is inserted on top. (See the product of the above reaction.) One way the epoxide ring can be opened is by an acid catalyzed oxidation-hydrolysis. Oxidation-hydrolysis gives a vicinal diol, a molecule with OH groups on neighboring carbons. For this reaction, the dihydroxylation is *anti* since, due to steric hindrance, the ring is attacked from the side opposite the existing oxygen atom. Thus, if the starting alkene is trans, the resulting vicinal diol will have one S and one R stereocenter. But, if the starting alkene is cis, the resulting vicinal diol will have a racemic mixture of S, S and R, R enantiomers.

EPOXIDATION EXERCISES

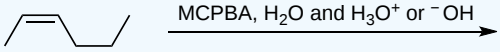
1. Predict the product of the reaction of cis-2-hexene with MCPBA (meta-chloroperoxybenzoic acid)

a) in acetone solvent.



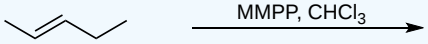
cis-2-hexene

b) in an aqueous medium with acid or base catalyst present.



cis-2-hexene

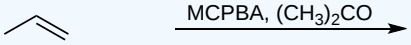
2. Predict the product of the reaction of trans-2-pentene with magnesium monoperoxyphthalate (MMPP) in a chloroform solvent.



trans-2-pentene

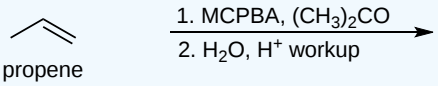
3. Predict the reaction of propene with MCPBA.

a) in acetone solvent



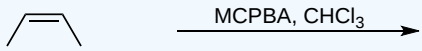
propene

b) after aqueous work-up.



propene

4. Predict the reaction of cis-2-butene in chloroform solvent.

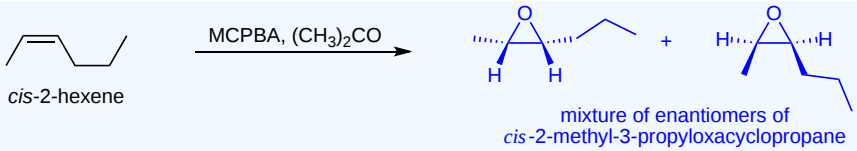


cis-2-butene

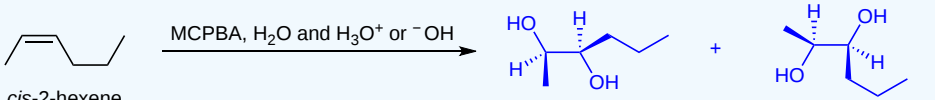
Answers

1. a) *Cis*-2-methyl-3-propyloxacyclopropane

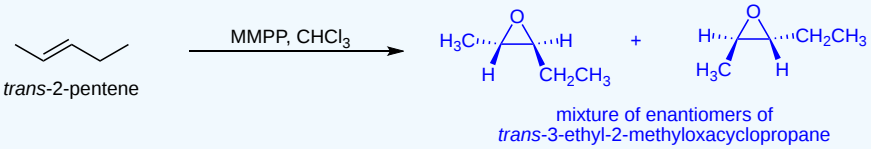
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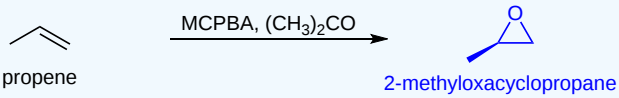
b) Racemic (2*R*,3*R*)-2,3-hexanediol and (2*S*,3*S*)-2,3-hexanediol



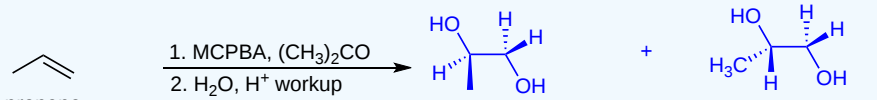
2. *Trans*-3-ethyl-2-methyloxacyclopropane.



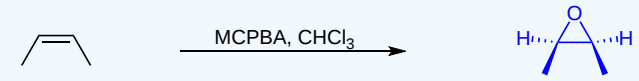
3. a) 2-methyl-oxacyclopropane



b) Racemic (2*S*)-1,2-propandiol and (2*R*)-1,2-propanediol

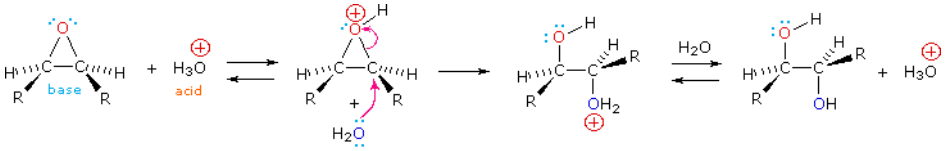


4. *Cis*-2,3-dimethyloxacyclopropane



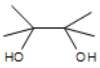
ANTI DIHYDROXYLATION

Epoxides may be cleaved by aqueous acid to give glycols that are often diastereomeric with those prepared by the syn-hydroxylation reaction described above. Proton transfer from the acid catalyst generates the conjugate acid of the epoxide, which is attacked by nucleophiles such as water in the same way that the cyclic bromonium ion described above undergoes reaction. The result is **anti-hydroxylation** of the double bond, in contrast to the syn-stereoselectivity of the earlier method. In the following equation this procedure is illustrated for a cis-disubstituted epoxide, which, of course, could be prepared from the corresponding cis-alkene. This hydration of an epoxide does not change the oxidation state of any atoms or groups.



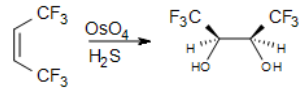
SYN DIHYDROXYLATION

Osmium tetroxide oxidizes alkenes to give glycols through syn addition. A glycol, also known as a vicinal diol, is a compound with two -OH groups on adjacent carbons.

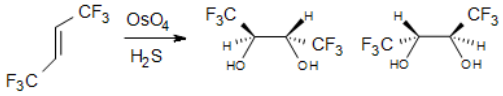


INTRODUCTION

The reaction with OsO_4 is a concerted process that has a cyclic intermediate and no rearrangements. Vicinal syn dihydroxylation complements the epoxide-hydrolysis sequence which constitutes an *anti* dihydroxylation of an alkene. When an alkene reacts with osmium tetroxide, stereocenters can form in the glycol product. Cis alkenes give meso products and trans alkenes give racemic mixtures.



Cis **Meso**



Trans **Racemic Mixture**

OsO_4 is formed slowly when osmium powder reacts with gasoues O_2 at ambient temperature. Reaction of bulk solid requires heating to 400 °C:

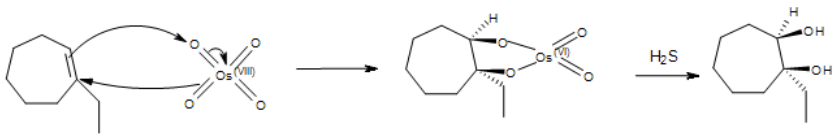
$$Os_{(s)} + 2O_{2\ (g)} \rightarrow OS_4 \tag{8.7.1}$$

Since Osmium tetroxide is expensive and highly toxic, the reaction with alkenes has been modified. Catalytic amounts of OsO_4 and stoichiometric amounts of an oxidizing agent such as hydrogen peroxide are now used to eliminate some hazards. Also, an older reagent that was used instead of OsO_4 was potassium permanganate, $KMnO_4$. Although syn diols will result from the reaction of $KMnO_4$ and an alkene, potassium permanganate is less useful since it gives poor yields of the product because of *overoxidation*.

MECHANISM

- Electrophilic attack on the alkene
  - Pi bond of the alkene acts as the nucleophile and reacts with osmium (VIII) tetroxide (OsO_4)
  - 2 electrons from the double bond flows toward the osmium metal
    - In the process, 3 electron pairs move simultaneously
  - Cyclic ester with Os (VI) is produced
- Reduction
  - H_2S reduces the cyclic ester
    - $NaHSO_4$ with H_2O may be used
  - Forms the syn-1,2-diol (glycol)

Example: Dihydroxylation of 1-ethyl-1-cycloheptene

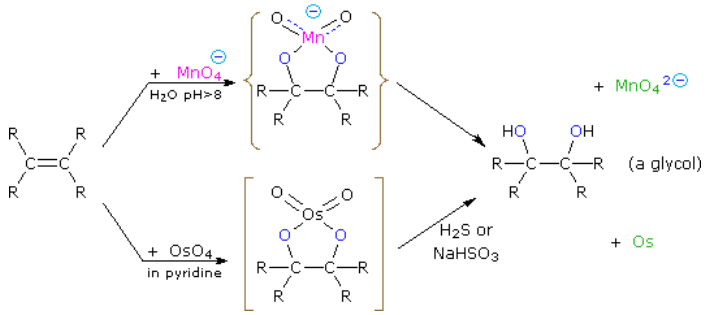


Electrophilic Attack **Intermediate** **Reduced Glycol**

HYDROXYLATION OF ALKENES

Dihydroxylated products (glycols) are obtained by reaction with aqueous potassium permanganate (pH > 8) or osmium tetroxide in pyridine solution. Both reactions appear to proceed by the same mechanism (shown below); the metallocyclic intermediate may be isolated in the

osmium reaction. In basic solution the purple permanganate anion is reduced to the green manganate ion, providing a nice color test for the double bond functional group. From the mechanism shown here we would expect syn-stereoselectivity in the bonding to oxygen, and regioselectivity is not an issue.



When viewed in context with the previously discussed addition reactions, the hydroxylation reaction might seem implausible. Permanganate and osmium tetroxide have similar configurations, in which the metal atom occupies the center of a tetrahedral grouping of negatively charged oxygen atoms. How, then, would such a species interact with the nucleophilic pi-electrons of a double bond? A possible explanation is that an empty d-orbital of the electrophilic metal atom extends well beyond the surrounding oxygen atoms and initiates electron transfer from the double bond to the metal, in much the same fashion noted above for platinum. Back-bonding of the nucleophilic oxygens to the antibonding π*-orbital completes this interaction. The result is formation of a metallocyclic intermediate, as shown above.

CHEMICAL HIGHLIGHT

Antitumor drugs have been formed by using dihydroxylation. This method has been applied to the enantioselective synthesis of ovalicin, which is a class of fungal-derived products called antiangiogenesis agents. These antitumor products can cut off the blood supply to solid tumors. A derivative of ovalicin, TNP-470, is chemically stable, nontoxic, and noninflammatory. TNP-470 has been used in research to determine its effectiveness in treating cancer of the breast, brain, cervix, liver, and prostate.

OUTSIDE LINKS

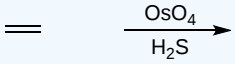
- http://en.Wikipedia.org/wiki/Osmium_tetroxide
- http://www.chm.bris.ac.uk/motm/oso4/oso4v.htm
- http://www.organic-chemistry.org/chemicals/oxidations/osmiumtetroxide.shtm

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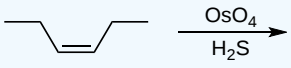
1. Dehestani, Ahmad et al. (2005). Ligand-assisted reduction of osmium tetroxide with molecular hydrogen via a [3+2] mechanism. *Journal of the American Chemical Society, 2005, 127 (10)*, 3423-3432.
2. Sorrell, Thomas, N. Organic Chemistry. New York: University Science Books, 2006.
3. Vollhardt, Peter, and Neil E. Schore. Organic Chemistry: Structure and Function. 5th Edition. New York: W. H. Freeman & Company, 2007.

? DIHYDROXYLATION EXERCISES

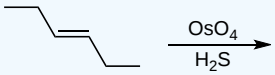
1. Give the major product.



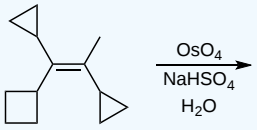
2. What is the product in the dihydroxylation of (Z)-3-hexene?



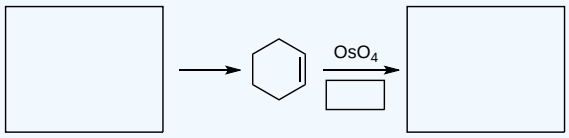
3. What is the product in the dihydroxylation of (E)-3-hexene?



4. Draw the intermediate of this reaction.

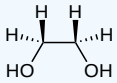


5. Fill in the missing reactants, reagents, and product. [Hint: First box requires knowledge of Section 14.4]

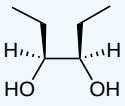


Answers

1. A syn-1,2-ethanediol is formed. There is no stereocenter in this particular reaction. The OH groups are on the same side.



2. Meso-3,4-hexanediol is formed. There are 2 stereocenters in this reaction.



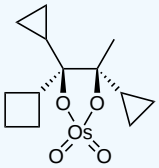
(3*S*,4*R*)

3. A racemic mixture of 3,4-hexanediol is formed. There are 2 stereocenters in both products.

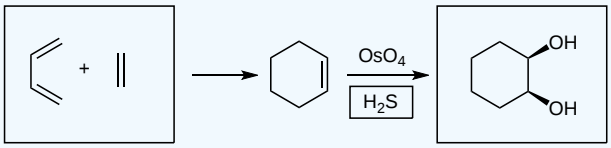


(3*R*,4*R*) (3*S*,4*S*)

4. A cyclic osmic ester is formed.



5. The Diels-Alder cycloaddition reaction is needed in the first box to form the cyclohexene (covered later in Section 14.4). The second box needs a reagent to reduce the intermediate cyclic ester (not shown). The third box has the product: 1,2-cyclohexanediol.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Shivam Nand
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Kristen Perano

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8.8: OXIDATION OF ALKENES - CLEAVAGE TO CARBONYL COMPOUNDS

Objective

After completing this section, you should be able to

1. write an equation to describe the cleavage of an alkene by ozone, followed by reduction of the ozonide so formed with either sodium borohydride or zinc and acetic acid.
2. predict the products formed from the ozonolysis-reduction of a given alkene.
3. write an equation to describe the cleavage of an alkene by potassium permanganate.
4. predict the products from the oxidative cleavage of a given alkene by potassium permanganate.
5. use the results of ozonolysis-reduction, or cleavage with permanganate, to deduce the structure of an unknown alkene.
6. identify the reagents that should be used in the oxidative cleavage of an alkene to obtain a given product or products.
7. write the equation for the cleavage of a 1,2-diol by periodic acid, and draw the structure of the probable intermediate.
8. predict the product or products that will be formed from the treatment of a given 1,2-diol with periodic acid.
9. use the results of hydroxylation/1,2-diol cleavage to deduce the structure of an unknown alkene.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

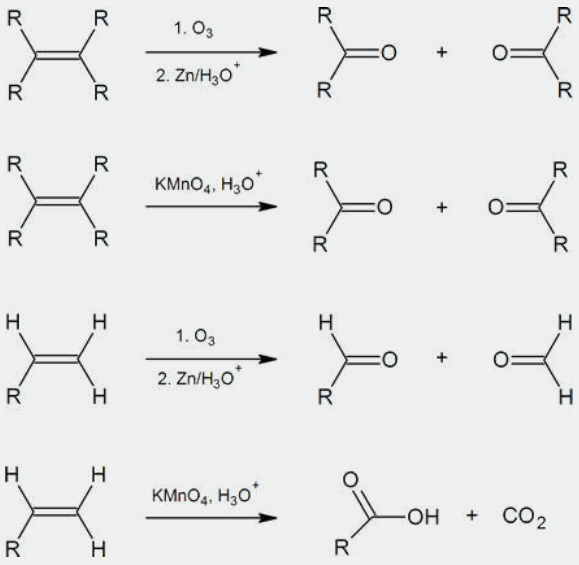
- molozonide
- ozonide
- ozonolysis

STUDY NOTES

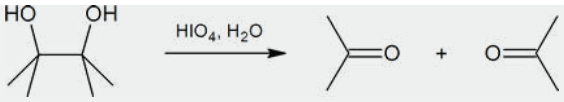
Ozonolysis, or ozonolysis-reduction, refers to the treatment of an alkene with ozone followed by a suitable reducing agent to break down complex double-bond-containing compounds into smaller, more easily identified products. From the identity of the products formed, it may be possible to deduce the structure of the original double-bond-containing substance. Ozonolysis will feature prominently in many of the road-map problems that you will encounter in this course.

A *molozonide* is an unstable, cyclic intermediate that is initially formed when an alkene reacts with ozone.

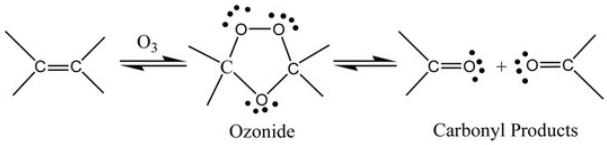
Alkenes can also be cleaved by other oxidizing agents such as potassium permanganate. However, $KMnO_4$ will carry the oxidation further than ozonolysis, so products can be slightly different. Note within the summary of the following reactions that ozonolysis produces aldehydes and ketones, while $KMnO_4$ can oxidize all the way to to carbon dioxide and carboxylic acid.



Diol cleavage is another example of a redox reaction; periodic acid, HIO_4, is reduced to iodic acid, HIO_3.



Ozonolysis is a method of oxidatively cleaving alkenes or alkynes using ozone (O_3), a reactive allotrope of oxygen. The process allows for carbon-carbon double or triple bonds to be replaced by double bonds with oxygen. This reaction is often used to identify the structure of unknown alkenes. by breaking them down into smaller, more easily identifiable pieces. Ozonolysis also occurs naturally and would break down repeated units used in rubber and other polymers. On an industrial scale, azelaic acid and pelargonic acids are produced from ozonolysis.

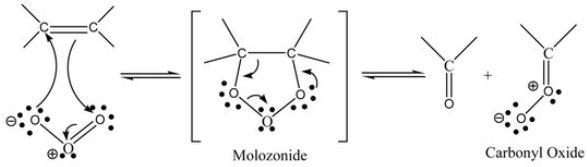


INTRODUCTION

The gaseous ozone is first passed through the desired alkene solution in either methanol or dichloromethane. The first intermediate product is an ozonide molecule which is then further reduced to carbonyl products. This results in the breaking of the Carbon-Carbon double bond and is replaced by a Carbon-Oxygen double bond instead.

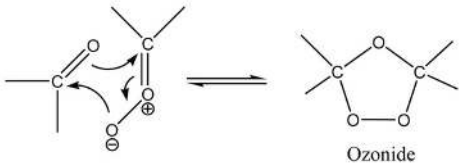
REACTION MECHANISM

Step 1:



The first step in the mechanism of ozonolysis is the initial electrophilic addition of ozone to the Carbon-Carbon double bond, which then form the molozonide intermediate. Due to the unstable molozonide molecule, it continues further with the reaction and breaks apart to form a carbonyl and a carbonyl oxide molecule.

Step 2:



The carbonyl and the carbonyl oxide rearranges itself and reforms to create the stable ozonide intermediate. A reductive workup could then be performed to convert convert the ozonide molecule into the desired carbonyl products.

REFERENCES

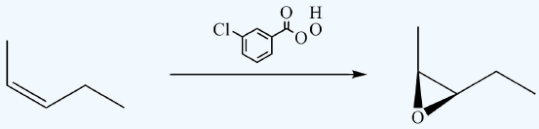
1. Vollhardt, K., Schore, N. Organic Chemistry: Structure and Function. 5th ed. New York, NY: W. H. Freeman and Company, 2007.
2. Shore, N. Study Guide and Solutions Manual for Organic Chemistry. 5th ed. New York, NY: W.H. Freeman and Company, 2007.

EXERCISES

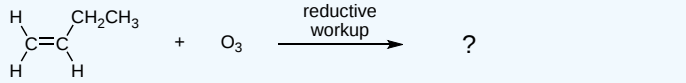
? EXERCISE \PageIndex1

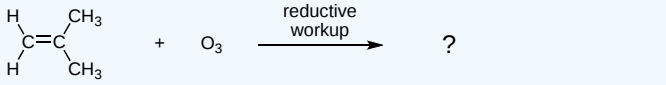
What would you expect the products to be from the reaction of *cis*-2-pentene with meta chloro-peroxybenzoic acid? Show the stereochemistry of the final product.

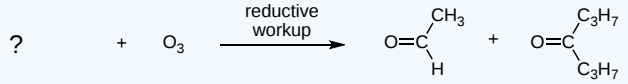
Answer

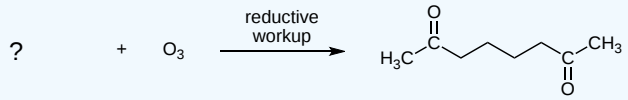


EXERCISE \PageIndex2

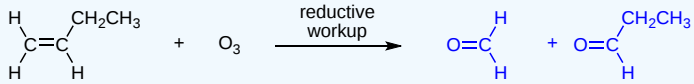
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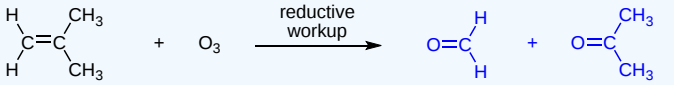
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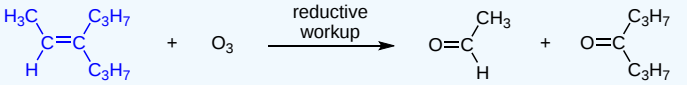
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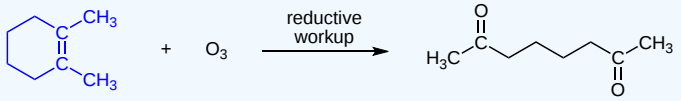
4. 

Answer

1. 

2. 

3. 

4. 

EXERCISE \PageIndex3

1. Draw the structure of the product or products obtained in each of the following reactions:

a. *cis*-2-butene $\xrightarrow[2.\ Zn/H_3O^+]{1.\ O_3}$

b. *trans*-2-butene $\xrightarrow[2.\ Zn/H_3O^+]{1.\ O_3}$

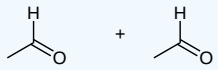
c. 2-methylpropene $\xrightarrow[2.\ Zn/H_3O^+]{1.\ O_3}$

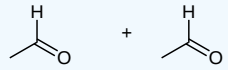
d. 2-methyl-1-pentene $\xrightarrow{\text{hot, acidic } KMnO_4}$

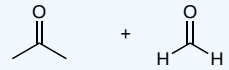
2. What important point did you learn from questions 1(*a*) and 1(*b*), above?

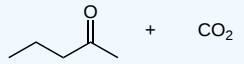
Answer

1.

a. 

b. 

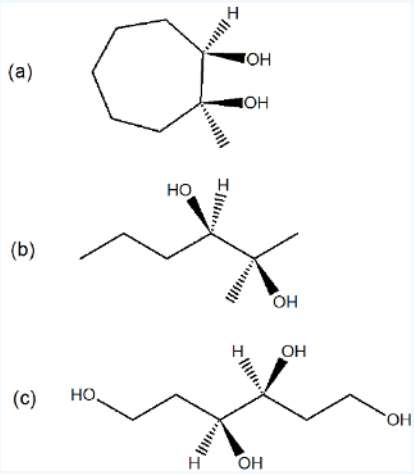
c. 

d. 

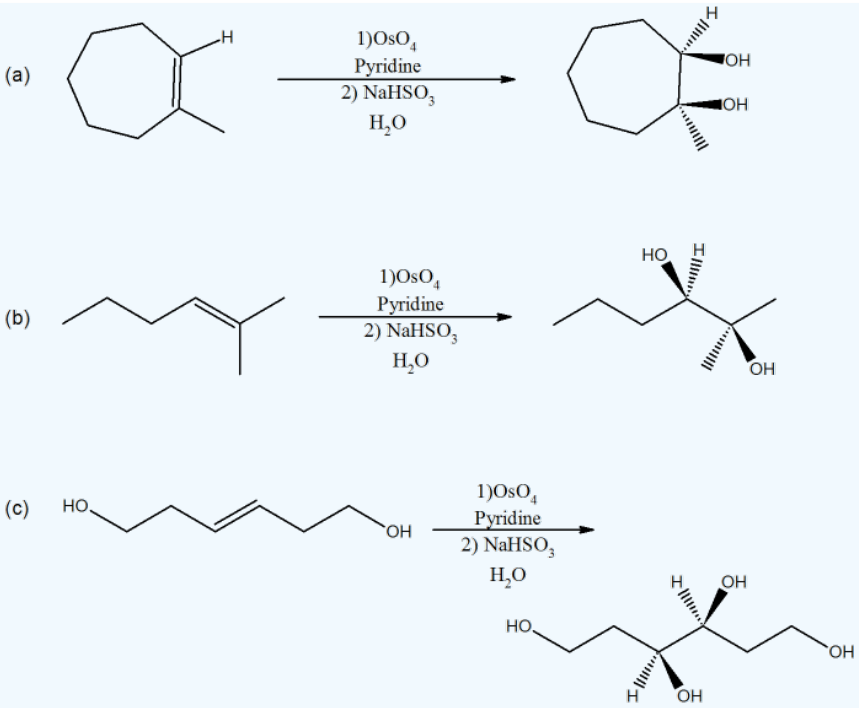
2. Exercises 1(*a*) and 1(*b*), above, indicate that it is not possible to distinguish between cis and trans isomers of alkenes using oxidative cleavage. Both isomers give the same product or products.

EXERCISE \PageIndex4

Give a reaction scheme with starting alkenes and required reagents to produce the following compounds.



Answer



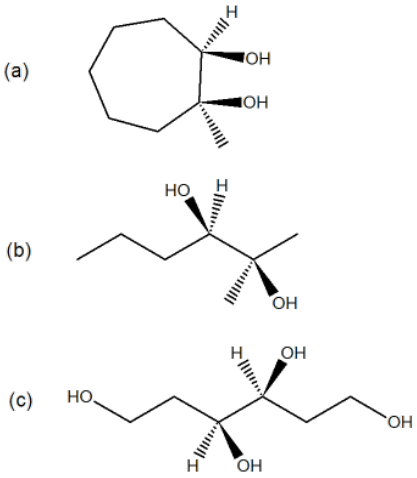
QUESTIONS

Q8.8.1

What would you expect the products to be from the reaction of *cis*-2-pentene with *m*-chloro-peroxybenzoic acid? Show the stereochemistry of the final product.

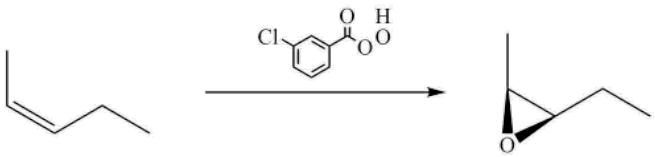
Q8.8.2

Give a reaction scheme with starting alkenes and required reagents to produce the following compounds.

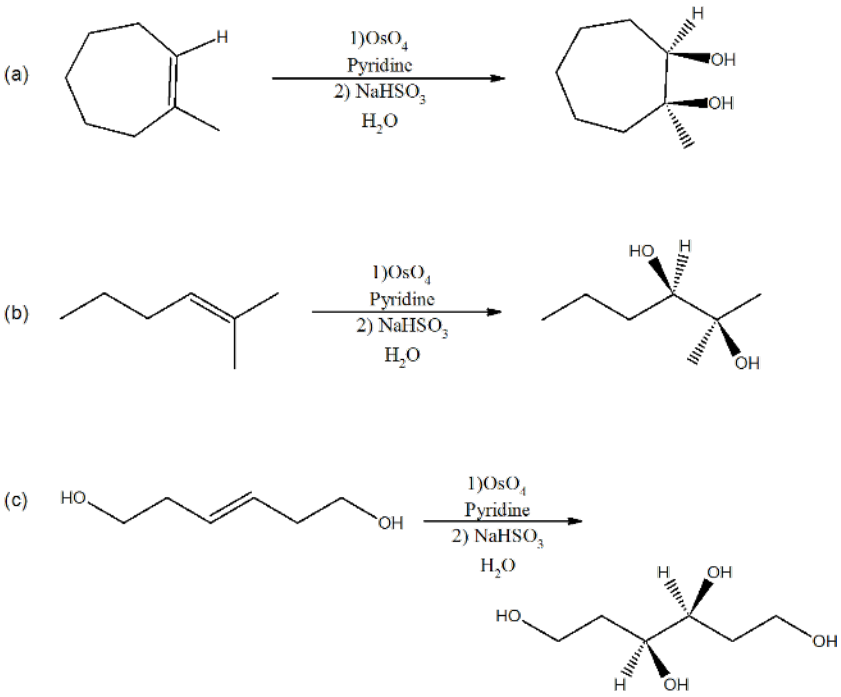


SOLUTIONS

S8.8.1



S8.8.2



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

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8.9: ADDITION OF CARBENES TO ALKENES - CYCLOPROPANE SYNTHESIS

Objectives

After completing this section, you should be able to

1. describe, and write the detailed mechanism for, the formation of a carbene, such as dichlorocarbene.
2. describe the structure of a carbene in terms of the hybridization of the central carbon atom.
3. write an equation for the formation of a substituted cyclopropane from an alkene and a carbene.
4. identify the reagents, the alkene, or both, needed to prepare a given substituted cyclopropane by addition of a carbene to a double bond.
5. identify the substituted cyclopropane formed from the reaction of a given alkene with the reagents necessary to form a carbene.

KEY TERMS

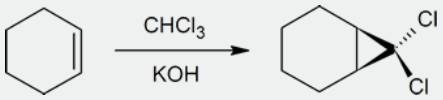
Make certain that you can define, and use in context, the key terms below.

- carbene (R_2C:)
- carbenoid
- Simmons-Smith reaction
- stereospecific

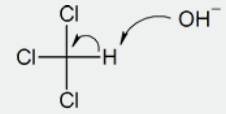
STUDY NOTES

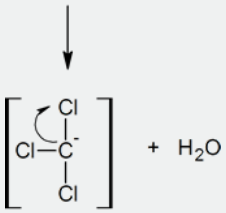
A *carbenoid* is best considered to be a reagent which, while not actually a carbene, behaves as if it were an intermediate of this type.

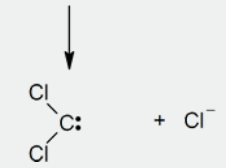
Dichlorocarbenes can also form cyclopropane structures and are created in situ from reagents such as chloroform and KOH.



The detailed mechanism of the formation of dichlorocarbene is given below. Note that the deprotonation of chloroform generates the trichloromethanide anion, which spontaneously expels the chloride anion.







The highly strained nature of cyclopropane compounds makes them very reactive and interesting synthetic targets. Additionally cyclopropanes are present in numerous biological compounds. One common method of cyclopropane synthesis is the reaction of carbenes with the double bond in alkenes or cycloalkenes. Methylene, H_2C, is simplest carbene, and in general carbenes have the formula R_2C. Other species that will also react with alkenes to form cyclopropanes but do not follow the formula of carbenes are referred to as carbenoids.

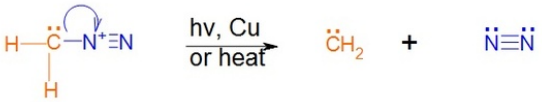
INTRODUCTION

Carbenes were once only thought of as short lived intermediates. The reactions of this section only deal with these short lived carbenes which are mostly prepared in situ, in conjunction with the main reaction. However, there do exist so called persistent carbenes. These persistent carbenes are stabilized by a variety of methods often including aromatic rings or transition metals. In general a carbene is neutral and has 6 valence electrons, 2 of which are non bonding. These electrons can either occupy the same sp^2 hybridized orbital to form a singlet carbene (with paired electrons), or two different sp^2 orbitals to from a triplet carbene (with unpaired electrons). The chemistry of triplet and singlet carbenes is quite different but can be oversimplified to the statement: singlet carbenes usually retain stereochemistry while triplet carbenes do not. The carbenes discussed in this section are singlet and thus retain stereochemistry.

The reactivity of a singlet carbene is concerted and similar to that of electrophilic or nucleophilic addition (although, triplet carbenes react like biradicals, explaining why sterochemistry is not retained). The highly reactive nature of carbenes leads to very fast reactions in which the rate determining step is generally carbene formation.

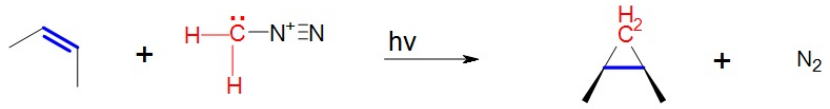
PREPARATION OF METHYLENE

The preparation of methylene starts with the yellow gas diazomethane, CH_2N_2. Diazomethane can be exposed to light, heat or copper to facilitate the loss of nitrogen gas and the formation of the simplest carbene methylene. The process is driven by the formation of the nitrogen gas which is a very stable molecule.

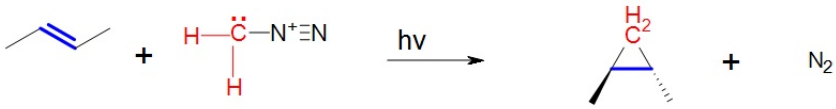


CARBENE REACTION WITH ALKENES

A carbene such as methlyene will react with an alkene which will break the double bond and result with a cyclopropane. The reaction will usually leave stereochemistry of the double bond unchanged. As stated before, carbenes are generally formed along with the main reaction; hence the starting material is diazomethane not methylene.



In the above case *cis*-2-butene is converted to *cis*-1,2-dimethylcyclopropane. Likewise, below the *trans* configuration is maintained.



ADDITIONAL TYPES OF CARBENES AND CARBENOIDS

In addition to the general carbene with formula R_2C there exist a number of other compounds that behave in much the same way as carbenes in the synthesis of cyclopropane. **Halogenated carbenes** are formed from halomethanes. An example is dicholorcarbene, Cl_2C. These halogenated carbenes will form cyclopropanes in the same manner as methylene but with the interesting presence of two halogen atoms in place of the hydrogen atoms.

Carbenoids are substances that form cyclopropanes like carbenes but are not technically carbenes. One common example is the stereospecific Simmons-Smith reaction which utilizes the carbenoid ICH_2ZnI. The carbenoid is formed in situ via the mixing of a Zn-Cu couple with CH_2I_2.Since this reacts the same as a carbene, the same methods can be applied to determine the product. An example of this is given as problem 5.

OUTSIDE LINKS

- http://en.Wikipedia.org/wiki/Simmons-Smith_reaction
- http://en.Wikipedia.org/wiki/Carbene

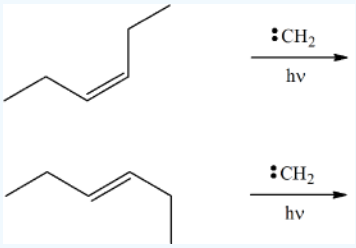
REFERENCES

1. Vollhardt, K. Peter C. and Schore, Neil E. Organic Chemistry: Structure and Function. New York: Bleyer, Brennan, 2007.
2. Abdel-Wahab, Aboel-Magd A. Ahmed, Saleh A. and Dürr, Heinz. "Carbene Formation by Extrusion of Nitrogen" in CRC Handbook of Organic Photochemistry and Photobiology. CRC Press, 2004.

EXERCISES

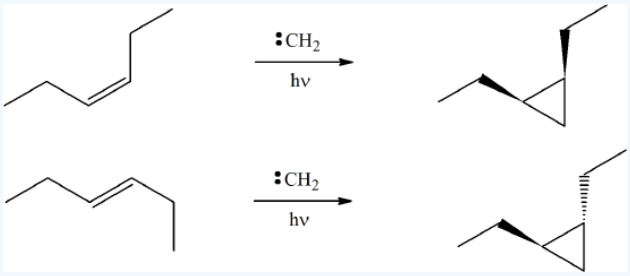
EXERCISE 8.9.1

Predict the resulting products. Will they be the same product?



Answer

No they will not be the same product, they will be isomers of each other.



EXERCISE 8.9.2

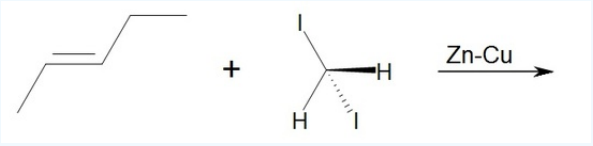
What would be the result of a Simmons-Smith reaction that used *trans*-3-pentene as a reagent?

Answer

The stereochemistry will be retained making a cyclopropane with trans methyl and ethyl groups. *Trans*-1-ethyl-2-methylcyclopropane

EXERCISE 8.9.3

Draw the product of this reaction. What type of reaction is this?



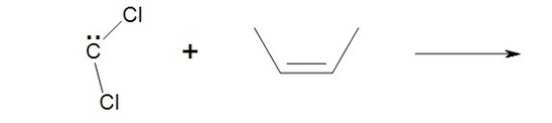
Answer

This is a Simmons-Smith reaction which uses the carbenoid formed by the CH_2I_2 and Zu-Cu. The reaction results in the same product as if methylene was used and retains stereospecificity. Iodine metal and the Zn-Cu are not part of the product. The product is *trans*-1,2-ethyl-methylcyclopropane.



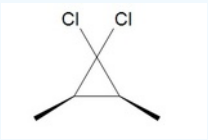
EXERCISE 8.9.4

What would the following reaction yield?



Answer

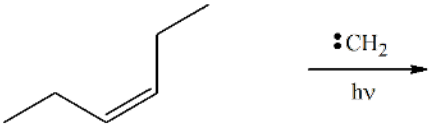
The halogenated carbene will react the same as methylene yielding, *cis*-1,1-dichloro-2,3dimethylcyclopropane.

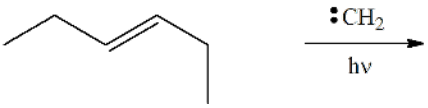


QUESTIONS

Q8.9.1

Predict the following products. Will they be the same product?

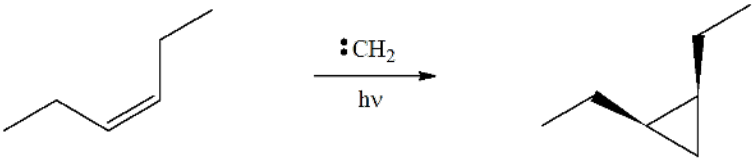


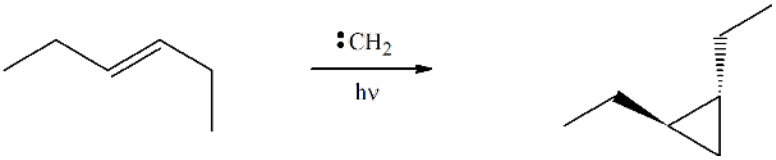


SOLUTIONS

S8.9.1

No they will not be the same product, they will be isomers of each other.





CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Paul Tisher

8.9: Addition of Carbenes to Alkenes - Cyclopropane Synthesis is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

8.10: RADICAL ADDITIONS TO ALKENES - CHAIN-GROWTH POLYMERS

Objectives

After completing this section, you should be able to

1. write the detailed mechanism for the radical polymerization of an alkene.
2. give examples of some common alkene monomers used in the manufacture of chain-growth polymers.
3. identify the alkene monomer used to prepare a specific chain-growth polymer, given the structure of the polymer.

KEY TERMS

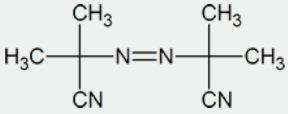
Make certain that you can define, and use in context, the key terms below.

- monomer
- polymer
- vinyl monomer

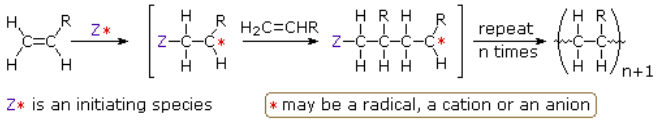
STUDY NOTES

Vinyl monomers are monomers of the type $CH_2{=}CHX$. Recall that the vinyl group is $CH_2{=}CH{-}$.

Although benzoyl peroxide is commonly used as an initiator in free-radical polymerization reactions, an alternative reagent is azobisisobutyronitrile, shown below.



All the monomers from which addition polymers are made are alkenes or functionally substituted alkenes. The most common and thermodynamically favored chemical transformations of alkenes are addition reactions. Many of these addition reactions are known to proceed in a stepwise fashion by way of reactive intermediates, and this is the mechanism followed by most polymerizations. A general diagram illustrating this assembly of linear macromolecules, which supports the name chain growth polymers, is presented here. Since a pi-bond in the monomer is converted to a sigma-bond in the polymer, the polymerization reaction is usually exothermic by 8 to 20 kcal/mol. Indeed, cases of explosively uncontrolled polymerizations have been reported.

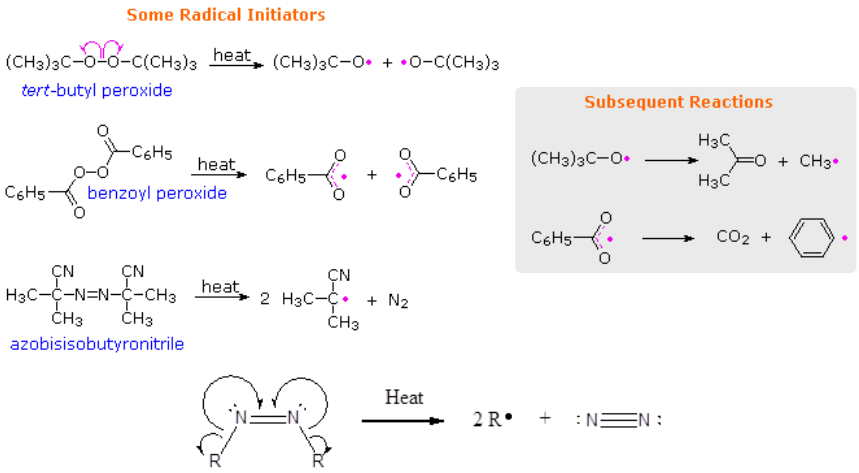


It is useful to distinguish four polymerization procedures fitting this general description.

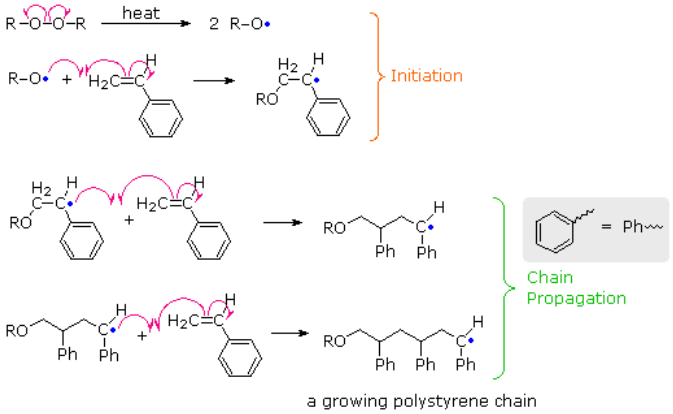
• Radical Polymerization The initiator is a radical, and the propagating site of reactivity (*) is a carbon radical.
• Cationic Polymerization The initiator is an acid, and the propagating site of reactivity (*) is a carbocation.
• Anionic Polymerization The initiator is a nucleophile, and the propagating site of reactivity (*) is a carbanion.
• Coordination Catalytic Polymerization The initiator is a transition metal complex, and the propagating site of reactivity (*) is a terminal catalytic complex.

RADICAL CHAIN-GROWTH POLYMERIZATION

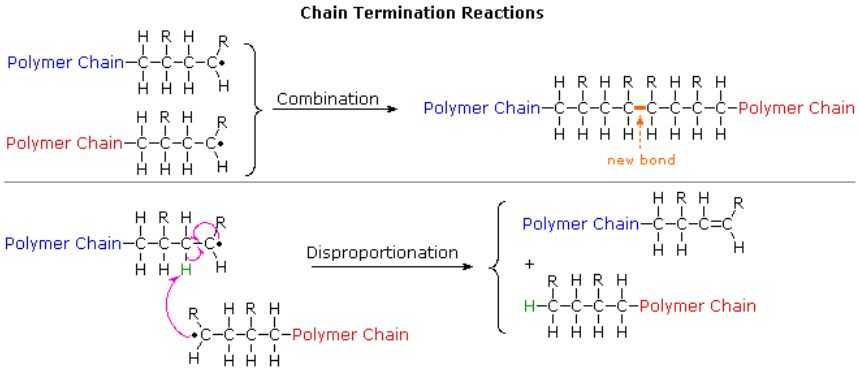
Virtually all of the monomers described above are subject to radical polymerization. Since this can be initiated by traces of oxygen or other minor impurities, pure samples of these compounds are often "stabilized" by small amounts of radical inhibitors to avoid unwanted reaction. When radical polymerization is desired, it must be started by using a radical initiator, such as a peroxide or certain azo compounds. The formulas of some common initiators, and equations showing the formation of radical species from these initiators are presented below.



By using small amounts of initiators, a wide variety of monomers can be polymerized. One example of this radical polymerization is the conversion of styrene to polystyrene, shown in the following diagram. The first two equations illustrate the initiation process, and the last two equations are examples of chain propagation. Each monomer unit adds to the growing chain in a manner that generates the most stable radical. Since carbon radicals are stabilized by substituents of many kinds, the preference for head-to-tail regioselectivity in most addition polymerizations is understandable. Because radicals are tolerant of many functional groups and solvents (including water), radical polymerizations are widely used in the chemical industry.



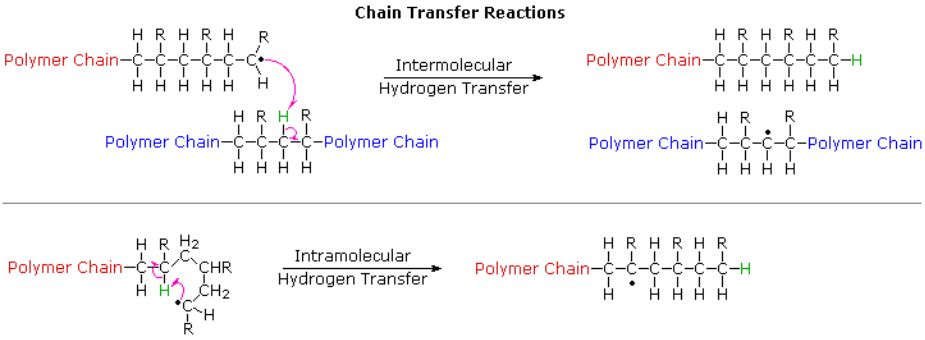
In principle, once started a radical polymerization might be expected to continue unchecked, producing a few extremely long chain polymers. In practice, larger numbers of moderately sized chains are formed, indicating that chain-terminating reactions must be taking place. The most common termination processes are Radical Combination and Disproportionation. These reactions are illustrated by the following equations. The growing polymer chains are colored blue and red, and the hydrogen atom transferred in disproportionation is colored green. Note that in both types of termination two reactive radical sites are removed by simultaneous conversion to stable product(s). Since the concentration of radical species in a polymerization reaction is small relative to other reactants (e.g. monomers, solvents and terminated chains), the rate at which these radical-radical termination reactions occurs is very small, and most growing chains achieve moderate length before termination.



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The relative importance of these terminations varies with the nature of the monomer undergoing polymerization. For acrylonitrile and styrene combination is the major process. However, methyl methacrylate and vinyl acetate are terminated chiefly by disproportionation.

Another reaction that diverts radical chain-growth polymerizations from producing linear macromolecules is called chain transfer. As the name implies, this reaction moves a carbon radical from one location to another by an intermolecular or intramolecular hydrogen atom transfer (colored green). These possibilities are demonstrated by the following equations

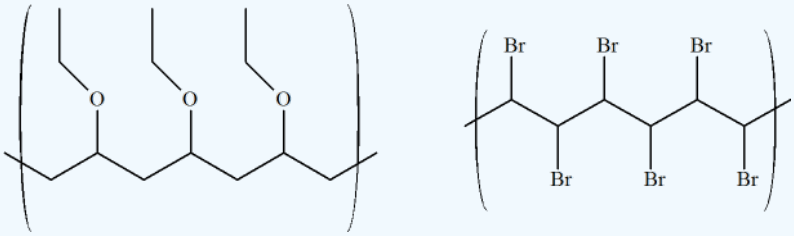


Chain transfer reactions are especially prevalent in the high pressure radical polymerization of ethylene, which is the method used to make LDPE (low density polyethylene). The 1º-radical at the end of a growing chain is converted to a more stable 2º-radical by hydrogen atom transfer. Further polymerization at the new radical site generates a side chain radical, and this may in turn lead to creation of other side chains by chain transfer reactions. As a result, the morphology of LDPE is an amorphous network of highly branched macromolecules.

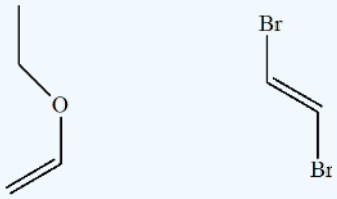
EXERCISE

? EXERCISE \PageIndex1

Propose the monomer units in the following polymers.



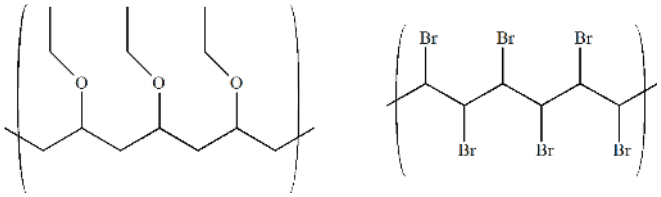
Answer



QUESTIONS

Q8.10.1

Propose the monomer units in the following polymers:



SOLUTIONS

S8.10.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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8.11: BIOLOGICAL ADDITIONS OF RADICALS TO ALKENES

Objective

After completing this section, you should be able to discuss, briefly, some of the addition reactions that take place in nature, and the role of enzymes in such processes.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

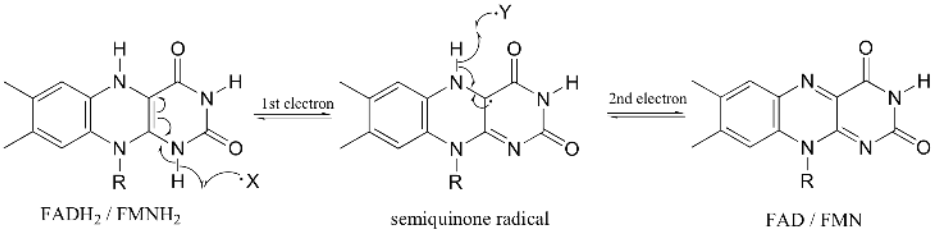
- enzyme
- coenzyme

STUDY NOTES

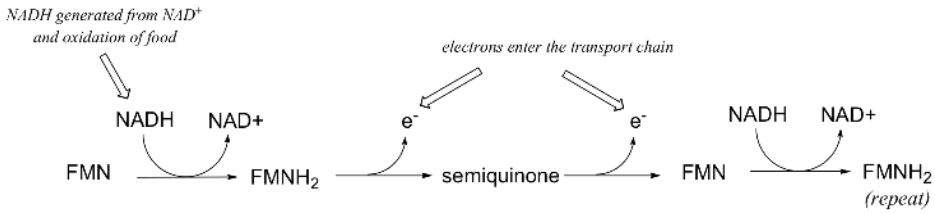
You need not memorize the reaction described in this section of the textbook. However, you should note how the names of enzymes are derived from the reactions they catalyze; for example, ascorbic acid oxidase is the enzyme that catalyzes the oxidation of ascorbic acid (vitamin C).

RADICAL MECHANISMS FOR FLAVIN-DEPENDENT REACTIONS

In chapter 16 we saw how flavin coenzymes, like their nicotinamide adenine dinucleotide counterparts, can act as hydride acceptors and donors. In these redox reactions, two electrons are transferred together in the form of a hydride ion. Flavin, however, is also capable of mediating chemical steps in which a single unpaired electron is transferred - in other words, radical chemistry. This is due to the ability of the flavin system to form a stabilized radical intermediate called a **semiquinone**, formed when $FADH_2$ (or $FMNH_2$) donates a single electron, or when FAD (or FMN) accepts a single electron.



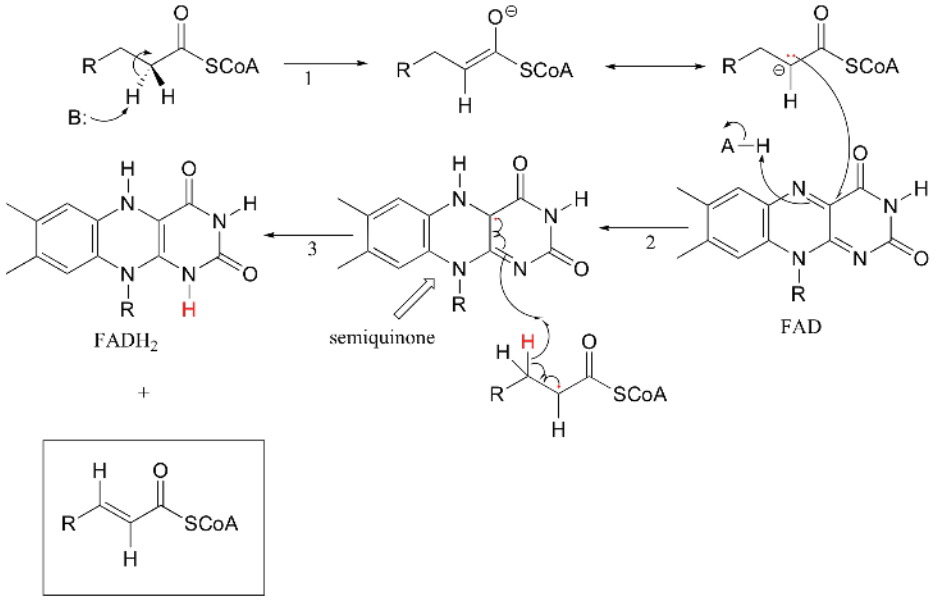
This single-electron transfer capability of flavins is critical to their metabolic role as the entry point of electrons into the electron transport phase of respiration. Electrons 'harvested' from the oxidation of fuel molecules are channeled, *one by one*, by $FMNH_2$ into the electron transport chain, where they eventually reduce molecular oxygen. NADH is incapable of single electron transfer - all it can do is transfer *two* electrons, in the form of a hydride, to FMN; the regenerated $FMNH_2$ is then able to continue sending single electrons into the transport chain.



You will learn more details about this process in a biochemistry class.

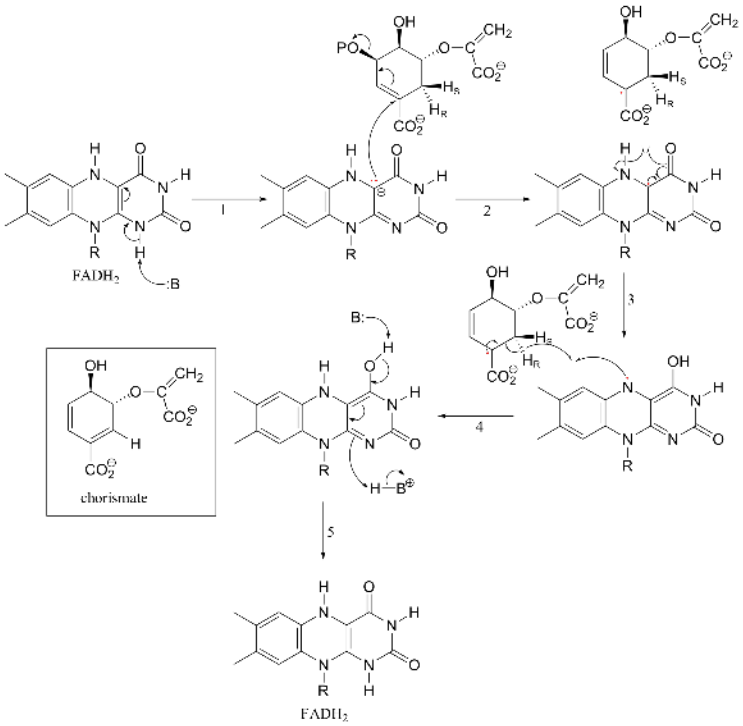
Because flavins are capable of single-electron as well as two-electron chemistry, the relevant mechanisms of flavoenzyme-catalyzed reactions are often more difficult to determine. Recall the dehydrogenation reaction catalyzed by acyl-CoA dehydrogenase (section 16.5C) - it involves the transfer of two electrons and two protons (ie. a hydrogen molecule) to FAD. Both electrons could be transferred together, with the FAD coenzyme simply acting as a hydride acceptor (this is the mechanism we considered previously). However, because the oxidizing coenzyme being used is FAD rather than NAD^+, it is also possible that the reaction could proceed by a single-electron, radical intermediate process. In the alternate radical mechanism proposed below, for example, the enolate intermediate first donates a *single*

electron to FAD, forming a radical semiquinone intermediate (step 2). The second electron is transferred when the semiquinone intermediate abstracts a hydrogen from C_b in a homolytic fashion (step 3).



Scientists are still not sure which mechanism - the hydride transfer mechanism that we saw in section 16.5B or the single electron transfer detailed above - more accurately depicts what is going on in this reaction.

The conjugated elimination catalyzed by chorismate synthase (section 14.3B) is another example of a reaction where the participation of flavin throws doubt on the question of what is the relevant mechanism. This could simply be a conjugated E1' reaction, with formation of an allylic carbocation intermediate. The question plaguing researchers studying this enzyme, however, is why $FADH_2$ is required. This is not a redox reaction, and correspondingly, $FADH_2$ is *not* used up in the course of the transformation - it just needs to be bound in the active site in order for the reaction to proceed. Given that flavins generally participate in single-electron chemistry, this is an indication that radical intermediates may be involved. Recently an alternative mechanism, involving a flavin semiquinone intermediate, has been proposed (*J. Biol. Chem* **2004**, *279*, 9451). Notice that a single electron is transferred from substrate to coenzyme in step 2, then transferred back in step 4.



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CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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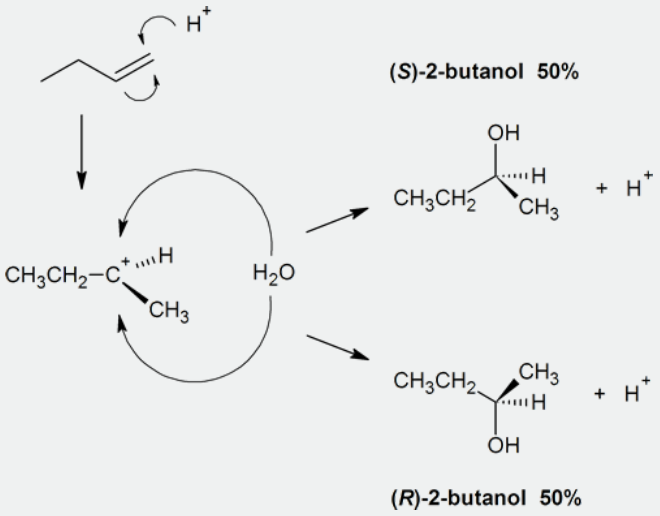
8.12: STEREOCHEMISTRY OF REACTIONS - ADDITION OF H_2O TO AN ACHIRAL ALKENE

Objective

After completing this section, you should be able to account for the stereochemistry of the product of the addition of water to an alkene in terms of the formation of a planar carbocation.

STUDY NOTES

Organic reactions in the laboratory or in living systems can produce chiral centres. Consider reaction of 1-butene with water (acid catalyzed). Markovnikov regiochemistry occurs and the OH adds to the second carbon. However, both *R* and *S* products occur giving a racemic (50/50) mixture of 2-butanol. How does this occur? The proton addition to 1-butene results in a planar carbocation intermediate. A molecule of water is then equally likely to attack from the top or the bottom of this cation to produce either (*S*)-2-butanol or (*R*)-2-butanol, respectively.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

8.12: Stereochemistry of Reactions - Addition of H_2O to an Achiral Alkene is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

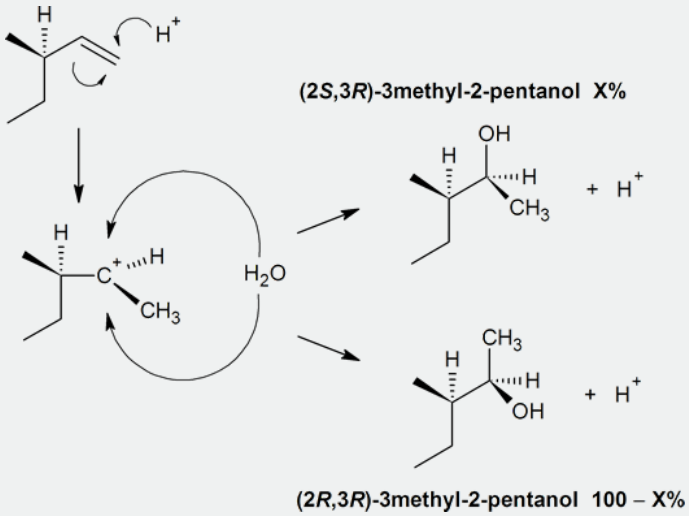
8.13: STEREOCHEMISTRY OF REACTIONS - ADDITION OF H_2O TO A CHIRAL ALKENE

Objective

After completing this section, you should be able to explain why the addition of H_2O to a chiral alkene leads to unequal amounts of diastereomeric products.

STUDY NOTES

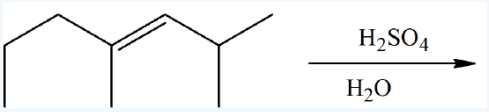
In the previous section, the addition of water to the achiral alkene produced a racemic mixture of two enantiomeric alcohols. They are produced in equal amounts so the mixture is optically inactive. What would occur if we carried out a similar reaction on a chiral alkene? Consider (*S*)-3-methyl-1-pentene reacting with water (acid catalyzed). Proton addition produces a carbocation intermediate that is chiral (* denotes stereogenic centre). That intermediate does not have a plane of symmetry and therefore attack by water is not equal from the top and bottom. This ultimately produces *R* and *S* products in a non 50:50 ratio.



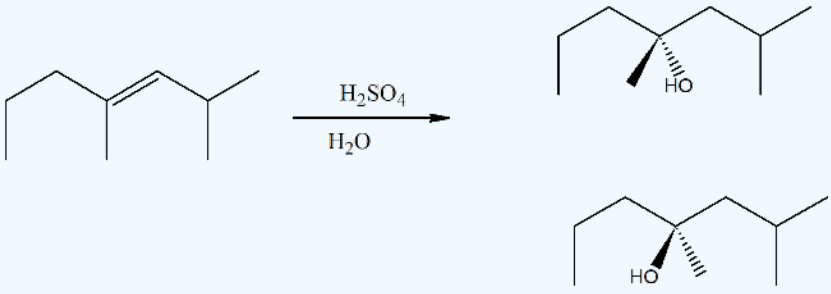
EXERCISE

EXERCISE 8.13.1

Predict the products of the following reaction showing stereochemistry.



Answer

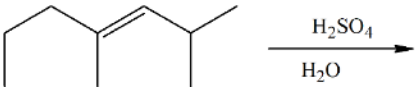


The products are diastereomers of one another.

QUESTIONS

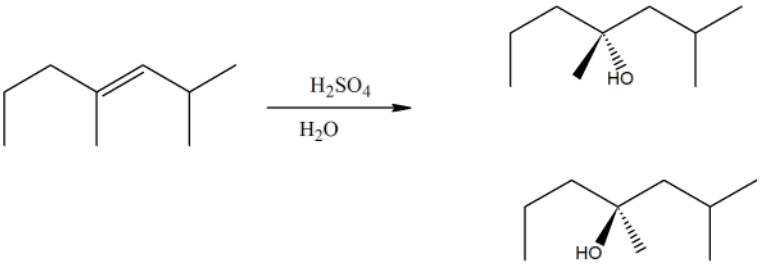
Q8.13.1

Predict the products of the following reaction showing stereochemistry.



SOLUTIONS

S8.13.1



The products (Markovnikov) are diastereomers of one another.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

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8.S: ALKENES - REACTIONS AND SYNTHESIS (SUMMARY)

CONCEPTS & VOCABULARY

8.1 Preparing Alkenes: A Preview of Elimination Reactions

- Alkenes can be prepared by either E1 or E2 elimination reactions of alkyl halides.

8.2 Halogenation of Alkenes: Addition of X_2

- Halogen molecules can react as **electrophiles** due to polarization of the halogen-halogen bond.
- During **electrophilic addition** of halogens to pi bonds, an intermediate halonium ion is formed.
- During electrophilic halogenation, ring opening of the halonium intermediate causes **anti** stereochemistry of the halogen atoms in the dihalide product.

8.3 Halohydrins from Alkenes: Addition of HOX

- **Halohydrins** have a halogen and a hydroxide on adjacent carbon atoms. Bromohydrin and chlorohydrin are the specific types of halohydrins where the halogen is bromine or chlorine respectively.
- In **halohydrin** formation a carbocation intermediate is formed on the more substituted carbon (when available). This causes the hydroxide to be added to the more substituted carbon of the original alkene and the halogen to add to the less substituted carbon.

8.4 Hydration of Alkenes: Addition of H_2O by Oxymercuration

- Electrophilic hydration is the addition of water to an alkene with one carbon adding a hydrogen and the other carbon a hydroxide.
- The mechanism begins with addition of a proton, yielding the more substituted **carbocation**.
- Carbocations can undergo **hydride shifts** and **alkyl shifts** to form a more stable **carbocation** when possible.
- **Markovnikov** addition through acid and water or oxymercuration-demercuration yields the more substituted alcohol product (when the two sides of the alkene are not equally substituted).
- Oxymercuration-demercuration avoids carbocation rearrangements through mercurinium ion bridge.

8.5 Hydration of Alkenes: Addition of H_2O by Hydroboration

- Hydroboration-oxidation proceeds through anti-**Markovnikov** addition of water to an alkene, yielding the less substituted alcohol.

8.6 Reduction of Alkenes: Hydrogenation

- Hydrogenation reactions increase the number of carbon-hydrogen bonds, therefore are reduction reactions.
- Addition of hydrogen to carbon-carbon pi bonds is called hydrogenation.
- Hydrogenation requires a catalyst to lower the activation energy allowing the reaction to proceed (commonly nickel, palladium or platinum).
- Hydrogenation reactions occur primarily with syn addition of the two hydrogen atoms, though potential for isomerization makes this uncertain.

8.7 Oxidation of Alkenes: Epoxidation and Hydroxylation

- **Epoxidation** can be carried out by reacting an alkene with a peroxy acid such as MCPBA.
- Anti **dihydroxylation** is achieved by ring opening an epoxide with water under acidic or basic conditions.
- Vicinal diols have hydroxy groups on adjacent carbon atoms.
- Syn dihydroxylation occurs through reaction with osmium tetraoxide, followed by reduction of the intermediate with sulfur compounds.

8.8 Oxidation of Alkenes: Cleavage to Carbonyl Compounds

- Ozonolysis is the cleavage of an alkene resulting in carbonyls at each carbon of the alkene.
- Alkenes can be cleaved by potassium permanganate, which also results in carbonyls at each alkene carbon, though potassium permanganate will oxidize every carbon-hydrogen bonds on the alkene to a carbon-oxygen bond.

8.9 Addition of Carbenes to Alkenes: Cyclopropane Synthesis

- Organic molecules that have a carbon with only two bonds and a lone pair of electrons are called carbenes.
- Most carbenes are highly reactive and short-lived and are often created *in situ*.
- Carbenes can be formed from diazo compounds by reacting wtih a copper catalyst.
- Carbenes will react with alkenes to form cyclopropane rings.

8.10 Radical Addition to Alkenes: Chain-Growth Polymers

- Monomers are units that repeat to form a polymer.

- In radical polymerization, the polymer chain reaction is initiated by a radical.
- Polymer chain reactions occur through a series of steps beginning with **initiation**, continuing through **propagation**, and ending in **termination**.

8.11 Biological Additions of Radicals to Alkenes

8.12 Reaction Stereochemistry: Addition of H_2O to an Achiral Alkene

- Since addition of water to an alkene proceeds through a planar carbocation intermediate, achiral alkenes lead to a racemic mixture of alcohol products.

8.13 Reaction Stereochemistry: Additon of H_2O to a Chiral Alkene

- Addition of water to alkenes which also contain a stereocenter does not lead to a 50:50 mixture of R and S products as the chiral center can reduce reactivity from one side of the carbocation. The products of this type of reaction will be diastereomers, since the original stereocenter will not change and the product will have an additional stereocenter.

SKILLS TO MASTER

- Skill 8.1 Draw accurate Electrophilic Addition Mechanisms incorporating halonium intermediates.
- Skill 8.2 Draw accurate Electrophilic Addition Mechanisms incorporating carbocation intermediates.
- Skill 8.3 Draw Markovnikov products of alkene additions based on the most substituted carbocation intermediate.
- Skill 8.4 Draw hydrogenation products of alkenes.
- Skill 8.5 Draw appropriate epoxidation products including sterechemistry.
- Skill 8.6 Describe how to prepare syn and anti diols from alkenes.
- Skill 8.7 Draw products of oxidative cleavage reactions.
- Skill 8.8 Describe radical chain reactions to form polymers.

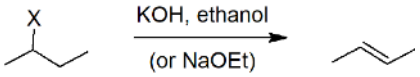
MEMORIZATION TASKS

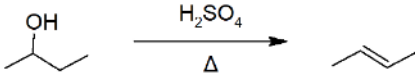
MT 8.1 Memorize reagents for alkene reactions.

MT 8.2 Memorize stability order of carbocations.

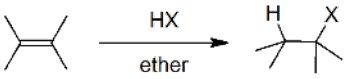
SUMMARY OF REACTIONS

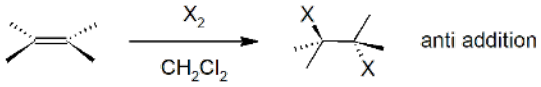
Preparation of Alkenes

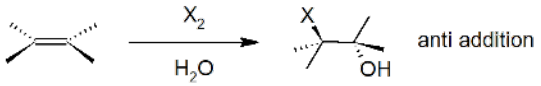


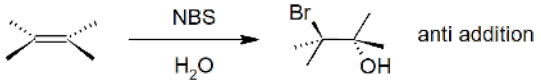


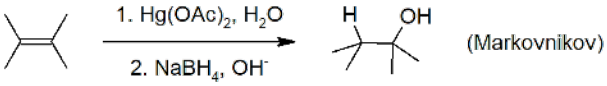
Addition Reactions

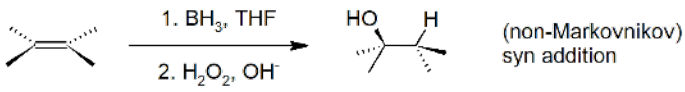


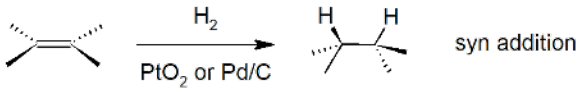


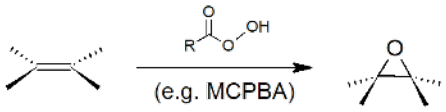


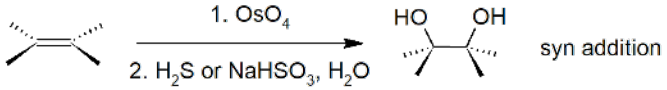


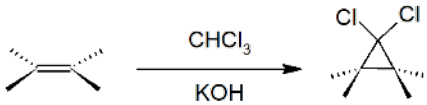


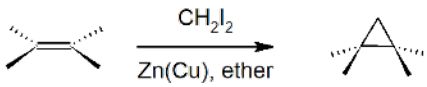


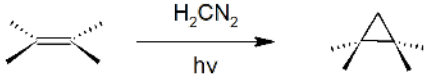




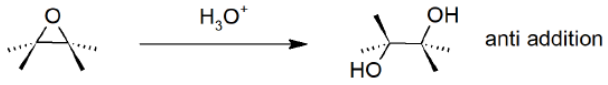




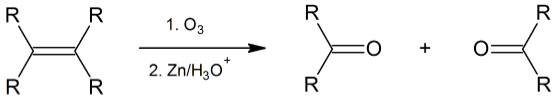


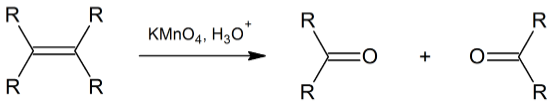


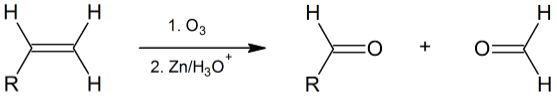
Anti-hydroxylation

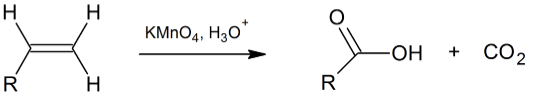


Oxidative Cleavage

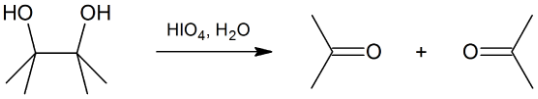








Diol Cleavage



CONTRIBUTORS

- Layne Morsch (University of Illinois Springfield)
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CHAPTER OVERVIEW

9: ALKYNES- AN INTRODUCTION TO ORGANIC SYNTHESIS

LEARNING OBJECTIVES

After you have completed Chapter 9, you should be able to

1. fulfill all of the detailed objectives listed under each individual section.
2. solve road-map problems involving any of the reactions introduced to this point.
3. design multistep syntheses using any of the reactions introduced to this point, and determine the viability of a given synthesis.
4. define, and use in context, the key terms introduced.

Addition reactions not only dominate the chemistry of alkenes, they are also the major class of reaction you will encounter. This chapter discusses an important difference between (terminal) alkynes and alkenes, that is, the acidity of the former; it also addresses the problem of devising organic syntheses. Once you have completed this chapter you will have increased the number of organic reactions in your repertoire, and should be able to design much more elaborate multistep syntheses. As you work through Chapter 9, you should notice the many similarities among the reactions described here and those in Chapters 7 and 8.

9.0: Prelude
9.1: Naming Alkynes
9.2: Preparation of Alkynes - Elimination Reactions of Dihalides
9.3: Reactions of Alkynes - Addition of HX and X_2
9.4: Hydration of Alkynes
9.5: Reduction of Alkynes
9.6: Oxidative Cleavage of Alkynes
9.7: Alkyne Acidity - Formation of Acetylide Anions
9.8: Alkylation of Acetylide Anions
9.9: An Introduction to Organic Synthesis
9.S: Alkynes - An Introduction to Organic Synthesis (Summary)

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9.0: Prelude

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9.1: NAMING ALKYNES

Objectives

After completing this section, you should be able to

1. provide the correct IUPAC name of an alkyne, given its Kekulé, condensed or shorthand structure.
2. provide the correct IUPAC name of a compound containing both double and triple bonds, given its Kekulé, condensed or shorthand structure.
3. draw the structure of a compound containing one or more triple bonds, and possibly one or more double bonds, given its IUPAC name.
4. name and draw the structure of simple alkynyl groups, and where appropriate, use these names as part of the IUPAC system of nomenclature.

STUDY NOTES

Simple alkynes are named by the same rules that are used for alkenes (see Section 7.3), except that the ending is *-yne* instead of *-ene*. Alkynes cannot exhibit *E,Z* (cis-trans) isomerism; hence, in this sense, their nomenclature is simpler than that of alkenes.

Alkynes are organic molecules made of the functional group carbon-carbon triple bonds and are written in the empirical formula of C_nH_{2n-2}. They are unsaturated hydrocarbons. Like alkenes have the suffix –ene, alkynes use the ending –yne; this suffix is used when there is only one alkyne in the molecule.



INTRODUCTION

Here are the molecular formulas and names of the first ten carbon straight chain alkynes.

Name	Molecular Formula
Ethyne	C_2H_2
Propyne	C_3H_4
1-Butyne	C_4H_6
1-Pentyne	C_5H_8
1-Hexyne	C_6H_{10}
1-Heptyne	C_7H_{12}
1-Octyne	C_8H_{14}
1-Nonyne	C_9H_{16}
1-Decyne	$C_{10}H_{18}$

The more commonly used name for ethyne is acetylene, which used industrially.

NAMING ALKYNES

Like previously mentioned, the IUPAC rules are used for the naming of alkynes.

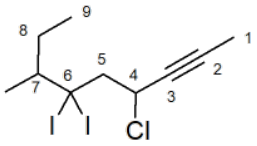
RULE 1

Find the longest carbon chain that includes both carbons of the triple bond.

RULE 2

Number the longest chain starting at the end closest to the triple bond. A 1-alkyne is referred to as a terminal alkyne and alkynes at any other position are called internal alkynes.

For example:

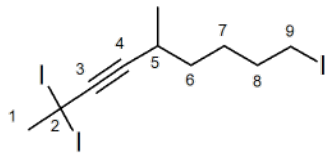


4-chloro-6,6-diiodo-7-methylnon-2-yne

RULE 3

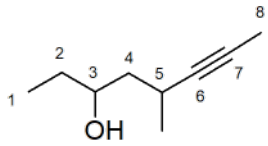
After numbering the longest chain with the lowest number assigned to the alkyne, label each of the substituents at its corresponding carbon. While writing out the name of the molecule, arrange the substituents in alphabetical order. If there are more than one of the same substituent use the prefixes di, tri, and tetra for two, three, and four substituents respectively. These prefixes are not taken into account in the alphabetical order.

For example:



2,2,9-triiodo-5-methylnon-3-yne

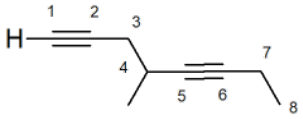
If there is an alcohol present in the molecule, number the longest chain starting at the end closest to it, and follow the same rules. However, the suffix would be –ynol, because the alcohol group takes priority over the triple bond.



5-methyl-6-octyn-3-ol

When there are two triple bonds in the molecule, find the longest carbon chain including both the triple bonds. Number the longest chain starting at the end closest to the triple bond that appears first. The suffix that would be used to name this molecule would be –diyne.

For example:

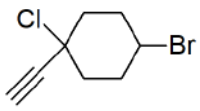


4-methyl-1,5-octadiyne

RULE 4

Substituents containing a triple bond are called alkynyl.

For example:



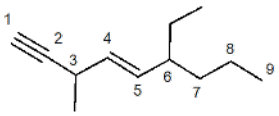
4-bromo-1-chloro-1-ethynylcyclohexane

Here is a table with a few of the alkynyl substituents:

Name	Molecule
Ethynyl	-C≡CH
2- Propynyl	$-CH_2C{\equiv}CH$
2-Butynyl	$-CH_3C{\equiv}CH_2CH_3$

RULE 5

A molecule that contains both double and triple bonds is called an alkenyne. The chain can be numbered starting with the end closest to the functional group that appears first. For example:



(*E*) 6-ethyl-3-methyl-non-4-en-1-yne

[NB If both functional groups are the exact same distance from the end the alkene takes precedence.]

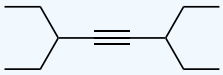
REFERENCE

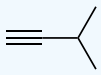
1. Vollhardt, Peter, and Neil E. Schore. Organic Chemistry: Structure and Function. 5th Edition. New York: W. H. Freeman & Company, 2007.

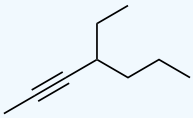
EXERCISES

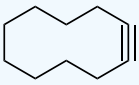
? EXERCISE 9.1.1

Name the following compounds:

a) 

b) 

c) 

d) 

Answer

A – 3,6-diethyl-4-octyne

B – 3-methylbutyne

C – 4-ethyl-2-heptyne

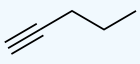
D – cyclodecyne

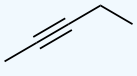
? EXERCISE 9.1.2

How many isomers are possible for C_5H_8? Draw them.

Answer

2 possible isomers





EXERCISE 9.1.3

Draw the following compounds:

a) 4,4-dimethyl-2-pentyne

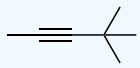
b) 3-octyne

c) 3-methyl-1-hexyne

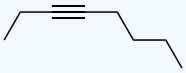
d) *trans* 3-hepten-1-yne

Answer

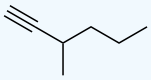
a)



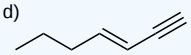
b)



c)



d)



EXERCISE 9.1.4

Do alkynes show *cis-trans* isomerism? Explain.

Answer

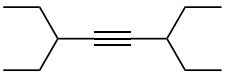
No. A triply bonded carbon atom can form only one other bond and has linear electron geometry so there are no "sides". Allkenes have two groups attached to each inyl carbon with a trigonal planar electron geometry that creates the possibility of cis-trans isomerism.

QUESTIONS

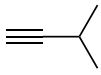
Q9.1.1

Name the following compounds:

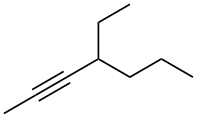
a)



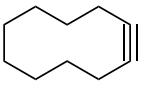
b)



c)



d)



Q9.1.2

How many isomers are possible for C_5H_8? Draw them.

Q9.1.3

Draw the following compounds:

A) 4,4-dimethyl-2-pentyne

B) 3-octyne

C) 3-methyl-1-hexyne

D) *trans* 3-hepten-1-yne

Q9.1.4

Do alkynes show cis-trans isomerism? Explain.

SOLUTIONS

S9.1.1

A – 3,6-diethyl-4-octyne

B – 3-methylbutyne

C – 4-ethyl-2-heptyne

D – cyclodecyne

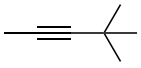
S9.1.2

2 possible isomers

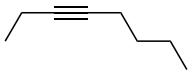


S9.1.3

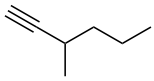
a)



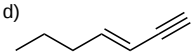
b)



c)



d)



S9.1.4

No. A triply bonded carbon atom can form only one other bond and has linear electron geometry so there are no "sides". Allkenes have two groups attached to each inyl carbon with a trigonal planar electron geometry that creates the possibility of cis-trans isomerism.

CONTRIBUTORS AND ATTRIBUTIONS

- A. Sheth and S. Sujit (UCD)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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9.2: PREPARATION OF ALKYNES - ELIMINATION REACTIONS OF DIHALIDES

Objectives

After completing this section, you should be able to

1. write an equation to describe the preparation of an alkyne by the dehydrohalogenation of a vicinal dihalide or vinylic halide.
2. identify the alkyne produced from the dehydrohalogenation of a given vicinal dihalide or vinylic halide.
3. write a reaction sequence to show how the double bond of an alkene can be transformed into a triple bond.
4. identify the vicinal dihalide (or vinylic halide) needed to synthesize a given alkyne by dehydrohalogenation.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- vicinal dihalide
- vinylic halide

Alkynes can be a useful functional group to synthesize due to some of their antibacterial, antiparasitic, and antifungal properties. One simple method for alkyne synthesis is by double elimination from a dihaloalkane.

INTRODUCTION

One case in which elimination can occur is when a haloalkane is put in contact with a nucleophile. The table below is used to determine which situations will result in elimination and the formation of a π bond.

Table 9.2.1: Elimination: Haloalkane-Nucleophile Reaction

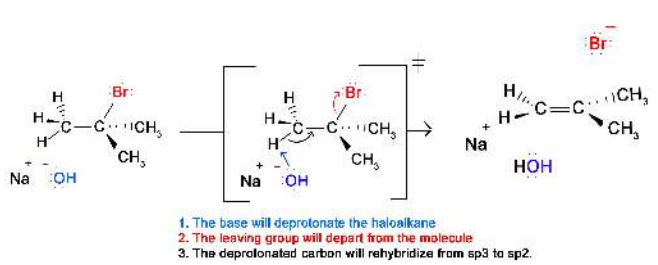
Type of Haloalkane	Weak Base, Poor Nucleophile	Weak Base, Good Nucleophile	Strong, Unhindered Base	Strong, Hindered Base
Primary				
Unhindered				E2
Branched			E2	E2
Secondary	E1		E2	E2
Tertiary	E1	E1	E2	E2

* Empty Box means no elimination or \9\pi\) bond forms

To synthesize alkynes from dihaloalkanes we use dehydrohalogenation. The majority of these reactions take place using alkoxide bases (other strong bases can also be used) with high temperatures. This combination results in the majority of the product being from the E2 mechanism.

E2 MECHANISM

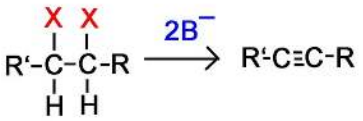
Recall that the E2 mechanism is a concerted reaction (occurs in 1 step). However, in this 1 step there are 3 different changes in the molecule. This is the reaction between 2-Bromo-2-methylpropane and Sodium Hydroxide.



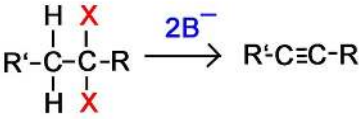
This is a brief review of the E2 reaction. For further information on why the reaction proceeds as it does visit the E2 reaction page. Now, if we apply this concept using 2 halides on vicinal or geminal carbons, the E2 reaction will take place twice resulting in the formation of 2 π bonds and thus an Alkyne.

DIHALOALKANE ELIMINATION

This is a general picture of the reaction taking place without any of the mechanisms shown.

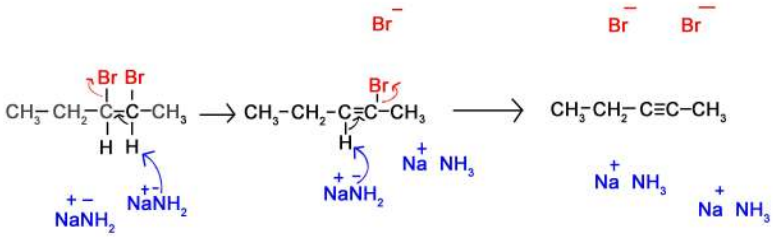


or



* With a terminal haloalkane the equation above is modified in that 3 equivalents of base will be used instead of 2.

Lets look at the mechanism of a reaction between 2,3-Dibromopentane with sodium amide in liquid ammonia.

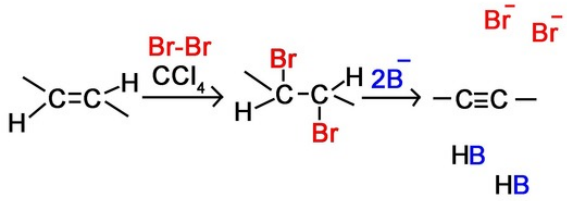


- Liquid ammonia is not part of the reaction, but is used as a solvent
- Notice the intermediate of the alkyne synthesis. It is stereospecifically in its anti form. Because the second proton and halogen are pulled off the molecule this is unimportant to the synthesis of alkynes. For more information on this see the page on preparation of alkenes from haloalkanes.

PREPARATION OF ALKYNES FROM ALKENES

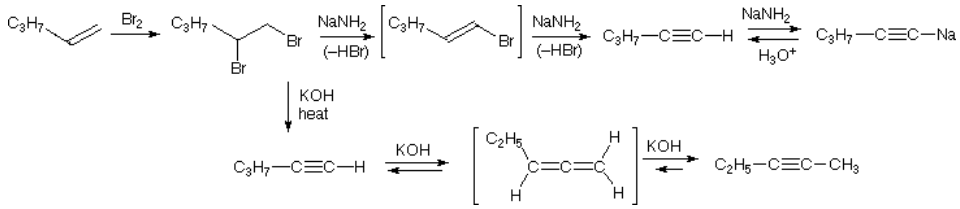
Lastly, we will briefly look at how to prepare alkynes from alkenes. This is a simple process using first halogenation of the alkene bond to form the dihaloalkane, and next, using the double elimination process to protonate the alkane and from the 2 π bonds.

This first process is gone over in much greater detail in the page on halogenation of an alkene. In general, chlorine or bromine is used with an inert halogenated solvent like chloromethane to create a vicinal dihalide from an alkene. The vicinal dihalide formed is the reactant needed to produce the alkyene using double elimination, as covered previously on this page.



TERMINAL ALKYNES

The acidity of terminal alkynes also plays a role in product determination when vicinal (or geminal) dihalides undergo base induced bis-elimination reactions. The following example illustrates eliminations of this kind starting from 1,2-dibromopentane, prepared from 1-pentene by addition of bromine. The initial elimination presumably forms 1-bromo-1-pentene, since base attack at the more acidic and less hindered 1 °-carbon should be favored. The second elimination then produces 1-pentyne. If the very strong base sodium amide is used, the terminal alkyne is trapped as its sodium salt, from which it may be released by mild acid treatment. (NB One cannot stop the reaction at the terminal alkyne with 2 equivalents of strong base.) However, if the weaker base KOH with heat is used for the elimination, the terminal alkyne salt is not formed, or is formed reversibly, and the initially generated 1-pentyne rearranges to the more stable 2-pentyne via an allene intermediate.



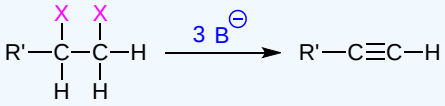
REFERENCES

1. Vollhardt, Peter, and Neil Shore. Organic Chemistry: Structure and Function. 5th. New York: W.H. Freeman and Company, 2007.
2. Daley, Richard, and Sally Daley. "13.8 Elimination of Organohalogens." Organic Chemistry. Daley. 5 July 2005. 21 Feb. 2009. <https://studylib.net/doc/8721401/13-elimination-reactions>.

EXERCISES

EXERCISE \PageIndex1

Why would we need 3 bases for every terminal dihaloalkane instead of 2 in order to form an alkyne?



Answer

Remember that hydrogen atoms on terminal alkynes make the alkyne acidic. One of the base molecules will pull off the terminal hydrogen instead of one of the halides like we want.

EXERCISE \PageIndex2

What are the major products of the following reactions:

a.) 1,2-Dibromopentane with sodium amide in liquid ammonia

b.) 1-Pentene first with Br_2 and chloromethane, followed by sodium ethoxide (Na^+ $^-O\text{-}CH_2CH_3$)

Answer

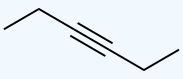
a) 1-Pentyne

b) 1-Pentyne

EXERCISE \PageIndex3

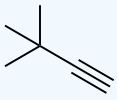
What would be good starting molecules for the synthesis of the following molecules:

a.



from an alkene

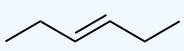
b.



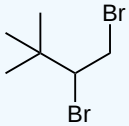
from a dihaloalkane

Answer

a.



b.

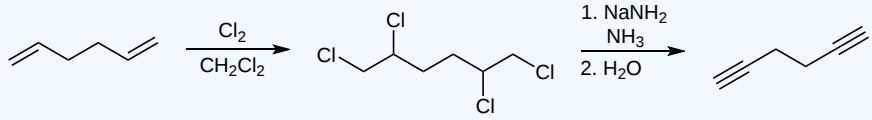


EXERCISE \PageIndex4

Use a 6 carbon diene to synthesize a 6 carbon molecule with 2 terminal alkynes.

Answer

Bromine or chlorine can be used with different inert solvents for the halogenation. This can be done using many different bases. Liquid ammonia is used as a solvent and needs to be followed by an aqueous work-up.



EXERCISE \PageIndex5

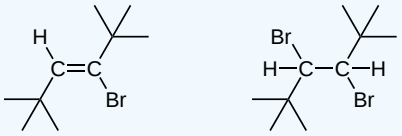
Identify the vinyl halide or halides and the vicinal dihalide or dihalides that could be used in the synthesis of:

a) 2,2,5,5-Tetramethyl-3-hexyne.

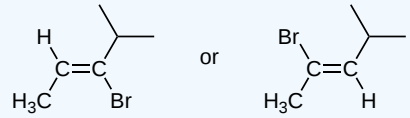
b) 4-Methyl-2-hexyne.

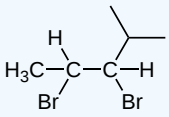
Answer

a)



b)





CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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9.3: REACTIONS OF ALKYNES - ADDITION OF HX AND X_2

Objectives

After completing this section, you should be able to

1. describe the bonding and geometry of the carbon-carbon triple bond in terms of the *sp*-hybridization of the carbon atoms involved.
2. explain the reactivity of alkynes based on the known strengths of carbon-carbon single, double and triple bonds.
3. write equations for the reaction of an alkyne with one or two equivalents of halogen (chlorine or bromine) or halogen acid (HCl, HBr or HI).
4. draw the structure of the product formed when an alkyne reacts with one equivalent of the halogens and halogen acids listed in Objective 3.
5. identify the alkyne which must have been used in an addition reaction with a halogen or halogen acid, given the product of such a reaction.

STUDY NOTES

You might find it useful to review Section 1.9 before you begin work on this chapter. If necessary, construct a molecular model of a simple alkyne. Notice the similarity between the behaviour of alkenes and that of alkynes. In the laboratory, you will observe that alkynes readily decolourize a solution of bromine in dichloromethane. Section 9.7 describes a test that allows you to distinguish between a terminal alkyne (i.e., one in which the triple bond occurs between the last two carbons in the chain) and nonterminal alkynes and alkenes.

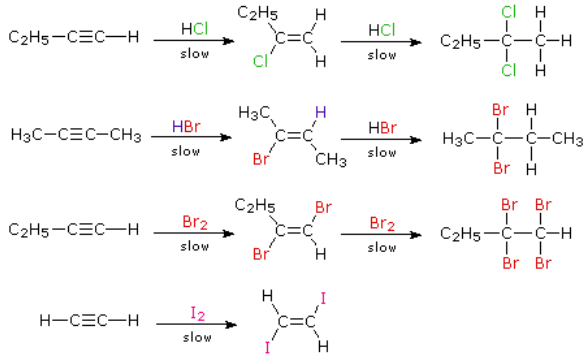
ADDITION BY ELECTROPHILIC REAGENTS

A carbon-carbon triple bond may be located at any unbranched site within a carbon chain or at the end of a chain, in which case it is called **terminal**. Because of its linear configuration (the bond angle of a sp-hybridized carbon is 180º), a ten-membered carbon ring is the smallest that can accommodate this function without excessive strain. Since the most common chemical transformation of a carbon-carbon double bond is an addition reaction, we might expect the same to be true for carbon-carbon triple bonds. Indeed, most of the alkene addition reactions also take place with alkynes, and with similar regio- and stereoselectivity.

When the addition reactions of electrophilic reagents, such as strong Brønsted acids and halogens, to alkynes are studied we find a curious paradox. The reactions are even more exothermic than the additions to alkenes, and yet the rate of addition to alkynes is slower by a factor of 100 to 1000 than addition to equivalently substituted alkenes. The reaction of one equivalent of bromine with 1-penten-4-yne, for example, gave 4,5-dibromo-1-pentyne as the chief product.

$HC{\equiv}C\text{-}CH_2\text{-}CH{=}CH_2 + Br_2 \rightarrow HC{\equiv}C\text{-}CH_2\text{-}CHBrCH_2Br$

Although these electrophilic additions to alkynes are sluggish, they do take place and generally display Markovnikov Rule regioselectivity and anti-stereoselectivity. One problem, of course, is that the products of these additions are themselves substituted alkenes and can therefore undergo further addition. Because of their high electronegativity, halogen substituents on a double bond act to reduce its nucleophilicity, and thereby decrease the rate of electrophilic addition reactions. Consequently, there is a delicate balance as to whether the product of an initial addition to an alkyne will suffer further addition to a saturated product. Although the initial alkene products can often be isolated and identified, they are commonly present in mixtures of products and may not be obtained in high yield. The following reactions illustrate many of these features. In the last example, 1,2-diodoethene does not suffer further addition inasmuch as vicinal-diiodoalkanes are relatively unstable.



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As a rule, electrophilic addition reactions to alkenes and alkynes proceed by initial formation of a **pi-complex**, in which the electrophile accepts electrons from and becomes weakly bonded to the multiple bond. Such complexes are formed reversibly and may then reorganize to a reactive intermediate in a slower, rate-determining step. Reactions with alkynes are more sensitive to solvent changes and catalytic influences than are equivalent alkenes. For examples and a discussion of mechanisms click here.

Why are the reactions of alkynes with electrophilic reagents more sluggish than the corresponding reactions of alkenes? After all, addition reactions to alkynes are generally more exothermic than additions to alkenes, and there would seem to be a higher π-electron density about the triple bond (two π-bonds versus one). Two factors are significant in explaining this apparent paradox. First, although there are more π-electrons associated with the triple bond, the sp-hybridized carbons exert a strong attraction for these π-electrons, which are consequently bound more tightly to the functional group than are the π-electrons of a double bond. This is seen in the ionization potentials of ethylene and acetylene.

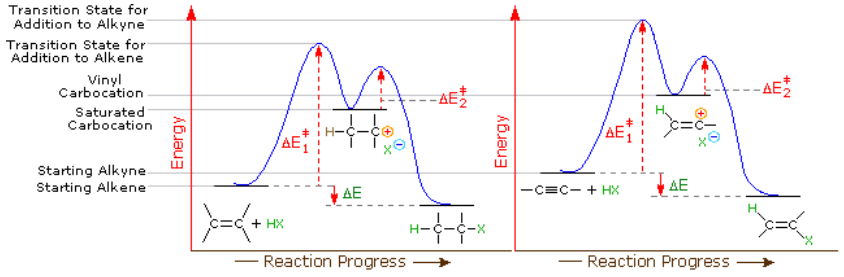
Acetylene	$HC{\equiv}CH + Energy \rightarrow [HC{\equiv}CH\ ^{\bullet(+)} + e^{(-)}$	ΔH = +264 kcal/mole
Ethylene	$H_2C{=}CH_2 + Energy \rightarrow [H_2C{=}CH_2]\ ^{\bullet(+)} + e^{(-)}$	ΔH = +244 kcal/mole
Ethane	$H_3C{-}CH_3 + Energy \rightarrow [H_3C{-}CH_3]\ ^{\bullet(+)} + e^{(-)}$	ΔH = +296 kcal/mole

As defined by the preceding equations, an **ionization potential** is the minimum energy required to remove an electron from a molecule of a compound. Since pi-electrons are less tightly held than sigma-electrons, we expect the ionization potentials of ethylene and acetylene to be lower than that of ethane, as is the case. Gas-phase proton affinities show the same order, with ethylene being more basic than acetylene, and ethane being less basic than either. Since the initial interaction between an electrophile and an alkene or alkyne is the formation of a pi-complex, in which the electrophile accepts electrons from and becomes weakly bonded to the multiple bond, the relatively slower reactions of alkynes becomes understandable.

A second factor is presumed to be the stability of the carbocation intermediate generated by sigma-bonding of a proton or other electrophile to one of the triple bond carbon atoms. This intermediate has its positive charge localized on an unsaturated carbon, and such **vinyl cations** are less stable than their saturated analogs. Indeed, we can modify our earlier ordering of carbocation stability to include these vinyl cations in the manner shown below. It is possible that vinyl cations stabilized by conjugation with an aryl substituent are intermediates in HX addition to alkynes of the type Ar-C≡C-R, but such intermediates are not formed in all alkyne addition reactions.

Carbocation Stability	$CH_3^{(+)} \approx RCH{=}CH^{(+)} < RCH_2^{(+)} \approx RCH{=}CR^{(+)} < R_2CH^{(+)} \approx CH_2{=}CH{-}CH_2^{(+)} < C_6H_5CH_2^{(+)} \approx R_3C^{(+)}$							
	Methyl	1°-Vinyl	1°	2°-Vinyl	2°	1°-Allyl	1°-Benzyl	3°

Application of the Hammond postulate indicates that the activation energy for the generation of a vinyl cation intermediate would be higher than that for a lower energy intermediate. This is illustrated for alkenes versus alkynes by the following energy diagrams.



A Comparison of Energy Profiles for Electrophilic Addition to Alkenes and Alkynes

Despite these differences, electrophilic additions to alkynes have emerged as exceptionally useful synthetic transforms.

ADDITION OF HYDROGEN HALIDE TO AN ALKYNE

Summary: Reactivity order of hydrogen halides: HI > HB r> HCl > HF.

Follows Markovnikov's rule:

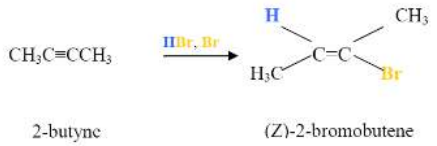
- Hydrogen adds to the carbon with the greatest number of hydrogens, the halogen adds to the carbon with fewest hydrogens.
- Protination occurs on the more stable carbocation. With the addition of HX, haloalkenes form.
- With the addition of excess HX, you get *anti* addition forming a geminal dihaloalkane.

ADDITION OF A HX TO AN INTERNAL ALKYNE

As described in Figure 1, the π electrons will attack the hydrogen of the HBr and because this is a symmetric molecule it does not matter which carbon it adds to, but in an asymmetric molecule the hydrogen will covalently bond to the carbon with the most hydrogens. Once the hydrogen is covalently bonded to one of the carbons, you will get a carbocation intermediate (not shown, but will look the same as depicted in Figure 1) on the other carbon. Again, this is a symmetric molecule and if it were asymmetric, which carbon would have the positive charge?

The final step is the addition of the Bromine, which is a good nucleophile because it has electrons to donate or share. Bromine, therefore attacks the carbocation intermediate placing it on the highly substituted carbon. As a result, you get 2-bromobutene from your 2-butyne reactant, as shown below.

Figure 2



Now, what if you have excess HBr?

ADDITION DUE TO EXCESS HX YIELDS A GEMINAL DIHALOALKANE

Figure 3



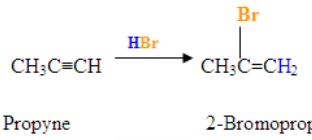
Here, the electrophilic addition proceeds with the same steps used to achieve the product in Addition of a HX to an Internal Alkyne. The π electrons attacked the hydrogen, adding it to the carbon on the left (shown in blue). Why was hydrogen added to the carbon on left and the one on the right bonded to the Bromine?

Now, you will have your carbocation intermediate, which is followed by the attack of the Bromine to the carbon on the right resulting in a haloalkane product.

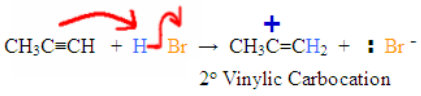
ADDITION OF HX TO TERMINAL ALKYNE

- Here is an addition of HBr to an asymmetric molecule.
- First, try to make sense of how the reactant went to product and then take a look at the mechanism.

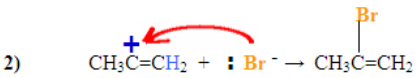
Figure 4



Mechanism:



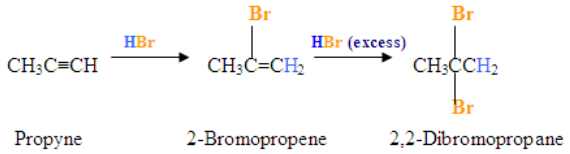
The π electrons are attacking the hydrogen, depicted by the electron pushing arrows and the Bromine gains a negative charge. The carbocation intermediate forms a positive charge on the left carbon after the hydrogen was added to the carbon with the most hydrogen substituents.



The Bromine, which has a negative charge, attacks the positively charged carbocation forming the final product with the nucleophile on the more substituted carbon.

ADDITION DUE TO EXCESS HBR PRESENT

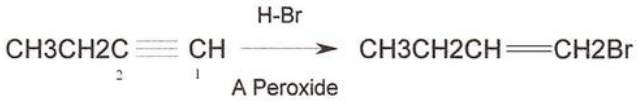
Figure 5



Most Hydrogen halide reactions with alkynes occur in a Markovnikov-manner in which the halide attaches to the most substituted carbon since it is the most positively polarized. A more substituted carbon has more bonds attached to 1) carbons or 2) electron-donating groups such as Fluorine and other halides. However, there are two specific reactions among alkynes where anti-Markovnikov reactions take place: the radical addition of HBr and Hydroboration Oxidation reactions. For alkynes, an anti-Markovnikov addition takes place on a terminal alkyne, an alkyne on the end of a chain.

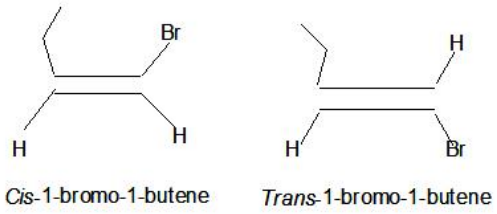
HBR ADDITION WITH RADICAL YIELDS 1-BROMOALKENE

The Br of the Hydrogen Bromide (H-Br) attaches to the less substituted 1-carbon of the terminal alkyne shown below in an anti-Markovnikov manner while the Hydrogen proton attaches to the second carbon. As mentioned above, the first carbon is the less substituted carbon since it has fewer bonds attached to carbons and other substituents. The H-Br reagent must also be reacted with heat or some other radicial initiator such as a peroxide in order for this reaction to proceed in this manner. This presence of the radical or heat leads to the anti-Markovnikov addition since it produces the most stable reaction. For more on Anti-Markovnikov additions:Radical Additions--Anti-Markovnikov Product Formation



The product of a terminal alkyne that is reacted with a peroxide (or light) and H-Br is a 1-bromoalkene.

Regioselectivity: The Bromine can attach in a ***syn*** or ***anti*** manner which means the resulting alkene can be both ***cis*** and ***trans***. ***Syn*** addition is when both Hydrogens attach to the same face or side of the double bond (i.e. ***cis***) while the ***anti*** addition is when they attach on opposite sides of the bond (***trans***).



REACTION: HALOGENATION OF ALKYNES

Summary:

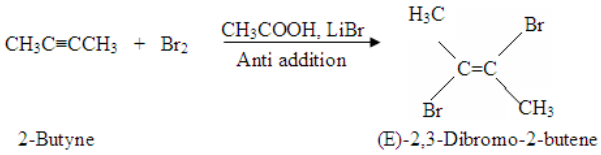


- Stereoslectivity: anti addition
- Reaction proceeds via cyclic halonium ion

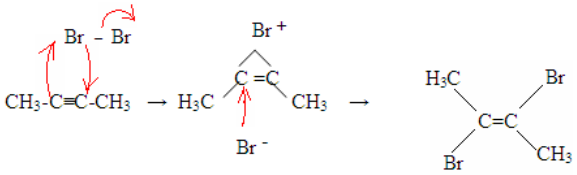
ADDITION OF BR_2

- The addition of Br_2 to an alkyne is analogous to adding Br_2 to an alkene.
- Once Br_2 approaches the nucleophilic alkyne, it becomes polarized.
- The π electrons, from the triple bond, can now attack the polarized bromine forming a C-Br bond and displacing the bromine ion.
- Now, you will get an intermediate electrophilic carbocation, which will immediately react with the bromine ion giving you the dibromo product.

Figure 6



Mechanism:

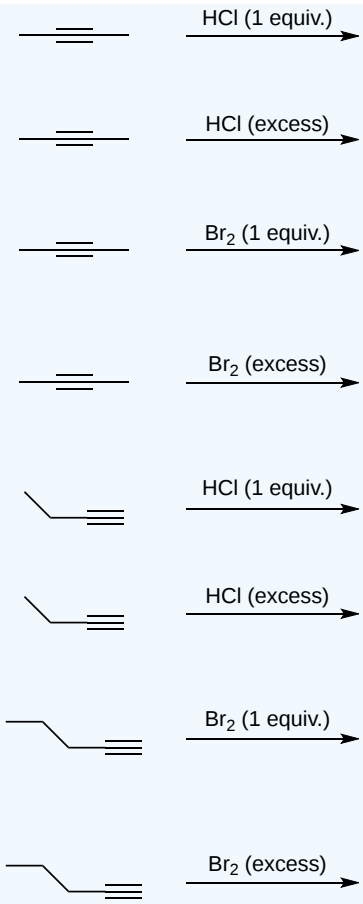


First, you see the polarized Br_2 being attacked by the π electrons. Once you form the C-Br bond, the other bromine is released as a bromine ion. The intermediate here is a bromonium ion, which is electrophilic and reacts with the bromine ion giving you the dibromo product.

EXERCISE

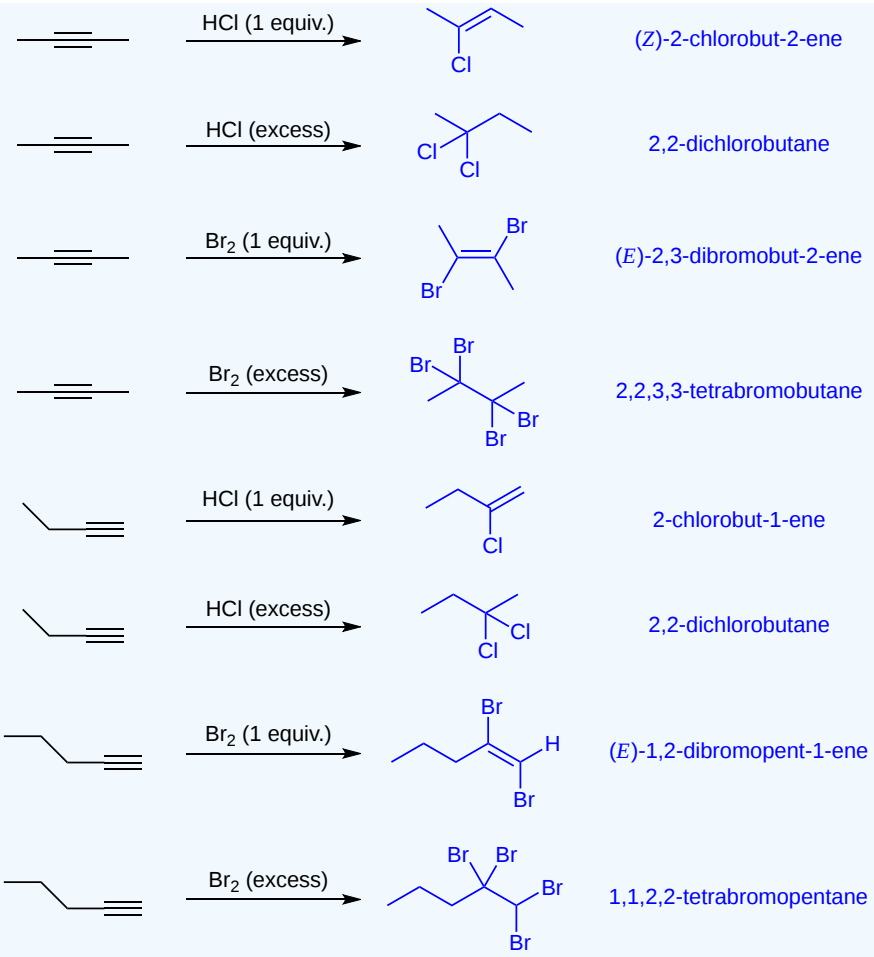
? EXERCISE \PageIndex1

Draw the structure and give the IUPAC name of the product formed in each of the reactions listed below:



Answer

https://chem.libretexts.org/@go/page/67215



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)

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9.4: HYDRATION OF ALKYNES

Objectives

After completing this section, you should be able to

1. write the equation for the reaction of water with an alkyne in the presence of sulfuric acid and mercury(II) sulfate.
2. describe keto-enol tautomerism.
3. predict the structure of the ketone formed when a given alkyne reacts with sulfuric acid in the presence of mercury(II) sulfate.
4. identify the reagents needed to convert a given alkyne to a given ketone.
5. identify the alkyne needed to prepare a given ketone by hydration of the triple bond.
6. write an equation for the reaction of an alkyne with borane.
7. write the equation for the reaction of a vinylic borane with basic hydrogen peroxide or hot acetic acid.
8. identify the reagents, the alkyne, or both, needed to prepare a given ketone or a given cis alkene through a vinylic borane intermediate.
9. identify the ketone produced when a given alkyne is reacted with borane followed by basic hydrogen peroxide.
10. identify the cis alkene produced when a given alkyne is reacted with borane followed by hot acetic acid.
11. explain why it is necessary to use a bulky, sterically hindered borane when preparing vinylic boranes from terminal alkynes.
12. predict the product formed when the vinylic borane produced from a terminal alkyne is treated with basic hydrogen peroxide.
13. identify the alkyne needed to prepare a given aldehyde by a vinylic borane.

KEY TERMS

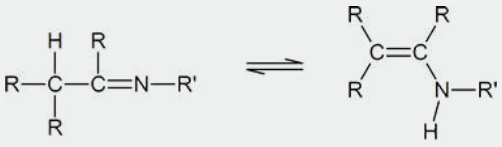
Make certain that you can define, and use in context, the key terms below.

- enol
- keto-enol tautomeric equilibrium
- tautomerism
- tautomers

STUDY NOTES

Rapid interconversion between tautomers is called *tautomerism*; however, as the two tautomers are in equilibrium, the term *tautomeric equilibrium* may be used. This section demonstrates the equilibrium between a ketone and an enol; hence, the term *keto-enol tautomeric equilibrium* is appropriate. The term “enol” indicates the presence of a carbon-carbon double bond and a hydroxyl (i.e., alcohol) group. Later in the course, you will see the importance of keto-enol tautomerism in discussions of the reactions of ketones, carbohydrates and nucleic acids.

It is important to note that tautomerism is not restricted to keto-enol systems. Other examples include imine-enamine tautomerism



imine enamine

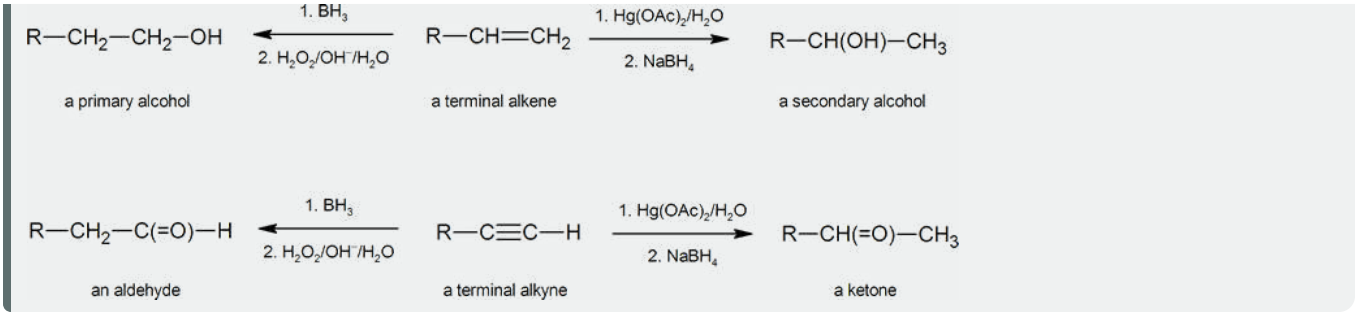
and nitroso-oxime tautomerism



nitroso oxime

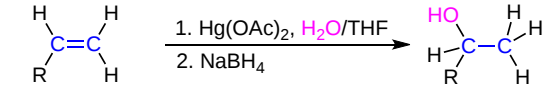
However, at the moment you need only concern yourself with keto-enol tautomerism.

Notice how hydroboration complements hydration in the chemistry of both alkenes and alkynes.



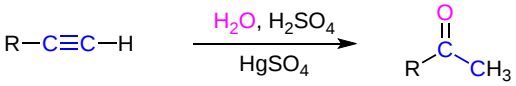
MERCURY(II)-CATALYZED HYDRATION OF ALKYNES

As with alkenes, hydration (addition of water) of alkynes requires a strong acid, usually sulfuric acid, and is facilitated by the mercuric ion (Hg^{2+}). However, the hydration of alkynes gives ketone products while the hydration of alkenes gives alcohol products. Notice that the addition of oxygen in both reactions follows Markovnikov rule.



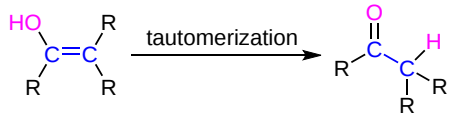
terminal alkene — 2° alcohol

During the hydration of an alkyne, the initial product is an enol intermediate (a compound having a hydroxyl substituent attached to a double-bond), which immediately rearranges to the more stable ketone through a process called **enol-keto tautomerization**.



terminal alkyne — ketone

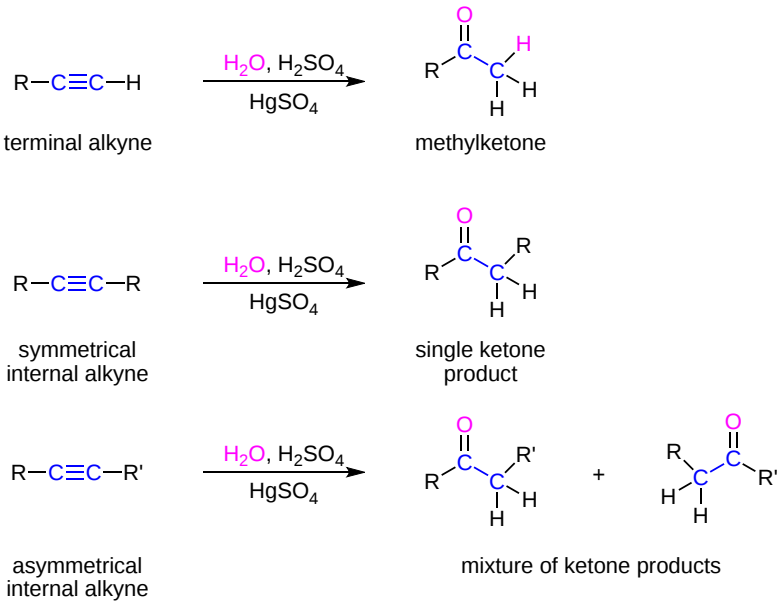
Tautomers are defined as rapidly inter-converted constitutional isomers, usually distinguished by a different bonding location for a labile hydrogen atom and a differently located double bond. The keto and enol tautomers are in equilibrium with each other and with few exceptions the keto tautomer is more thermodynamically stable and therefor favored by the equilibrium. This mechanism for tautomerization will be discussed in greater detail in **Section 22-1**.



enol tautomer — keto tautomer **(favored)**

GENERAL REACTION

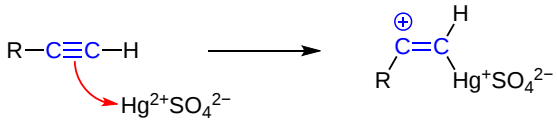
For terminal alkynes, the addition of water follows the Markovnikov rule, and the final product is a methyl ketone. For internal alkynes the addition of water is not regioselective. Hydration of symmetrical internal alkynes produces a single ketone product. However, hydration of asymmetrical alkynes, (i.e. if R & R' are not the same) produces two isomeric ketone products.



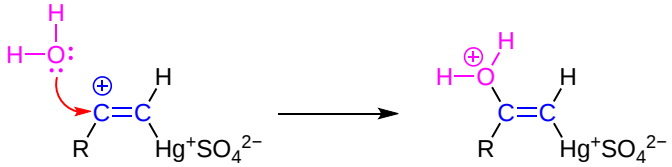
MECHANISM

The mechanism starts with the eletrophilic addition of the mercuric ion (Hg^{2+}) to the alkyne producing a mercury-containing vinylic carbocation intermediate. Nucleophilic attack of water on the vinylic carbocation forms a C-O bond to produce a protonated enol. Deprotonation of the enol by water then produces a organomurcury enol. The murcury is substituted with H^+ to produced a neutral enol and regenerate the Hg^{2+} catalyst. The enol is converted to the ketone product through keto-enol tautomerization the mechanism of which is provided in **Section 22-1**.

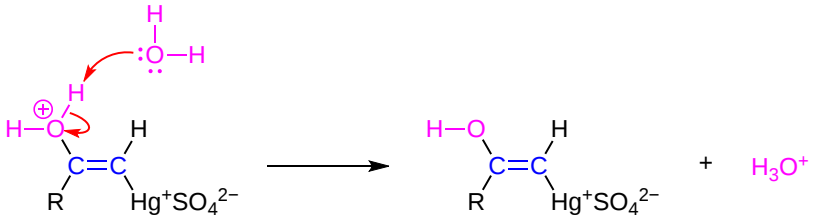
1) Electrophilic addition of Hg^{2+}



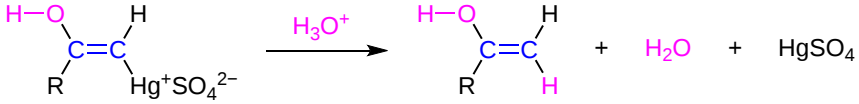
2) Nucleophilic attack by water



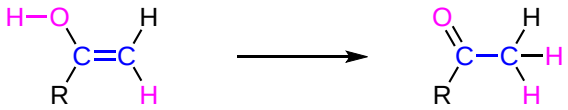
3) Deprotonation



4) Substitution

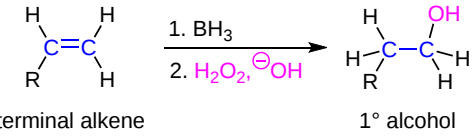


5) Tautomerization

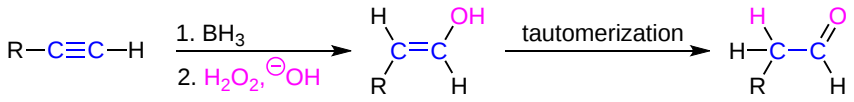


HYDROBORATION–OXIDATION OF ALKYNES

The hydroboration-oxidation of alkynes is analagous to the reaction with alkenes. However, where alkenes for alcohol products, alkynes for aldehyde or ketone products. In both cases the addition is anti-Markovnikov and an oxygen is placed on the less alkyl substituted carbon. With the hydroboration of an alkyne the presences of a second pi bond allows the initial product to under tautomerization to become the final aldehyde product.

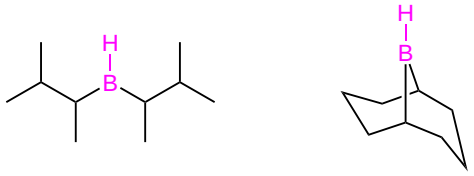


terminal alkene — 1° alcohol



terminal alkyne — enol — aldehyde

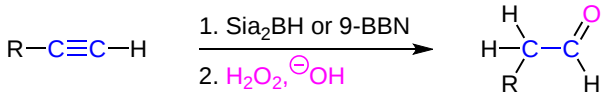
Alkynes have two pi bonds both of which are capable of reacting with borane (BH_3). To limit the reactivity to only one alkyne pi bond, a dialkyl borane reagent (R_2BH) is used. Replacing two of the hydrogens on the borane with alkyl groups also creates steric hindrance which enhances the anti-Markovnikov regioselective of the reaction. Disiamylborane (Sia_2BH) and 9-borabicyclo[3.3.1]nonane (9-BBN) are two common reagents for this hydroboration reaction. The oxidation reagents (a basic hydrogen peroxide solution) are the same for both alkenes and alkynes.



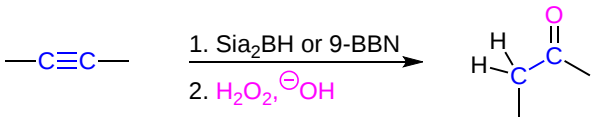
disiamylborane (Sia_2BH) — 9-borabicyclo[3.3.1]nonane (9-BBN)

GENERAL REACTION

The hydroboration of terminal alkynes produces aldehyde products while internal alkynes produce ketone products. The hydroboration of symmetrical alkynes produces one ketone product and asymmetrical alkynes produce a mixture of product ketones.



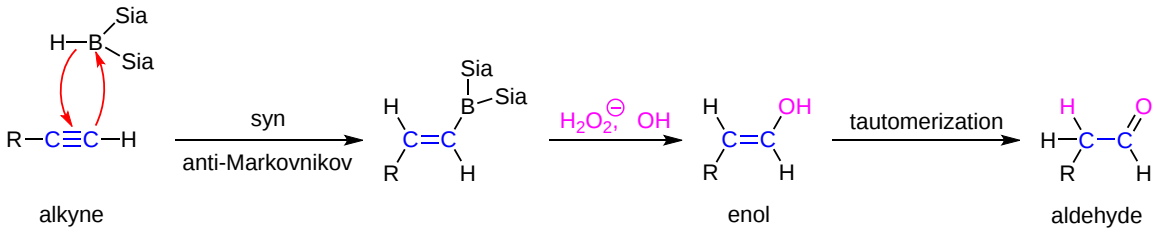
terminal alkyne — aldehyde



internal alkyne — ketone

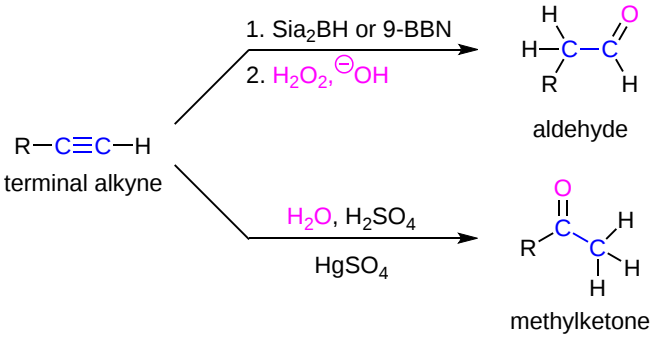
MECHANISM

The mechanism starts with the electrophilic addition of the B-H bond of the borane. The hydrogen atom and the borane all on the same side of the alkyne creating a syn addition configuration in the alkene product. Also, the addition is anti-Markovnikov regioselective which means the borane adds to the less substituted carbon of the alkyne and the hydrogen atom adds to the more substituted. The oxidative work-up replaces the borane with a hydroxy group (-OH) creating an enol intermediate. The enol immediately tautomerizes to the product aldehyde for terminal alkynes and the product ketone for internal alkynes.

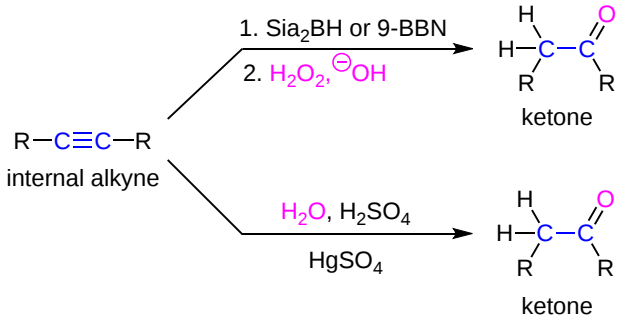


COMPARISON OF MERCURY(II)-CATALYZED HYDRATION AND HYDROBORATION–OXIDATION OF ALKYNES

These two reactions are complementary for the reaction of a terminal alkyne because the produce distinctly different products. The mercury(II) catalyzed hydration of a terminal alkyne produces a methyl ketone, while the hydroboration-oxidation produces an aldehyde.



For internal alkynes, the regioslectivity of these reactions are rendered ineffective. The reactions are redundant in that they both produce the same ketone products.



EXERCISES

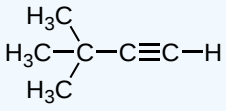
? EXERCISE \PageIndex1

Draw the structure of the product formed when each of the substances below is treated with H_2O/H_2SO_4 in the presence of $HgSO_4$.

a)

$H_3CH_2C—C≡C—H$

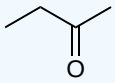
b)



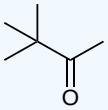
Answer

a)

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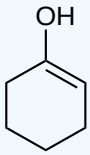


b)

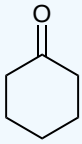


EXERCISE \PageIndex2

Draw the structure of the keto form of the compound shown below. Which form would you expect to be the most stable?



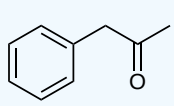
Answer

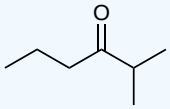


The keto form should be the most stable.

EXERCISE \PageIndex3

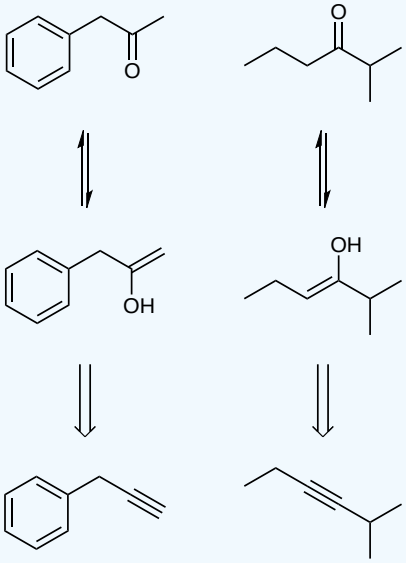
What alkyne would you start with to gain the following products?

a) 

b) 

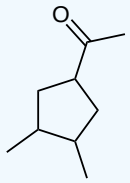
Answer

a) b)

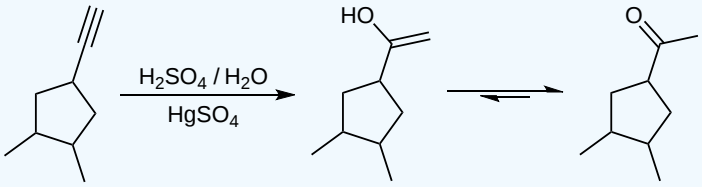


EXERCISE \PageIndex4

What alkyne would you start with to gain the following product?



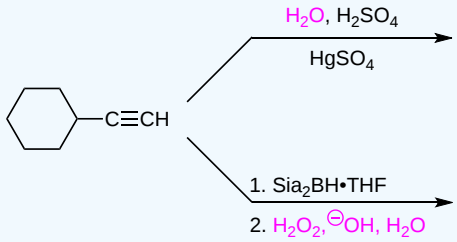
Answer



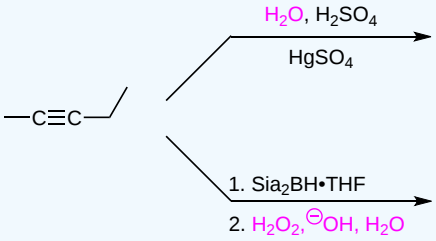
EXERCISE \PageIndex5

Draw the product(s) of the following reactions:

a)

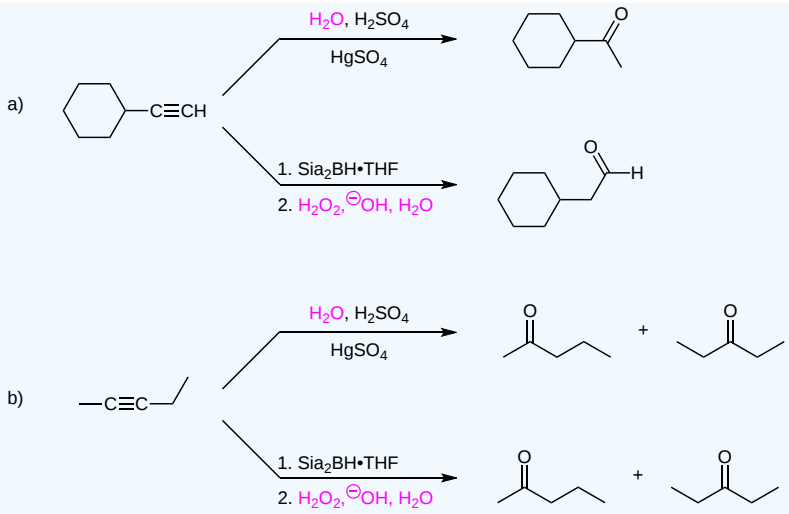


b)



Answer

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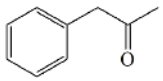
For internal alkynes, there is no difference in the reaction products.

QUESTIONS

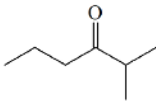
Q9.4.1

What alkyne would you start with to gain the following products, in an oxidation reaction? Keep in mind resonance.

A

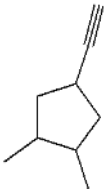


B



Q9.4.2

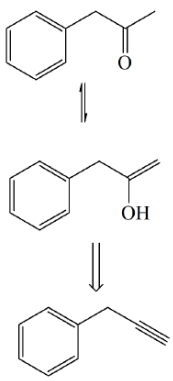
Propose a reaction scheme for the following compound starting from the alkyne and showing required reagents and intermediates.



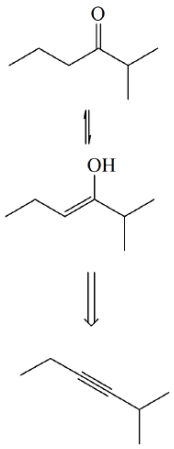
SOLUTIONS

S9.4.1

A

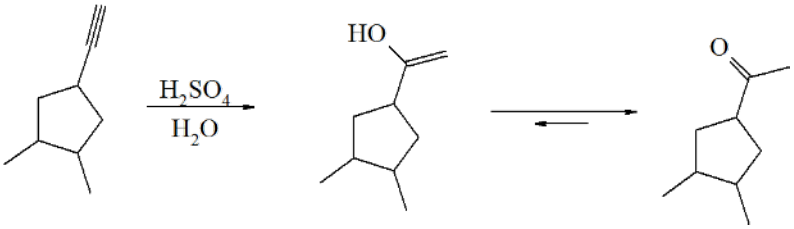


B



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S9.4.2



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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9.5: REDUCTION OF ALKYNES

Objectives

After completing this section, you should be able to

1. write equations for the catalytic hydrogenation of alkynes to alkanes and cis alkenes.
2. identify the reagent and catalyst required to produce a given alkane or cis alkene from a given alkyne.
3. identify the product formed from the reaction of a given alkyne with hydrogen and a specified catalyst.
4. identify the alkyne that must be used to produce a given alkane or cis alkene by catalytic hydrogenation.
5. write the equation for the reduction of an alkyne with an alkali metal and liquid ammonia.
6. predict the structure of the product formed when a given alkyne is reduced with an alkali metal and liquid ammonia.
7. identify the alkyne that must be used to produce a given alkene by reduction with an alkali metal and ammonia.

KEY TERMS

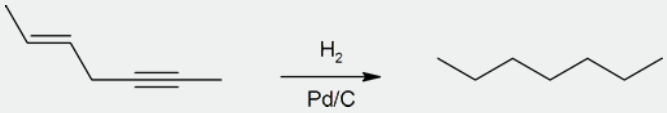
Make certain that you can define, and use in context, the key terms below.

- anion radical
- Lindlar catalyst

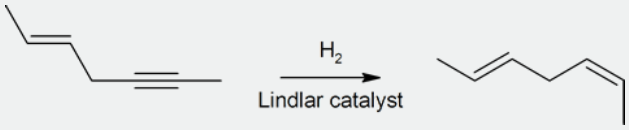
STUDY NOTES

The Lindlar catalyst allows a chemist to reduce a triple bond in the presence of a double bond.

Thus



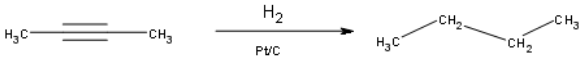
but



Reactions between alkynes and catalysts are a common source of alkene formation. Because alkynes differ from alkenes on account of their two procurable π bonds, alkynes are more susceptible to additions. Aside from turning them into alkenes, these catalysts affect the arrangement of substituents on the newly formed alkene molecule. Depending on which catalyst is used, the catalysts cause anti- or syn-addition of hydrogens. Alkynes can readily undergo additions because of their availability of two π bonds.

HYDROGENATION OF AN ALKYNE

Alkynes can be fully hydrogenated into alkanes with the help of a platinum catalyst. However, the use of two other catalysts can be used to hydrogenate alkynes to alkanes. These catalysts are: Palladium dispersed on carbon (Pd/C) and finely dispersed nickel (Raney-Ni).

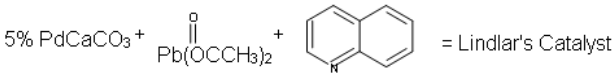


HYDROGENATION OF AN ALKYNE TO A CIS-ALKENE

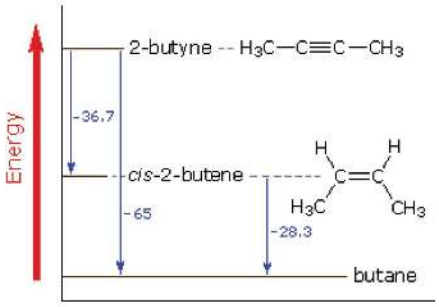
Because hydrogenation is an interruptible process involving a series of steps, hydrogenation can be stopped, using modified catalysts (e.g., Lindlar's Catalyst) at the transitional alkene stage. Lindar's catalyst has three components: Palladium-Calcium Carbonate, lead acetate and quinoline. The quinoline serves to prevent complete hydrogenation of the alkyne to an alkane. Lindlar's Catalyst transforms an alkyne to a cis-alkene.

R-C≡C-R + H_2 & Lindlar catalyst ⟶ *cis* R-CH=CH-R

LINDLAR'S CATALYST:



Like alkenes, alkynes readily undergo catalytic hydrogenation, either to cis or trans alkenes, or to alkanes, depending on the reaction employed.



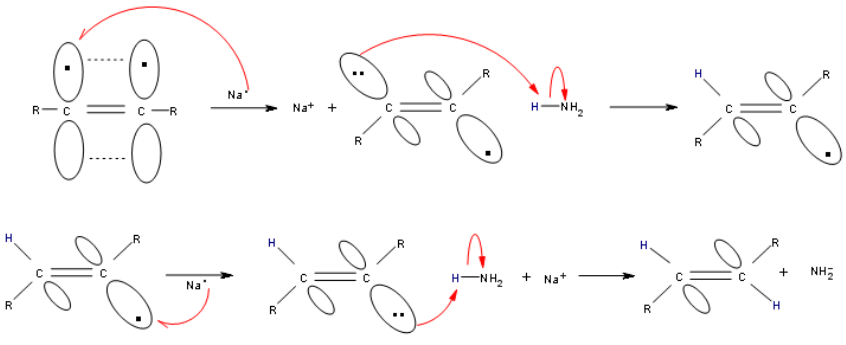
The catalytic addition of hydrogen to 2-butyne provides heat of reaction data that reflect the relative thermodynamic stabilities of these hydrocarbons, as shown in the diagram to the right. From the heats of hydrogenation, shown in blue in units of kcal/mole, it would appear that alkynes are thermodynamically less stable than alkenes to a greater degree than alkenes are less stable than alkanes. The standard bond energies for carbon-carbon bonds confirm this conclusion. Thus, a double bond is stronger than a single bond, but not twice as strong. The difference (63 kcal/mole) may be regarded as the strength of the π-bond component. Similarly, a triple bond is stronger than a double bond, but not 50% stronger. Here the difference (54 kcal/mole) may be taken as the strength of the second π-bond. The 9 kcal/mole weakening of this second π-bond is reflected in the heat of hydrogenation numbers (36.7 - 28.3 = 8.4).

Since alkynes are thermodynamically less stable than alkenes, we might expect addition reactions of the former to be more exothermic and relatively faster than equivalent reactions of the latter. In the case of catalytic hydrogenation, the usual Pt and Pd hydrogenation catalysts are so effective in promoting addition of hydrogen to both double and triple carbon-carbon bonds that the alkene intermediate formed by hydrogen addition to an alkyne cannot be isolated. A less efficient catalyst, Lindlar's catalyst, prepared by deactivating (or poisoning) a conventional palladium catalyst by treating it with lead acetate and quinoline, permits alkynes to be converted to alkenes without further reduction to an alkane.

HYDROGENATION OF AN ALKYNE TO A TRANS-ALKENE

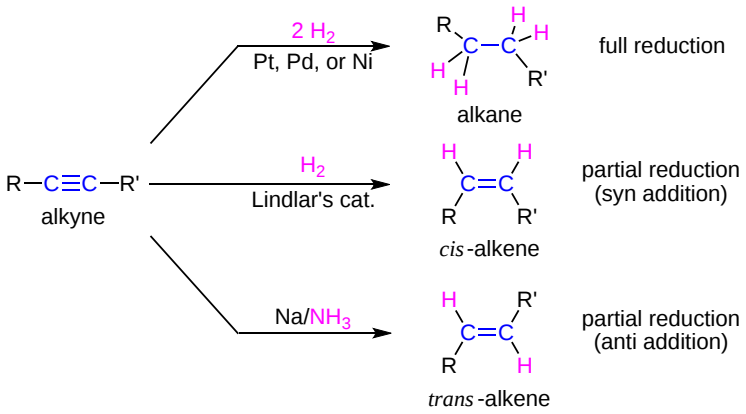
Alkynes can be reduced to trans-alkenes with the use of sodium or lithium dissolved in an ammonia solvent. An Na (Li) radical donates an electron to one of the P bonds in a carbon-carbon triple bond. This forms an anion, which can be protonated by a hydrogen in an ammonia solvent. This prompts another Na radical to donate an electron to the second P orbital. Soon after this anion is also protonated by a hydrogen from the ammonia solvent, resulting in a trans-alkene.

MECHANISM



OVERVIEW OF REDUCTION OF ALKYNES

Alkynes can undergo reductive hydrogenation reactions similar to alkenes. With the presence of two pi bonds within alkynes, the reduction reactions can be partial to form an alkene or complete to form an alkane. Since partial reduction of an alkyne produces an alkene, the stereochemistry provided by the reaction's mechanism determines whether a *cis*- or *trans*- alkene is formed. The three most significant alkyne reduction reactions are summarized below:

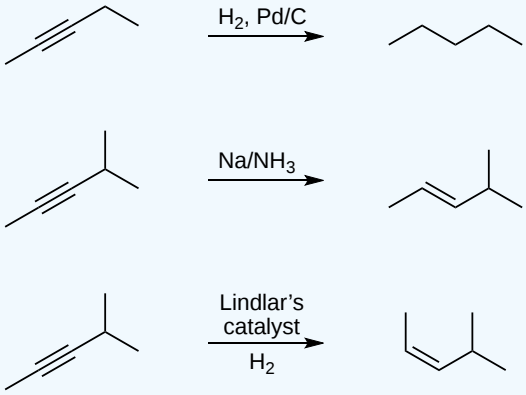


EXERCISE

? EXERCISE 9.5.1

Using any alkyne how would you prepare the following compounds: pentane, *trans*-4-methyl-2-pentene, *cis*-4-methyl-2-pentene.

Answer



QUESTIONS

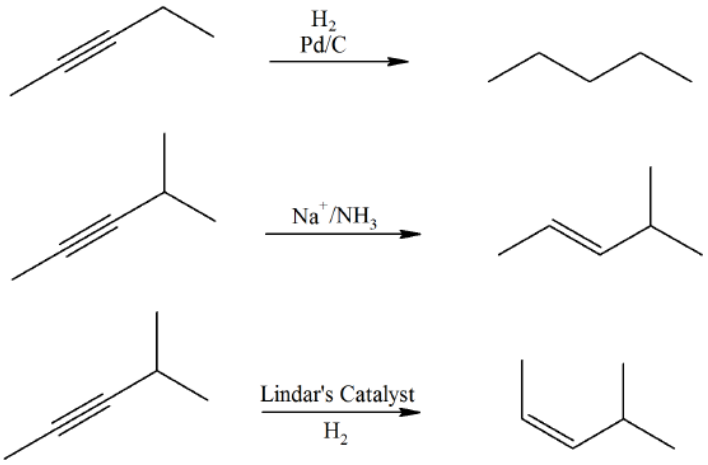
Q9.5.1

Usng any alkyne how would you prepare the following compounds:

pentane, *trans*-4-methyl-2-pentene, *cis*-4-methyl-2-pentene.

SOLUTIONS

S9.5.1



CONTRIBUTORS AND ATTRIBUTIONS

- Ravjot Takhar (UCD)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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9.6: OXIDATIVE CLEAVAGE OF ALKYNES

Objectives

After completing this section, you should be able to

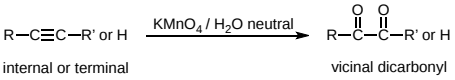
1. write an equation to represent the oxidative cleavage of an alkyne with potassium permanganate or ozone.
2. identify the products that result from the oxidative cleavage of a given alkyne.
3. identify the reagents needed to carry out the oxidative cleavage of an alkyne.
4. use the results of an oxidative cleavage to determine the identity of an alkyne of unknown structure.

STUDY NOTES

Compare the oxidative cleavage of alkynes with the oxidative cleavage of alkenes, discussed in Section 8.8.

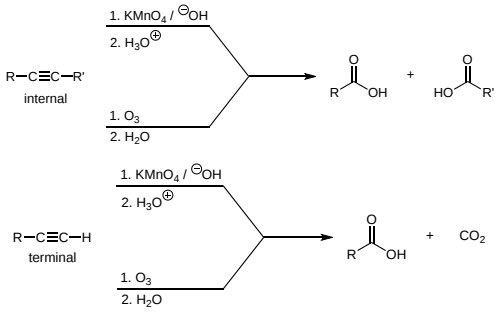
Alkynes, much like alkene, can be cleaved with as powerful oxidizing agents such as ozone or KMnO4. Because triple bonds are generally less reactive than double bonds the yields of the is reaction are sometimes low.

Gentle Alkyne Oxidation



Strong Alkyne Oxidation - Oxidative Cleavage

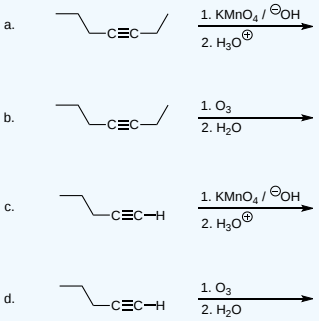
During strong oxidation with ozone or basic potassium permanganate, the alkyne is cleaved into two products. Because at least one of the reaction products is a carboxylic acid, it is important to consider the acid-base chemistry of the product in the reaction solution. Carboxylic acids are deprotonated in basic solutions to carboxylates. A second reaction step is required to protonate the carboxylate to the neutral form of the carboxylic acid.



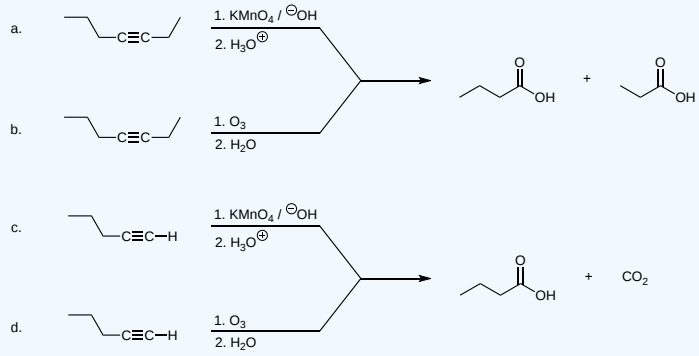
EXERCISE

EXERCISE 9.6.1

Draw the bond-line structures for the product(s) of the following reactions.



Answer



> Oxidative cleavage of alkynes produces carboxylic acids and/or carbon dioxide. **Aldehydes are not produced.**

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

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9.7: ALKYNE ACIDITY - FORMATION OF ACETYLIDE ANIONS

Objectives

After completing this section, you should be able to

1. write an equation for the reaction that occurs between a terminal alkyne and a strong base, such as sodamide, $NaNH_2$.
2. rank a given list of compounds, including water, acetylene and ammonia, in order of increasing or decreasing acidity.
3. rank a given list of hydrocarbons, such as acetylene, ethylene and ethane, in order of increasing or decreasing acidity.
4. describe a general method for determining which of two given compounds is the stronger acid.
5. provide an acceptable explanation of why terminal alkynes are more acidic than alkanes or alkenes.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- acetylide anion
- acidity order

STUDY NOTES

An *acetylide anion* is an anion formed by removing the proton from the end carbon of a terminal alkyne:

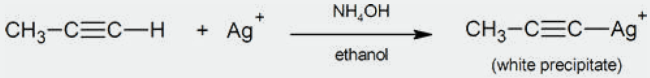


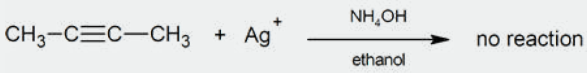
An *acidity order*is a list of compounds arranged in order of increasing or decreasing acidity.

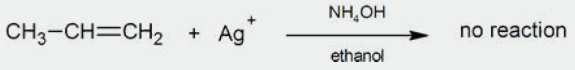
The general ideas discussed in this section should already be familiar to you from your previous exposure to chemistry and from the review in Section 2.8. A slightly different account of why terminal alkynes are stronger acids than are alkenes or alkanes is given below. However, the argument is still based on the differences between *sp*-, sp^2- and sp^3-hybrid orbitals.

The carbons of a triple bond are *sp*-hybridized. An *sp*-hybrid orbital has a 50% *s* character and a 50% *p* character, whereas an sp^2-hybrid orbital is 33% *s* and 67% *p*, and an sp^3-hybrid orbital is 25% *s* and 75% *p*. The greater the *s* character of the orbital, the closer the electrons are to the nucleus. Thus in a C(*sp*)—H bond, the bonding electrons are closer to the carbon nucleus than they are in a C(sp^2)—H bond. In other words, compared to a C(sp^2)—H bond (or a C(sp^3)—H bond), a C(*sp*)—H bond is very slightly polar: $C^{\delta-}—H^{\delta+}$. This slight polarity makes it easier for a base to remove a proton from a terminal alkyne than from a less polar or non-polar alkene or alkane.

As you will appreciate, the reaction between sodium amide and a terminal alkyne is an acid-base reaction. The sodium acetylide product is, of course, a salt. Terminal alkynes can also form salts with certain heavy-metal cations, notably silver(I) and copper(I). In the laboratory component of this course, you will use the formation of an insoluble silver acetylide as a method for distinguishing terminal alkynes from alkenes and non-terminal alkynes:







Metal acetylides are explosive when dry. They should be destroyed while still wet by warming with dilute nitric acid:



ACIDITY OF TERMINAL ALKYNES: FORMATION OF ACETYLIDE ANIONS

Terminal alkynes are much more acidic than most other hydrocarbons. Removal of the proton leads to the formation of an acetylide anion, $RC{\equiv}C{:}^-$. The origin of the enhanced acidity can be attributed to the stability of the acetylide anion, which has the unpaired electrons in an sp hybridized orbital. The stability results from occupying an orbital with a high degree of s-orbital character. There is a strong correlation

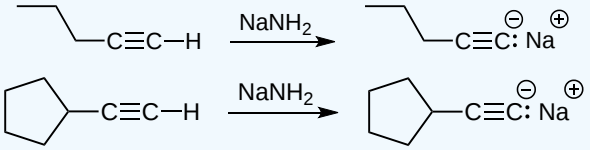
between s-character in the orbital containing the non-bonding electrons in the anion and the acidity of hydrocarbons. The enhanced acidity with greater s-character occurs despite the fact that the homolytic C-H BDE is larger.

Table 9.7.1: Akynes

Compound	Conjugate Base	Hybridization	"s Character"	pKa	C-H BDE (kJ/mol)
CH_3CH_3	$CH_3CH_2^-$	sp^3	25%	50	410
CH_2CH_2	CH_2CH^-	sp^2	33%	44	473
HCCH	HCC^-	sp	50%	25	523

Consequently, acetylide anions can be readily formed by deprotonation using a sufficiently strong base. Amide anion (NH_2^-), in the form of $NaNH_2$ is commonly used for the formation of acetylide anions.

EXAMPLE \PageIndex1



EXERCISE

EXERCISE 9.7.1

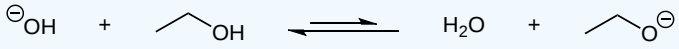
Given that the p*K*a of water is 14.00, would you expect hydroxide ion to be capable of removing a proton from each of the substances listed below? Justify your answers, briefly.

a. ethanol (p*K*a = 16)
b. acetic acid (p*K*a = 4.72)
c. acetylene (p*K*a = 25)

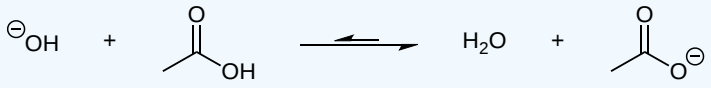
Answer

1.

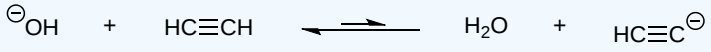
a. No, not very well. The p*K*a of ethanol is greater than that of water, thus the equilibrium lies to the left rather than to the right.Add texts here. Do not delete this text first.



b. Yes, very well. There is a difference of 11 p*K*a units between the p*K*a of water and the p*K*a of acetic acid. The equilibrium lies well to the right.



c. No, hardly at all. The hydroxide ion is too weak a base to remove a proton from acetylene. The equilibrium lies well to the left.



QUESTIONS

Q9.7.1

If OH^- has a pKa of 14.00 in water, what pKa be required to deprotonate OH^-?

SOLUTIONS

S9.7.1

Need a stronger base, or a compound with a pKa > 14.00 to deprotonate.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Prof. Paul G. Wenthold (Purdue University)

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9.8: ALKYLATION OF ACETYLIDE ANIONS

Objectives

After completing this section, you should be able to

1. write an equation to describe the reaction of an acetylide ion with an alkyl halide.
2. discuss the importance of the reaction between acetylide ions and alkyl halides as a method of extending a carbon chain.
3. identify the alkyne (and hence the acetylide ion) and the alkyl halide needed to synthesize a given alkyne.
4. determine whether or not the reaction of an acetylide ion with a given alkyl halide will result in substitution or elimination, and draw the structure of the product formed in either case.

KEY TERMS

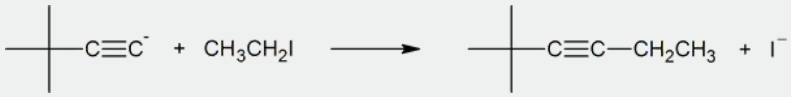
Make certain that you can define, and use in context, the key term below.

- alkylation

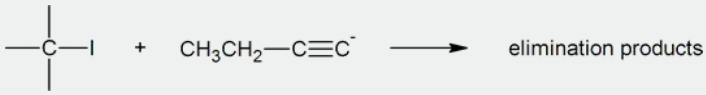
STUDY NOTES

The alkylation of acetylide ions is important in organic synthesis because it is a reaction in which a new carbon-carbon bond is formed; hence, it can be used when an organic chemist is trying to build a complicated molecule from much simpler starting materials.

The alkyl halide used in this reaction must be primary. Thus, if you were asked for a suitable synthesis of 2,2-dimethyl-3-hexyne, you would choose to attack iodoethane with the anion of 3,3- dimethyl-1-butyne



rather than to attack 2-iodo-2-methylpropane with the anion of 1-butyne.

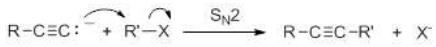


The reasons will be made clear in Chapter 11.

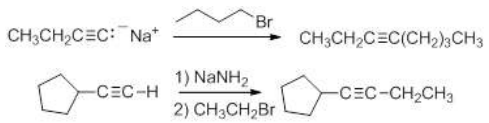
NUCLEOPHILIC SUBSTITUTION REACTIONS OF ACETYLIDES

EDIT SECTION

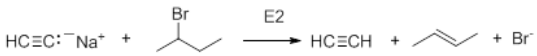
Acetylide anions are strong bases and strong nucleophiles. Therefore, they are able to displace halides and other leaving groups in substitution reactions. The product is a substituted alkyne.



Because the ion is a very strong base, the substitution reaction is most efficient with methyl or primary halides without substitution near the reaction center,

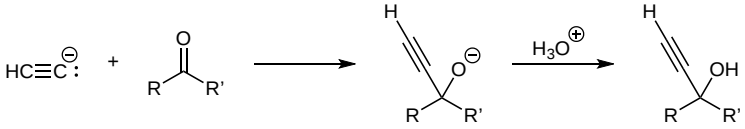


Secondary, tertiary or even bulky primary substrates will give elimination by the E2 mechanism.



NUCLEOPHILIC ADDITION OF ACETYLIDES TO CARBONYLS

Acetylide anions will add to aldehydes and ketones to form alkoxides, which, upon protonation, give propargyl alcohols.

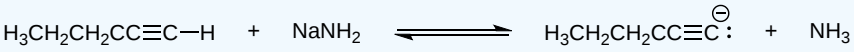


With aldehydes and non-symmetric ketones, in the absence of chiral catalyst, the product will be a racemic mixture of the two enantiomers.

EXERCISES

EXERCISE 9.8.1

The pK_a of ammonia is 35. Estimate the equilibrium constant for the deprotonation of pent-1-yne by sodium amide, as shown below.

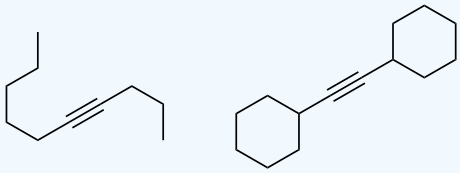


Answer

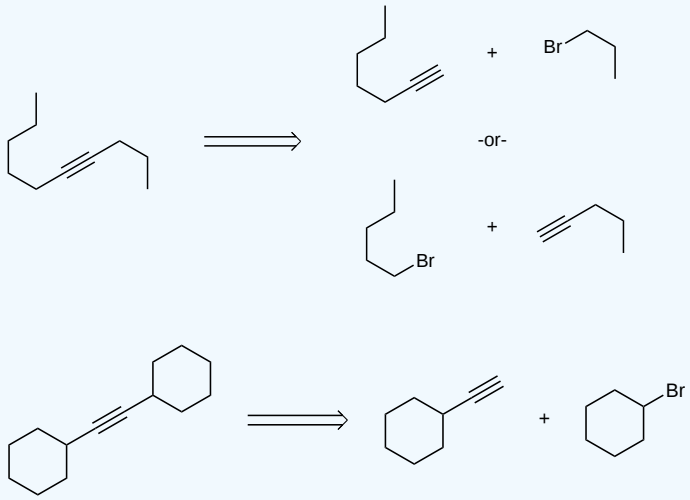
Assuming the pK_a of pent-1-yne is about 25, then the difference in pK_as is 10. Since pentyne is more acidic, the formation of the acetylide will be favored at equilibrium, so the equilibrium constant for the reaction is about 10^{10}.

EXERCISE 9.8.2

Give the possible reactants which could form the following molecules by an alkylation.



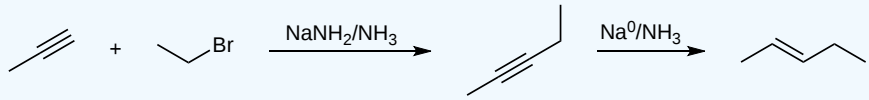
Answer



EXERCISE 9.8.3

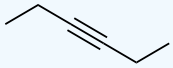
Propose a synthetic route to produce 2-pentene from propyne and an alkyl halide.

Answer

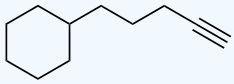


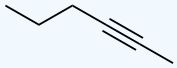
EXERCISE 9.8.4

Using acetylene as the starting material, show how you would synthesize the following compounds

a) 

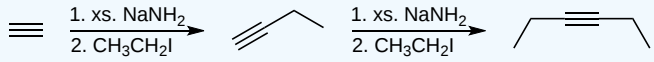
b) but-2-yne

c) 

d) 

Answer

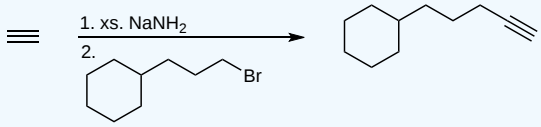
a)



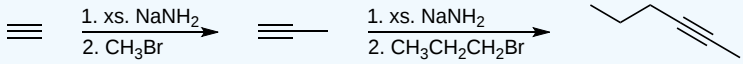
b)



c)

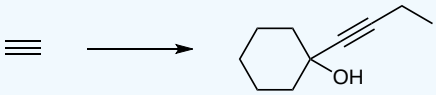


d)

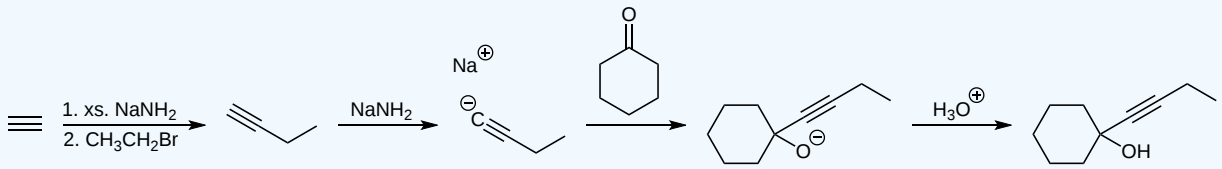


EXERCISE 9.8.5

Show how you would accomplish the following synthetic transformation.



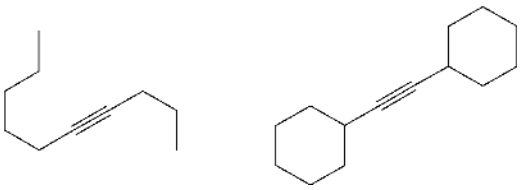
Answer



QUESTIONS

Q9.8.1

Give the possible reactants for the following formations:

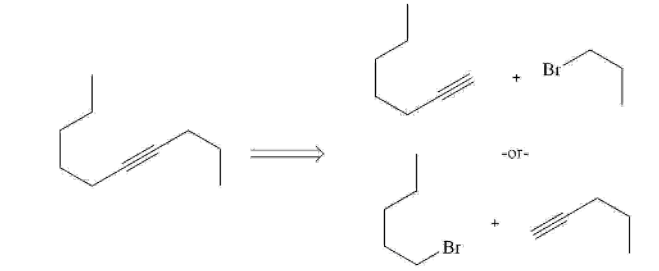


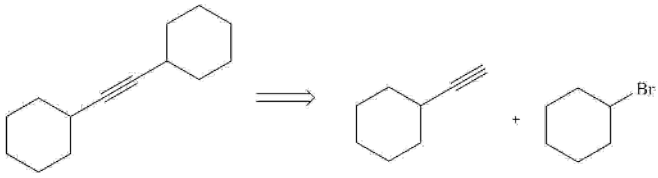
Q9.8.2

Propose a synthetic route to produce 2-pentene from propyne and an alkyl halide.

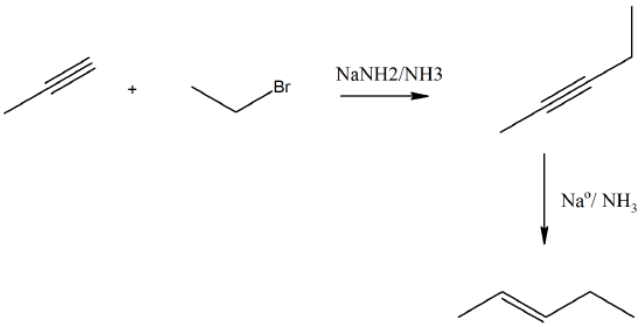
SOLUTIONS

S9.8.1





S9.8.2



CONTRIBUTORS AND ATTRIBUTIONS

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9.9: AN INTRODUCTION TO ORGANIC SYNTHESIS

Objective

After completing this section, you should be able to design a multistep synthesis to prepare a given product from a given starting material, using any of the reactions introduced in the textbook up to this point.

STUDY NOTES

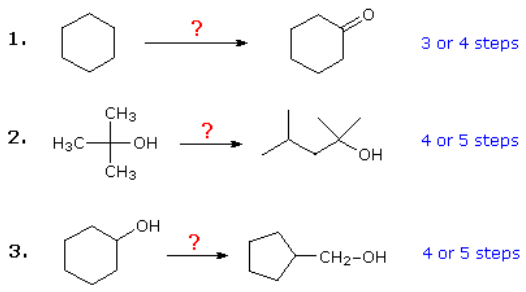
You should have noticed that some of the assigned problems have required that you string together a number of organic reactions to convert one organic compound to another when there is no single reaction to achieve this goal. Such a string of reactions is called an "organic synthesis." One of the major objectives of this course is to assist you in designing such syntheses. To achieve this objective, you will need to have all of the reactions described in the course available in your memory. You will need to recall some reactions much more frequently than others, and the only way to master this objective is to practise. The examples given in this chapter will be relatively simple, but you will soon see that you can devise some quite sophisticated syntheses using a limited number of basic reactions.

The study of organic chemistry exposes a student to a wide range of interrelated reactions. Alkenes, for example, may be converted to structurally similar alkanes, alcohols, alkyl halides, epoxides, glycols and boranes; cleaved to smaller aldehydes, ketones and carboxylic acids; and enlarged by carbocation and radical additions as well as cycloadditions. All of these products may be transformed subsequently to a host of new compounds incorporating a wide variety of functional groups, and thereby open to even further elaboration. Consequently, the logical conception of a multistep synthesis for the construction of a designated compound from a specified starting material becomes one of the most challenging problems that may be posed.

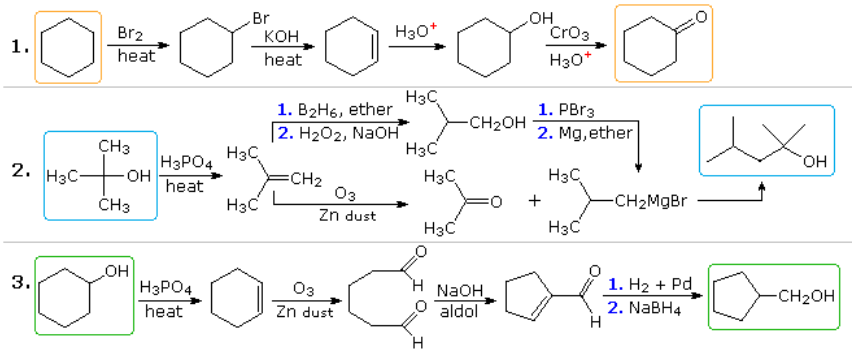
A one or two step sequence of simple reactions is not that difficult to deduce. If, for example, one is asked to prepare meso-3,4-hexanediol from 3-hexyne, most students realize it will be necessary to reduce the alkyne to cis or trans-3-hexene before undertaking glycol formation. Permanaganate or osmium tetroxide hydroxylation of cis-3-hexene would form the desired meso isomer. From trans-3-hexene it would be necessary to first epoxidize the alkene with a peracid, followed by ring opening with hydroxide ion. This example illustrates a common feature in synthesis: **often there is more than one effective procedure that leads to the desired product**.

Longer multistep syntheses require careful analysis and thought, since many options need to be considered. Like an expert chess player evaluating the long range pros and cons of potential moves, the chemist must appraise the potential success of various possible reaction paths, focussing on the scope and limitations constraining each of the individual reactions being employed. This can be a daunting task, the skill for which is acquired by experience, and often trial and error.

The three examples shown below are illustrative. The first is a simple functional group conversion problem, that may initially seem difficult. It is often helpful to work such problems backwards, starting from the product. In this case it should be apparent that cyclohexanol may be substituted for cyclohexanone, since the latter could then be made by a simple oxidation. Also, since cyclohexane (and alkanes in general) is relatively unreactive, bromination (or chlorination) would seem to be an obvious first step. At this point one is tempted to convert bromocyclohexane to cyclohexanol by an S_N2 reaction with hydroxide ion. This reaction would undoubtedly be accompanied by E2 elimination, so it would be cleaner, although one step longer, to first make cyclohexene and then hydrate it by any of several methods (e.g. oxymercuration and hydroboration) including the one shown by clicking on the diagram



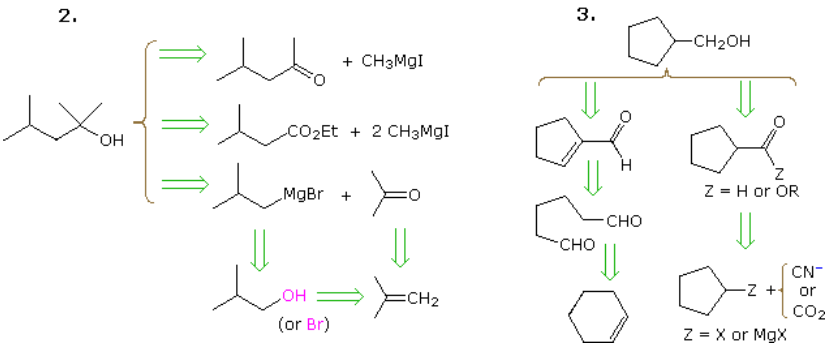
Answer



Plausible solutions for the second and third problem will also appear above at this point. In problem 2 the desired product has seven carbon atoms and the starting material has four. Clearly, two intermediates derived from the starting compound must be joined together, and one carbon must be lost, either before or after this bonding takes place. The 3º-alcohol function in the product suggests formation by a Grignard addition to a ketone, and isobutene appears to be a good precursor to each of these reactants, as shown. The reactant and product compounds in the third problem are isomers, but some kind of bond-breaking and bond-making sequence is clearly necessary for this structural change to occur. One possible procedure is shown above. Acid-catalyzed rearrangement of cyclohexene oxide, followed by reduction might also serve.

The useful approach of working out syntheses starting from the target molecule and working backward toward simpler starting materials has been formalized by Prof. E. J. Corey (Harvard) and termed **retrosynthetic analysis**. In this procedure the target molecule is transformed progressively into simpler structures by disconnecting selected carbon-carbon bonds. These disconnections rest on **transforms**, which are the reverse of plausible synthetic constructions. Each simpler structure, so generated, becomes the starting point for further disconnections, leading to a branched set of interrelated intermediates. A retrosynthetic transform is depicted by the => symbol, as shown below for previous examples 2 & 3. Once a complete analysis has been conducted, the desired synthesis may be carried out by application of the reactions underlying the transforms.

Examples of Retrosynthetic Analysis



The above diagram does not provide a complete set of transforms for these target compounds. When a starting material is specified, as in the above problems, the proposed pathways must reflect that constraint. Thus the 4-methyl-2-pentanone and 3-methylbutyrate ester options in example 2, while entirely reasonable, do not fit well with a *tert*-butanol start. Likewise, a cyclopentyl intermediate might provide an excellent route to the product in example 3, but does not meet the specified conditions of the problem.

Retrosynthetic analysis is especially useful when considering relatively complex molecules without starting material constraints. If it is conducted without bias, unusual and intriguing possibilities sometimes appear. Unfortunately, molecular complexity (composed of size, functionality, heteroatom incorporation, cyclic connectivity and stereoisomerism) generally leads to very large and extensively branched transform trees. Computer assisted analysis has proven helpful, but in the end the instincts and experience of the chemist play a critical role in arriving at a successful synthetic plan. Some relatively simple examples, most having starting material restrictions, are provided below.

EXERCISES

EXERCISE 9.9.1

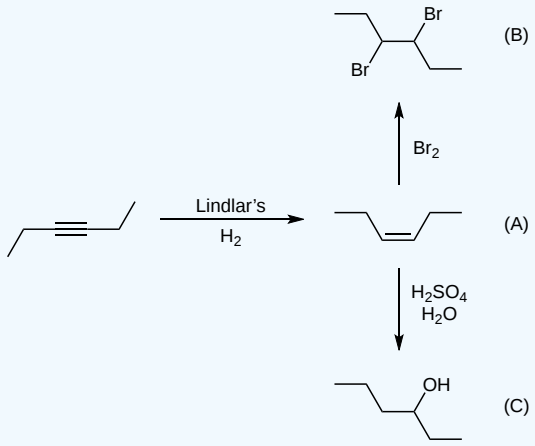
Starting at 3-hexyne predict synthetic routes to achieve:

a) trans-3-hexene

b) 3,4-dibromohexane

c) 3-hexanol.

Answer



EXERCISE 9.9.2

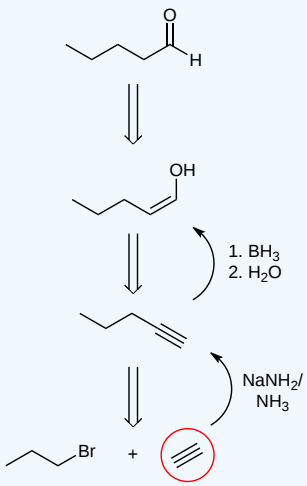
Starting with acetylene and any alkyl halides propose a synthesis to make

a) pentanal

b) hexane.

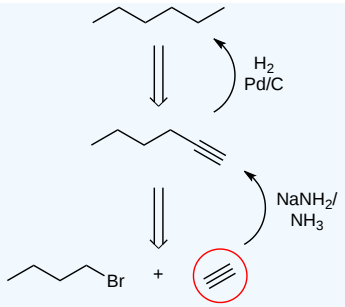
Answer

a)



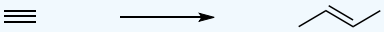
[NB: Hydroboration of the alkyne requires H_2O_2, OH^- in the second step of the oxidative work-up not just H_2O.]

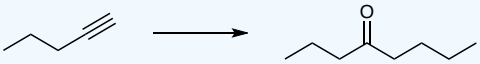
b)



EXERCISE 9.9.3

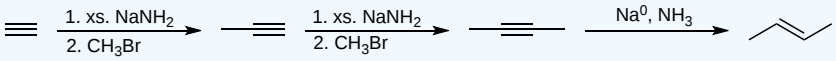
Show how you would accomplish the following synthetic transformations.

a) 

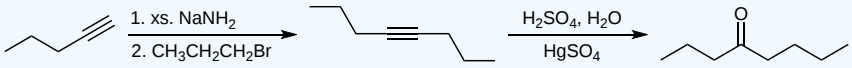
b) 

Answer

a)



b)



QUESTIONS

Q9.9.1

Starting at 3-hexyne predict synthetic routes to achieve:

A – *cis*-3-hexene

B – 3,4-dibromohexane

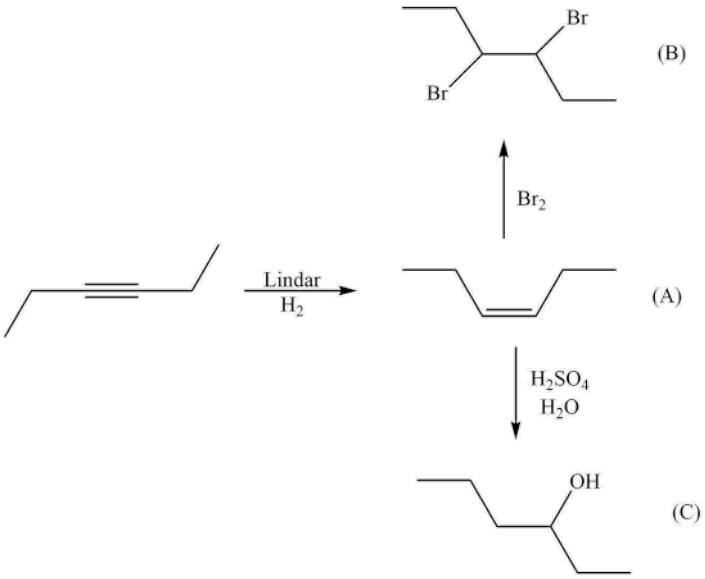
C – 3-hexanol

Q9.9.2

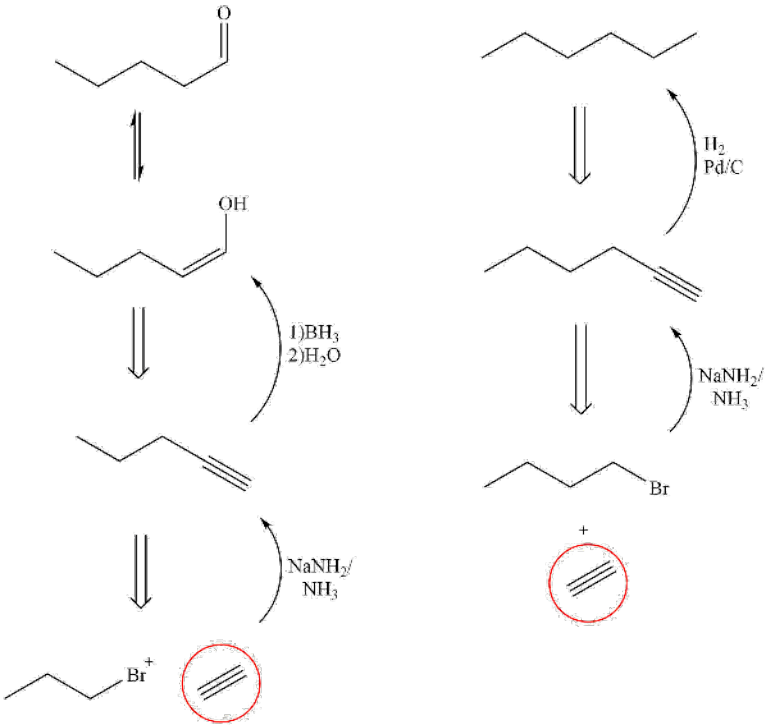
Starting with acetylene and any alkyl halides propose a synthesis to make (a) pentanal and (b) hexane.

SOLUTIONS

S9.9.1



S9.9.2



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9.S: ALKYNES - AN INTRODUCTION TO ORGANIC SYNTHESIS (SUMMARY)

CONCEPTS & VOCABULARY

9.1 Naming Alkynes

- Follow IUPAC rules in naming alkynes.

9.2 Preparation of Alkynes - Elimination Reactions of Dihalides

- **Vicinal** describes two groups on adjacent carbon atoms.
- **Geminal** describes two groups on the same carbon atom.
- Alkynes can be prepared by two successive eliminations of HX from either **vicinal** or **geminal** dihalides.

9.3 Reactions of Alkynes - Addition of HX and X_2

- **Alkynes** undergo addition reactions similarly to alkenes yielding Markovnikov products.

9.4 Hydration of Alkynes

- Enols have a hydroxyl group bonded to a sp^2 hybrid carbon (double-bonded carbon).
- Enols are usually not stable and undergo **keto-enol tautomerization** to form a ketone or aldehyde.
- Hydration of alkynes leads to an enol product which then rapidly tautomerizes into a ketone or aldehyde.

9.5 Reduction of Alkynes

- Alkynes can be hydrogenated with hydrogen gas and strong catalysts to yield alkanes.
- Alkynes can be hydrogenated with hydrogen gas and Lindlar's catalyst to yield Z alkenes.
- Alkynes can be hydrogenated with sodium metal and liquid ammonia to yield E alkenes.

9.6 Oxidative Cleavage of Alkynes

- Oxidative cleavage of internal alkynes forms two molecules of carboxylic acids.
- Oxidative cleavage of terminal alkynes forms one molecule of carbon dioxide and one carboxylic acid.

9.7 Alkyne Acidity - Formation of Acetylide Anions

- Terminal alkynes are relatively acidic compared to alkene and alkane carbon-hydrogen bonds.
- Deprotonation of a terminal alkyne forms an acetylide ion, which is a good nucleophile.

9.8 Alkylation of Acetylide Anions

- Acetylide ions can be alkylated by adding to alkyl halides and carbonyl compounds.

9.9 An Introduction to Organic Synthesis

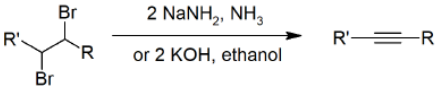
- Desired products cannot always be made from available starting materials through one reaction. Formation of these materials may require multiple reactions completed in sequence. This type of reaction sequence is termed synthesis.

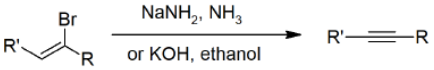
SKILLS TO MASTER

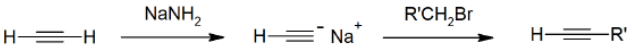
- Skill 9.1 Use IUPAC rules to accurately name alkynes.
- Skill 9.2 Draw elimination mechanisms to form alkynes.
- Skill 9.3 Draw addition mechanisms to alkynes incorporating carbocation intermediates.
- Skill 9.4 Draw addition mechanisms to alkynes incorporating halonium intermediates.
- Skill 9.5 Describe relative stability of enols to ketones and aldehydes.
- Skill 9.6 Draw keto-enol tautomerism mechanism.
- Skill 9.7 Draw products that differentiate between multiple reduction reactions of alkynes.
- Skill 9.8 Draw products of oxidative cleavage of alkynes.
- Skill 9.9 Draw mechanism for deprotonation of terminal alkynes.
- Skill 9.10 Compare acidity of terminal alkynes with other organic compounds.
- Skill 9.11 Draw reaction mechanisms using acetylide ions as nucleophiles.
- Skill 9.12 Describe schemes to accomplish synthesis of organic products given a starting material.

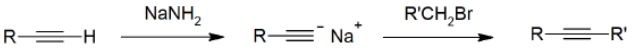
SUMMARY OF REACTIONS

Preparation of Alkynes

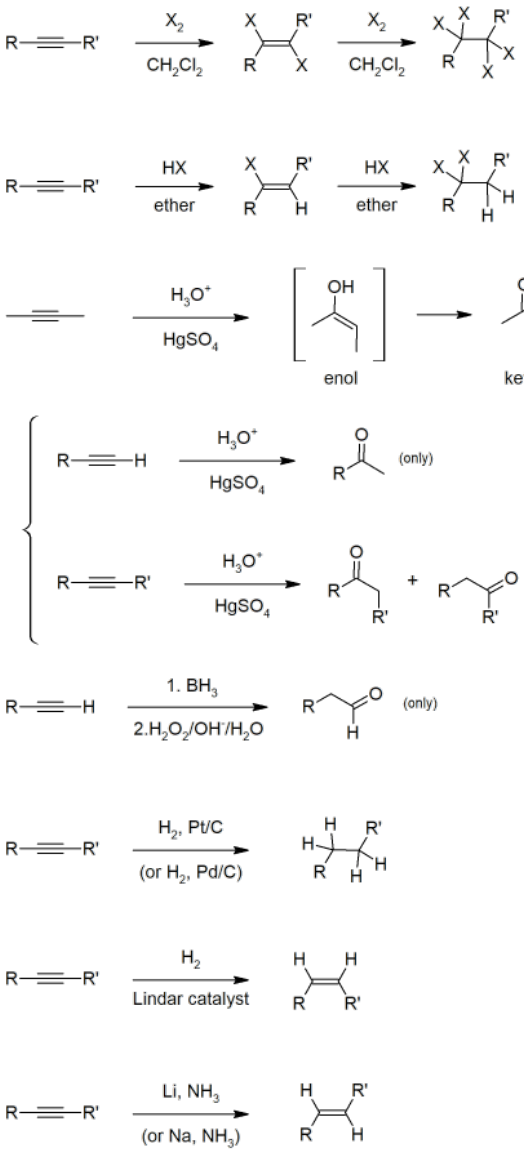








Reactions of Alkynes



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CHAPTER OVERVIEW

10: ORGANOHALIDES

LEARNING OBJECTIVES

After you have completed Chapter 10, you should be able to

1. fulfill all of the detailed objectives listed under each individual section.
2. design a multistep synthesis to prepare a given compound from a given starting material using any of the reactions studied up to this point in the course, including those which involve alkyl halides.
3. solve road-map problems requiring a knowledge of any of the reactions or concepts studied up to this point, including those introduced in this chapter.
4. define, and use in context, the key terms introduced.

You have already encountered alkyl halides several times in this course. In this chapter, you will examine in some detail the methods that are used to prepare these important compounds. For chemists involved in the synthesis of new organic compounds, alkyl halides are extremely useful, particularly because of their ability to react with certain metals and form organometallic compounds. However, a detailed discussion of the reactions of alkyl halides will be delayed until Chapter 11.

10.0: Introduction
10.1: Names and Properties of Alkyl Halides
10.2: Preparing Alkyl Halides from Alkanes - Radical Halogenation
10.3: Preparing Alkyl Halides from Alkenes - Allylic Bromination
10.4: Stability of the Allyl Radical - Resonance Revisited
10.5: Preparing Alkyl Halides from Alcohols
10.6: Reactions of Alkyl Halides - Grignard Reagents
10.7: Organometallic Coupling Reactions
10.8: Oxidation and Reduction in Organic Chemistry
10.S: Organohalides (Summary)

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10.0: INTRODUCTION

Objectives

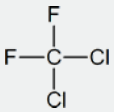
After completing this section, you should be able to

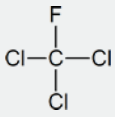
1. list the industrial uses of some important halogenated hydrocarbons including 1,1,1-trichloroethane, tetrafluoroethylene and dichlorodifluoromethane.
2. outline, briefly, how the chemistry of vinyl halides and aryl halides differs from that of the alkyl halides discussed.

STUDY NOTES

There are several different types of halogen-substituted organic compounds, including aryl halides, acyl halides, vinyl halides and alkynyl halides. The primary focus of this chapter is on alkyl halides.

Freons™, also called fluorocarbons or chlorofluorocarbons, have been a source of concern to environmentalists since 1974, when Frank S. Rowland and Mario J. Molina suggested that these substances might be contributing to the destruction of Earth's ozone layer. The stratospheric ozone layer filters out much of the ultraviolet radiation from the sun's rays. It is believed that extensive depletion of this layer, and the consequent increase in the amount of ultraviolet radiation reaching Earth, could result in the destruction of certain crops, in climate modification, and in an increase in the incidence of skin cancer. In recent years, the manufacture and use of freons has declined sharply as the general public has become more aware of the problems that might be caused by these substances.

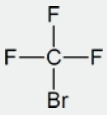


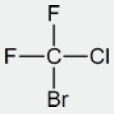


Note: "Freon" is a DuPont trademark.

Related to the freons are the halons—now used in some fire extinguishers, particularly in areas where foams or dry-chemical extinguishers cannot be used (e.g., in and around computers). If you examine such extinguishers, you will find that the halon is identified by a number; for example, halon 1301 or halon 1211. The first number represents the number of carbon atoms present, the second is the number of fluorines, the third is the number of chlorines and the fourth is the number of bromines.

Thus the halons given as examples above have the following structures:





You need not remember the names of the various freons and halons, but you should be prepared to name them by the IUPAC system according to the rules developed in the next section.

Many organic compounds are closely related to the alkanes. Alkanes react with halogens to produce halogenated hydrocarbons, the simplest of which have a single halogen atom substituted for a hydrogen atom of the alkane. Even more closely related are the cycloalkanes, compounds in which the carbon atoms are joined in a ring, or cyclic fashion.

The reactions of alkanes with halogens produce **halogenated hydrocarbons**, compounds in which one or more hydrogen atoms of a hydrocarbon have been replaced by halogen atoms:



The replacement of only one hydrogen atom gives an **alkyl halide (or haloalkane)**. A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two,

three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table 10.1, along with some of their uses.

Table 10.1: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

TO YOUR HEALTH: HALOGENATED HYDROCARBONS

Once widely used in consumer products, many chlorinated hydrocarbons are suspected carcinogens (cancer-causing substances) and also are known to cause severe liver damage. An example is carbon tetrachloride (CCl_4), once used as a dry-cleaning solvent and in fire extinguishers but no longer recommended for either use. Even in small amounts, its vapor can cause serious illness if exposure is prolonged. Moreover, it reacts with water at high temperatures to form deadly phosgene ($COCl_2$) gas, which makes the use of CCl_4 in fire extinguishers particularly dangerous.

Ethyl chloride, in contrast, is used as an external local anesthetic. When sprayed on the skin, it evaporates quickly, cooling the area enough to make it insensitive to pain. It can also be used as an emergency general anesthetic.

Bromine-containing compounds are widely used in fire extinguishers and as fire retardants on clothing and other materials. Because they too are toxic and have adverse effects on the environment, scientists are engaged in designing safer substitutes for them, as for many other halogenated compounds.

CONTRIBUTORS AND ATTRIBUTIONS

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10.1: NAMES AND PROPERTIES OF ALKYL HALIDES

OBJECTIVES

After completing this section, you should be able to

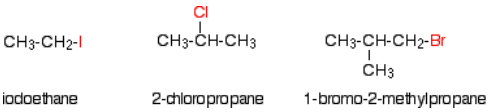
1. write the IUPAC name of a halogenated aliphatic hydrocarbon, given its Kekulé, condensed or shorthand structure.
2. draw the Kekulé, condensed or shorthand structure of a halogenated aliphatic hydrocarbon, given it IUPAC name.
3. write the IUPAC name and draw the Kekulé, condensed or shorthand structure of a simple alkyl halide, given a systematic, non-IUPAC name (e.g., sec-butyl iodide).
4. arrange a given series of carbon-halogen bonds in order of increasing or decreasing length and strength.

STUDY NOTES

This section contains little that is new. If you mastered the IUPAC nomenclature of alkanes, you should have little difficulty in naming alkyl halides. Notice that when a group such as CH_2Br must be regarded as a substituent, rather than as part of the main chain, we may use terms such as bromomethyl.

You will find it easier to understand the reactions of the alkyl halides if you keep the polarity of the $C-X$ bond fixed permanently in your mind (see "The Polar C—X Bond" shown in the reading below).

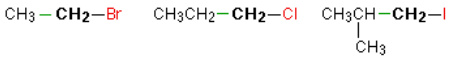
Alkyl halides are also known as haloalkanes. This page explains what they are and discusses their physical properties. alkyl halides are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine or iodine). We will only look at compounds containing one halogen atom. For example:



alkyl halides fall into different classes depending on how the halogen atom is positioned on the chain of carbon atoms. There are some chemical differences between the various types.

PRIMARY ALKYL HALIDES

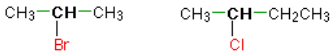
In a primary (1°) halogenoalkane, the carbon which carries the halogen atom is only attached to one other alkyl group.Some examples of primary alkyl halides include:



Notice that it doesn't matter how complicated the attached alkyl group is. In each case there is only one linkage to an alkyl group from the CH_2 group holding the halogen. There is an exception to this: CH_3Br and the other methyl halides are often counted as primary alkyl halides even though there are **no** alkyl groups attached to the carbon with the halogen on it.

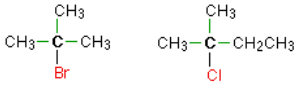
SECONDARY ALKYL HALIDES

In a secondary (2°) halogenoalkane, the carbon with the halogen attached is joined directly to two other alkyl groups, which may be the same or different. Examples:



TERTIARY ALKYL HALIDES

In a tertiary (3°) halogenoalkane, the carbon atom holding the halogen is attached directly to three alkyl groups, which may be any combination of same or different. Examples:



The Learning Objective is to name halogenated hydrocarbons given formulas and write formulas for these compounds given names.

Many organic compounds are closely related to the alkanes. As we noted in Section 12.7, alkanes react with halogens to produce halogenated hydrocarbons, the simplest of which have a single halogen atom substituted for a hydrogen atom of the alkane. Even more closely related are the cycloalkanes, compounds in which the carbon atoms are joined in a ring, or cyclic fashion.

The reactions of alkanes with halogens produce halogenated hydrocarbons, compounds in which one or more hydrogen atoms of a hydrocarbon have been replaced by halogen atoms:

CH_3CH_2Cl $CH_3CHBrCH_2Br$ CH_3CHICH_2Cl

The replacement of only one hydrogen atom gives an alkyl halide (or haloalkane). The *common names* of alkyl halides consist of two parts: the name of the alkyl group plus the stem of the name of the halogen, with the ending *-ide*. The IUPAC system uses the name of the parent alkane with a prefix indicating the halogen substituents, preceded by number indicating the substituent's location. The prefixes are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. Thus CH_3CH_2Cl has the common name ethyl chloride and the IUPAC name chloroethane. Alkyl halides with simple alkyl groups (one to four carbon atoms) are often called by common names. Those with a larger number of carbon atoms are usually given IUPAC names.

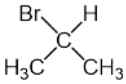
EXAMPLE 10.1.1

Please indicate if the following haloalkanes are methyl, 1°, 2°, or 3°:

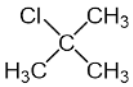
a) CH_3I

b) CH_3CH_2Br

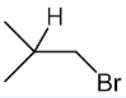
c)



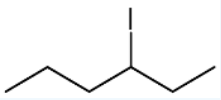
d)



e)



f)



Solution

a) methyl

b) 1°

c) 2°

d) 3°

e) 1°

f) 2°

The haloalkanes, also known as alkyl halides, are a group of chemical compounds comprised of an alkane with one or more hydrogens replaced by a halogen atom (fluorine, chlorine, bromine, or iodine). There is a fairly large distinction between the structural and physical properties of haloalkanes and the structural and physical properties of alkanes. As mentioned above, the structural differences are due to the replacement of one or more hydrogens with a halogen atom. The differences in physical properties are a result of factors such as electronegativity, bond length, bond strength, and molecular size.

HALOGENS AND THE CHARACTER OF THE CARBON-HALOGEN BOND

With respect to electronegativity, halogens are more electronegative than carbons. This results in a carbon-halogen bond that is polarized. As shown in the image below, carbon atom has a partial positive charge, while the halogen has a partial negative charge.

The Polar C-X Bond



The following image shows the relationship between the halogens and electronegativity. Notice, as we move up the periodic table from iodine to fluorine, electronegativity increases.

Electronegativity I < Br < Cl < F

The following image shows the relationships between bond length, bond strength, and molecular size. As we progress down the periodic table from fluorine to iodine, molecular size increases. As a result, we also see an increase in bond length. Conversely, as molecular size increases and we get longer bonds, the strength of those bonds decreases.

Bond length C-F < C-Cl < C-Br < C-I

Bond strength C-I < C-Br < C-Cl < C-F

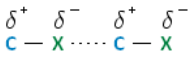
Molecular size F < Cl < Br < I

HALOALKANES HAVE HIGHER BOILING POINTS THAN ALKANES

When comparing alkanes and haloalkanes, we will see that haloalkanes have higher boiling points than alkanes containing the same number of carbons. London dispersion forces are the first of two types of forces that contribute to this physical property. You might recall from general chemistry that London dispersion forces increase with molecular surface area. In comparing haloalkanes with alkanes, haloalkanes exhibit an increase in surface area due to the substitution of a halogen for hydrogen. The incease in surface area leads to an increase in London dispersion forces, which then results in a higher boiling point.

Dipole-dipole interaction is the second type of force that contributes to a higher boiling point. As you may recall, this type of interaction is a coulombic attraction between the partial positive and partial negative charges that exist between carbon-halogen bonds on separate haloalkane molecules. Similar to London dispersion forces, dipole-dipole interactions establish a higher boiling point for haloalkanes in comparison to alkanes with the same number of carbons.

Dipole-Dipole Interaction



The table below illustrates how boiling points are affected by some of these properties. Notice that the boiling point increases when hydrogen is replaced by a halogen, a consequence of the increase in molecular size, as well as an increase in both London dispersion forces and dipole-dipole attractions. The boiling point also increases as a result of increasing the size of the halogen, as well as increasing the size of the carbon chain.

Boiling Points of Haloalkanes (°C)

R	X = H	F	Cl	Br	I
CH_3	-161.7	-78.4	-24.2	3.6	42.4
CH_3CH_2	-88.6	-37.7	12.3	38.4	72.3
$CH_3(CH_2)_2$	-42.1	-2.5	46.6	71.0	102.5
$CH_3(CH_2)_3$	-0.5	32.5	78.4	101.6	130.5
$CH_3(CH_2)_4$	36.1	62.8	107.8	129.6	157.0
$CH_3(CH_2)_7$	125.7	142.0	182.0	200.3	225.5

SOLUBILITY

SOLUBILITY IN WATER

The alkyl halides are at best only slightly soluble in water. For a halogenoalkane to dissolve in water you have to break attractions between the halogenoalkane molecules (van der Waals dispersion and dipole-dipole interactions) and break the hydrogen bonds between water

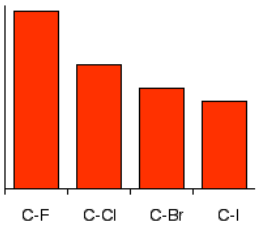
molecules. Both of these cost energy. Energy is released when ne These will only be dispersion forces and dipole-dipole interactions. These aren't as strong as the original hydrogen bonds in the water, and so not as much energy is released as was used to separate the water molecules. The energetics of the change are sufficiently "unprofitable" that very little dissolves.

SOLUBILITY IN ORGANIC SOLVENTS

Alkyl halides tend to dissolve in organic solvents because the new intermolecular attractions have much the same strength as the ones being broken in the separate halogenoalkane and solvent.

CHEMICAL REACTIVITY

The pattern in strengths o



Notice that bond strength orine bond is than the rest. To react with the alkyl halides, the carbon-halogen bond has got to be broken. Because that gets easier as you go from fluoride to chloride to bromide to iodide, the compounds get more reactive in that order. Iodoalkanes are the most reactive and fluoroalkanes are the least. In fact, fluoroalkanes are so unreactive that we shall pretty well ignore them completely from now on in this section!

EXERCISES

? EXERCISE 10.1.1

Give the common and IUPAC names for each compound.

a. $CH_3CH_2CH_2Br$
b. $(CH_3)_2CHCl$
c. CH_3CH_2I
d. $CH_3CH_2CH_2CH_2F$

Answer

a. The alkyl group ($CH_3CH_2CH_2$–) is a propyl group, and the halogen is bromine (Br). The common name is therefore propyl bromide. For the IUPAC name, the prefix for bromine (bromo) is combined with the name for a three-carbon chain (propane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-bromopropane.

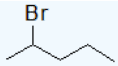
b. The alkyl group [$(CH_3)_2CH$–] has three carbon atoms, with a chlorine (Cl) atom attached to the middle carbon atom. The alkyl group is therefore isopropyl, and the common name of the compound is isopropyl chloride. For the IUPAC name, the Cl atom (prefix *chloro*-) attached to the middle (second) carbon atom of a propane chain results in 2-chloropropane.

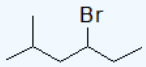
c. The alkyl group (CH_3CH_2–) is a ethyl group, and the halogen is iodide (I). The common name is therefore ethyl iodide. For the IUPAC name, the prefix for Iodide (Iodod) is combined with the name for a two-carbon chain (ethane), preceded by a number identifying the carbon atom to which the I atom is attached, so the IUPAC name is 1-bromoethane

d. The alkyl group ($CH_3CH_2CH_2CH_2$–) is a butyl group, and the halogen is fluorine (F). The common name is therefore butyl fluoride. For the IUPAC name, the prefix for Fluorine (Fluoro) is combined with the name for a four-carbon chain (butane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-fluorobutane.

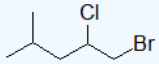
? EXERCISE 10.1.2

Give the IUPAC name for each compound.

A 

B 

C 

D 

Answer

A) The parent alkane has five carbon atoms in the longest continuous chain; it is pentane. A bromo (Br) group is attached to the second carbon atom of the chain. The IUPAC name is 2-bromopentane.

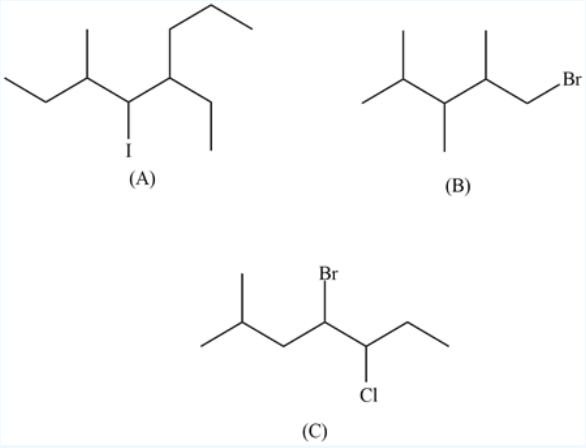
B) The parent alkane is hexane. Methyl ($CH_{3)}$ and bromo (Br) groups are attached to the second and fourth carbon atoms, respectively. Listing the substituents in alphabetical order gives the name 4-bromo-2-methylhexane.

C) 2-Chloro-3-methylbutane

D) 1-Bromo-2-chloro-4-methylpentane rine (F). The common name is therefore butyl fluoride. For the IUPAC name, the prefix for Fluorine (Fluoro) is combined with the name for a four-carbon chain (butane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-fluorobutane.

? EXERCISE 10.1.3

Give the names of the following organohalides:



Answer

(A) 5-ethyl-4-iodo-3methyl-octane

(B) 1-bromo-2,3,4-trimethyl-pentane

(C) 4-bromo-5-chloro-2-methyl-heptane

? EXERCISE 10.1.4

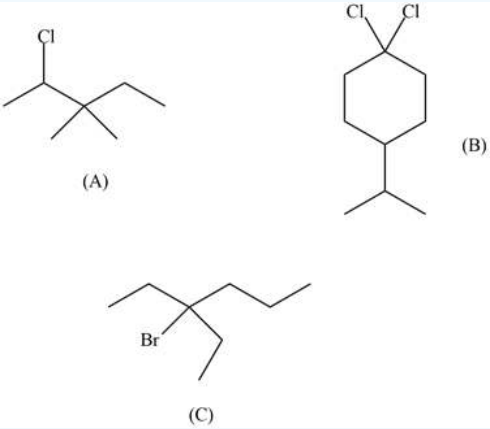
Draw the structures of the following compounds:

(A) 2-Chloro-3,3-dimethylpentane

(B) 1,1-Dichloro-4-isopropylcyclohexane

(C) 3-bromo-3-ethylhexane

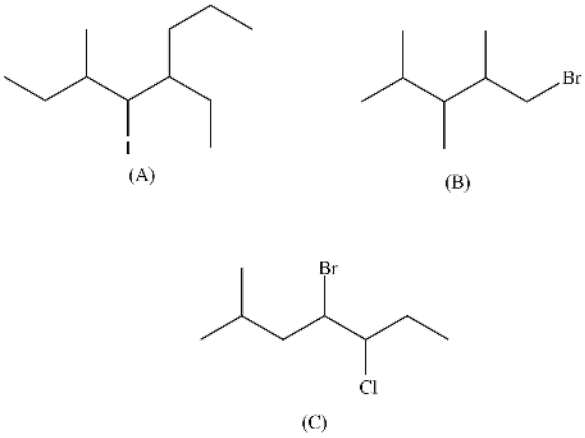
Answer



QUESTIONS

Q10.1.1

Give the names of the following organohalides:



Q10.1.2

Draw the structures of the following compounds:

A – 2-Chloro-3,3-dimethylpentane

B – 1,1-Dichloro-4-isopropylcyclohexane

C – 3-bromo-3-ethylhexane

SOLUTIONS

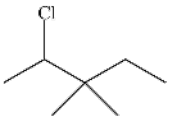
S10.1.1

A – 5-ethyl-4-iodo-3methyl-octane

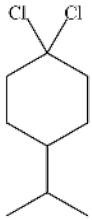
B – 1-bromo-2,3,4-trimethyl-pentane

C – 4-bromo-5-chloro-2-methyl-heptane

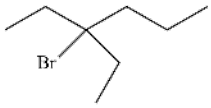
S10.1.2



(A)



(B)



(C)

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Jim Clark (Chemguide.co.uk)
- Rachael Curtis (UC Davis)

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10.2: PREPARING ALKYL HALIDES FROM ALKANES - RADICAL HALOGENATION

OBJECTIVES

After completing this section, you should be able to

1. explain why the radical halogenation of alkanes is not usually a particularly good method of preparing pure samples of alkyl halides.
2. use **C — H** bond energies to account for the fact that in radical chlorinations, the reactivity of hydrogen atoms decreases in the order tertiary > secondary > primary.
3. predict the approximate ratio of the expected products from the monochlorination of a given alkane.

STUDY NOTES

The following terms are synonymous:

1. methyl hydrogens, primary hydrogens, and 1° hydrogens.
2. methylene hydrogens, secondary hydrogens, and 2° hydrogens.
3. methine hydrogens, tertiary hydrogens, and 3° hydrogens.

Note that in radical chlorination reactions, the reactivity of methine, methylene and methyl hydrogens decreases in the ratio of approximately 5 : 3.5 : 1. This will aid in the prediction of expected products from the monochlorination of a given alkane.

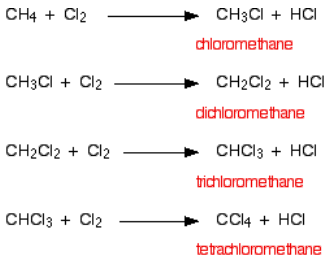
METHANE AND CHLORINE

If a mixture of methane and chlorine is exposed to a flame, it explodes - producing carbon and hydrogen chloride. This is not a very useful reaction! The reaction we are going to explore is a more gentle one between methane and chlorine in the presence of ultraviolet light - typically sunlight. This is a good example of a photochemical reaction - a reaction brought about by light.

$$CH_4 + Cl_2 + energy \rightarrow CH_3Cl + HCl \tag{10.2.1}$$

The organic product is chloromethane. One of the hydrogen atoms in the methane has been replaced by a chlorine atom, so this is a substitution reaction. However, the reaction doesn't stop there, and all the hydrogens in the methane can in turn be replaced by chlorine atoms. Multiple substitution is dealt with on a separate page, and you will find a link to that at the bottom of this page.

Substitution reactions happen in which hydrogen atoms in the methane are replaced one at a time by chlorine atoms. You end up with a mixture of chloromethane, dichloromethane, trichloromethane and tetrachloromethane.



The original mixture of a colorless and a green gas would produce steamy fumes of hydrogen chloride and a mist of organic liquids. All of the organic products are liquid at room temperature with the exception of the chloromethane which is a gas.

If you were using bromine, you could either mix methane with bromine vapor, or bubble the methane through liquid bromine - in either case, exposed to UV light. The original mixture of gases would, of course, be red-brown rather than green.

You wouldn't choose to use these reactions as a means of preparing these organic compounds in the lab because the mixture of products would be too tedious to separate. The mechanisms for the reactions are explained on separate pages.

Alkanes (the most basic of all organic compounds) undergo very few reactions. One of these reactions is halogenation, or the substitution of a single hydrogen on the alkane for a single halogen to form a haloalkane. This reaction is very important in organic chemistry because it opens a gateway to further chemical reactions.

HALOGENATION REACTION

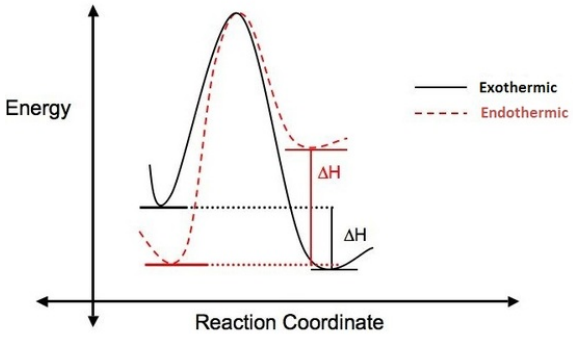
While the reactions possible with alkanes are few, there are many reactions that involve haloalkanes. In order to better understand the mechanism (a detailed look at the step by step process through which a reaction occurs), we will closely examine the chlorination of methane. When methane (CH_4) and chlorine (Cl_2) are mixed together in the absence of light at room temperature nothing happens. However, if the conditions are changed, so that either the reaction is taking place at high temperatures (denoted by Δ) or there is ultra violet irradiation, a product is formed, chloromethane (CH_3Cl).

ENERGETICS

Why does this reaction occur? Is the reaction favorable? A way to answer these questions is to look at the change in enthalpy (ΔH) that occurs when the reaction takes place.

$$\Delta H = (\text{Energy put into reaction}) - (\text{Energy given off from reaction})$$

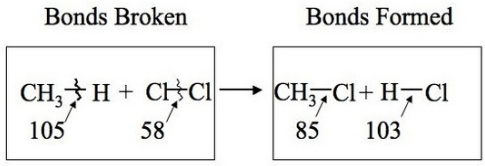
If more energy is put into a reaction than is given off, the ΔH is positive, the reaction is endothermic and not energetically favorable. If more energy is given off in the reaction than was put in, the ΔH is negative, the reaction is said to be exothermic and is considered favorable. The figure below illustrates the difference between endothermic and exothermic reactions.



ΔH can also be calculated using bond dissociation energies (ΔH°):

$$\Delta H = \sum \Delta H^\circ \text{ of bonds broken} - \sum \Delta H^\circ \text{ of bonds formed} \qquad (10.2.2)$$

Let's look at our specific example of the chlorination of methane to determine if it is endothermic or exothermic:



Change in enthalpy = (105 + 58) - (85 + 103)
= -25kcal/mol

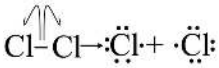
Since, the ΔH for the chlorination of methane is negative, the reaction is exothermic. Energetically this reaction is favorable. In order to better understand this reaction we need to look at the mechanism (a detailed step by step look at the reaction showing how it occurs) by which the reaction occurs.

RADICAL CHAIN MECHANISM

The reaction proceeds through the radical chain mechanism. The radical chain mechanism is characterized by three steps: **initiation**, **propagation** and **termination**. Initiation requires an input of energy but after that the reaction is self-sustaining. The first propagation step uses up one of the products from initiation, and the second propagation step makes another one, thus the cycle can continue until indefinitely.

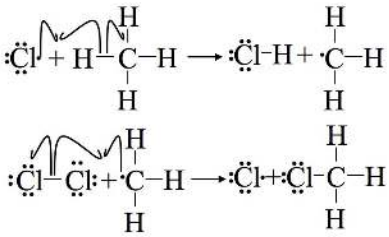
STEP 1: INITIATION

Initiation breaks the bond between the chlorine molecule (Cl_2). For this step to occur energy must be put in, this step is not energetically favorable. After this step, the reaction can occur continuously (as long as reactants provide) without input of more energy. It is important to note that this part of the mechanism cannot occur without some external energy input, through light or heat.

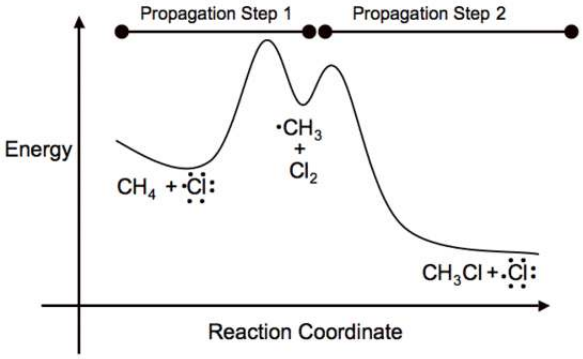


STEP 2: PROPAGATION

The next two steps in the mechanism are called propagation steps. In the first propagation step, a chlorine radical combines with a hydrogen on the methane. This gives hydrochloric acid (HCl, the inorganic product of this reaction) and the methyl radical. In the second propagation step more of the chlorine starting material (Cl_2) is used, one of the chlorine atoms becomes a radical and the other combines with the methyl radical.

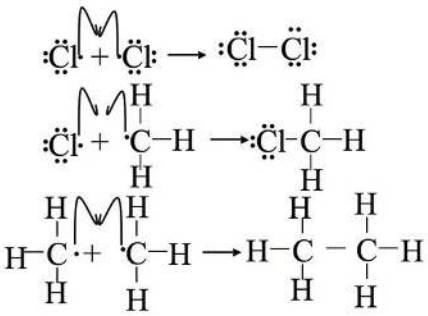


The first propagation step is endothermic, meaning it takes in heat (requires 2 kcal/mol) and is not energetically favorable. In contrast the second propagation step is exothermic, releasing 27 kcal/mol. Since the second propagation step is so exothermic, it occurs very quickly. The second propagation step uses up a product from the first propagation step (the methyl radical) and following Le Chatelier's principle, when the product of the first step is removed the equilibrium is shifted towards it's products. This principle is what governs the unfavorable first propagation step's occurance.



STEP 3: TERMINATION

In the termination steps, all the remaining radicals combine (in all possible manners) to form more product (CH_3Cl), more reactant (Cl_2) and even combinations of the two methyl radicals to form a side product of ethane (CH_3CH_3).



PROBLEMS WITH THE CHLORINATION OF METHANE

The chlorination of methane does not necessarily stop after one chlorination. It may actually be very hard to get a monosubstituted chloromethane. Instead di-, tri- and even tetra-chloromethanes are formed. One way to avoid this problem is to use a much higher

concentration of methane in comparison to chloride. This reduces the chance of a chlorine radical running into a chloromethane and starting the mechanism over again to form a dichloromethane. Through this method of controlling product ratios one is able to have a relative amount of control over the product.

CHLORINATION OF OTHER ALKANES

When alkanes larger than ethane are halogenated, isomeric products are formed. Thus chlorination of propane gives both 1-chloropropane and 2-chloropropane as mono-chlorinated products. Four constitutionally isomeric dichlorinated products are possible, and **five constitutional isomers** exist for the trichlorinated propanes. Can you write structural formulas for the four dichlorinated isomers?

$$CH_3CH_2CH_3 + 2Cl_2 \rightarrow \text{Four } C_3H_6Cl_2 \text{ isomers} + 2HCl \tag{10.2.3}$$

The halogenation of propane discloses an interesting feature of these reactions. **All the hydrogens in a complex alkane do not exhibit equal reactivity**. For example, propane has eight hydrogens, six of them being structurally equivalent **primary**, and the other two being **secondary**. If all these hydrogen atoms were equally reactive, halogenation should give a 3:1 ratio of 1-halopropane to 2-halopropane mono-halogenated products, reflecting the primary/secondary numbers. This is not what we observe. Light-induced gas phase chlorination at 25 ºC gives 45% 1-chloropropane and 55% 2-chloropropane.

CH_3-CH_2-CH_3 + Cl_2 → 45% CH_3-CH_2-CH_2Cl + 55% CH_3-$CHCl$-CH_3

These results suggest strongly that 2º-hydrogens are inherently more reactive than 1º-hydrogens, by a factor of about 3:1. Further experiments showed that 3º-hydrogens are even more reactive toward halogen atoms. Thus, light-induced chlorination of 2-methylpropane gave predominantly (65%) 2-chloro-2-methylpropane, the substitution product of the sole 3º-hydrogen, despite the presence of nine 1º-hydrogens in the molecule.

$(CH_3)_3CH$ + Cl_2 → 65% $(CH_3)_3CCl$ + 35% $(CH_3)_2CHCH_2Cl$

If you are uncertain about the terms primary (1º), secondary (2º) & tertiary (3º) Click Here.

It should be clear from a review of the two steps that make up the free radical chain reaction for halogenation that the first step (hydrogen abstraction) is the **product determining step**. Once a carbon radical is formed, subsequent bonding to a halogen atom (in the second step) can only occur at the radical site. Consequently, an understanding of the preference for substitution at 2º and 3º-carbon atoms must come from an analysis of this first step.

First Step: R_3CH + $X\cdot$ → $R_3C\cdot$ + H-X

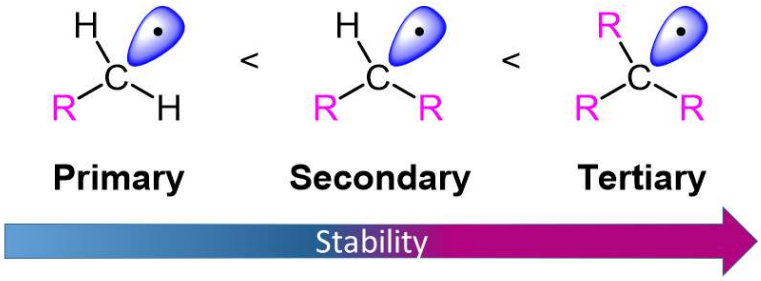
Second Step: $R_3C\cdot$ + X_2 → R_3CX + $X\cdot$

Since the H-X product is common to all possible reactions, differences in reactivity can only be attributed to differences in C-H bond dissociation energies. In our previous discussion of bond energy we assumed average values for all bonds of a given kind, but now we see that this is not strictly true. In the case of carbon-hydrogen bonds, there are significant differences, and the specific dissociation energies (energy required to break a bond homolytically) for various kinds of C-H bonds have been measured. These values are given in the following table.

R (in R–H)	methyl	ethyl	i-propyl	t-butyl	phenyl	benzyl	allyl	vinyl
Bond Dissociation Energy (kcal/mole)	103	98	95	93	110	85	88	112

The difference in C-H bond dissociation energy reported for primary (1º), secondary (2º) and tertiary (3º) sites agrees with the halogenation observations reported above, in that we would expect weaker bonds to be broken more easily than are strong bonds. By this reasoning we would expect benzylic and allylic sites to be exceptionally reactive in free radical halogenation, as experiments have shown. The methyl group of toluene, $C_6H_5CH_3$, is readily chlorinated or brominated in the presence of free radical initiators (usually peroxides), and ethylbenzene is similarly chlorinated at the benzylic location exclusively. The hydrogens bonded to the aromatic ring (referred to as phenyl hydrogens above) have relatively high bond dissociation energies and are not substituted.

$C_6H_5CH_2CH_3$ + Cl_2 → $C_6H_5CHClCH_3$ + HCl



Relative Stability of Free Radicals

EXERCISES

? EXERCISE 10.2.1

Write out the complete mechanism for the chlorination of methane.

Answer

The answer to this problem is actually above in the initiation, propagation and termination descriptions.

? EXERCISE 10.2.2

Explain, in your own words, how the first propagation step can occur without input of energy if it is energetically unfavorable.

Answer

Since the second step in propagation is energetically favorable and fast, it drives the equilibrium toward products, even though the first step is not favorable.

? EXERCISE 10.2.3

Which step of the radical chain mechanism requires outside energy? What can be used as this energy?

Answer

Initiation step requires energy which can be in the form of light or het.

? EXERCISE 10.2.4

Having learned how to calculate the change in enthalpy for the chlorination of methane apply your knowledge and using the table provided below calculate the change in enthalpy for the bromination of ethane.

Compound	Bond Dissociation Energy (kcal/mol)
CH_3CH_2-H	101
CH_3CH_2-Br	70
H-Br	87
Br_2	46

Answer

To calculate the enthalpy of reaction, you subtract the BDE of the bonds formed from the BDE of the bonds broken.

Bonds broken are C-H and Br-Br.

Bonds formed are H-Br adn C-Br.

Bonds broken - bonds formed = change in enthalpy

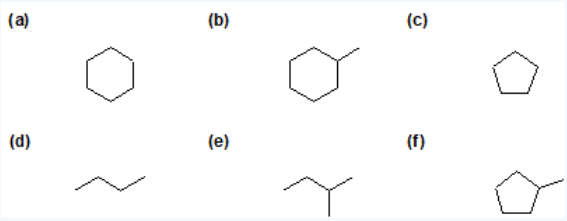
(101 kcal/mol + 46 kcal/mol) - (87 kcal/mol + 70 kcal/mol) = change in enthalpy

-10 kcal/mol = change in enthalpy for bromination of ethane.

EXERCISE 10.2.5

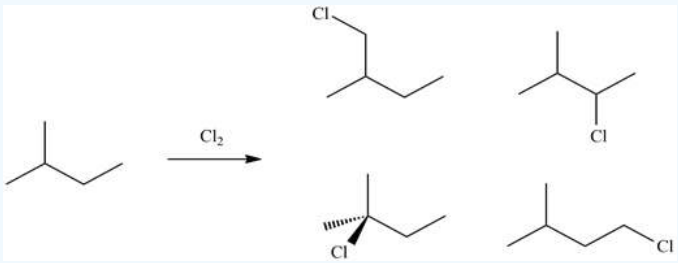
1) Predict the mono-substituted halogenated product(s) of chlorine gas reacting with 2-methylbutane.

2) For the following compounds, give all possible monochlorinated derivatives.

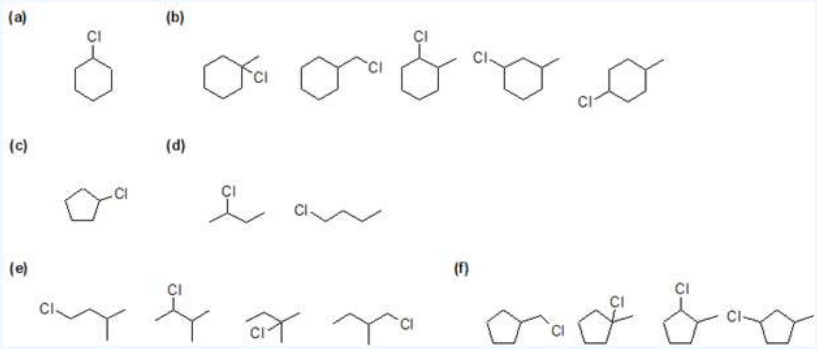


Answer

1)



2)



QUESTIONS

Q10.2.1

Predict the mono-substituted halogenated product(s) of chlorine gas reacting with 2-methylbutane.

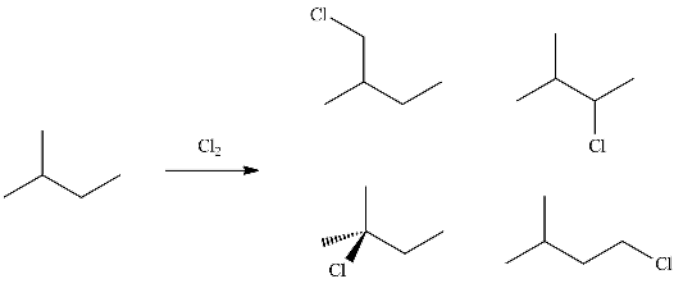
Q10.2.2

Predict the relative amount of each mono-brominated product when 3-methylpentane is reacted with Br_2. Consider 1°, 2°, 3° hydrogen.

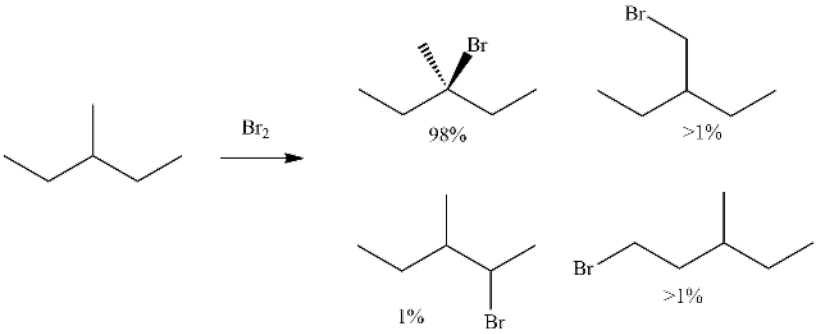
SOLUTIONS

S10.2.1

https://chem.libretexts.org/@go/page/67252



S10.2.2



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Jim Clark (Chemguide.co.uk)
- Kristen Kelley and Britt Farquharson

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10.3: PREPARING ALKYL HALIDES FROM ALKENES - ALLYLIC BROMINATION

Objectives

After completing this section, you should be able to

1. write the equation for the bromination of a symmetrical alkene using N-bromosuccinimide.
2. predict the product formed when a given symmetrical alkene is treated with N-bromosuccinimide.
3. identify the reagent, the symmetrical alkene, or both, needed to produce a given allyl halide by allylic bromination.
4. list the following radicals in order of increasing or decreasing stability: allyl, vinyl, primary alkyl, secondary alkyl, tertiary alkyl, methyl.
5. explain the ease of forming an allyl radical, and the difficulty of forming a vinyl radical, in terms of relative C–H bond dissociation energies.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- allylic carbon

STUDY NOTES

We have discussed the electrophilic addition of X_2 and HX to alkenes as a route to forming alkyl halides (Sections 7.7 and 8.2). In this section we introduce bromination at the allyic position with N-bromosuccinimide (NBS). Notice that at the moment we are restricting our studies to the allylic bromination of symmetrical alkenes, such as cyclohexene. When we introduce an element of asymmetry, we find that more than one allyl radical can be formed; therefore, we must assess the relative stability of each radical when trying to predict which product will predominate. The method of doing this assessment is described in the next section.

R (in R–H)	methyl	ethyl	i-propyl	t-butyl	phenyl	benzyl	allyl	vinyl
Bond Dissociation Energy (kcal/mole)	103	98	95	93	110	85	88	112

The covalent bond homolyses that define the bond dissociation energies listed above may are described by the general equation:

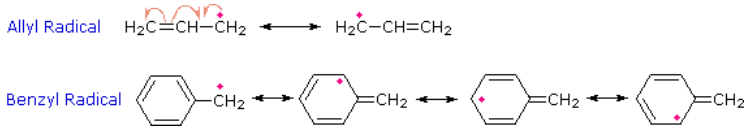
$R_3C\text{-}H + \text{energy} \longrightarrow R_3C\cdot + H\cdot$

Since the hydrogen atom is common to all the cases cited here, we can attribute the differences in bond dissociation energies to differences in the stability of the alkyl radicals ($R_3C\cdot$) as the carbon substitution changes. This leads us to the conclusion that:

alkyl radical stability increases in the order: phenyl < primary (1°) < secondary (2°) < tertiary (3°) < allyl ≈ benzyl.

Because alkyl radicals are important intermediates in many reactions, this stability relationship will prove to be very useful in future discussions. The enhanced stability of allyl and benzyl radicals may be attributed to resonance stabilization. If you wish to review the principles of resonance Click Here.

Formulas for the allyl and benzyl radicals are shown below. Draw structural formulas for the chief canonical forms contributing to the resonance hybrid in each case.

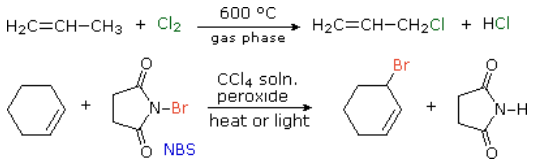


The poor stability of phenyl radicals, $C_6H_5\cdot$, may in turn be attributed to the different hybridization state of the carbon bearing the unpaired electron (sp^2 vs. sp^3).

We noted that benzylic and allylic sites are exceptionally reactive in free radical halogenation reactions. Since carbon-carbon double bonds add chlorine and bromine in liquid phase solutions, radical substitution reactions by these halogens are often carried out at elevated

temperature in the gas phase (first equation below). Formation of the ionic π-complexes that are intermediates in halogen addition is unfavorable in the absence of polar solvents, and entropy generally favors substitution over addition.

The brominating reagent, N-bromosuccinimide (NBS), has proven useful for achieving allylic or benzylic substitution in CCl_4 solution at temperatures below its boiling point (77 ºC). One such application is shown in the second equation.



The predominance of allylic substitution over addition in the NBS reaction is interesting. The N–Br bond is undoubtedly weak (probably less than 50 kcal/mol) so bromine atom abstraction by radicals should be very favorable. The resulting succinimyl radical might then establish a chain reaction by removing an allylic hydrogen from the alkene. One problem with this mechanism is that NBS is very insoluble in CCl_4, about 0.006 mole / liter at reflux. Although it is possible that the allylic bromination occurs at a solid-liquid interface, evidence for another pathway has been obtained. In the non-polar solvent used for these reactions, very low concentrations of bromine may be generated from NBS. This would serve as a source of bromine atoms, which would abstract allylic hydrogens irreversibly (an exothermic reaction) in competition with reversible addition to the double bond. The HBr produced in this way is known to react with NBS, giving a new bromine molecule and succinimide, as shown here. Ionic addition of bromine to the double bond would be very slow in these circumstances (CCl_4 is a nonpolar solvent).

$$HBr + (CH_2CO)_2NBr \rightarrow Br_2 + (CH_2CO)_2NH$$

This mechanism is essentially the same as that for the free radical halogenation of alkanes, with NBS serving as a source of very low concentrations of bromine. Unsymmetrical allylic radicals will react to give two regioisomers. Thus, 1-octene on bromination with NBS yields a mixture of 3-bromo-1-octene (ca. 18%) and 1-bromo-2-octene (82%) - both cis and trans isomers.

$$RCH_2CH=CH_2 + (CH_2CO)_2NBr \rightarrow RCHBrCH=CH_2 + RCH=CHCH_2Br + (CH_2CO)_2N$$

CONTRIBUTORS

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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10.4: STABILITY OF THE ALLYL RADICAL - RESONANCE REVISITED

Objectives

After completing this section, you should be able to

1. explain the stability of the allyl radical in terms of resonance.
2. explain the difference between resonance and tautomerism.
3. write an equation for the reaction of an unsymmetrical alkene with N-bromosuccinimide.
4. draw the structure of each of the possible products that could be obtained from the reaction of a given unsymmetrical alkene with N-bromosuccinimide, and predict which product will predominate.
5. explain the formation of more than one product from the reaction of N-bromosuccinimide with a given unsymmetrical alkene.
6. explain the observed product ratio when a given unsymmetrical alkene is treated with N-bromosuccinimide.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- delocalized
- resonance forms
- resonance hybrid

STUDY NOTES

You will have encountered the concept of resonance if you have taken general first-year chemistry course. You should also briefly review Section 2.5.

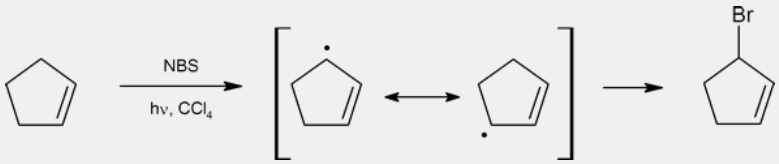
When we can represent a species by two or more different Lewis or Kekulé structures, neither of which represents the true structure of the species, these structures are referred to as *resonance forms*. A common example used in general chemistry courses to illustrate the concept of resonance is ozone, O3. The two resonance forms of ozone may be represented as follows:



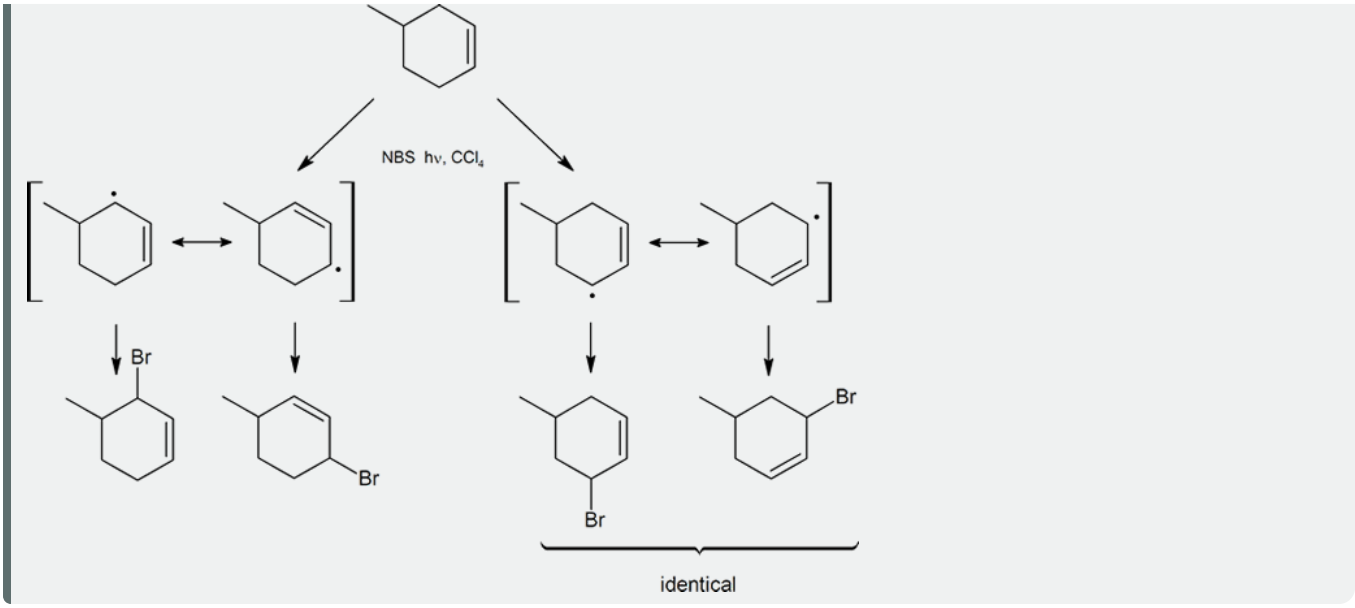
The concept of resonance is quite important, and will be used frequently throughout the remainder of this course. The guidelines below may assist you in drawing resonance contributors.

1. Resonance occurs whenever a molecule, radical or ion can be represented by two or more structures differing only in the arrangement of electrons (no atoms may be moved).
2. The true structure of a species is a hybrid of the resonance contributors and is more stable (i.e., lower in energy) than any of the contributors.
3. The most important contributors are those containing the most covalent bonds. Another way of saying the same thing is that the most important contributors have the least amount of charge separation.
4. Contributors in which all the atoms (except hydrogen) have a complete octet (i.e., are surrounded by eight electrons) are particularly important.

In the previous section we discussed the allylic bromination of a symmetrical alkene with NBS such as this cyclopentene, which affords one product.

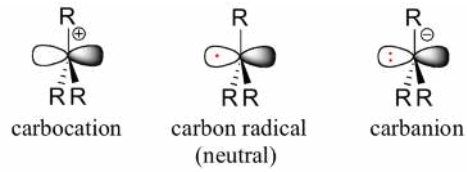


However, with an unsymmetrical alkene and the delocalized unpaired electron forming various allylic resonances, several products are possible. For example, the NBS bromination of 4-methyl-cyclohexene leads to three products.

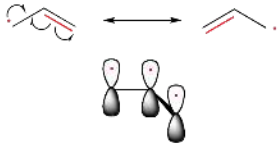


THE GEOMETRY AND RELATIVE STABILITY OF CARBON RADICALS

As organic chemists, we are particularly interested in radical intermediates in which the unpaired electron resides on a carbon atom. Experimental evidence indicates that the three bonds in a carbon radical have trigonal planar geometry, and therefore the carbon is considered to be sp^2-hybridized with the unpaired electron occupying the perpendicular, unhybridized $2p_z$orbital. Contrast this picture with carbocation and carbanion intermediates, which are both also trigonal planar but whose $2p_z$ orbitals contain zero or two electrons, respectively.



The trend in the stability of carbon radicals parallels that of carbocations (section 8.4B): tertiary radicals, for example, are more stable than secondary radicals, followed by primary and methyl radicals. This should make intuitive sense, because radicals, like carbocations, can be considered to be electron deficient, and thus are stabilized by the electron-donating effects of nearby alkyl groups. Benzylic and allylic radicals are more stable than alkyl radicals due to resonance effects - an unpaired electron can be delocalized over a system of conjugated pi bonds. An allylic radical, for example, can be pictured as a system of three parallel $2p_z$ orbitals sharing three electrons.



INTRODUCTION

Electrons have no fixed position in atoms, compounds and molecules (see image below) but have probabilities of being found in certain spaces (orbitals). Resonance forms illustrate areas of higher probabilities (electron densities). This is like holding your hat in either your right hand or your left. The term Resonance is applied when there are two or more possibilities available. Resonance structures do not change the relative positions of the atoms like your arms in the metaphor. The skeleton of the Lewis Structure remains the same, only the electron locations change. A double headed arrow on both ends of the arrow (↔) between Lewis structures is used to show their inter-connectivity. It is different from the double harpoons (⇌) used for designating equilibria. A double headed arrow on only one end (→) is used to indicate the movement of two electrons in a single resonance structure.

EXAMPLE 10.4.1

Consider ozone (O_3)

Solution

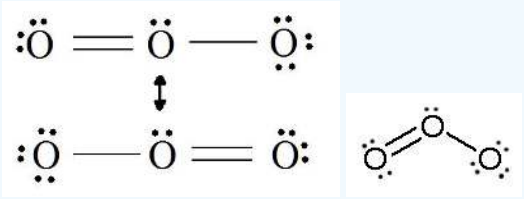


Figure: This is an animation of how one can do a resonance with ozone by moving electrons:

DELOCALIZATION AND RESONANCE STRUCTURES RULES

In resonance structures, the electrons are able to move to help stabilize the molecule. This movement of the electrons is called delocalization.

1. Resonance structures should have the same number of electrons, do not add or subtract any electrons. (You can check the number of electrons by counting them)
2. All resonance structures must follow the rules of writing Lewis Structures.
3. The hybridization of the structure must stay the same.
4. The skeleton of the structure can not be changed (only the electrons move).
5. Resonance structures must also have the same amount of lone pairs.

FORMAL CHARGE

Even though the structures look the same, the formal charge (FC) may not be. Formal charges are charges that are assigned to a specific atom in a molecule. If computed correctly, the overall formal charge of the molecule should be the same as the oxidation charge of the molecule (the charge when you write out the empirical and molecular formula) We want to choose the resonance structure with the least formal charges that add up to zero or the charge of the overall molecule.

The equation for finding Formal Charge is:

Formal Charge = (number of valence electrons in free orbital) - (number of lone-pair electrons) - ($\frac{1}{2}$ number bond pair electrons)

The formal charge has to equal the molecule's overall charge.

Ex.) CNS^- has an overall charge of -1, so the Lewis structure's formal charge has to equal -1.

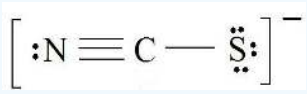
See Lewis Structure for more information.

EXAMPLE 10.4.2: THIOCYANATE ION

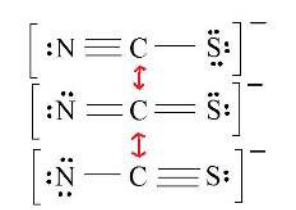
Consider the thiocyanate (CNS^-) ion.

Solution

1. Find the Lewis Structure of the molecule. (Remember the Lewis Structure rules.)



2. Resonance: All elements want an octet, and we can do that in multiple ways by moving the terminal atom's electrons around (bonds too).

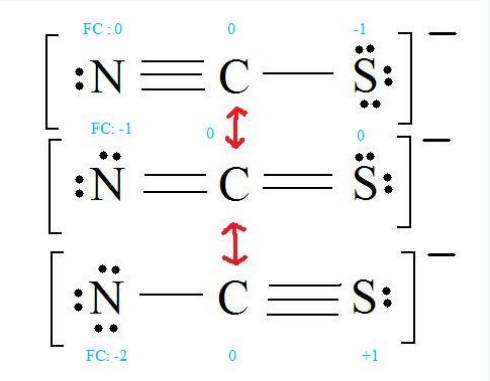


3. Assign Formal Charges

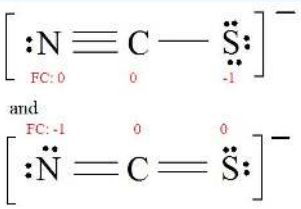
Formal Charge = (number of valence electrons in free orbital) - (number of lone-pair electrons) - ($\frac{1}{2}$ number bond pair electrons)

Remember to determine the number of valence electron each atom has before assigning Formal Charges

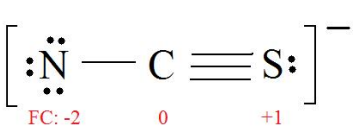
C = 4 valence e$^-$, N = 5 valence e$^-$, S = 6 valence e$^-$, also add an extra electron for the (-1) charge. The total of valence electrons is 16.



4. Find the most ideal resonance structure. (Note: It is the one with the least formal charges that adds up to zero or to the molecule's overall charge.)



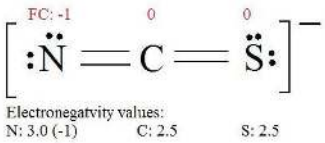
are the most ideal structures because of their minimal formal charges.



Is not that commonly used because of it's formal charge, but it is still a resonance structure.

5. Now we have to look at electronegativity for the "Correct" Lewis structure.

The most electronegative atom usually has the negative formal charge, while the least electronegative atom usually has the positive formal charges.



Electronegatvity values:
N: 3.0 (-1) C: 2.5 S: 2.5

Is the "correct" Lewis structure out of all the other resonances because of the electronegativity values.

RESONANCE HYBRIDS

Resonance Structures are a representation of a *Resonance Hybrid*, which is the combination of all resonance structures. Though the Formal Charge closest to zero is the most accepted structure, in reality the correct Lewis structure is actually a combination of all the resonance structures (and hence is not solely describe as one).

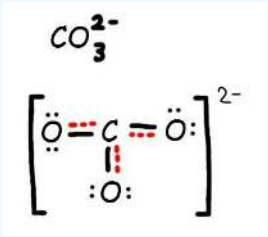
1. Draw the Lewis Structure & Resonance for the molecule (using solid lines for bonds).
2. Where there **can** be a double or triple bond, draw a dotted line (-----) for a bond.

3. Draw only the lone pairs found in all resonance structures, do not include the lone pairs that are not on all of the resonance structures.

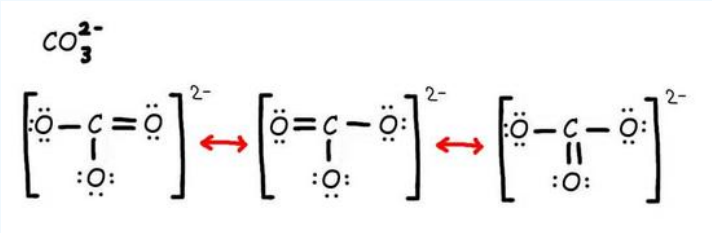
EXAMPLE 10.4.3

Consider the carbonate ion: CO_3^{2-}

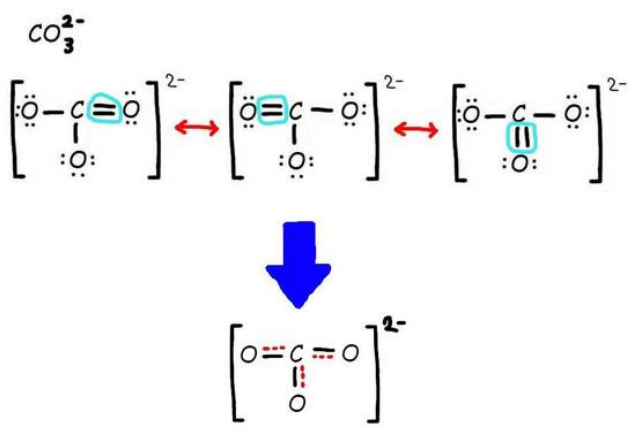
Solution



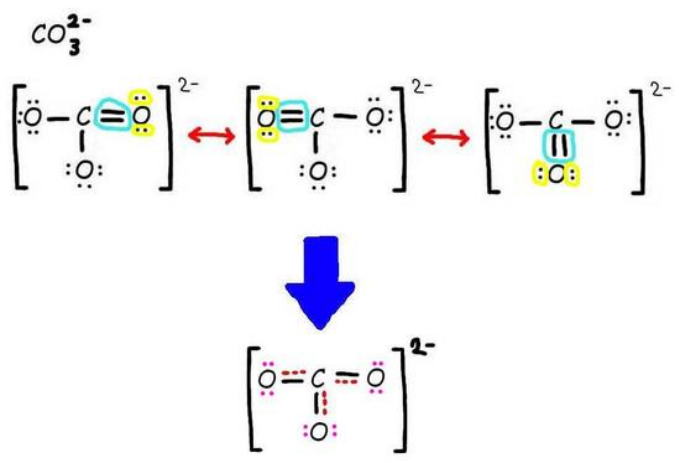
Step 1: Draw the Lewis Structure & Resonance.



Step 2: Combine the resonance structures by adding (dotted) bonds where other resonance bonds can be formed.



Step 3: Add only the lone pairs found on **ALL** resonance structures.

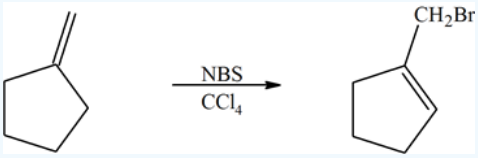


The bottom is the finished resonance hybrid for CO_3^{2-}.

EXERCISES

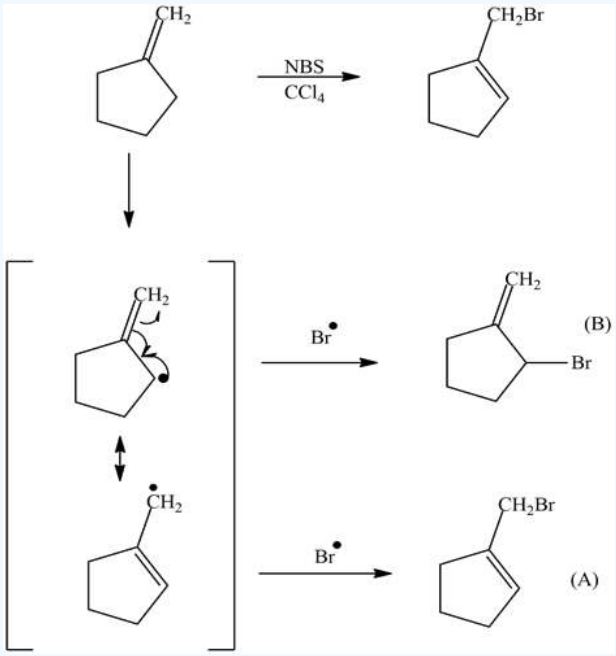
EXERCISE 10.4.1

The following reaction shows the major product. Explain why this would be the final product and why the 2° bromo product is not the major product.



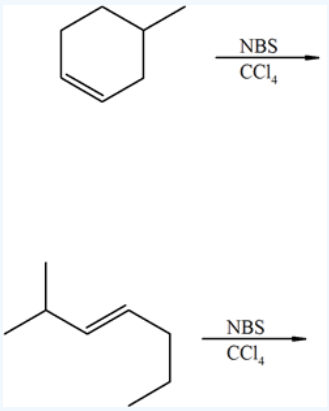
Answer

The product (A) is a 1° halogen which is more predominant product even though the (B) had a better transition state with a 2° radical. The 1° radical intermediate is not as sterically hindered.



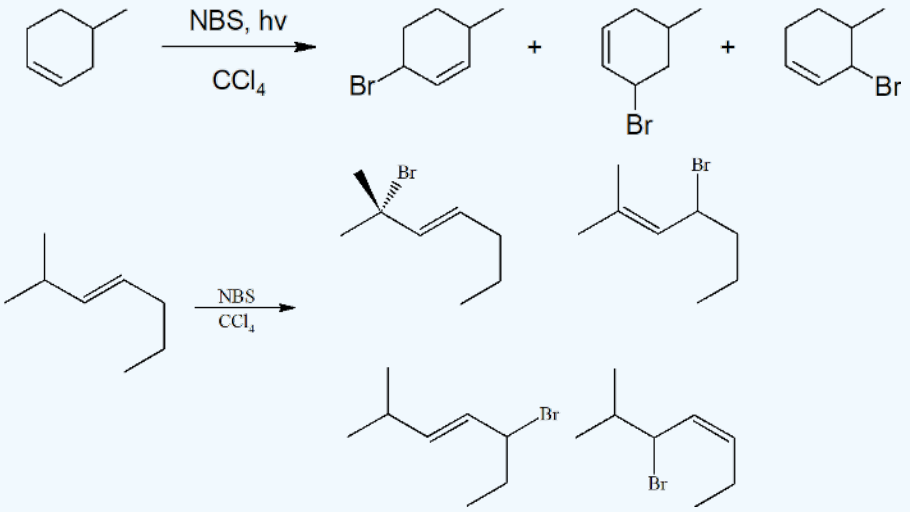
EXERCISE 10.4.2

Predict the products of the following reactions:



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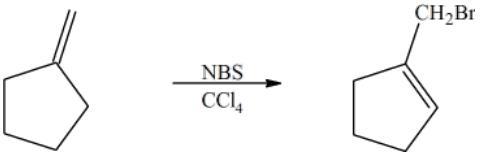
Answer



QUESTIONS

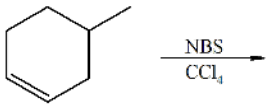
Q10.4.1

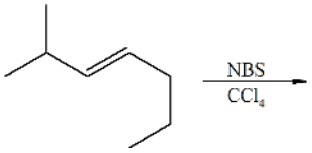
The following reaction shows the major product. Explain why this would be the final product and why the 2° bromo product is not the major product.



Q10.4.2

Predict the products of the following reactions:

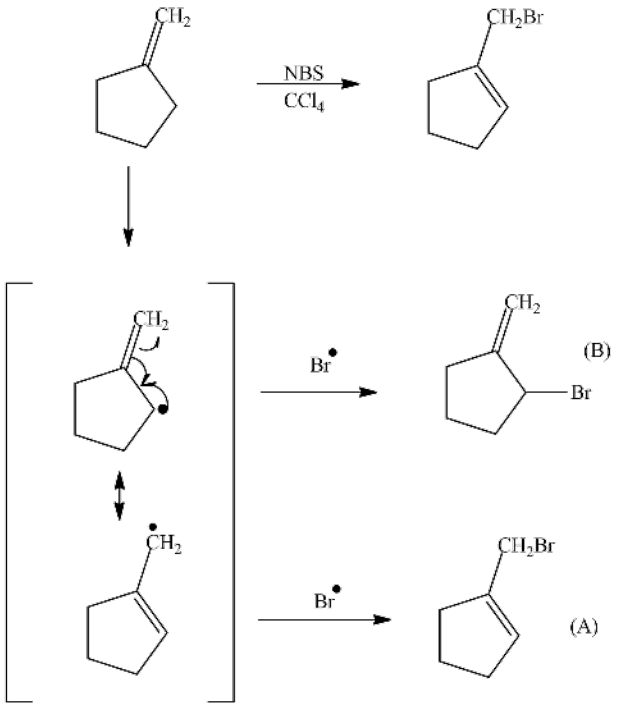




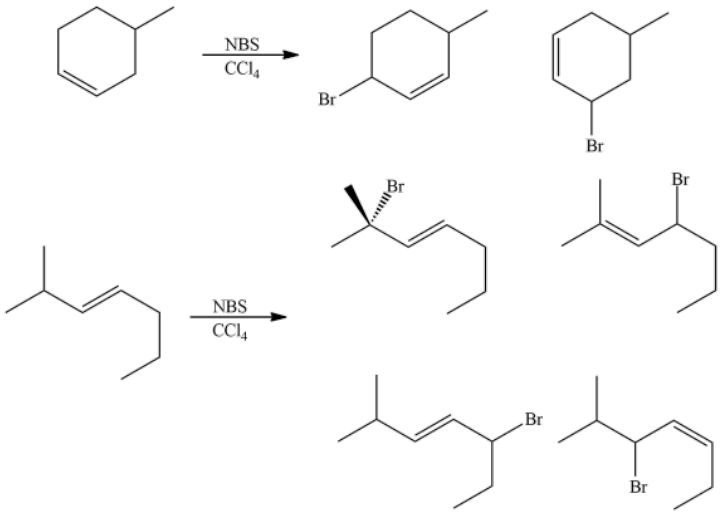
SOLUTIONS

S10.4.1

The product (A) is a 1° halogen which is more predominant product even though the (B) had a better transition state with a 2° radical. The 1° radical intermediate is not as sterically hindered.



S10.4.2



CONTRIBUTORS AND ATTRIBUTIONS

- Sharon Wei (UCD), Liza Chu (UCD)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
-

10.4: Stability of the Allyl Radical - Resonance Revisited is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

10.5: PREPARING ALKYL HALIDES FROM ALCOHOLS

Objectives

After completing this section, you should be able to

1. write an equation for the conversion of an alcohol to an alkyl halide.
2. list a given series of alcohols in increasing or decreasing order of reactivity with hydrogen halides.
3. identify the alkyl halide formed when a given alcohol reacts with thionyl chloride, phosphorus tribromide, or a hydrogen halide.
4. identify the alcohol which should be used to prepare a given alkyl halide using one of the reagents specified in Objective 3.
5. select the most appropriate reagent for converting a given alcohol to a given alkyl halide.

STUDY NOTES

The use of thionyl chloride for converting alcohols to alkyl chlorides has the added benefit that both of the by-products, sulfur dioxide and hydrogen chloride, are gases. This characteristic simplifies the isolation and purification of the reaction product.

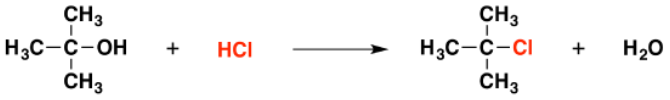
In the laboratory, one can test for the presence of alcohols with Lucas reagent (a mixture of concentrated hydrochloric acid and zinc chloride). Lucas reagent converts alcohols to alkyl chlorides: tertiary alcohols give an immediate reaction, indicated when the alcohol solution turns cloudy; secondary alcohols usually show evidence of reacting within five minutes; primary alcohols do not react to any significant extent. Thus, Lucas reagent can help distinguish among primary, secondary and tertiary alcohols.

This page looks at reactions in which the -OH group in an alcohol is replaced by a halogen such as chlorine or bromine. It includes a simple test for an -OH group using phosphorus(V) chloride. The general reaction looks like this:

$$ROH + HX \rightarrow RX + H_2O \tag{10.5.1}$$

REACTION WITH HYDROGEN CHLORIDE

Tertiary alcohols react reasonably rapidly with concentrated hydrochloric acid, but for primary or secondary alcohols the reaction rates are too slow for the reaction to be of much importance. A tertiary alcohol reacts if it is shaken with with concentrated hydrochloric acid at room temperature. A tertiary halogenoalkane (haloalkane or alkyl halide) is formed.



REPLACING -OH BY BROMINE

Rather than using hydrobromic acid,the alcohol is typically treated with a mixture of sodium or potassium bromide and concentrated sulfuric acid. This produces hydrogen bromide, which reacts with the alcohol. The mixture is warmed to distil off the bromoalkane.

$$CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br + H_2O \tag{10.5.2}$$

REPLACING -OH BY IODINE

In this case, the alcohol is reacted with a mixture of sodium or potassium iodide and concentrated phosphoric(V) acid, H_3PO_4, and the iodoalkane is distilled off. The mixture of the iodide and phosphoric(V) acid produces hydrogen iodide, which reacts with the alcohol.

$$CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O \tag{10.5.3}$$

Phosphoric(V) acid is used instead of concentrated sulfuric acid because sulfuric acid oxidizes iodide ions to iodine and produces hardly any hydrogen iodide. A similar phenomenon occurs to some extent with bromide ions in the preparation of bromoalkanes but not enough to interfere with the main reaction. There is no reason why you could not use phosphoric(V) acid in the bromide case instead of sulfuric acid if desired.

When alcohols react with a hydrogen halide, a substitution takes place producing an alkyl halide and water:

Figure

SCOPE OF REACTION

- The order of reactivity of alcohols is 3° > 2° > 1° methyl.
- The order of reactivity of the hydrogen halides is HI > HBr > HCl (HF is generally unreactive).

The reaction is acid catalyzed. Alcohols react with the strongly acidic hydrogen halides HCl, HBr, and HI, but they do not react with nonacidic NaCl, NaBr, or NaI. Primary and secondary alcohols can be converted to alkyl chlorides and bromides by allowing them to react with a mixture of a sodium halide and sulfuric acid:



REACTING ALCOHOLS WITH PHOSPHORUS HALIDES

Alcohols react with liquid phosphorus(III) chloride (also called phosphorus trichloride) to yield chloroalkanes.

$$3CH_3CH_2CH_2OH + PCl_3 \rightarrow 3CH_3CH_2CH_2Cl + H_3PO_3 \tag{10.5.4}$$

Alcohols also violently react with solid phosphorus(V) chloride (phosphorus pentachloride) at room temperature, producing clouds of hydrogen chloride gas. While it is not a good approach to make chloroalkanes, it is a good test for the presence of -OH groups. To show that a substance was an alcohol, you would first have to eliminate all the other groups that also react with phosphorus(V) chloride. For example, carboxylic acids (containing the -COOH group) also react with it (because of the -OH in -COOH) as does water (H-OH).

If you have a neutral liquid not contaminated with water, and clouds of hydrogen chloride are produced when you add phosphorus(V) chloride, then you have an alcohol group present.

$$CH_3CH_2CH_2OH + PCl_5 \rightarrow CH_3CH_2CH_2Cl + POCl_3 + HCl \tag{10.5.5}$$

There are also side reactions involving the $POCl_3$ reacting with the alcohol.

OTHER REACTIONS INVOLVING PHOSPHORUS HALIDES

Instead of using phosphorus(III) bromide or iodide, the alcohol is usually heated under reflux with a mixture of red phosphorus and either bromine or iodine. The phosphorus first reacts with the bromine or iodine to give the phosphorus(III) halide.

$$2P_{(s)} + 3Br_2 \rightarrow 2PBr_3 \tag{10.5.6}$$

$$2P_{(s)} + 3I_2 \rightarrow 2PI_3 \tag{10.5.7}$$

These then react with the alcohol to give the corresponding halogenoalkane, which can be distilled off.

$$3CH_3CH_2CH_2OH + PBr_3 \rightarrow 3CH_3CH_2CH_2Br + H_3PO_3 \tag{10.5.8}$$

$$3CH_3CH_2CH_2OH + PI_3 \rightarrow 3CH_3CH_2CH_2I + H_3PO_3 \tag{10.5.9}$$

REACTING ALCOHOLS WITH THIONYL CHLORIDE

Sulfur dichloride oxide (thionyl chloride) has the formula $SOCl_2$. Traditionally, the formula is written as shown, despite the fact that the modern name writes the chlorine before the oxygen (alphabetical order). The sulfur dichloride oxide reacts with alcohols at room temperature to produce a chloroalkane. Sulfur dioxide and hydrogen chloride are given off. Care would have to be taken because both of these are poisonous.

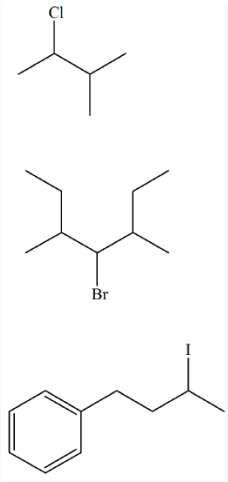
$$CH_3CH_2CH_2OH + SOCl_2 \rightarrow CH_3CH_2CH_2Cl + SO_2 + HCl \tag{10.5.10}$$

The advantage that this reaction has over the use of either of the phosphorus chlorides is that the two other products of the reaction (sulfur dioxide and HCl) are both gases. That means that they separate themselves from the reaction mixture.

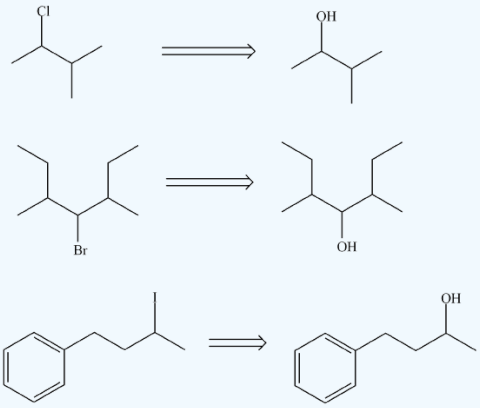
EXERCISE

? EXERCISE 10.5.1

Predict the alcohol required for the synthesis of the following halides:



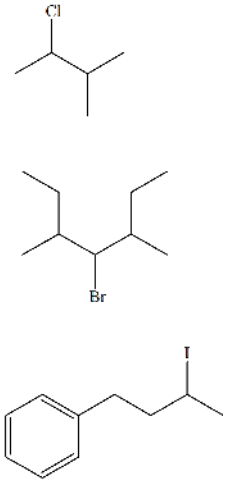
Answer



QUESTIONS

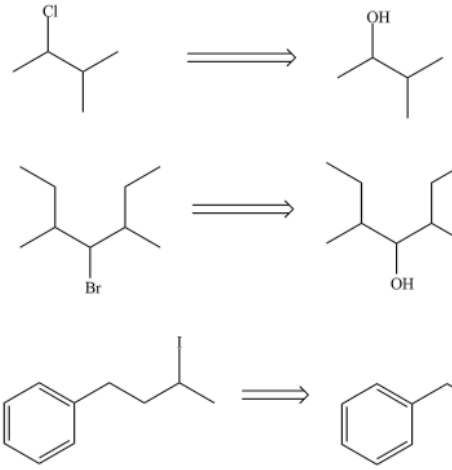
Q10.5.1

Predict the alcohol required for the synthesis of the following halides:



SOLUTIONS

S10.5.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)

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10.6: REACTIONS OF ALKYL HALIDES - GRIGNARD REAGENTS

OBJECTIVES

After completing this section, you should be able to

1. write an equation to describe the formation of a Grignard reagent.
2. give examples of Grignard reagents formed from aryl and vinyl halides as well as from alkyl halides.
3. explain the reactivity of Grignard reagents in terms of the polarity of the carbon-magnesium bond.
4. write an equation for the reaction of a Grignard reagent with a proton donor, such as water.
5. predict the product formed from the reaction of a given organohalide with magnesium followed by a proton donor.
6. identify the organohalide, the reagents, or both, needed to prepare a given alkane.
7. describe how a deuterium atom may be introduced at a specific location in an organic molecule through use of a Grignard reagent.
8. describe at least one limitation on the use of Grignard reagents in organic synthesis.
9. write an equation for the direct conversion of an alkyl halide to an alkane using a hydride donor, such as lithium aluminum hydride.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

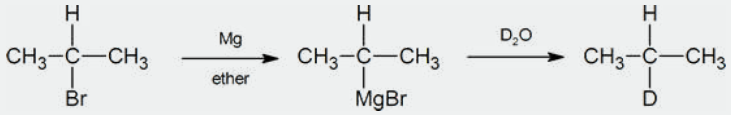
- carbanion
- Grignard reagent

STUDY NOTES

The organomagnesium compounds formed by the reaction of an alkyl or aryl halide with magnesium are called *Grignard reagents*. As you will see throughout the remainder of this course, Grignard reagents can be used to synthesize a wide range of organic compounds and are extremely useful to the organic chemist.

In the introductory section, we tried to stress that the chemistry of alkyl halides is quite different from that of aryl (or vinyl) halides. However, both alkyl and aryl halides react with magnesium to form Grignard reagents.

The reaction of a Grignard reagent with D_2O ("heavy water") provides a convenient method for introducing a deuterium atom (remember D is equivalent to ^2H) into a molecule at a specific location. For example:



The alkali metals (Li, Na, K etc.) and the alkaline earth metals (Mg and Ca, together with Zn) are good reducing agents, the former being stronger than the latter. These same metals reduce the carbon-halogen bonds of alkyl halides. The halogen is converted to a halide anion, and the carbon bonds to the metal which has characteristics similar to a carbanion (R:-).

FORMATION OF ORGANOMETALLIC REAGENTS

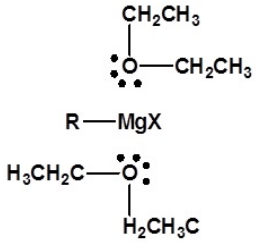
EDIT SECTION

Many organometallic reagents are commercially available, however, it is often necessary to make then. The following equations illustrate these reactions for the commonly used metals lithium and magnesium (R may be hydrogen or alkyl groups in any combination).

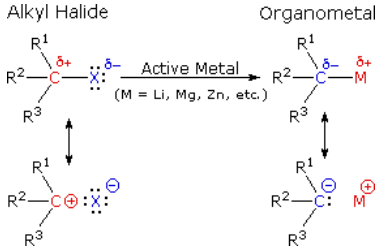
- **An Alkyl Lithium Reagent** $R_3C\text{-}X + 2Li \longrightarrow R_3C\text{-}Li + LiX$
- **A Grignard Regent** $R_3C\text{-}X + Mg \longrightarrow R_3C\text{-}MgX$

Halide reactivity in these reactions increases in the order: Cl < Br < I and Fluorides are usually not used. The alkyl magnesium halides described in the second reaction are called Grignard Reagents after the French chemist, Victor Grignard, who discovered them and received the Nobel prize in 1912 for this work. The other metals mentioned above react in a similar manner, but Grignard and Alky Lithium Reagents most widely used. Although the formulas drawn here for the alkyl lithium and Grignard reagents reflect the stoichiometry of the reactions and are widely used in the chemical literature, they do not accurately depict the structural nature of these remarkable substances. Mixtures of polymeric and other associated and complexed species are in equilibrium under the conditions normally used for their preparation.

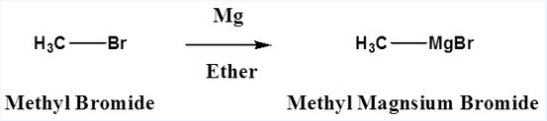
A suitable solvent must be used. For alkyl lithium formation pentane or hexane are usually used. Diethyl ether can also be used but the subsequent alkyl lithium reagent must be used immediately after preparation due to an interaction with the solvent. Ethyl ether or THF are essential for Grignard reagent formation. Lone pair electrons from two ether molecules form a complex with the magnesium in the Grignard reagent (As pictured below). This complex helps stabilize the organometallic and increases its ability to react.

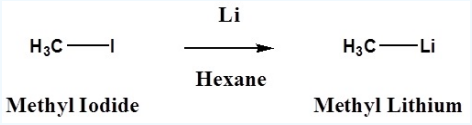


These reactions are obviously substitution reactions, but they cannot be classified as nucleophilic substitutions, as were the earlier reactions of alkyl halides. Because the functional carbon atom has been reduced, the polarity of the resulting functional group is inverted (an originally electrophilic carbon becomes nucleophilic). This change, shown below, makes alkyl lithium and Grignard reagents excellent nucleophiles and useful reactants in synthesis.

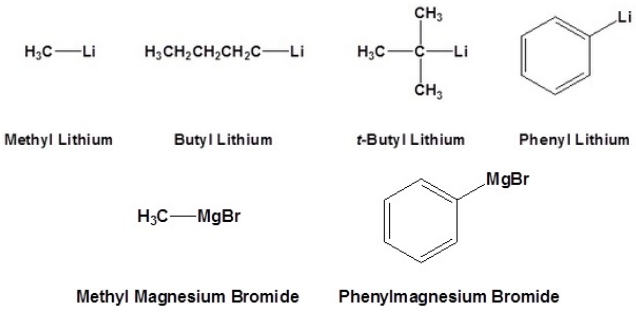


EXAMPLE 10.6.1





COMMON ORGANOMETALLIC REAGENTS

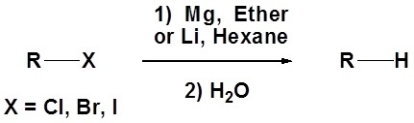


ORGANOMETALLIC REAGENTS AS BASES

These reagents are very strong bases (pKa's of saturated hydrocarbons range from 42 to 50). Although not usually done with Grignard reagents, organolithium reagents can be used as strong bases. Both Grignard reagents and organolithium reagents react with water to form the corresponding hydrocarbon. This is why so much care is needed to insure dry glassware and solvents when working with organometallic reagents.



In fact, the reactivity of Grignard reagents and organolithium reagents can be exploited to create a new method for the conversion of halogens to the corresponding hydrocarbon (illustrated below). The halogen is converted to an organometallic reagent and then subsequently reacted with water to from an alkane.



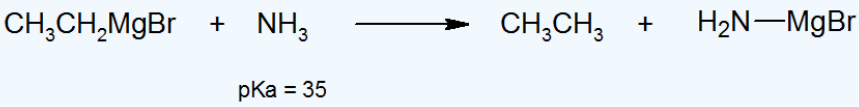
Conjugate base anions of terminal alkynes (acetylide anions) are nucleophiles, and can do both nucleophilic substitution and nucleophilic addition reactions.

EXERCISES

EXERCISE 10.6.1

How strong of a base would you expect ethyl Grignard to be? Would the following reactions be able to take place?





Answer

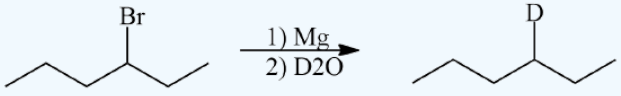
Because hydrocarbons like ethane are very weak acids (pKa = 50), then the corresponding carbanion ($CH_3CH_2^-$) is expected to be a strong base. Both reactions will occur.

EXERCISE 10.6.2

How would you make a deuterated compound from an alkyl halide?

Answer

By first making a Grignard and then exposing it to heavy water.

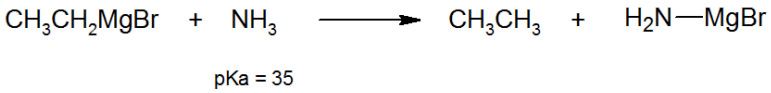


QUESTIONS

Q10.6.1

How strong of a base would you expect ethyl Grignard to be? Would the following reactions be able to take place?





Q10.6.2

How would you make a deuterated compound from an alkyl halide?

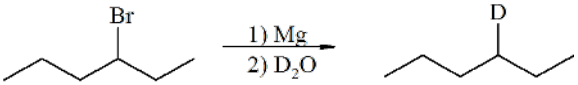
SOLUTIONS

S10.6.1

Because hydrocarbons like ethane are very weak acids (pKa = 50), then the corresponding carbanion ($CH_3CH_2^-$) is expected to be a strong base. Both reactions will occur.

S10.6.2

By first making a Grignard and then exposing it to heavy water.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

10.6: Reactions of Alkyl Halides - Grignard Reagents is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

10.7: ORGANOMETALLIC COUPLING REACTIONS

Objectives

After completing this section, you should be able to

1. write an equation for the formation of an alkyllithium from an alkyl halide.
2. write an equation for the formation of a lithium dialkylcopper (Gilman) reagent from an alkyllithium and copper(I) iodide.
3. write an equation for the coupling of a lithium dialkylcopper reagent with an alkyl halide (i.e., a Corey-House synthesis).
4. draw the structure of the product formed from a given Corey-House synthesis.
5. identify the reagents needed to convert two given organohalides to a specified hydrocarbon through a Corey-House synthesis.

KEY TERMS

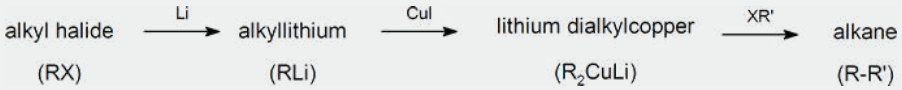
Make certain that you can define, and use in context, the key terms below.

- Corey-House synthesis
- pheromone

STUDY NOTES

A *pheromone* is a chemical released by members of one species to cause specific behavioural or physiological changes in other members of the same species. Examples include sex pheromones, alarm pheromones and trail pheromones.

The *Corey-House synthesis* provides us with a method of coupling together two alkyl groups through the formation of a new carbon-carbon bond. The product of such a reaction is an alkane, and this synthetic method gives us a route for the preparation of unsymmetrical alkanes. The method was developed during the late 1960s by E. J. Corey and Herbert House working independently at Harvard University and Massachusetts Institute of Technology, respectively. The overall synthetic route is shown on the next page. Note that R and R′ represent alkyl groups, which can be the same or different, and X represents a halogen (preferably bromine or iodine).



In order to obtain a good yield of alkane, both R′X and RX should be primary alkyl halides. However, the experimental procedure can be modified so that this synthesis can be carried out using a wide range of alkyl, aryl, vinyl, benzyl and allyl halides. A detailed discussion of these modifications is beyond the scope of this course, but you should be aware of possible limitations in the use of the Corey-House synthesis.

Note: In some textbooks, lithium diorganocoppers are referred to as lithium dialkylcoppers, or cuprates.

GILMAN REAGENTS

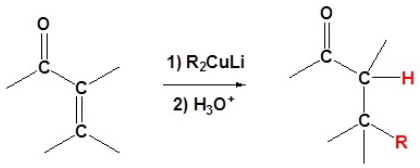
Another important reaction exhibited by organometallic reagents is metal exchange. Organolithium reagents react with cuprous iodide to give a lithium dimethylcopper reagent, which is referred to as a Gilman reagent. Gilman reagents are a source of carbanion like nucleophiles similar to Grignard and Organo lithium reagents. However, the reactivity of organocuprate reagents is slightly different and this difference will be exploited in different situations. In the case of α, β unsaturated carbonyls organocuprate reagents allow for an 1,4 addition of an alkyl group. As we will see later Grignard and Organolithium reagents add alkyl groups 1,2 to α, β unsaturated carbonyls

Organocuprate reagents are made from the reaction of organolithium reagents and CuI

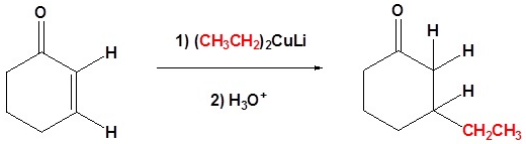
$$2RLi + CuI \rightarrow R_2CuLi + LiI \tag{10.7.1}$$

This acts as a source of R:$^-$

$$2Ch_3Li + CuI \rightarrow (CH_3)_2CuLi + LiI \tag{10.7.2}$$

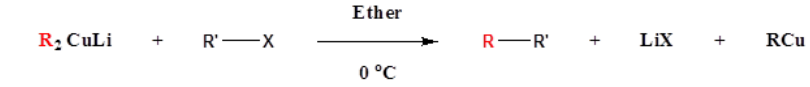


Example



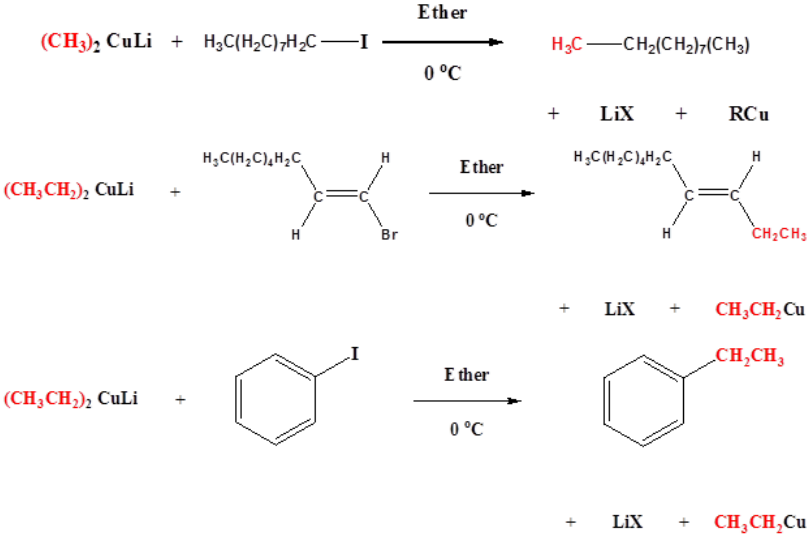
COUPLING REACTIONS WITH GILMAN REAGENTS

The coupling of Giman reactions with organochlorides, organobromides, and organoiodides is useful in organic synthesis because it forms a carbon bond. During the reaction one of the alkyl groups fromt he Gilman reagent replaces the halogen for the organohalide.



Gilman Reagent X = Cl, Br, or I

EXAMPLES



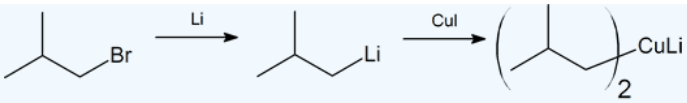
EXERCISE

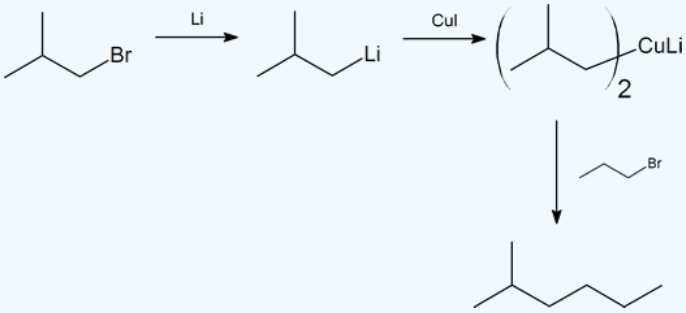
? EXERCISE 10.7.1

1. Starting with alkyl halides containing no more than four carbon atoms, how would you synthesize each of the following alkanes?
   a. 2,5-dimethylhexane
   b. 2-methylhexane

Answer

https://chem.libretexts.org/@go/page/67257





a.

Notice that in (*a*), both the alkyl halides are primary. This fact should ensure a good yield of product. In (*b*) we have the choice of using 2-bromopropane and 1-bromobutane, or 1-bromo-2-methylpropane and 1-bromopropane. We chose the latter as it enables us to use two primary alkyl halides, and hence a simpler procedure

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

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10.8: OXIDATION AND REDUCTION IN ORGANIC CHEMISTRY

Objectives

After completing this section, you should be able to

1. identify organic reactions as being oxidations, reductions, or neither.
2. rank given compounds in order of their oxidation level.

KEY TERMS

Make certain that you can define, and use in context, the terms below.

- oxidation
- reduction

You are undoubtedly already familiar with the general idea of oxidation and reduction: you learned in general chemistry that when a compound or atom is oxidized it loses electrons, and when it is reduced it gains electrons. You also know that oxidation and reduction reactions occur in pairs: if one species is oxidized, another must be reduced at the same time - thus the term 'redox reaction'.

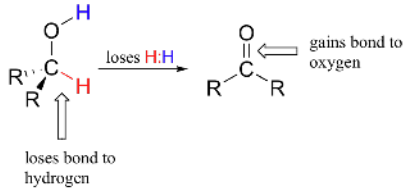
Most of the redox reactions you have seen previously in general chemistry probably involved the flow of electrons from one metal to another, such as the reaction between copper ion in solution and metallic zinc:

$$Cu^{+2}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{+2}_{(aq)} \tag{10.8.1}$$

In organic chemistry, redox reactions look a little different. Electrons in an organic redox reaction often are transferred in the form of a hydride ion - a proton and two electrons. Because they occur in conjunction with the transfer of a proton, these are commonly referred to as **hydrogenation** and **dehydrogenation** reactions: a hydride plus a proton adds up to a hydrogen (H_2) molecule. Be careful - do not confuse the terms hyd**rogen**ation and dehy**drogen**ation with hydration and dehydration - the latter refer to the gain and loss of a *water* molecule (and are *not* redox reactions), while the former refer to the gain and loss of a *hydrogen* molecule.

When a carbon atom in an organic compound loses a bond to hydrogen and gains a new bond to a heteroatom (or to another carbon), we say the compound has been dehydrogenated, or oxidized. A very common biochemical example is the oxidation of an alcohol to a ketone or aldehyde:

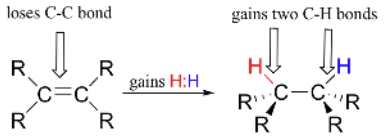
Dehydrogenation (oxidation) of an alcohol



When a carbon atom loses a bond to hydrogen and gains a bond to a heteroatom (or to another carbon atom), it is considered to be an oxidative process because hydrogen, of all the elements, is the least electronegative. Thus, in the process of dehydrogenation the carbon atom undergoes an overall loss of electron density - and loss of electrons is oxidation.

Conversely, when a carbon atom in an organic compound gains a bond to hydrogen and loses a bond to a heteroatom (or to another carbon atom), we say that the compound has been hydrogenated, or reduced. The hydrogenation of a ketone to an alcohol, for example, is overall the reverse of the alcohol dehydrogenation shown above. Illustrated below is another common possibility, the hydrogenation (reduction) of an alkene to an alkane.

Hydrogenation (reduction) of an alkene

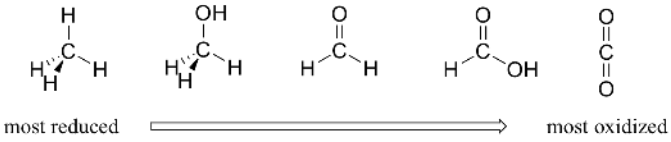


Hydrogenation results in *higher* electron density on a carbon atom(s), and thus we consider process to be one of reduction of the organic molecule.

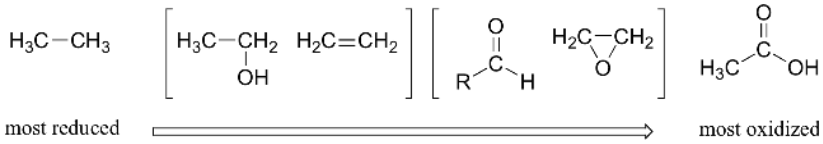
Notice that neither hydrogenation nor dehydrogenation involves the gain or loss of an oxygen *atom*. Reactions which *do* involve gain or loss of one or more oxygen atoms are usually referred to as 'oxygenase' and 'reductase' reactions, and are the subject of section 16.10 and section

17.3.

For the most part, when talking about redox reactions in organic chemistry we are dealing with a small set of very recognizable functional group transformations. It is therefore very worthwhile to become familiar with the idea of 'oxidation states' as applied to organic functional groups. By comparing the relative number of bonds to hydrogen atoms, we can order the familiar functional groups according to oxidation state. We'll take a series of single carbon compounds as an example. Methane, with four carbon-hydrogen bonds, is highly reduced. Next in the series is methanol (one less carbon-hydrogen bond, one more carbon-oxygen bond), followed by formaldehyde, formate, and finally carbon dioxide at the highly oxidized end of the group.



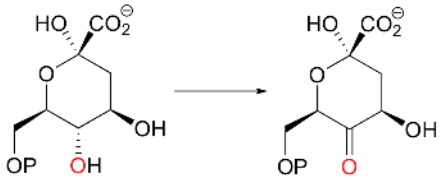
This pattern holds true for the relevant functional groups on organic molecules with two or more carbon atoms:



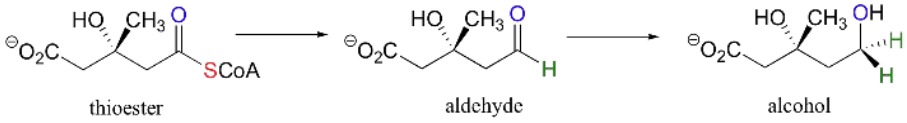
Alkanes are highly reduced, while alcohols - as well as alkenes, ethers, amines, sulfides, and phosphate esters - are one step up on the oxidation scale, followed by aldehydes/ketones/imines and epoxides, and finally by carboxylic acid derivatives (carbon dioxide, at the top of the oxidation list, is specific to the single carbon series).

Notice that in the series of two-carbon compounds above, ethanol and ethene are considered to be in the same oxidation state. You know already that alcohols and alkenes are interconverted by way of addition or elimination of water (section 14.1). When an alcohol is dehydrated to form an alkene, one of the two carbons loses a C-H bond and gains a C-C bond, and thus is oxidized. However, the other carbon loses a C-O bond and gains a C-C bond, and thus is considered to be reduced. Overall, therefore, there is no change to the oxidation state of the molecule.

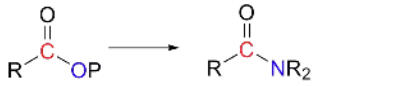
You should learn to recognize when a reaction involves a change in oxidation state in an organic reactant . Looking at the following transformation, for example, you should be able to quickly recognize that it is an oxidation: an alcohol functional group is converted to a ketone, which is one step up on the oxidation ladder.



Likewise, this next reaction involves the transformation of a carboxylic acid derivative (a thioester) first to an aldehyde, then to an alcohol: this is a *double* reduction, as the substrate loses two bonds to heteroatoms and gains two bonds to hydrogens.



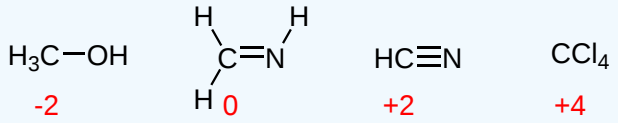
An acyl transfer reaction (for example the conversion of an acyl phosphate to an amide) is *not* considered to be a redox reaction - the oxidation state of the organic molecule is does not change as substrate is converted to product, because a bond to one heteroatom (oxygen) has simply been traded for a bond to another heteroatom (nitrogen).



It is important to be able to recognize when an organic molecule is being oxidized or reduced, because this information tells you to look for the participation of a corresponding redox agent that is being reduced or oxidized- remember, oxidation and reduction always occur in tandem! We will soon learn in detail about the most important biochemical and laboratory redox agents.

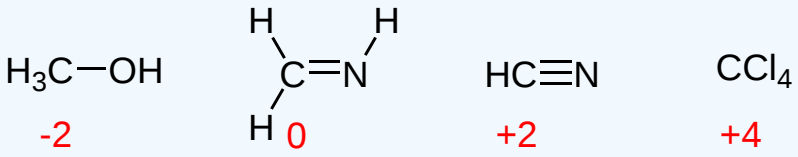
Worked Example 10.8.1

1) Rank the following compounds in order of increasing oxidation level:



Answer

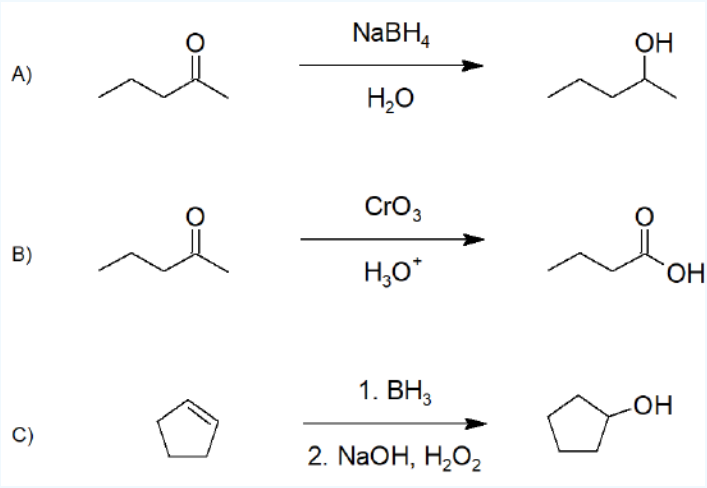
The easiest way to solve this problem is to calculate the oxidation level of the carbon in each compound. Remembering that hydrogens decrease the oxidation level by one, electronegative elements increase the oxidation level by one, and carbons do not change the oxidation level, the oxidation level of each carbon can be calculate. The carbon in CH_3OH has three bonds to hydrogens and one bond to oxygen so it oxidation level is 3(-1) + 1(+1) = -2. The carbon in HCN has one bond to hydrogens and three bonds to nitrogen so it oxidation level is 1(-1) + 3(+1) = +2. The carbon in CH_2NH has two bonds to hydrogens and two bond to nitrogen so it oxidation level is 2(-1) + 2(+1) = 0. The carbon in CCl_4 has zero bonds to hydrogens and four bonds to chlorine so it oxidation level is o(-1) + 4(+1) = +4. The compounds now can be listing in the following order of increasing oxidation level.



EXERCISE

? EXERCISE 10.8.1

In each case state whether the reaction is an oxidation or reduction of the organic compound.



Answer

A – Reduction

B – Oxidation

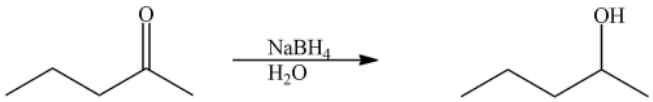
C – Neither. One carbon is reduced from alkene to alkane and another carbon is oxidized from alkene to the alcohol.

QUESTIONS

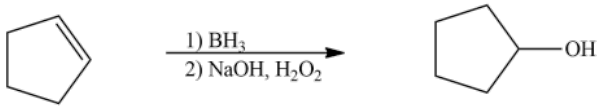
Q10.8.1

In each case state whether the reaction is an oxidation or reduction of the organic compound.

A)



B)



SOLUTIONS

S10.8.1

A – Reduction

B – Oxidation

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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10.S: ORGANOHALIDES (SUMMARY)

CONCEPTS & VOCABULARY

10.1 Introduction to Organohalides

- Alkyl halides (and allyl and benzyl halides) are more reactive than vinyl and aryl halides.

10.2 Names and Properties of Alkyl Halides

- Reactivity of alkyl halides is often related to the substitution of the carbon atom the halogen is attached to.
- Alkyl halides are categorized by the number of bonds to other alkyl groups (**primary**, **secondary**, and **tertiary**).
- Carbon-halogen bonds are polarized with partial positive charges on carbon and partial negative charges on the halogen.
- Fluorine is the most electronegative of the halogens while iodine is the least electronegative.
- Iodine is the largest of the halogens yielding the longest/weakest bonds to carbon of the halogens.
- Since haloalkanes have dipole-dipole interactions, they have greater intermolecular forces than similar sized alkanes and therefore higher boiling points.
- Alkyl halides are either slightly soluble or insoluble in water, but are soluble in organic solvents.

10.3 Preparing Alkyl Halides from Alkanes - Radical Halogenation

- Halogenation of alkanes is exothermic, so it is energetically favorable.
- Radical chain mechanisms consist of three steps: **initiation**, **propagation** and **termination**.
- Hydrogens on more substituted carbon atoms are more reactive to radical halogenation.

10.4 Preparing Alkyl Halides from Alkenes - Allylic Bromination

- More substituted radicals and radicals with resonance structures are more stable than other radicals.
- Radical substitution can be carried out at the allylic or benzylic carbon by reacting with NBS.

10.5 Stability of the Allyl Radical - Resonance Revisited

- Allyl cations, anions and radicals have resonance structures. To draw these resonance structures non-bonded and pi-bond electrons can be moved.
- Resonance hybrids are used to show the combination of all resonance structures for a molecule or ion.

10.6 Preparing Alkyl Halides form Alcohols

- Alcohols can be reacted with hydrohalogen acids or a mixture of halogen salts and a stronger acid (to form hydrohalogen acids *in situ*).
- Alcohols will also react with thionyl chloride or with phosphorus halides to from haloalkanes.

10.7 Reactions of Alkyl Halides - Grignard Reactions

- Organometallic reagents can be formed from alkyl halides and reactive metals (such as lithium and magnesium).
- Alkyl magnesium halide compounds are callled Grignard reagents.
- Grignard reagents react as bases where the alkyl group gets protonated and the metal complexes to the conjugate base of the reacting acid.

10.8 Organometallic Coupling Reactions

- Lithium dialkyl copper compounds are called Gilman reagents.
- Gilman reagents have different reactivity from the other organometallics (lithium and Grignard reagents).
- Organometallics can be reacted with alkyl halides to join to alkyl groups (coupling reactions).

10.9 Oxidation and Reduction in Organic Chemistry

- Gaining bonds to hydrogen for organic molecules is reduction.
- Losing bonds to hydrogen for organic molecules is oxidation.

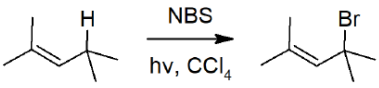
SKILLS TO MASTER

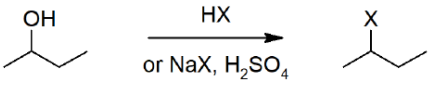
- Skill 10.1 Differentiate between types of halides (alkyl, allyl, aryl, benzyl, and vinyl).
- Skill 10.2 Differentiate between substitution of alkyl halides (primary, secondary, and tertiary).
- Skill 10.3 Identify relative reactivity of carbon-hydrogen bonds to radical halogenation.
- Skill 10.4 Draw resonance structures for radical compounds.

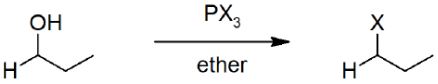
- Skill 10.5 Draw mechanisms for radical halogenation of alkanes (initiation, propagation and termination).
- Skill 10.6 Calculate the enthalpy change of a reaction using bond dissociation energies of reactants and products.
- Skill 10.7 Determine products for allylic bromination reactions.
- Skill 10.8 Draw resonance structures for allylic and other similar compounds and ions.
- Skill 10.9 Draw products of reactions of alcohols to form alkyl halides.
- Skill 10.10 Write equations to form Grignard reagents from alkyl halides.
- Skill 10.11 Draw reaction products for Grignard reagents acting as bases.
- Skill 10.12 Write equations for the formation of Gilman reagents.
- Skill 10.13 Draw reaction products of organometallic coupling reactions.
- Skill 10.14 Explain oxidation and reduction in organic molecules.

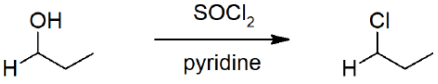
SUMMARY OF REACTIONS

Preparation of Alkyl Halides

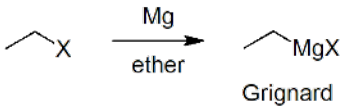


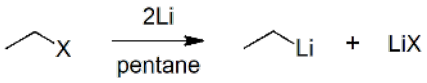


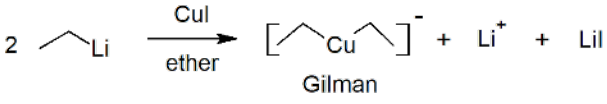


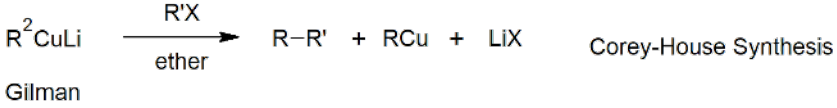


Reactions Alkyl Halides









CONTRIBUTORS

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- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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CHAPTER OVERVIEW

11: REACTIONS OF ALKYL HALIDES- NUCLEOPHILIC SUBSTITUTIONS AND ELIMINATIONS

LEARNING OBJECTIVES

After you have completed Chapter 11, you should be able to

1. fulfill all of the detailed objectives listed under each individual section.
2. use the reactions studied in this chapter with those from earlier ones when designing multistep syntheses.
3. use the reactions and concepts discussed in this chapter to solve road map problems.
4. define, and use in context, the key terms introduced.

In this course, you have already seen several examples of nucleophilic substitution reactions; now you will see that these reactions can occur by two different mechanisms. You will study the factors that determine which mechanism will be in operation in a given situation, and examine possible ways for increasing or decreasing the rates at which such reactions occur. The stereochemical consequences of both mechanisms will also be discussed.

Elimination reactions often accompany nucleophilic substitution; so these reactions are also examined in this chapter. Again you will see that two different mechanisms are possible, and, as in the case of nucleophilic substitution reactions, chemists have learned a great deal about the factors that determine which mechanism will be observed when a given alkyl halide undergoes such a reaction.

11.0: Introduction
11.1: The Discovery of Nucleophilic Substitution Reactions
11.2: The SN2 Reaction
11.3: Characteristics of the SN2 Reaction
11.4: The SN1 Reaction
11.5: Characteristics of the SN1 Reaction
11.6: Biological Substitution Reactions
11.7: Elimination Reactions - Zaitsev's Rule
11.8: The E2 Reaction and the Deuterium Isotope Effect
11.9: The E2 Reaction and Cyclohexane Conformation
11.10: The E1 and E1cB Reactions
11.11: Biological Elimination Reactions
11.12: A Summary of Reactivity - SN1, SN2, E1, E1cB, and E2
11.S: Reactions of Alkyl Halides - Nucleophilic Substitutions and Eliminations (Summary)

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11.0: INTRODUCTION

Objective

After completing this section, you should be able to identify substitution and elimination as being the two most important reactions of alkyl halides.

STUDY NOTES

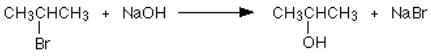
Alkyl halides are electrophiles, which means they can undergo nucleophilic substitution and base-induced elimination reactions. These reaction types offer a large and useful range of reactions for organic synthesis in the laboratory.

THE REACTIONS

Both reactions involve heating the halogenoalkane under reflux with sodium or potassium hydroxide solution.

NUCLEOPHILIC SUBSTITUTION

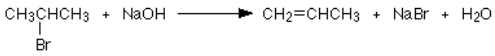
The hydroxide ions present are good nucleophiles, and one possibility is a replacement of the halogen atom by an -OH group to give an alcohol via a nucleophilic substitution reaction.



In the example, 2-bromopropane is converted into propan-2-ol.

ELIMINATION

Halogenoalkanes also undergo elimination reactions in the presence of sodium or potassium hydroxide.



The 2-bromopropane has reacted to give an alkene - propene.

Notice that a hydrogen atom has been removed from one of the end carbon atoms together with the bromine from the centre one. In all simple elimination reactions the things being removed are on adjacent carbon atoms, and a double bond is set up between those carbons.

WHAT DECIDES WHETHER YOU GET SUBSTITUTION OR ELIMINATION?

The reagents you are using are the same for both substitution or elimination - the halogenoalkane and either sodium or potassium hydroxide solution. In all cases, you will get a mixture of both reactions happening - some substitution and some elimination. What you get most of depends on a number of factors.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Jim Clark (Chemguide.co.uk)

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11.1: THE DISCOVERY OF NUCLEOPHILIC SUBSTITUTION REACTIONS

Objectives

After completing this section, you should be able to

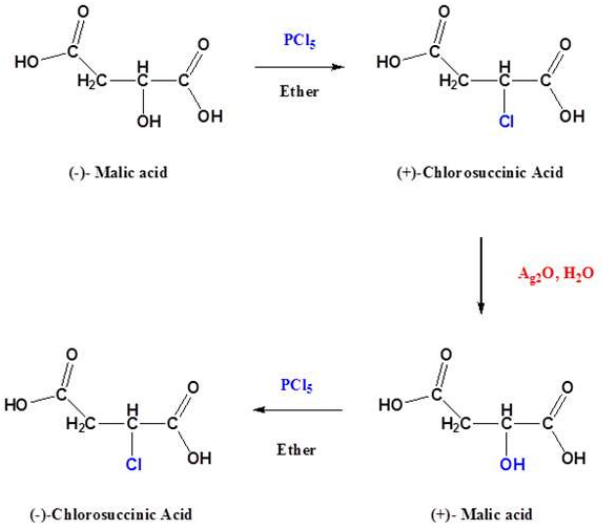
1. write an equation to represent the Walden inversion.
2. write a short paragraph describing the Walden inversion.
3. describe, using equations, a series of reactions interconverting two enantiomers of 1-phenyl-2-propanol which led to the conclusion that nucleophilic substitution of primary and secondary alkyl halides proceeds with inversion of configuration.

STUDY NOTES

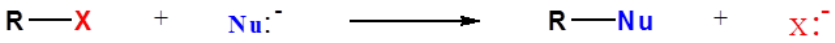
The IUPAC name for malic acid is 2-hydroxybutanedioic acid. This acid is produced by apples, a fact which seems to have been appreciated by the British novelist Thomas Hardy in *The Woodlanders*:

Up, upward they crept, a stray beam of the sun alighting every now and then like a star on the blades of the pomace-shovels, which had been converted to steel mirrors by the action of the malic acid.

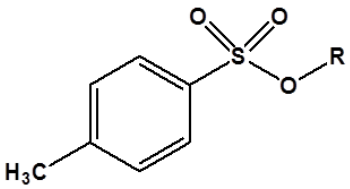
In 1896, the German chemist Paul Walden discovered that he could interconvert pure enantiomeric (+) and (-) malic acids through a series of reactions. This conversion meant that there was some kind of change in the stereo chemistry made during the reaction.



There reactions are currently referred to as nucleophilic substitution reaction because each step involves the substitution of one nucleophile by another. Therese reactions are one of the most common and versatile reaction types in organic chemistry.

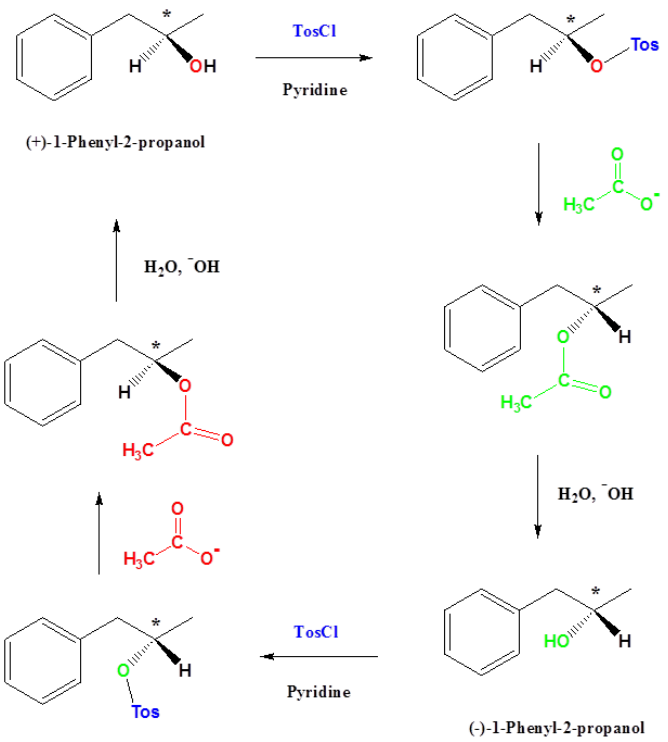


Further investigations into these reaction were under taken during the 1920's and 1930's to clarify the mechanism and clarify how the inversion of configurations occur. These reactions involved the nucleophilic substitution of an alkyl p-toluenesulfonate (called a tosylate group). For this purpose the tosylate groups acts as a halogen substituent. In the series of reactions (+)-1-phenyl-2-propanol is interconverted with (-)-1-phenyl-2-propanol.

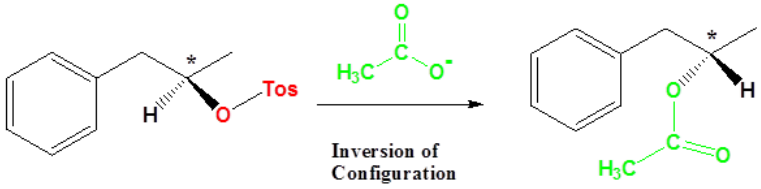


p-Toluenesulfonate (Tosylate)

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It was determined that the reaction with acetate was causing the stereochemical configuration to be inverted.



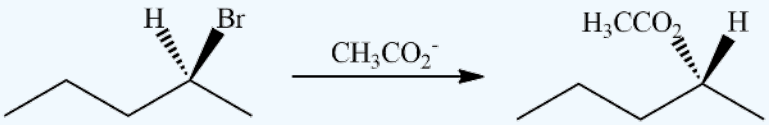
EXERCISE

? EXERCISE 11.1.1

1) Predict the product of a nucleophilic substitution of (S)-2-bromopentane reacting with $CH_3CO_2^-$, Show stereochemistry.

Answer

1)



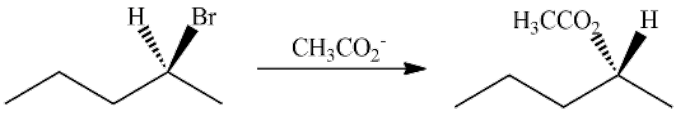
QUESTIONS

Q11.1.1

Predict the product of a nucleophilic substitution of (S)-2-bromopentane reacting with $CH_3CO_2^-$, Show stereochemistry.

SOLUTIONS

S11.1.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

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11.2: THE SN2 REACTION

Objectives

After completing this section, you should be able to

1. write an expression relating reaction rate to the concentration of reagents for a second-order reaction.
2. determine the order of a chemical reaction from experimentally obtained rate data.
3. describe the essential features of the S_N2 mechanism, and draw a generalized transition state for such a reaction.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- bimolecular
- kinetics
- rate coefficient
- rate equation
- reaction rate
- second-order reaction
- S_N2

STUDY NOTES

Most of the key terms introduced in this section should already be familiar to you from your previous general chemistry course.

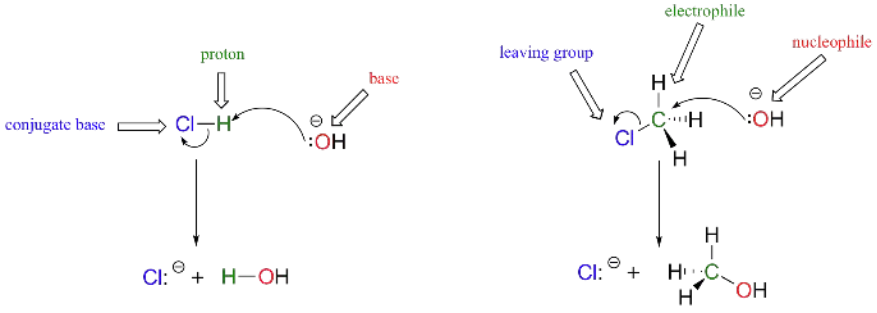
Reaction rate refers to the change in concentration of a reactant or product per unit of time. Using strict SI units, reaction rates are expressed in mol · L^{-1} · s^{-1}, but in some textbooks you will find this value written as M/s. In general, the reaction rate of a given reaction changes with time, as it is dependent on the concentration of one or more of the reactants.

An equation which shows the relationship between the reaction rate and the concentrations of the reactants is known as the rate equation. All rate equations contain a proportionality constant, usually given the symbol *k*, which is known as the rate coefficient. Some textbooks refer to this value as the "rate constant," but this name is a little misleading as it is not a true constant. The rate coefficient of a given reaction depends on such factors as temperature and the nature of the solvent.

S_N2 is short for "bimolecular nucleophilic substitution." You will encounter abbreviations for other types of reactions later in this chapter.

If you are unclear on the point about the inversion of configuration during an S_N2 reaction, construct a molecular model of a chiral alkyl halide, the transition state formed when this substance reacts with a nucleophile in an S_N2 process, and the product obtained from this reaction.

In many ways, the proton transfer process in a Brønsted-Lowry acid-base reaction can be thought of as simply a special kind of nucleophilic substitution reaction, one in which the electrophile is a hydrogen rather than a carbon.



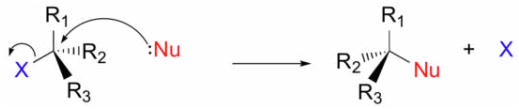
acid-base reaction **nucleophilic substitution**

In both reaction types, we are looking at very similar players: an electron-rich species (the nucleophile/base) attacks an electron-poor species (the electrophile/proton), driving off the leaving group/conjugate base.

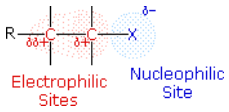
In the next few sections, we are going to be discussing some general aspects of nucleophilic substitution reactions, and in doing so it will simplify things greatly if we can use some abbreviations and generalizations before we dive into real examples.

Instead of showing a specific nucleophile like hydroxide, we will simply refer to the nucleophilic reactant as 'Nu'. In a similar fashion, we will call the leaving group 'X'. We will see as we study actual reactions that leaving groups are sometimes negatively charged, sometimes neutral, and sometimes positively charged. We will also see some examples of nucleophiles that are negatively charged and some that are neutral. Therefore, in this general picture we will not include a charge designation on the 'X' or 'Nu' species. In the same way, we will see later that nucleophiles and leaving groups are sometimes protonated and sometimes not, so for now, for the sake of simplicity, we will not include protons on 'Nu' or 'X'. We will generalize the three other groups bonded on the electrophilic central carbon as R_1, R_2, and R_3: these symbols could represent hydrogens as well as alkyl groups. Finally, in order to keep figures from becoming too crowded, we will use in most cases the line structure convention in which the central, electrophilic carbon is not drawn out as a 'C'.

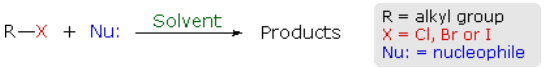
Here, then, is the generalized picture of a concerted (single-step) nucleophilic substitution reaction:



The functional group of alkyl halides is a carbon-halogen bond, the common halogens being fluorine, chlorine, bromine and iodine. With the exception of iodine, these halogens have electronegativities significantly greater than carbon. Consequently, this functional group is polarized so that the carbon is electrophilic and the halogen is nucleophilic, as shown in the drawing on the right. Two characteristics other than electronegativity also have an important influence on the chemical behavior of these compounds. The first of these is covalent bond strength. The strongest of the carbon-halogen covalent bonds is that to fluorine. Remarkably, this is the strongest common single bond to carbon, being roughly 30 kcal/mole stronger than a carbon-carbon bond and about 15 kcal/mole stronger than a carbon-hydrogen bond. Because of this, **alkyl fluorides and fluorocarbons in general are chemically and thermodynamically quite stable**, and do not share any of the reactivity patterns shown by the other alkyl halides. The carbon-chlorine covalent bond is slightly weaker than a carbon-carbon bond, and the bonds to the other halogens are weaker still, the bond to iodine being about 33% weaker. The second factor to be considered is the relative stability of the corresponding halide anions, which is likely the form in which these electronegative atoms will be replaced. This stability may be estimated from the relative acidities of the H-X acids, assuming that the strongest acid releases the most stable conjugate base (halide anion). With the exception of HF ($pK_a = 3.2$), all the hydrohalic acids are very strong, small differences being in the direction HCl < HBr < HI.

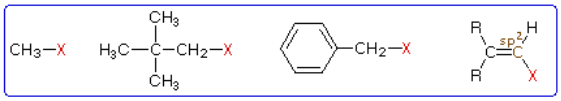


In order to understand why some combinations of alkyl halides and nucleophiles give a substitution reaction, whereas other combinations give elimination, and still others give no observable reaction, we must investigate systematically the way in which changes in reaction variables perturb the course of the reaction. The following general equation summarizes the factors that will be important in such an investigation.

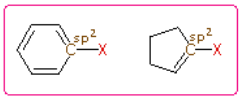


One conclusion, relating the structure of the R-group to possible products, should be immediately obvious. **If R- has no beta-hydrogens an elimination reaction is not possible**, unless a structural rearrangement occurs first. The first four halides shown on the left below do not give elimination reactions on treatment with base, because they have no β-hydrogens. The two halides on the right do not normally undergo such reactions because the potential elimination products have highly strained double or triple bonds.

It is also worth noting that sp^2 hybridized C–X compounds, such as the three on the right, do not normally undergo nucleophilic substitution reactions, unless other functional groups perturb the double bond(s).



no β-hydrogens



strained elimination product

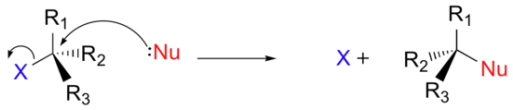
Using the general reaction shown above as our reference, we can identify the following variables and observables.

Variables	**R** change α-carbon from 1º to 2º to 3º if the α-carbon is a chiral center, set as (*R*) or (*S*) **X** change from Cl to Br to I (F is relatively unreactive) **Nu:** change from anion to neutral; change basicity; change polarizability **Solvent** polar vs. non-polar; protic vs. non-protic
Observables	**Products** substitution, elimination, no reaction. **Stereospecificity** if the α-carbon is a chiral center what happens to its configuration? **Reaction Rate** measure as a function of reactant concentration.

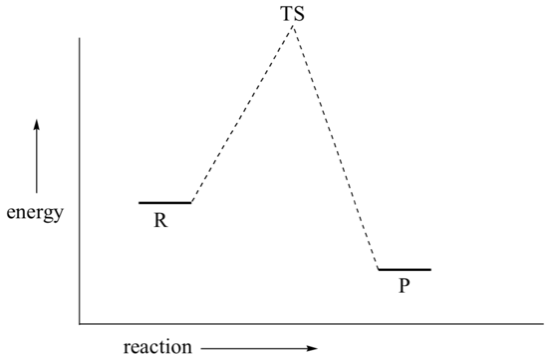
When several reaction variables may be changed, it is important to isolate the effects of each during the course of study. In other words: **only one variable should be changed at a time**, the others being held as constant as possible. For example, we can examine the effect of changing the halogen substituent from Cl to Br to I, using ethyl as a common R–group, cyanide anion as a common nucleophile, and ethanol as a common solvent. We would find a common substitution product, C_2H_5–CN, in all cases, but the speed or rate of the reaction would increase in the order: Cl < Br < I. This reactivity order reflects both the strength of the C–X bond, and the stability of $X^{(-)}$ as a leaving group, and leads to the general conclusion that alkyl iodides are the most reactive members of this functional class.

THE S_N2 MECHANISM

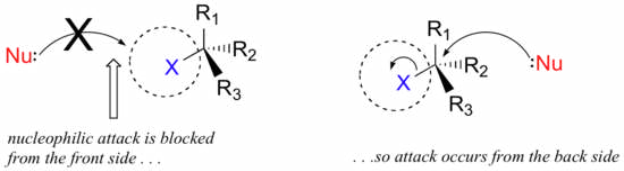
There are two mechanistic models for how an alkyl halide can undergo nucleophilic substitution. In the first picture, the reaction takes place in a single step, and bond-forming and bond-breaking occur simultaneously. (In all figures in this section, 'X' indicates a halogen substituent).



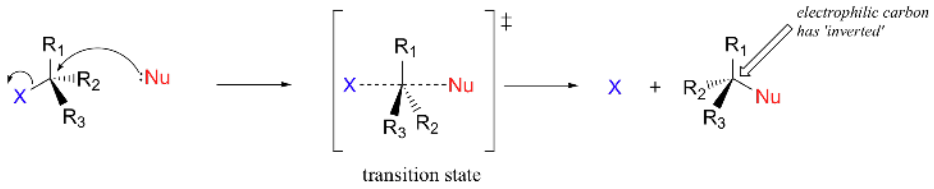
This is called an '**S_N2**' mechanism. In the term S_N2, S stands for 'substitution', the subscript N stands for 'nucleophilic', and the number 2 refers to the fact that this is a **bimolecular reaction**: the overall rate depends on a step in which two separate molecules (the nucleophile and the electrophile) collide. A potential energy diagram for this reaction shows the transition state (TS) as the highest point on the pathway from reactants to products.



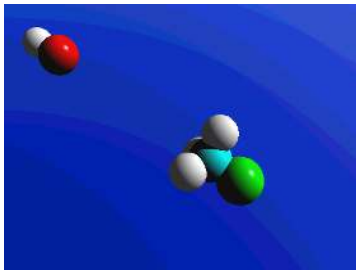
If you look carefully at the progress of the S_N2 reaction, you will realize something very important about the outcome. The nucleophile, being an electron-rich species, must attack the electrophilic carbon from the *back side* relative to the location of the leaving group. Approach from the front side simply doesn't work: the leaving group - which is also an electron-rich group - blocks the way.



The result of this backside attack is that the stereochemical configuration at the central carbon *inverts* as the reaction proceeds. In a sense, the molecule is turned inside out. At the transition state, the electrophilic carbon and the three 'R' substituents all lie on the same plane.



What this means is that S_N2 reactions whether enzyme catalyzed or not, are inherently stereoselective: when the substitution takes place at a stereocenter, we can confidently predict the stereochemical configuration of the product. Below is an animation illustrating the principles we have just learned, showing the S_N2 reaction between hydroxide ion and methyl iodide. Notice how backside attack by the hydroxide nucleophile results in inversion at the tetrahedral carbon electrophile.



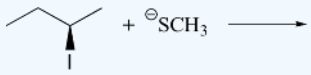
EXAMPLE \PageIndex1



(S)-2-Chlorobutane **(R)-2-Butanol**

EXERCISE \PageIndex1

Predict the structure of the product in this S_N2 reaction. Be sure to specify stereochemistry.



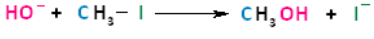
Answer



We will be contrasting about two types of nucleophilic substitution reactions. One type is referred to as **unimolecular nucleophilic substitution (S_N1)**, whereby the rate determining step is unimolecular and **bimolecular nucleophilic substitution (S_N2)**, whereby the rate determining step is bimolecular. We will begin our discussion with S_N2 reactions, and discuss S_N1 reactions elsewhere.

BIOMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTIONS AND KINETICS

In the term S_N2, the S stands for substitution, the N stands for nucleophilic, and the number two stands for bimolecular, meaning there are two molecules involved in the rate determining step. The rate of bimolecular nucleophilic substitution reactions depends on the concentration of both the haloalkane and the nucleophile. To understand how the rate depends on the concentrations of both the haloalkane and the nucleophile, let us look at the following example. The hydroxide ion is the nucleophile and methyl iodide is the haloalkane.



$$\text{Rate} = k[CH_3{-}I][HO^-]$$

If we were to double the concentration of either the haloalkane or the nucleophile, we can see that the rate of the reaction would proceed twice as fast as the initial rate.

$$\text{Rate}_1 = k[CH_3-I][HO^-]$$
$$\text{Rate}_2 = 2k[CH_3-I][HO^-]$$
$$\text{Rate}_2 = 2\,\text{Rate}_1$$

If we were to double the concentration of both the haloalkane and the nucleophile, we can see that the rate of the reaction would proceed four times as fast as the initial rate.

$$\text{Rate}_1 = k[CH_3-I][HO^-]$$
$$\text{Rate}_2 = 4k[CH_3-I][HO^-]$$
$$\text{Rate}_2 = 4\,\text{Rate}_1$$

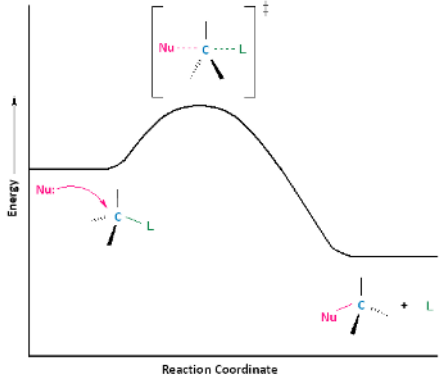
The bimolecular nucleophilic substitution reaction follows second-order kinetics; that is, the rate of the reaction depends on the concentration of two first-order reactants. In the case of bimolecular nucleophilic substitution, these two reactants are the haloalkane and the nucleophile. For further clarification on reaction kinetics, the following links may facilitate your understanding of rate laws, rate constants, and second-order kinetics:

- Definition of a Reaction Rate
- Rate Laws and Rate Constants
- The Determination of the Rate Law
- Second-Order Reactions

BIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTIONS ARE CONCERTED

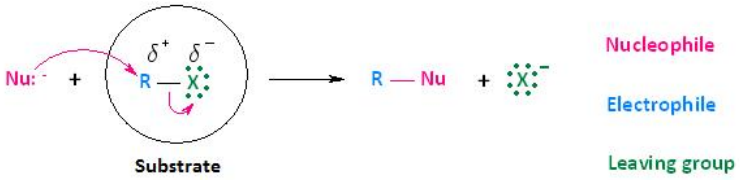
Bimolecular nucleophilic substitution (SN_2) reactions are **concerted**, meaning they are a **one step process**. This means that the process whereby the nucleophile attacks and the leaving group leaves is simultaneous. Hence, the bond-making between the nucleophile and the electrophilic carbon occurs at the same time as the bond-breaking between the electophilic carbon and the halogen.

The potential energy diagram for an SN_2 reaction is shown below. Upon nucleophilic attack, a single transition state is formed. A transition state, unlike a reaction intermediate, is a very short-lived species that cannot be isolated or directly observed. Again, this is a single-step, concerted process with the occurrence of a single transition state.

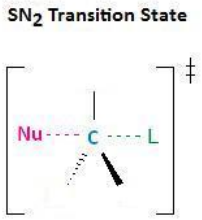


STERICALLY HINDERED SUBSTRATES WILL REDUCE THE S_N2 REACTION RATE

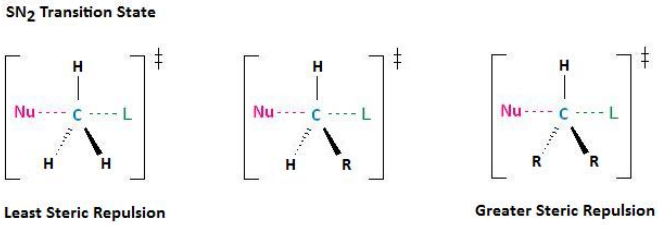
Now that we have discussed the effects that the leaving group, nucleophile, and solvent have on biomolecular nucleophilic substitution (S_N2) reactions, it's time to turn our attention to how the substrate affects the reaction. Although the substrate, in the case of nucleophilic substitution of haloalkanes, is considered to be the entire molecule circled below, we will be paying particular attention to the alkyl portion of the substrate. In other words, we are most interested in the electrophilic center that bears the leaving group.



In the section Kinetics of Nucleophilic Substitution Reactions, we learned that the SN_2 transition state is very crowded. Recall that there are a total of five groups around the electrophilic center, the nucleophile, the leaving group, and three substituents.

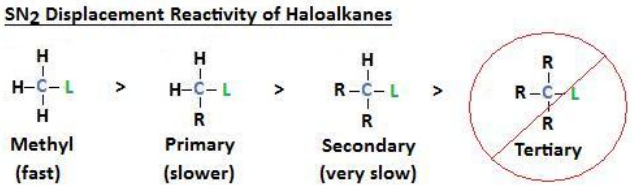


If each of the three substituents in this transition state were small hydrogen atoms, as illustrated in the first example below, there would be little steric repulsion between the incoming nucleophile and the electrophilic center, thereby increasing the ease at which the nucleophilic substitution reaction can occur. Remember, for the SN_2 reaction to occur, the nucleophile must be able to attack the electrophilic center, resulting in the expulsion of the leaving group. If one of the hydrogens, however, were replaced with an R group, such as a methyl or ethyl group, there would be an increase in steric repulsion with the incoming nucleophile. If two of the hydrogens were replaced by R groups, there would be an even greater increase in steric repulsion with the incoming nucleophile.



How does steric hindrance affect the rate at which an SN_2 reaction will occur? As each hydrogen is replaced by an R group, the rate of reaction is significantly diminished. This is because the addition of one or two R groups shields the backside of the electrophilic carbon, impeding nucleophilic attack.

The diagram below illustrates this concept, showing that electrophilic carbons attached to three hydrogen atoms results in faster nucleophilic substitution reactions, in comparison to primary and secondary haloalkanes, which result in nucleophilic substitution reactions that occur at slower or much slower rates, respectively. Notice that a tertiary haloalkane, that which has three R groups attached, does not undergo nucleophilic substitution reactions at all. The addition of a third R group to this molecule creates a carbon that is entirely blocked.



SUBSTITUTES ON NEIGHBORING CARBONS SLOW NUCLEOPHILIC SUBSTITUTION REACTIONS

Previously we learned that adding R groups to the electrophilic carbon results in nucleophilic substitution reactions that occur at a slower rate. What if R groups are added to neighboring carbons? It turns out that the addition of substitutes on neighboring carbons will slow nucleophilic substitution reactions as well.

In the example below, 2-methyl-1-bromopropane differs from 1-bromopropane in that it has a methyl group attached to the carbon that neighbors the electrophilic carbon. The addition of this methyl group results in a significant decrease in the rate of a nucleophilic substitution reaction.



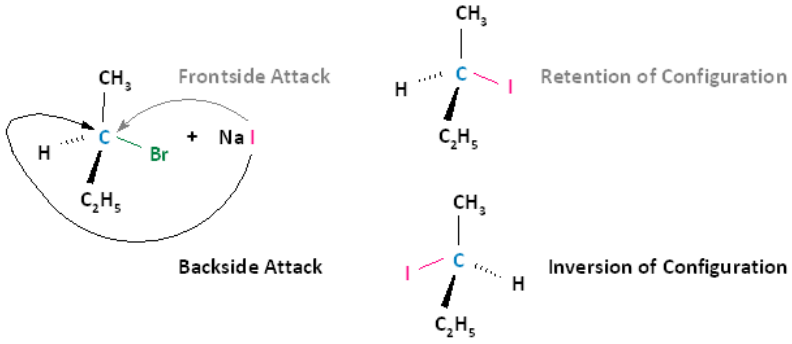
If R groups were added to carbons farther away from the electrophilic carbon, we would still see a decrease in the reaction rate. However, branching at carbons farther away from the electrophilic carbon would have a much smaller effect.

FRONTSIDE VS. BACKSIDE ATTACKS

A biomolecular nucleophilic substitution (S_N2) reaction is a type of nucleophilic substitution whereby a lone pair of electrons on a nucleophile attacks an electron deficient electrophilic center and bonds to it, resulting in the expulsion of a leaving group. It is possible for the nucleophile to attack the electrophilic center in two ways.

- **Frontside Attack:** In a frontside attack, the nucleophile attacks the electrophilic center on the same side as the leaving group. When a frontside attack occurs, the stereochemistry of the product remains the same; that is, we have retention of configuration.
- **Backside Attack:** In a backside attack, the nucleophile attacks the electrophilic center on the side that is opposite to the leaving group. When a backside attack occurs, the stereochemistry of the product does not stay the same. There is inversion of configuration.

The following diagram illustrates these two types of nucleophilic attacks, where the frontside attack results in retention of configuration; that is, the product has the same configuration as the substrate. The backside attack results in inversion of configuration, where the product's configuration is opposite that of the substrate.

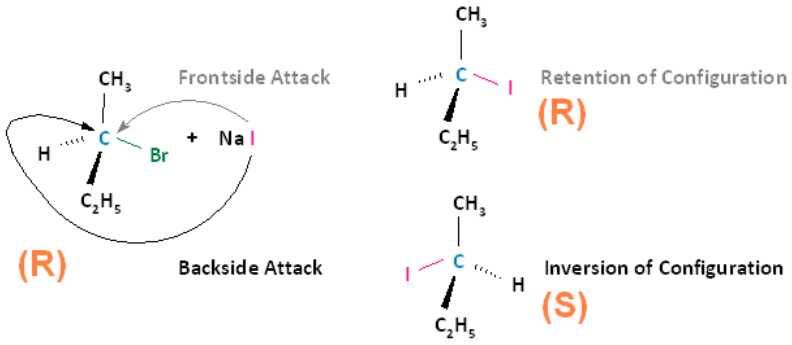


Experimental Observation: All S_N2 Reactions Proceed With Nucleophilic Backside Attacks

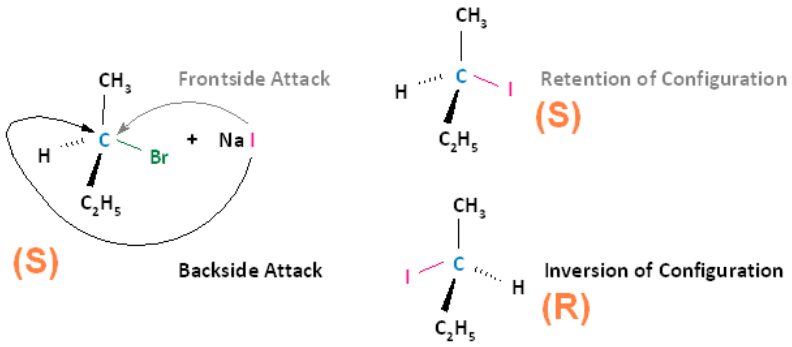
Experimental observation shows that all S_N2 reactions proceed with inversion of configuration; that is, the nucleophile will always attack from the backside in all S_N2 reactions. To think about why this might be true, remember that the nucleophile has a lone pair of electrons to be shared with the electrophilic center, and the leaving group is going to take a lone pair of electrons with it upon leaving. Because like charges repel each other, the nucleophile will always proceed by a backside displacement mechanism.

S_N2 REACTIONS ARE STEREOSPECIFIC

The S_N2 reaction is stereospecific. A stereospecific reaction is one in which different stereoisomers react to give different stereoisomers of the product. For example, if the substrate is an R enantiomer, a frontside nucleophilic attack results in retention of configuration, and the formation of the R enantiomer. A backside nucleophilic attack results in inversion of configuration, and the formation of the S enantiomer.



Conversely, if the substrate is an S enantiomer, a frontside nucleophilic attack results in retention of configuration, and the formation of the S enantiomer. A backside nucleophilic attack results in inversion of configuration, and the formation of the R enantiomer.



In conclusion, S_N2 reactions that begin with the R enantiomer as the substrate will form the S enantiomer as the product. Those that begin with the S enantiomer as the substrate will form the R enantiomer as the product. This concept also applies to substrates that are *cis* and substrates that are *trans*. If the *cis* configuration is the substrate, the resulting product will be *trans*. Conversely, if the *trans* configuration is the substrate, the resulting product will be *cis*.

EXERCISES

? EXERCISE \PageIndex2

1) The reaction below follows the S_N2 mechanism.



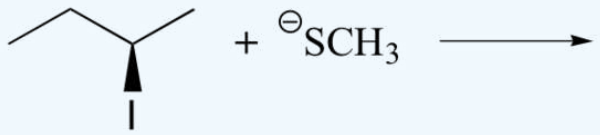
a) Write the rate law for this reaction.

b) Determine the value of the rate coefficient, k, if the initial concentrations are 0.01 M CH_3Cl, 0.01 M NaOH, and the initial reaction rate is 6 x 10^{-10} M/s.

c) Calculate the initial reaction rate if the initial reactant concentrations are changed to 0.02 M CH_3Cl and 0.0005 M NaOH.

2) Predict the product of a nucleophilic substitution of (S)-2-bromopentane reacting with $CH_3CO_2^-$, Show stereochemistry.

3) Predict the structure of the product in this S_N2 reaction. Be sure to specify stereochemistry.



4) Since everything is relative in chemistry, one reaction's nucleophile can be another reaction's leaving group. Some functional groups can only react as a nucleophile or electrophile, while other functional groups can react as either a nucleophile or electrophile depending on the reaction conditions. Classify the following compounds as nucleophile, electrophile, or leaving groups. More than one answer may be possible.

a) bromoethane

b) hydroxide

c) water

d) chlorocyclohexane

e) ethanol

f) bromide

Answer

1) a) rate = k [CH_3Cl] [OH^-]

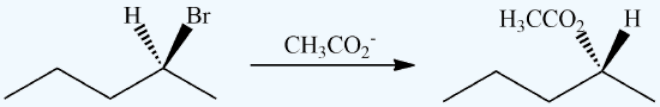
b) substitute the data into the rate expression above and apply algebra to solve for k

k = 6 x 10^{-6} $Lmol^{-1}s^{-1}$

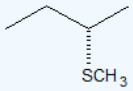
c) Using the rate law above, substitute the value for k from the previous question along with the new concentrations to determine the new initial rate.

rate = 6 x 10^{-10} M/s

2)



3)



4)

a) electrophile (Alkyl halides are always electrophiles - one reason they are an o-chem student's best friend.)

b) strong nucleophile

c) weak nucleophile and good leaving group

d) electrophile (Alkyl halides are always electrophiles - one reason they are an o-chem student's best friend.)

e) weak nucleophile, a poor electrophile without clever chemistry (stay tuned for future chapters), good leaving group

f) good nucleophile and a good leaving group

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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11.3: CHARACTERISTICS OF THE SN2 REACTION

Objectives

After completing this section, you should be able to

1. discuss the role of steric effects in S_N2 reactions.
2. arrange a given series of alkyl halides in order of increasing or decreasing reactivity towards nucleophilic substitution through the S_N2 mechanism.
3. suggest a reason why vinyl halides and aryl halides do not undergo S_N2 reactions.
4. discuss how the nature of the nucleophile affects the rate of an S_N2 reaction.
5. arrange a given series of common nucleophiles (e.g., CN^-, I^-, Br^- Cl^-, H_2O) in order of increasing or decreasing nucleophilicity.
6. discuss how the nature of the leaving group affects the rate of an S_N2 reaction.
7. arrange a given series of leaving groups in order of increasing or decreasing ability to leave during an S_N2 reaction.
8. discuss the role played by the solvent in an S_N2 reaction.
9. give examples of the solvents which are commonly used for S_N2 reactions, and identify those that promote a high reaction rate.
10. predict which of two given S_N2 reactions will proceed faster, by taking into account the structure of the substrates, the nucleophiles involved, leaving-group ability, solvent effects, or any combination of these factors.

KEY TERMS

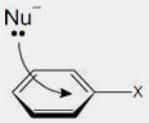
Make certain that you can define, and use in context, the key terms below.

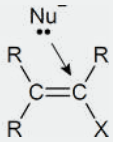
- leaving group
- polar aprotic solvent
- solvation

STUDY NOTES

You may wish to review the discussion of acid-base theory given in Sections 2.7-2.11.

Both aryl and vinylic halides are relatively unreactive in S_N2 displacement mechanisms, mostly because during the backside attack of the molecule the incoming nucleophile is sterically hindered by both substituents and electron density from any double bonds present. Also, leaving groups on sp^2-hybridized carbons tend to be held tighter than sp^3-hybridized carbons.



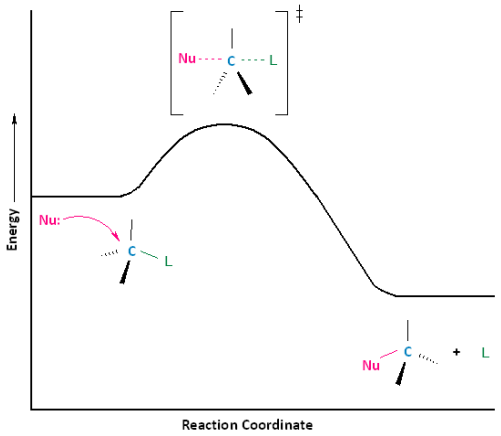


Solvation may be defined as the interaction between molecules of solvent and particles of solute. The result of solvation is to stabilize (i.e., lower the energy of) the solute particles. Solvents with lone pairs of electrons are good at solvating cations. Protic (i.e., hydroxylic) solvents are able to solvate anions through hydrogen bonding. As water has two lone pairs of electrons and is also protic, it is good at solvating both anions and cations.

BIMOLECULAR NUCLEOPHILIC SUBSTITUTION REACTIONS ARE CONCERTED

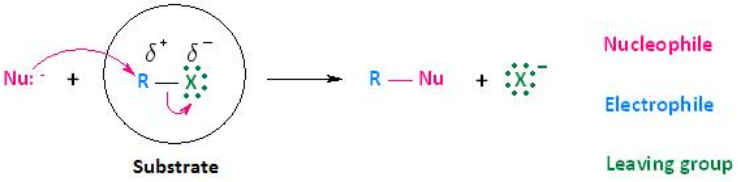
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The potential energy diagram for an SN_2 reaction is shown below. Upon nucleophilic attack, a single transition state is formed. A transition state, unlike a reaction intermediate, is a very short-lived species that cannot be isolated or directly observed. Again, this is a single-step, concerted process with the occurrence of a single transition state.

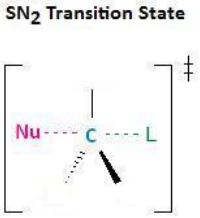


STERICALLY HINDERED SUBSTRATES WILL REDUCE THE S_N2 REACTION RATE

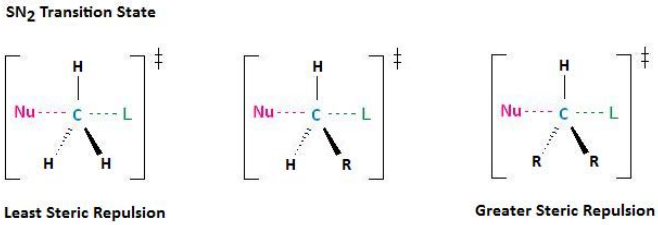
Now that we have discussed the effects that the leaving group, nucleophile, and solvent have on biomolecular nucleophilic substitution (S_N2) reactions, it's time to turn our attention to how the substrate affects the reaction. Although the substrate, in the case of nucleophilic substitution of haloalkanes, is considered to be the entire molecule circled below, we will be paying particular attention to the alkyl portion of the substrate. In other words, we are most interested in the electrophilic center that bears the leaving group.



In the section Kinetics of Nucleophilic Substitution Reactions, we learned that the SN_2 transition state is very crowded. Recall that there are a total of five groups around the electrophilic center, the nucleophile, the leaving group, and three substituents.

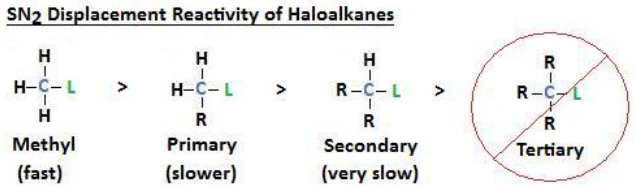


If each of the three substituents in this transition state were small hydrogen atoms, as illustrated in the first example below, there would be little steric repulsion between the incoming nucleophile and the electrophilic center, thereby increasing the ease at which the nucleophilic substitution reaction can occur. Remember, for the SN_2 reaction to occur, the nucleophile must be able to attack the electrophilic center, resulting in the expulsion of the leaving group. If one of the hydrogens, however, were replaced with an R group, such as a methyl or ethyl group, there would be an increase in steric repulsion with the incoming nucleophile. If two of the hydrogens were replaced by R groups, there would be an even greater increase in steric repulsion with the incoming nucleophile.



How does steric hindrance affect the rate at which an SN_2 reaction will occur? As each hydrogen is replaced by an R group, the rate of reaction is significantly diminished. This is because the addition of one or two R groups shields the backside of the electrophilic carbon, impeding nucleophilic attack.

The diagram below illustrates this concept, showing that electrophilic carbons attached to three hydrogen atoms results in faster nucleophilic substitution reactions, in comparison to primary and secondary haloalkanes, which result in nucleophilic substitution reactions that occur at slower or much slower rates, respectively. Notice that a tertiary haloalkane, that which has three R groups attached, does not undergo nucleophilic substitution reactions at all. The addition of a third R group to this molecule creates a carbon that is entirely blocked.



SUBSTITUTES ON NEIGHBORING CARBONS SLOW NUCLEOPHILIC SUBSTITUTION REACTIONS

Previously we learned that adding R groups to the electrophilic carbon results in nucleophilic substitution reactions that occur at a slower rate. What if R groups are added to neighboring carbons? It turns out that the addition of substitutes on neighboring carbons will slow nucleophilic substitution reactions as well.

In the example below, 2-methyl-1-bromopropane differs from 1-bromopropane in that it has a methyl group attached to the carbon that neighbors the electrophilic carbon. The addition of this methyl group results in a significant decrease in the rate of a nucleophilic substitution reaction.



If R groups were added to carbons farther away from the electrophilic carbon, we would still see a decrease in the reaction rate. However, branching at carbons farther away from the electrophilic carbon would have a much smaller effect.

WHAT IS A NUCLEOPHILE?

Nucleophilic functional groups are those which have electron-rich atoms able to donate a pair of electrons to form a new covalent bond. In both laboratory and biological organic chemistry, the most relevant nucleophilic atoms are oxygen, nitrogen, and sulfur, and the most common nucleophilic functional groups are water, alcohols, phenols, amines, thiols, and occasionally carboxylates.

More specifically in laboratory reactions, halide and azide (N_3^-) anions are commonly seen acting as nucleophiles.

When thinking about nucleophiles, the first thing to recognize is that, for the most part, the same quality of 'electron-richness' that makes a something nucleophilic also makes it basic: *nucleophiles can be bases, and bases can be nucleophiles*. It should not be surprising, then, that most of the trends in basicity that we have already discussed also apply to nucleophilicity.

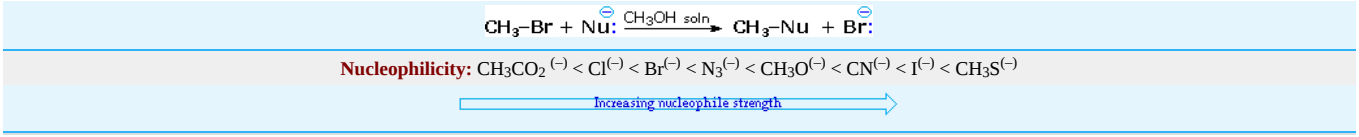
Some confusion in distinguishing basicity (base strength) and nucleophilicity (nucleophile strength) is inevitable. Since basicity is a less troublesome concept; it is convenient to start with it. Basicity refers to the ability of a base to accept a proton. Basicity may be related to the pKa of the corresponding conjugate acid, as shown below. The strongest bases have the weakest conjugate acids and vice versa. The range of basicities included in the following table is remarkable, covering over fifty powers of ten!

In an acid-base equilibrium the weakest acid and the weakest base will predominate (they will necessarily be on the same side of the equilibrium). Learning the pKa values for common compounds provides a useful foundation on which to build an understanding of acid-base factors in reaction mechanisms.

Base	$I^{(-)}$	$Cl^{(-)}$	H_2O	$CH_3CO_2^{(-)}$	$RS^{(-)}$	$CN^{(-)}$	$RO^{(-)}$	$NH_2^{(-)}$	$CH_3^{(-)}$
Conj. Acid	HI	HCl	$H_3O^{(+)}$	CH_3CO_2H	RSH	HCN	ROH	NH_3	CH_4
pK_a	-9	-7	-1.7	4.8	8	9.1	16	33	48

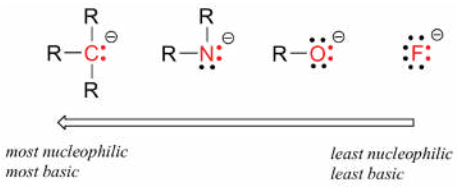
Increasing base strength

Nucleophilicity is a more complex property. It commonly refers to the rate of substitution reactions at the halogen-bearing **carbon atom** of a reference alkyl halide, such as CH_3-Br. Thus the nucleophilicity of the $Nu:^{(-)}$ reactant in the following substitution reaction varies as shown in the chart below:



PERIODIC TRENDS AND SOLVENT EFFECTS IN NUCLEOPHILICITY

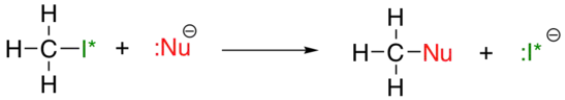
There are predictable periodic trends in nucleophilicity. Moving horizontally across the second row of the table, the trend in nucleophilicity parallels the trend in basicity:



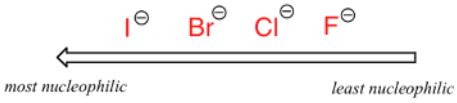
The reasoning behind the horizontal nucleophilicity trend is the same as the reasoning behind the basicity trend: more electronegative elements hold their electrons more tightly, and are less able to donate them to form a new bond. This horizontal trend also tells us that amines are more nucleophilic than alcohols, although both groups commonly act as nucleophiles in both laboratory and biochemical reactions.

Recall that the basicity of atoms decreases as we move vertically down a column on the periodic table: thiolate ions are less basic than alkoxide ions, for example, and bromide ion is less basic than chloride ion, which in turn is less basic than fluoride ion. Recall also that this trend can be explained by considering the increasing size of the 'electron cloud' around the larger ions: the electron density inherent in the negative charge is spread around a larger area, which tends to increase stability (and thus reduce basicity).

The vertical periodic trend for nucleophilicity is somewhat more complicated that that for basicity: depending on the solvent that the reaction is taking place in, the nucleophilicity trend can go in either direction. Let's take the simple example of the SN2 reaction below:



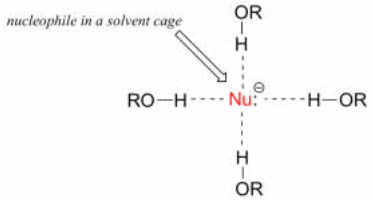
. . .where Nu^- is one of the halide ions: fluoride, chloride, bromide, or iodide, and the leaving group I* is a radioactive isotope of iodine (which allows us to distinguish the leaving group from the nucleophile in that case where both are iodide). If this reaction is occurring in a **protic solvent** (that is, a solvent that has a hydrogen bonded to an oxygen or nitrogen - water, methanol and ethanol are the most important examples), then the reaction will go fastest when iodide is the nucleophile, and slowest when fluoride is the nucleophile, reflecting the relative strength of the nucleophile.



Relative nucleophilicity in a protic solvent

This of course, is opposite that of the vertical periodic trend for basicity, where iodide is the *least* basic. What is going on here? Shouldn't the stronger base, with its more reactive unbonded valence electrons, also be the stronger nucleophile?

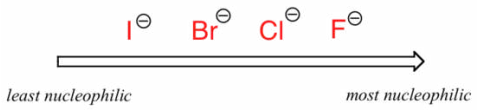
As mentioned above, it all has to do with the solvent. Remember, we are talking now about the reaction running in a *protic* solvent like ethanol. Protic solvent molecules form very strong ion-dipole interactions with the negatively-charged nucleophile, essentially creating a 'solvent cage' around the nucleophile:



In order for the nucleophile to attack the electrophile, it must break free, at least in part, from its solvent cage. The lone pair electrons on the larger, less basic iodide ion interact less tightly with the protons on the protic solvent molecules - thus the iodide nucleophile is better able to

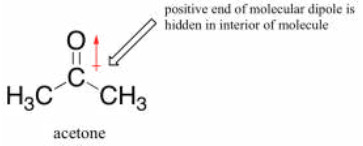
break free from its solvent cage compared the smaller, more basic fluoride ion, whose lone pair electrons are bound more tightly to the protons of the cage.

The picture changes if we switch to a **polar aprotic solvent**, such as acetone, in which there is a molecular dipole but *no hydrogens bound to oxygen or nitrogen*. Now, fluoride is the best nucleophile, and iodide the weakest.



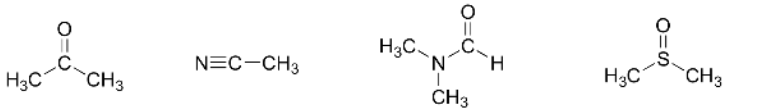
Relative nucleophilicity in a polar aprotic solvent

The reason for the reversal is that, with an aprotic solvent, the ion-dipole interactions between solvent and nucleophile are much weaker: the positive end of the solvent's dipole is hidden in the interior of the molecule, and thus it is shielded from the negative charge of the nucleophile.



A weaker solvent-nucleophile interaction means a weaker solvent cage for the nucleophile to break through, so the solvent effect is much less important, and the more basic fluoride ion is also the better nucleophile.

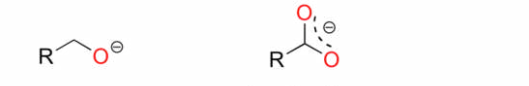
Why not use a completely nonpolar solvent, such as hexane, for this reaction, so that the solvent cage is eliminated completely? The answer to this is simple - the nucleophile needs to be in solution in order to react at an appreciable rate with the electrophile, and a solvent such as hexane will not solvate an a charged (or highly polar) nucleophile at all. That is why chemists use polar aprotic solvents for nucleophilic substitution reactions in the laboratory: they are polar enough to solvate the nucleophile, but not so polar as to lock it away in an impenetrable solvent cage. In addition to acetone, three other commonly used polar aprotic solvents are acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).



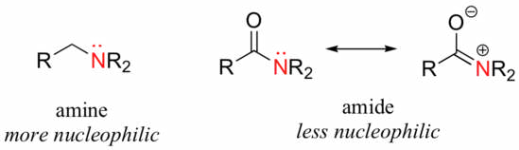
In biological chemistry, where the solvent is protic (water), the most important implication of the periodic trends in nucleophilicity is that thiols are more powerful nucleophiles than alcohols. The thiol group in a cysteine amino acid, for example, is a powerful nucleophile and often acts as a nucleophile in enzymatic reactions, and of course negatively-charged thiolates (RS^-) are even more nucleophilic. This is not to say that the hydroxyl groups on serine, threonine, and tyrosine do not also act as nucleophiles - they do.

RESONANCE EFFECTS ON NUCLEOPHILICITY

Resonance effects also come into play when comparing the inherent nucleophilicity of different molecules. The reasoning involved is the same as that which we used to understand resonance effects on basicity. If the electron lone pair on a heteroatom is delocalized by resonance, it is inherently less reactive - meaning less nucleophilic, and also less basic. An alkoxide ion, for example, is more nucleophilic and more basic than a carboxylate group, even though in both cases the nucleophilic atom is a negatively charged oxygen. In the alkoxide, the negative charge is localized on a single oxygen, while in the carboxylate the charge is delocalized over two oxygen atoms by resonance.

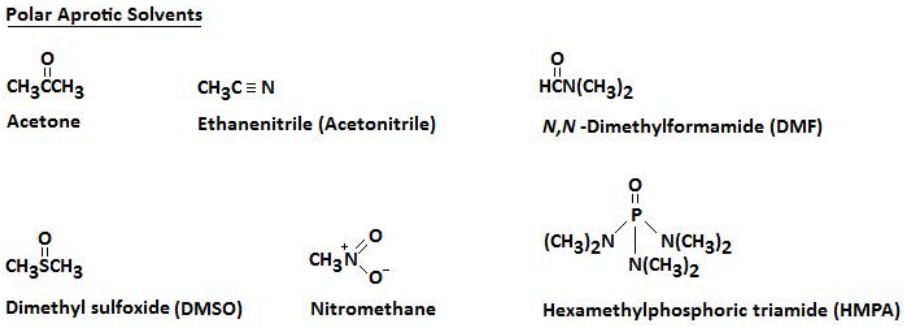


The nitrogen atom on an amide is less nucleophilic than the nitrogen of an amine, due to the resonance stabilization of the nitrogen lone pair provided by the amide carbonyl group.

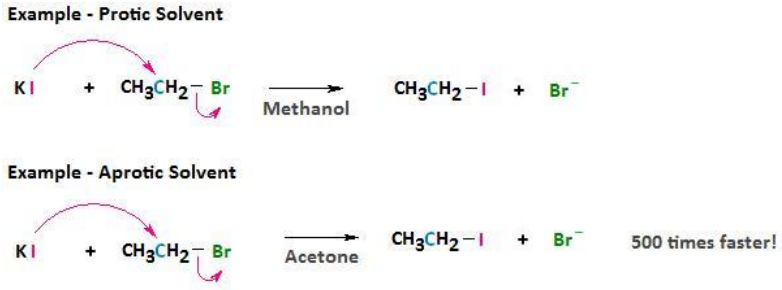


INFLUENCE OF THE SOLVENT IN AN S_N2 REACTION

The rate of an SN2 reaction is significantly influenced by the solvent in which the reaction takes place. The use of **protic solvents** (those, such as water or alcohols, with hydrogen-bond donating capability) decreases the power of the nucleophile, because of strong hydrogen-bond interactions between solvent protons and the reactive lone pairs on the nucleophile. A less powerful nucleophile in turn means a slower S_N2 reaction. S_N2 reactions are faster in **polar, aprotic solvents:** those that lack hydrogen-bond donating capability. Below are several polar aprotic solvents that are commonly used in the laboratory:

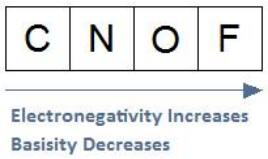


These aprotic solvents are polar but, because they do not form hydrogen bonds with the anionic nucleophile, there is a relatively weak interaction between the aprotic solvent and the nucleophile. By using an aprotic solvent we can raise the reactivity of the nucleophile. This can sometimes have dramatic effects on the rate at which a nucleophilic substitution reaction can occur. For example, if we consider the reaction between bromoethane and potassium iodide, the reaction occurs 500 times faster in acetone than in methanol.

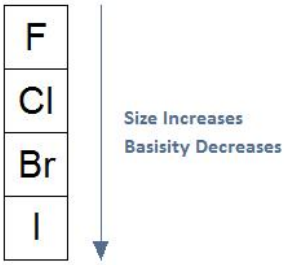


THE LEAVING GROUP

As Electronegativity Increases, Basicity Decreases: In general, if we move from the left of the periodic table to the right of the periodic table as shown in the diagram below, electronegativity increases. As electronegativity increases, basicity will decrease, meaning a species will be less likely to act as base; that is, the species will be less likely to share its electrons.



As Size Increases, Basicity Decreases: In general, if we move from the top of the periodic table to the bottom of the periodic table as shown in the diagram below, the size of an atom will increase. As size increases, basicity will decrease, meaning a species will be less likely to act as a base; that is, the species will be less likely to share its electrons.

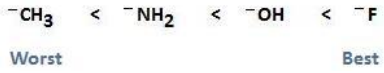


Resonance Decreases Basicity: The third factor to consider in determining whether or not a species will be a strong or weak base is resonance. As you may remember from general chemistry, the formation of a resonance stabilized structure results in a species that is less willing to share its electrons. Since strong bases, by definition, want to share their electrons, resonance stabilized structures are weak bases.

Now that we understand how electronegativity, size, and resonance affect basicity, we can combine these concepts with the fact that weak bases make the best leaving groups. Think about why this might be true. In order for a leaving group to leave, it must be able to accept electrons. A strong bases wants to donate electrons; therefore, the leaving group must be a weak base. We will now revisit electronegativity, size, and resonance, moving our focus to the leaving group, as well providing actual examples.

As Electronegativity Increases, The Ability of the Leaving Group to Leave Increases

As mentioned previously, if we move from left to right on the periodic table, electronegativity increases. With an increase in electronegativity, basisity decreases, and the ability of the leaving group to leave increases. This is because an increase in electronegativity results in a species that wants to hold onto its electrons rather than donate them. The following diagram illustrates this concept, showing $^-CH_3$ to be the worst leaving group and F^- to be the best leaving group. This particular example should only be used to facilitate your understanding of this concept. In real reaction mechanisms, these groups are not good leaving groups at all. For example, fluoride is such a poor leaving group that S_N2 reactions of fluoroalkanes are rarely observed.

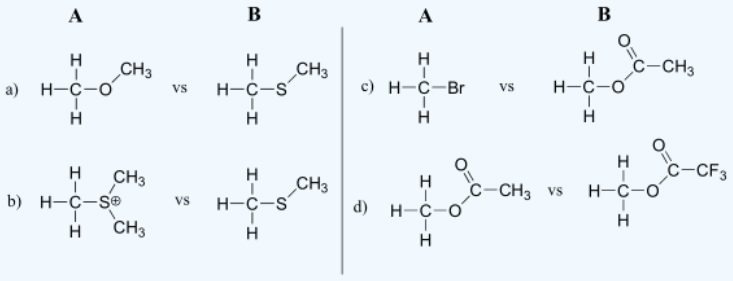


As Size Increases, The Ability of the Leaving Group to Leave Increases: Here we revisit the effect size has on basicity. If we move down the periodic table, size increases. With an increase in size, basicity decreases, and the ability of the leaving group to leave increases. The relationship among the following halogens, unlike the previous example, is true to what we will see in upcoming reaction mechanisms.



EXAMPLE 11.3.1

In each pair (A and B) below, which electrophile would be expected to react more rapidly in an S_N2 reaction with the thiol group of cysteine as the common nucleophile?



Solution

a) B (thiolate is a weaker base/better leaving group than alcohol)

b) A (sulfide is better leaving group than thiolate (sulfide is neutral and not at all basic)

c) A (bromide ion is a weaker base/better leaving group than acetate – compare pK_a values of HBr and acetic acid).

d) B (inductive electron-withdrawing effect of fluorines make trifluoroacetate a weaker base/better leaving group)

EXERCISES

EXERCISE 11.3.1

What product(s) do you expect from the reaction of 1-bromopentane with each of the following reagents in an S_N2 reaction?

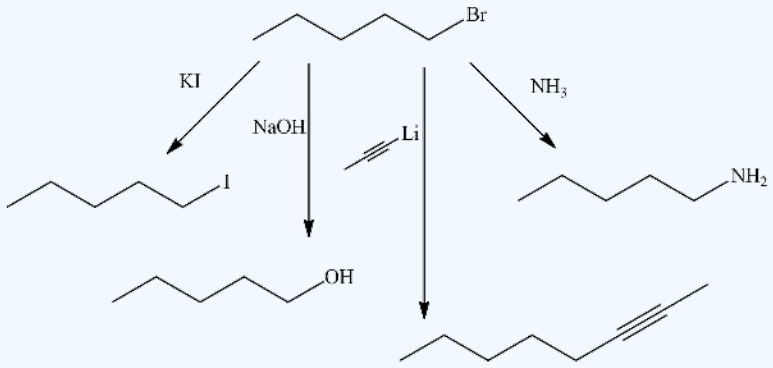
a) KI

b) NaOH

c) $CH_3C{\equiv}C\text{-}Li$

d) NH_3

Answer



EXERCISE 11.3.2

Which in the following pairs is a better nuceophile?

a) $(CH_3CH_2)_2N^-$ or $(CH_3CH_2)_2NH$

b) $(CH_3CH_2)_3N$ or $(CH_3CH_2)_3B$

c) H_2O or H_2S

Answer

a) $(CH_3CH_2)_2N^-$ as there is a charge present on the nitrogen.

b) $(CH_3CH_2)_3N$ because a lone pair of electrons is present.

c) H_2S as nucleophilicity generally increases going down the periodic table. [Assumes the absence of a polar aprotic solvent.]

EXERCISE 11.3.3

Order the following in increasing reactivity for an S_N2 reaction.

CH_3CH_2Br CH_3CH_2OTos $(CH_3CH_2)_3CCl$ $(CH_3CH_2)_2CHCl$

Answer

$(CH_3CH_2)_3CCl$ -or- $(CH_3CH_2)_2CHCl$ $\longrightarrow$ CH_3CH_2Br $\longrightarrow$ CH_3CH_2OTos

EXERCISE 11.3.4

Solvents benzene, ether, chloroform are non-polar and not strongly polar solvents. What effects do these solvents have on an S_N2 reaction?

Answer

They will decrease the reactivity of the reaction.

QUESTIONS

Q11.3.1

What product(s) do you expect from the reaction of 1-bromopentane with each of the following reagents in an S_N2 reaction?

A – KI

B – NaOH

C - $CH_3C{\equiv}C\text{-}Li$

D – NH_3

Q11.3.2

Which in the following pairs is a better nuceophile?

A - $(CH_3CH_2)_2N^-$ or $(CH_3CH_2)_2NH$

B - $(CH_3CH_2)_3N$ or $(CH_3CH_2)_3B$

C – H_2O or H_2S

Q11.3.3

Order the following in increasing reactivity for an S_N2 reaction.

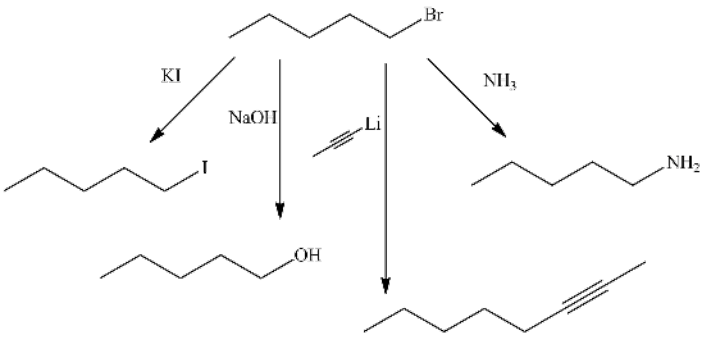
CH_3CH_2Br CH_3CH_2OTos $(CH_3CH_2)_3CCl$ $(CH_3CH_2)_2CHCl$

Q11.3.4

Solvents benzene, ether, chloroform are non-polar and not strongly polar solvents. What effects do these solvents have on an S_N2 reaction?

SOLUTIONS

S11.3.1



S11.3.2

A - $(CH_3CH_2)_2N^-$ as there is a charge present on the nitrogen.

B - $(CH_3CH_2)_3N$ because a lone pair of electrons is present.

C - H_2O as oxygen is more electronegative.

S11.3.3

$(CH_3CH_2)_3CCl$ -or- $(CH_3CH_2)_2CHCl$ $\longrightarrow$ CH_3CH_2Br $\longrightarrow$ CH_3CH_2OTos

S11.3.4

They will decrease the reactivity of the reaction.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)

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11.4: THE SN1 REACTION

Objectives

After completing this section, you should be able to

1. write an expression relating reaction rate and reactant concentration for a first-order reaction.
2. compare the kinetics of S_N1 and S_N2 reactions.
3. identify the rate-limiting step for a reaction, given the reaction energy diagram.
4. sketch a reaction energy diagram for a reaction, given the mechanism and sufficient information to identify the rate-limiting step.
5. write the mechanism of a typical S_N1 reaction, and discuss the important features of the mechanism.
6. discuss the stereochemistry of an S_N1 reaction, and explain why a racemic mixture is expected when substitution takes place at the chiral carbon atom of an optically pure substrate.
7. explain why unimolecular nucleophilic substitution at the chiral carbon atom of an optically pure substrate does not result in complete racemization.
8. compare the stereochemical consequences of the S_N1 mechanism with those of the S_N2 mechanism.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- first-order reaction
- rate-limiting step
- S_N1

STUDY NOTES

You should recognize that certain compounds (notably tertiary alkyl halides) which react very slowly by the S_N2 mechanism can undergo rapid nucleophilic substitution by an alternative mechanism.

The abbreviation S_N1 refers to "unimolecular nucleophilic substitution." In a *first-order reaction*, the rate of the reaction depends on the concentration of only one of the reactants. Thus, when an alkyl halide reacts by an S_N1 mechanism, the rate of reaction is dependent on the concentration of the alkyl halide, but is independent of the concentration of the attacking nucleophile.

Note: In many textbooks the "rate-limiting step" is called the "rate-determining step."

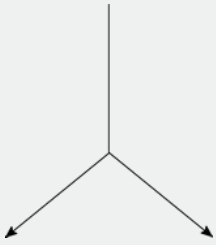
Racemization problems can be a potential source of confusion. Most students entering an introductory organic chemistry course have a reasonable background in mathematics, and feel comfortable if they have a formula or equation they can use in this type of situation. Thus, we recommend that you consider the following approach.

1. In a given mixture of enantiomers, let x = the fraction of the (+)-enantiomer, and $1 - x$ = the fraction of the (−)-enantiomer. [Remember that the fraction can be obtained by dividing the percentage by 100%.]
2. The observed $[\alpha]_D$ of the mixture is then given by:

   Observed $[\alpha]_D = x$ ($[\alpha]_D$ of the (+)-enantiomer)

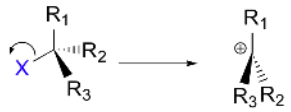
   + $(1 - x)$($[\alpha]_D$ of the (−)-enantiomer)

Another source of confusion is the way in which the terms "percentage racemization" and "percentage inversion" are used. You must be clear in your mind that 80% racemized means that we have 40% of the original configuration and 60% (40% + 20%) of the inverted configuration. This point is illustrated in the diagram below.

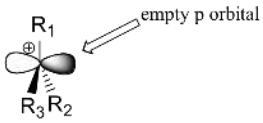


THE S_N1 MECHANISM

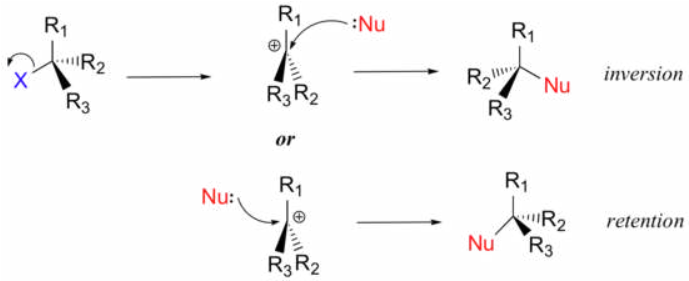
A second model for a nucleophilic substitution reaction is called the '**dissociative**', or '**S_N1**' mechanism: in this picture, the C-X bond breaks *first*, before the nucleophile approaches:



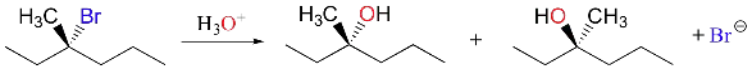
This results in the formation of a carbocation: because the central carbon has only three bonds, it bears a formal charge of +1. Recall that a carbocation should be pictured as sp^2 hybridized, with trigonal planar geometry. Perpendicular to the plane formed by the three sp^2 hybrid orbitals is an empty, unhybridized *p* orbital.



In the second step of this two-step reaction, the nucleophile attacks the empty, 'electron hungry' *p* orbital of the carbocation to form a new bond and return the carbon to tetrahedral geometry.



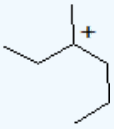
We saw that S_N2 reactions result specifically in inversion of stereochemistry at the electrophilic carbon center. What about the stereochemical outcome of S_N1 reactions? In the model S_N1 reaction shown above, the leaving group dissociates completely from the vicinity of the reaction before the nucleophile begins its attack. Because the leaving group is no longer in the picture, the nucleophile is free to attack from either side of the planar, sp^2-hybridized carbocation electrophile. This means that about half the time the product has the same stereochemical configuration as the starting material (retention of configuration), and about half the time the stereochemistry has been inverted. In other words, *racemization* has occurred at the carbon center. As an example, the tertiary alkyl bromide below would be expected to form a racemic mix of *R* and *S* alcohols after an S_N1 reaction with water as the incoming nucleophile.



? EXERCISE 11.4.1

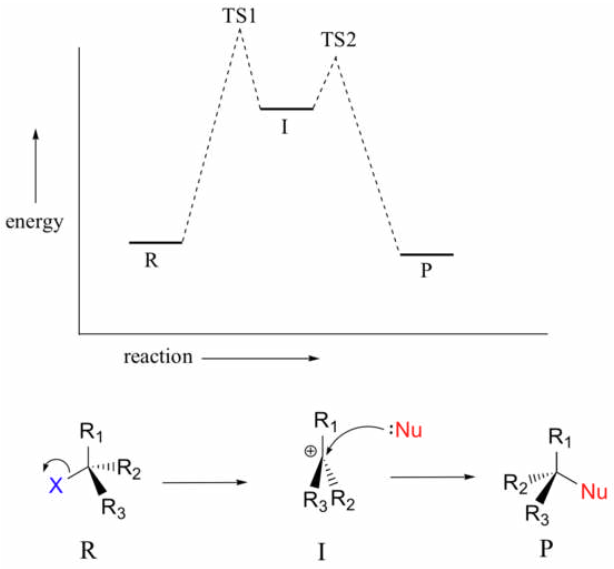
Draw the structure of the intermediate in the two-step nucleophilic substitution reaction above.

Answer



Planar cation intermediate that can be attacked by OH^- from either side (i.e., into or out of the plane of the screen)

The S_N1 reaction we see an example of a reaction intermediate, a very important concept in the study of organic reaction mechanisms that was introduced earlier in the module on organic reactivity Recall that many important organic reactions do not occur in a single step; rather, they are the sum of two or more discreet bond-forming / bond-breaking steps, and involve transient intermediate species that go on to react very quickly. In the S_N1 reaction, the carbocation species is a reaction intermediate. A potential energy diagram for an S_N1 reaction shows that the carbocation intermediate can be visualized as a kind of valley in the path of the reaction, higher in energy than both the reactant and product but lower in energy than the two transition states.



Recall that the first step of the reaction above, in which two charged species are formed from a neutral molecule, is much the slower of the two steps, and is therefore rate-determining. This is illustrated by the energy diagram, where the activation energy for the first step is higher than that for the second step. Also recall that an S_N1 reaction has *first order* kinetics, because the rate determining step involves one molecule splitting apart, not two molecules colliding.

EXERCISE 11.4.2

Consider two nucleophilic substitutions that occur uncatalyzed in solution. Assume that reaction A is S_N2, and reaction B is S_N1. Predict, in each case, what would happen to the rate of the reaction if the concentration of the nucleophile were doubled, while all other conditions remained constant.

A: $CH_3I + CH_3S^{\ominus} \xrightarrow{S_N2}$

B: $(CH_3)_3CBr + CH_3SH \xrightarrow{S_N1}$

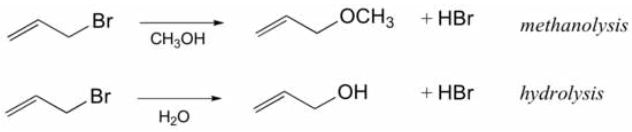
Answer

For Reaction A, the rate law is rate = $k[CH_3I][CH_3S^-]$. Therefore, if the concentration of the nucleophile, CH_3S^-, is doubled and the concentration of the alkyl halide remains the same, then the reaction rate will double.

For Reaction B, the rate law is rate = $k[(CH_3)_3Br]$. Therefore, if the concentration of the nucleophile, CH_3SH, is doubled and the concentration of the alkyl halide remains the same, then reaction rate stays the same.

INFLUENCE OF THE SOLVENT IN AN S_N1 REACTION

Since the hydrogen atom in a polar protic solvent is highly positively charged, it can interact with the anionic nucleophile which would negatively affect an SN2, but it does not affect an SN1 reaction because the nucleophile is not a part of the rate-determining step. Polar protic solvents actually speed up the rate of the unimolecular substitution reaction because the large dipole moment of the solvent helps to stabilize the transition state. The highly positive and highly negative parts interact with the substrate to lower the energy of the transition state. Since the carbocation is unstable, anything that can stabilize this even a little will speed up the reaction. Sometimes in an SN1 reaction the solvent acts as the nucleophile. This is called a solvolysis reaction.The S_N1 reaction of allyl bromide in methanol is an example of what we would call **methanolysis**, while if water is the solvent the reaction would be called **hydrolysis**:

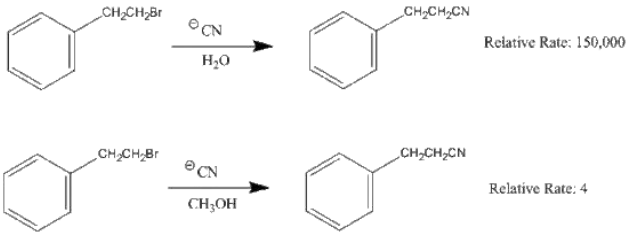


The polarity and the ability of the solvent to stabilize the intermediate carbocation is very important as shown by the relative rate data for the solvolysis (see table below). The dielectric constant of a solvent roughly provides a measure of the solvent's polarity. A dielectric

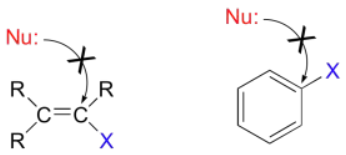
constant below 15 is usually considered non-polar. Basically, the dielectric constant can be thought of as the solvent's ability to reduce the internal charge of the solvent. So for our purposes, the higher the dielectric constant the more polar the substance and in the case of S_N1 reactions, the faster the rate.

Solvent	Dielectric Constant	Relative Rate
• CH_3CO_2H • CH_3OH • H_2O	• 6 • 33 • 78	• 1 • 4 • 150,000

Below is the same reaction conducted in two different solvents and the relative rate that corresponds with it.



One more important point must be made before continuing: nucleophilic substitutions as a rule occur at sp^3-hybridized carbons, and *not* where the leaving group is attached to an sp^2-hybridized carbon::



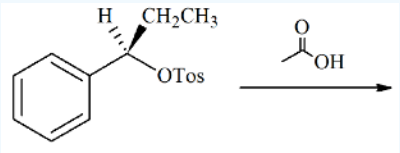
Bonds on sp^2-hybridized carbons are inherently shorter and stronger than bonds on sp^3-hybridized carbons, meaning that it is harder to break the C-X bond in these substrates. S_N2 reactions of this type are unlikely also because the (hypothetical) electrophilic carbon is protected from nucleophilic attack by electron density in the p bond. S_N1 reactions are highly unlikely, because the resulting carbocation intermediate, which would be sp-hybridized, would be very unstable (we'll discuss the relative stability of carbocation intermediates in a later section of this module).

Before we look at some real-life nucleophilic substitution reactions in the next chapter, we will spend some time in the remainder of this module focusing more closely on the three principal partners in the nucleophilic substitution reaction: the nucleophile, the electrophile, and the leaving group.

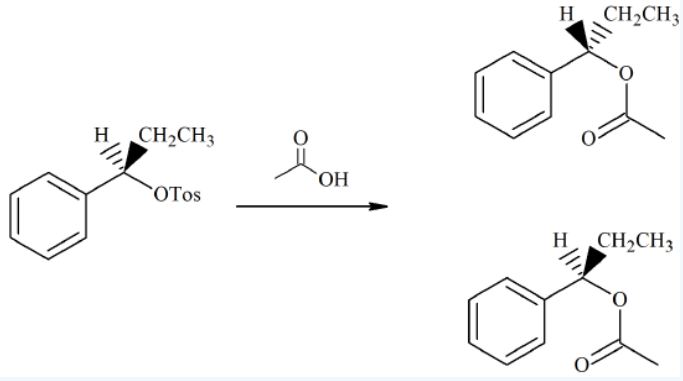
EXERCISES

? EXERCISE 11.4.3

Give the products of the following S_N1 reaction. Show stereochemistry.



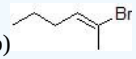
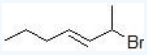
Answer



EXERCISE 11.4.4

Predict with compound in each pair will undergo an SN1 reaction more quickly.

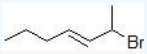
a)  or 

b)  or 

c)  or

Answer

a) 

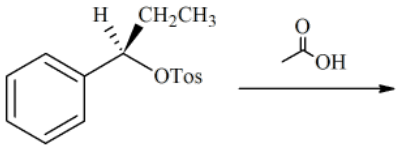
b) 

c) 

QUESTIONS

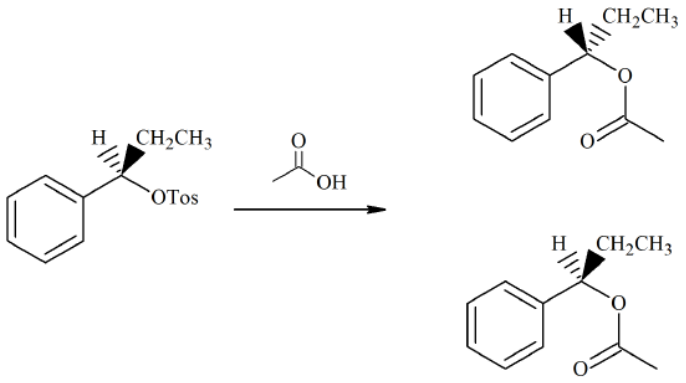
Q11.4.1

Give the products of the following S_N1 reaction. Show stereochemistry.



SOLUTIONS

S11.4.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)

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11.5: CHARACTERISTICS OF THE SN1 REACTION

Objectives

After completing this section, you should be able to

1. discuss how the structure of the substrate affects the rate of a reaction occurring by the S_N1 mechanism.
2. arrange a given list of carbocations (including benzyl and allyl) in order of increasing or decreasing stability.
3. explain the high stability of the allyl and benzyl carbocations.
4. arrange a given series of compounds in order of increasing or decreasing reactivity in S_N1 reactions, and discuss this order in terms of the Hammond postulate.
5. discuss how the nature of the leaving group affects the rate of an S_N1 reaction, and in particular, explain why S_N1 reactions involving alcohols are carried out under acidic conditions.
6. explain why the nature of the nucleophile does not affect the rate of an S_N1 reaction.
7. discuss the role played by the solvent in an S_N1 reaction, and hence determine whether a given solvent will promote reaction by this mechanism.
8. compare the roles played by the solvent in S_N1 and in S_N2 reactions.
9. determine which of two S_N1 reactions will occur faster, by taking into account factors such as the structure of the substrate and the polarity of the solvent.
10. determine whether a given reaction is most likely to occur by an S_N1 or S_N2 mechanism, based on factors such as the structure of the substrate, the solvent used, etc.

KEY TERMS

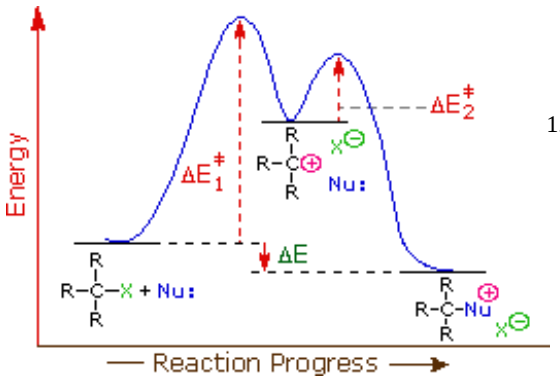
Make certain that you can define, and use in context, the key terms below.

- benzylic
- dielectric constant
- polarity

CONTENT

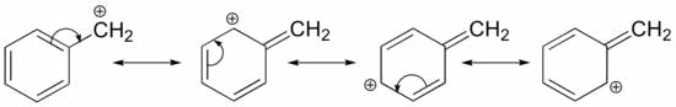
S_N1 MECHANISM

The first order kinetics of S_N1 reactions suggests a two-step mechanism in which the rate-determining step consists of the ionization of the alkyl halide, as shown in the diagram below. In this mechanism, a carbocation is formed as a high-energy intermediate, and this species bonds immediately to nearby nucleophiles. If the nucleophile is a neutral molecule, the initial product is an "onium" cation, as drawn above for t-butyl chloride, and presumed in the energy diagram. In evaluating this mechanism, we may infer several outcomes from its function.

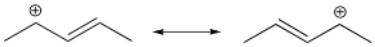


The only reactant that is undergoing change in the first (rate-determining) step is the alkyl halide, so we expect such reactions would be unimolecular and follow a first-order rate equation. Hence the name **S_N1** is applied to this mechanism.

1. Since nucleophiles only participate in the fast second step, their relative molar concentrations rather than their nucleophilicities should be the primary product-determining factor. If a nucleophilic solvent such as water is used, its high concentration will assure that alcohols are the major product. Recombination of the halide anion with the carbocation intermediate simply reforms the starting compound. Note that S_N1 reactions in which the nucleophile is also the solvent are commonly called **solvolysis** reactions. The hydrolysis of t-butyl chloride is an example.
2. The Hammond postulate suggests that the activation energy of the rate-determining first step will be inversely proportional to the stability of the carbocation intermediate. The stability of carbocations was discussed earlier, and a qualitative relationship is given below.



Benzyl Carbocation



an allylic carbocation

Carbocation Stability	$CH_3^{(+)}$	$< CH_3CH_2^{(+)} < (CH_3)_2CH^{(+)} \approx \underset{CH_2^{(+)}}{CH_2{=}CH{-}} < C_6H_5CH_2^{(+)} \approx (CH_3)_3C^{(+)}$

Consequently, we expect that 3º-alkyl halides will be more reactive than their 2º and 1º-counterparts in reactions that follow an S_N1 mechanism. This is opposite to the reactivity order observed for the S_N2 mechanism. Allylic and benzylic halides are exceptionally reactive by either mechanism.

Fourth, in order to facilitate the charge separation of an ionization reaction, as required by the first step, a good ionizing solvent will be needed. Two solvent characteristics will be particularly important in this respect. The first is the ability of solvent molecules to orient themselves between ions so as to attenuate the electrostatic force one ion exerts on the other. This characteristic is related to the **dielectric constant, ε,** of the solvent. Solvents having high dielectric constants, such as water (ε=81), formic acid (ε=58), dimethyl sulfoxide (ε=45) & acetonitrile (ε=39) are generally considered better ionizing solvents than are some common organic solvents such as ethanol (ε=25), acetone (ε=21), methylene chloride (ε=9) & ether (ε=4). The second factor is **solvation**, which refers to the solvent's ability to stabilize ions by encasing them in a sheath of weakly bonded solvent molecules. Anions are solvated by hydrogen-bonding solvents, as noted earlier. Cations are often best solvated by nucleophilic sites on a solvent molecule (e.g. oxygen & nitrogen atoms), but in the case of carbocations these nucleophiles may form strong covalent bonds to carbon, thus converting the intermediate to a substitution product. This is what happens in the hydrolysis reactions described above.

Fifth, the stereospecificity of these reactions may vary. The positively-charged carbon atom of a carbocation has a trigonal (flat) configuration (it prefers to be sp^2 hybridized), and can bond to a nucleophile equally well from either face. If the intermediate from a chiral alkyl halide survives long enough to encounter a random environment, the products are expected to be racemic (a 50:50 mixture of enantiomers). On the other hand, if the departing halide anion temporarily blocks the front side, or if a nucleophile is oriented selectively at one or the other face, then the substitution might occur with predominant inversion or even retention of configuration.

Just as with S_N2 reactions, the nucleophile, solvent and leaving group also affect S_N1 (Unimolecular Nucleophilic Substitution) reactions. Polar protic solvents have a hydrogen atom attached to an electronegative atom so the hydrogen is highly polarized. Polar aprotic solvents have a dipole moment, but their hydrogen is not highly polarized. Polar aprotic solvents are not used in S_N1 reactions because some of them can react with the carbocation intermediate and give you an unwanted product. Rather, polar protic solvents are preferred.

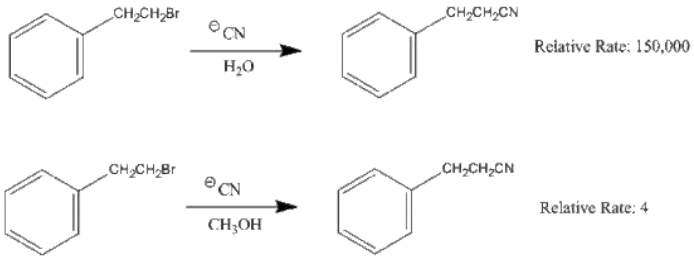
SOLVENT EFFECTS ON THE S_N1 REACTION

Since the hydrogen atom in a polar protic solvent is highly positively charged, it can interact with the anionic nucleophile which would negatively affect an S_N2, but it does not affect an SN1 reaction because the nucleophile is not a part of the rate-determining step (See S_N2 Nucleophile). Polar protic solvents actually speed up the rate of the unimolecular substitution reaction because the large dipole moment of the solvent helps to stabilize the transition state. The highly positive and highly negative parts interact with the substrate to lower the energy of the transition state. Since the carbocation is unstable, anything that can stabilize this even a little will speed up the reaction.

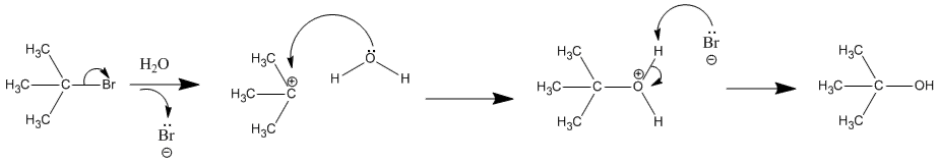
Sometimes in an S_N1 reaction the solvent acts as the nucleophile. This is called a solvolysis reaction (see example below). The polarity and the ability of the solvent to stabilize the intermediate carbocation is very important as shown by the relative rate data for the solvolysis (see table below). The dielectric constant of a solvent roughly provides a measure of the solvent's polarity. A dielectric constant below 15 is usually considered non-polar. Basically, the dielectric constant can be thought of as the solvent's ability to reduce the internal charge of the solvent. So for our purposes, the higher the dielectric constant the more polar the substance and in the case of S_N1 reactions, the faster the rate.

Solvent	Dielectric Constant	Relative Rate
• CH_3CO_2H • CH_3OH • H_2O	• 6 • 33 • 78	• 1 • 4 • 150,000

Below is the same reaction conducted in two different solvents and the relative rate that corresponds with it.



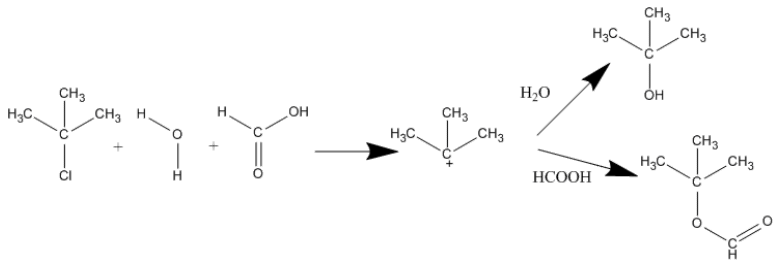
The figure below shows the mechanism of an S_N1 reaction of an alkyl halide with water. Since water is also the solvent, this is an example of a solvolysis reaction.



Examples of polar protic solvents are: acetic acid, isopropanol, ethanol, methanol, formic acid, water, etc.

EFFECTS OF NUCLEOPHILE

The strength of the nucleophile does not affect the reaction rate of SN1 because, as stated above, the nucleophile is not involved in the rate-determining step. However, if you have more than one nucleophile competing to bond to the carbocation, the strengths and concentrations of those nucleophiles affects the distribution of products that you will get. For example, if you have $(CH_3)_3CCl$ reacting in water and formic acid where the water and formic acid are competing nucleophiles, you will get two different products: $(CH_3)_3COH$ and $(CH_3)_3COCOH$. The relative yields of these products depend on the concentrations and relative reactivities of the nucleophiles.

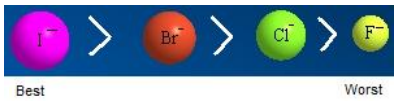


EFFECTS OF LEAVING GROUP

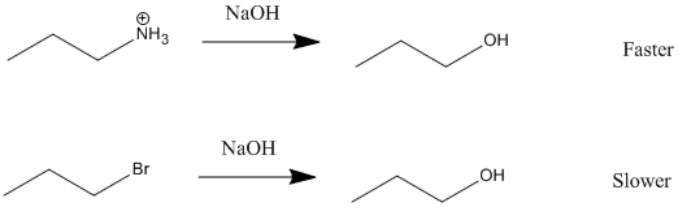
An S_N1 reaction speeds up with a good leaving group. This is because the leaving group is involved in the rate-determining step. A good leaving group wants to leave so it breaks the C-Leaving Group bond faster. Once the bond breaks, the carbocation is formed and the faster the carbocation is formed, the faster the nucleophile can come in and the faster the reaction will be completed.

A good leaving group is a weak base because weak bases can hold the charge. They're happy to leave with both electrons and in order for the leaving group to leave, it needs to be able to accept electrons. Strong bases, on the other hand, donate electrons which is why they can't be good leaving groups. As you go from left to right on the periodic table, electron donating ability decreases and thus ability to be a good leaving group increases. Halides are an example of a good leaving group whos leaving-group ability increases as you go down the column.

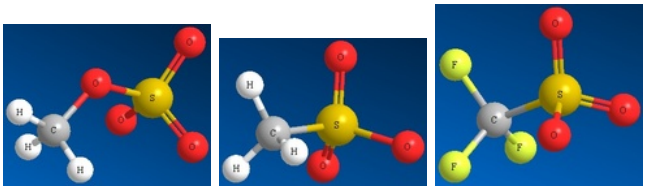
Excellent	• TsO^- • NH_3
Very Good	• I^- • H_2O
Good	• Br^-
Fair	• Cl^-
Poor	• F^-
Very Poor	• OH^- • NH_2^-



The two reactions below is the same reaction done with two different leaving groups. One is significantly faster than the other. This is because the better leaving group leaves faster and thus the reaction can proceed faster.



Other examples of good leaving groups are sulfur derivatives such as methyl sulfate ion and other sulfonate ions (See Figure below)



Methyl Sulfate Ion Mesylate Ion Triflate Ion Tosylate Ion

PREDICTING S_N1 VS. S_N2 MECHANISMS; COMPETITION BETWEEN NUCLEOPHILIC SUBSTITUTION AND ELIMINATION REACTIONS

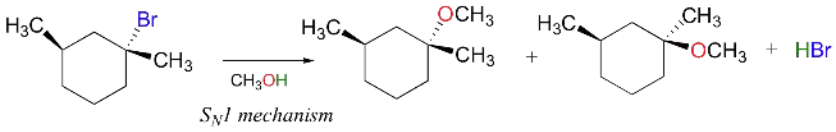
When considering whether a nucleophilic substitution is likely to occur via an S_N1 or S_N2 mechanism, we really need to consider three factors:

1) **The electrophile:** when the leaving group is attached to a methyl group or a primary carbon, an S_N2 mechanism is favored (here the electrophile is unhindered by surrounded groups, and any carbocation intermediate would be high-energy and thus unlikely). When the leaving group is attached to a tertiary, allylic, or benzylic carbon, a carbocation intermediate will be relatively stable and thus an S_N1 mechanism is favored.

2) **The nucleophile**: powerful nucleophiles, especially those with negative charges, favor the S_N2 mechanism. Weaker nucleophiles such as water or alcohols favor the S_N1 mechanism.

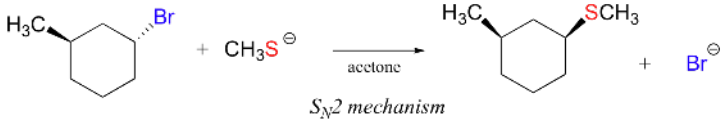
3) **The solvent**: Polar aprotic solvents favor the S_N2 mechanism by enhancing the reactivity of the nucleophile. Polar protic solvents favor the S_N1 mechanism by stabilizing the carbocation intermediate. S_N1 reactions are frequently solvolysis reactions.

For example, the reaction below has a tertiary alkyl bromide as the electrophile, a weak nucleophile, and a polar protic solvent (we'll assume that methanol is the solvent). Thus we'd confidently predict an S_N1 reaction mechanism. Because substitution occurs at a chiral carbon, we can also predict that the reaction will proceed with racemization.



S_N1 mechanism

In the reaction below, on the other hand, the electrophile is a secondary alkyl bromide – with these, both S_N1 and S_N2 mechanisms are possible, depending on the nucleophile and the solvent. In this example, the nucleophile (a thiolate anion) is strong, and a polar aprotic solvent is used – so the S_N2 mechanism is heavily favored. The reaction is expected to proceed with inversion of configuration.

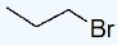


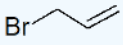
S_N2 mechanism

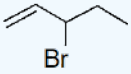
EXERCISES

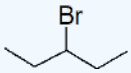
EXERCISE 11.5.1

Rank the following by increasing reactivity in an S_N1 reaction.

A 

B 

C 

D 

Answer

Consider the stability of the intermediate, the carbocation.

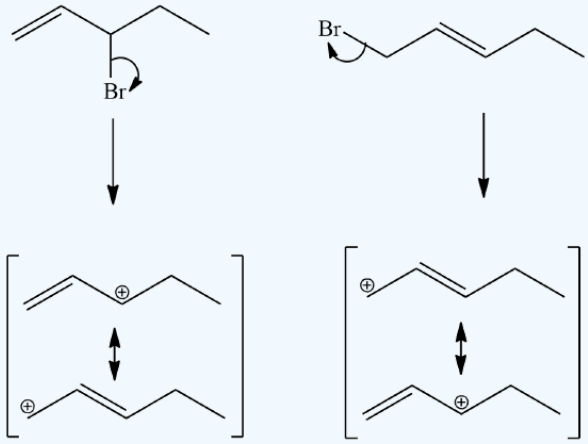
A, D, B, C (most reactive)

EXERCISE 11.5.2

3-bromo-1-pentene and 1-bromo-2-pentene undergo S_N1 reaction at almost the same rate, but one is a secondary halide while the other is a primary halide. Explain why this is.

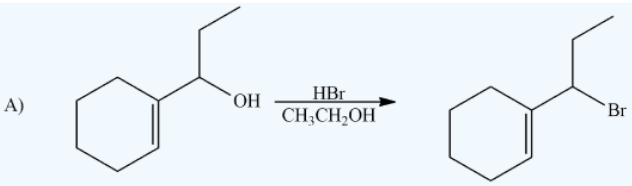
Answer

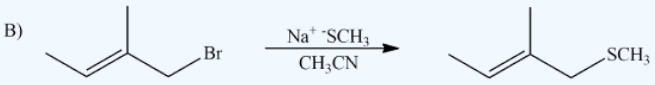
They have the same intermediates when you look at the resonance forms.



EXERCISE 11.5.3

Label the following reactions as most likely occuring by an S_N1 or S_N2 mechanism. Suggest why.





Answer

A) S_N1 -> poor leaving group, protic solvent, secondary cation intermediate

B) S_N2 -> good leaving group, polar solvent, primary position.

EXERCISE 11.5.4

Which solvent would an S_N1 reaction occur faster in? H_2O or CH_3CN

Answer

An S_N1 reaction would occur faster in H_2O because it's polar protic and would stailize the carbocation and CH_3CN is polar aprotic.

EXERCISE 11.5.5

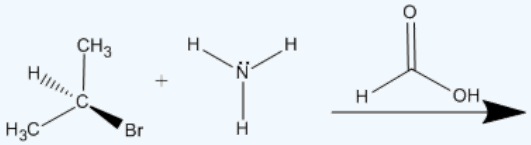
What kind of conditions disfavor S_N1 reactions?

Answer

Polar aprotic solvents, a weak leaving group and primary substrates disfavor S_N1 reactions.

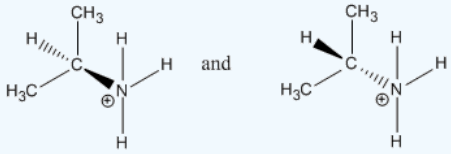
EXERCISE 11.5.6

What are the products of the following reaction and does it proceed via S_N1 or S_N2?



Answer

Reaction proceeds via S_N1 because a tertiary carbocation was formed, the solvent is polar protic and Br^- is a good leaving group.

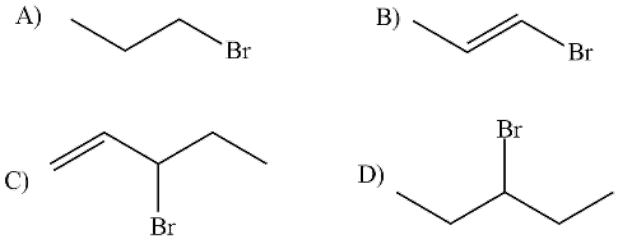


Racemic Mixture

QUESTIONS

Q11.5.1

Rank the following by increasing reactivity in an S_N1 reaction.

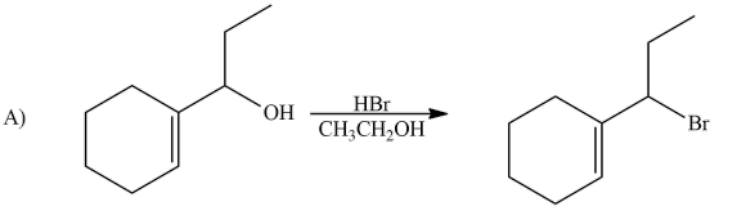


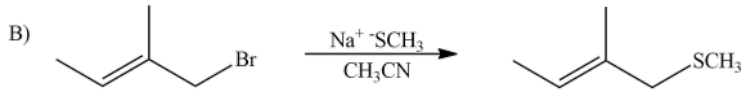
Q11.5.2

3-bromo-1-pentene and 1-bromo-2-pentene undergo S_N1 reaction at almost the same rate, but one is a secondary halide while the other is a primary halide. Explain why this is.

Q11.5.3

Label the following reactions as most likely occuring by an S_N1 or S_N2 mechanism. Suggest why.





SOLUTIONS

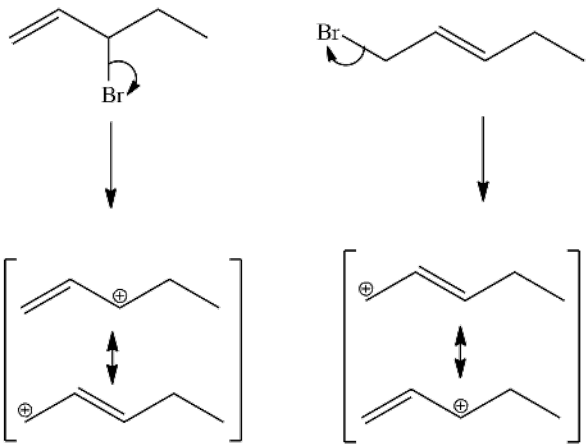
S11.5.1

Consider the stability of the intermediate, the carbocation.

A < D < B < C (most reactive)

S11.5.2

They have the same intermediates when you look at the resonance forms.



S11.5.3

A – S_N1 *poor leaving group, protic solvent, secondary cation intermediate

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B – S_N2 *good leaving group, polar solvent, primary position.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Ashiv Sharma

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11.6: BIOLOGICAL SUBSTITUTION REACTIONS

Objective

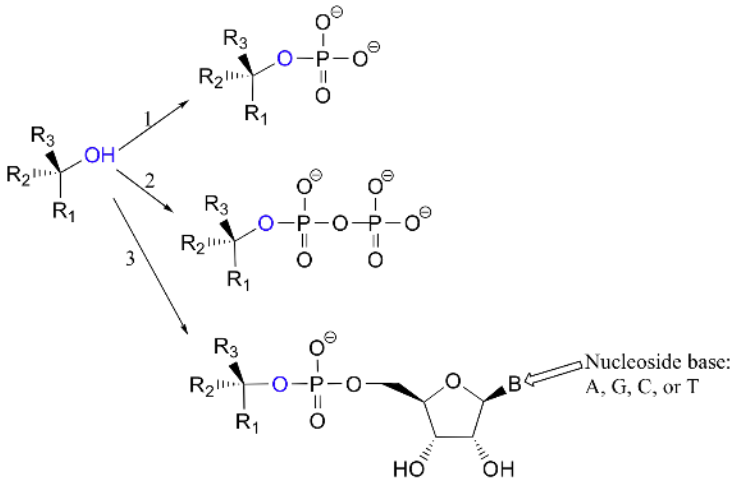
After completing this section, you should have an appreciation that S_N1 and S_N2 mechanisms exist and are well-known in biological chemistry.

LEAVING GROUPS IN BIOCHEMICAL REACTIONS

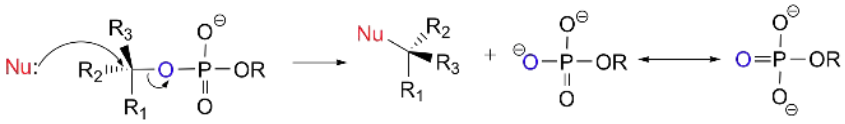
In biological reactions, we do not often see halides serving as leaving groups (in fact, outside of some marine organisms, halogens are fairly unusual in biological molecules). More common leaving groups in biochemical reactions are phosphates, water, alcohols, and thiols. In many cases, the leaving group is protonated by an acidic group on the enzyme as bond-breaking occurs. For example, hydroxide ion itself seldom acts as a leaving group – it is simply too high in energy (too basic). Rather, the hydroxide oxygen is generally protonated by an enzymatic acid before or during the bond-breaking event, resulting in a (very stable) water leaving group.



More often, however, the hydroxyl group of an alcohol is first converted enzymatically to a phosphate ester in order to create a better leaving group. This phosphate ester can take the form of a simple monophosphate (arrow 1 in the figure below), a diphosphate (arrow 2), or a nucleotide monophosphate (arrow 3).

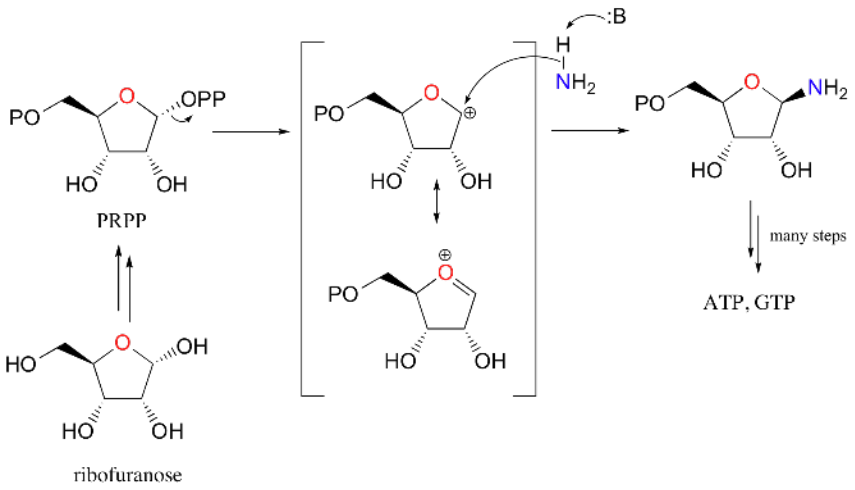


Due to resonance delocalization of the developing negative charge, phosphates are excellent leaving groups.



Here's a specific example (from DNA nucleotide biosynthesis) that we will encounter in more detail in section 11.5:

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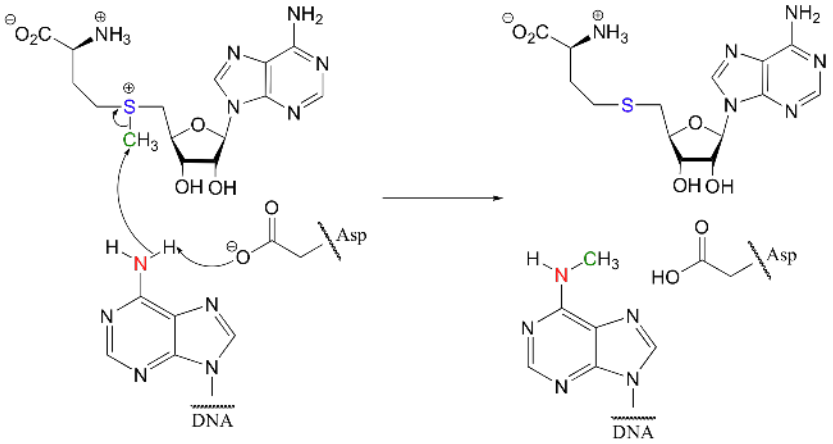


Here, the OH group on ribofuranose is converted to a diphosphate, a much better leaving group. Ammonia is the nucleophile in the second step of this S_N1-like reaction.

We will learn much more about phosphates in chapter 10. What is important for now is that in each case, an alcohol has been converted into a much better leaving group, and is now primed for a nucleophilic substitution reaction.

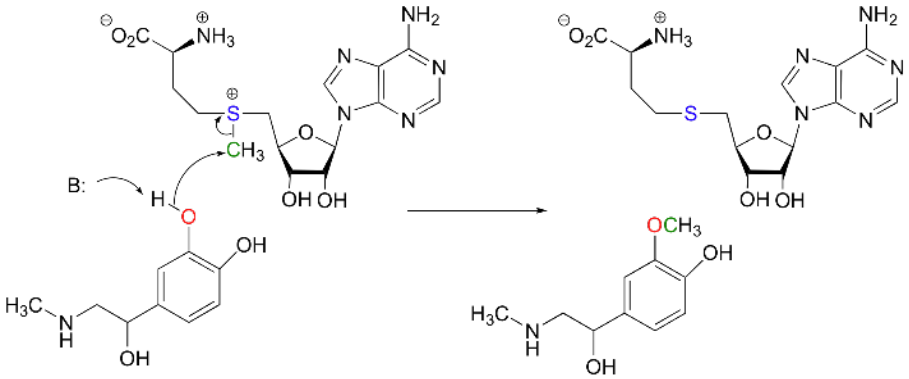
SAM METHYLTRANSFERASES

Some of the most important examples of S_N2 reactions in biochemistry are those catalyzed by S-adenosyl methionine (SAM) – dependent methyltransferase enzymes. We have already seen, in chapter 6 and again in chapter 8, how a methyl group is transferred in an S_N2 reaction from SAM to the amine group on the nucleotide base adenosine:



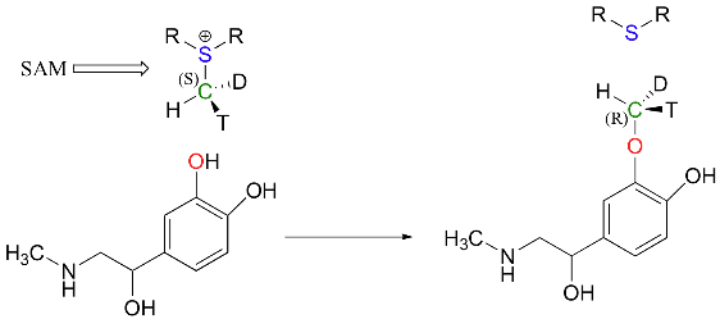
(*Nucleic Acids Res.* **2000**, *28*, 3950).

Another SAM-dependent methylation reaction is catalyzed by an enzyme called catechol-O-methyltransferase. The substrate here is epinephrine, also known as adrenaline.



Notice that in this example, the attacking nucleophile is an alcohol rather than an amine (that's why the enzyme is called an O-methyltransferase). In both cases, though, a basic amino acid side chain is positioned in the active site in just the right place to deprotonate the nucleophilic group as it attacks, increasing its nucleophilicity. The electrophile in both reactions is a methyl carbon, so there is little steric hindrance to slow down the nucleophilic attack. The methyl carbon is electrophilic because it is bonded to a positively-charged sulfur, which is a powerful electron withdrawing group. The positive charge on the sulfur also makes it an excellent leaving group, as the resulting product will be a neutral and very stable sulfide. All in all, in both reactions we have a reasonably good nucleophile, an electron-poor, unhindered electrophile, and an excellent leaving group.

Because the electrophilic carbon in these reactions is a methyl carbon, a stepwise S_N1-like mechanism is extremely unlikely: a methyl carbocation is very high in energy and thus is not a reasonable intermediate to propose. We can confidently predict that this reaction is S_N2. Does this S_N2 reaction occur, as expected, with inversion of stereochemistry? Of course, the electrophilic methyl carbon in these reactions is achiral, so inversion is not apparent. To demonstrate inversion, the following experiment has been carried out with catechol-O-methyltransferase:



Here, the methyl group of SAM was made to be chiral by incorporating hydrogen isotopes tritium (^{3}H, T) and deuterium (^{2}H, D). The researchers determined that the reaction occurred with inversion of configuration, as expected for an S_N2 displacement (*J. Biol. Chem.* **1980,** *255,* 9124).

CONTRIBUTORS AND ATTRIBUTIONS

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- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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11.7: ELIMINATION REACTIONS - ZAITSEV'S RULE

Objective

After completing this section, you should be able to apply Zaitsev's rule to predict the major product in a base-induced elimination of an unsymmetrical halide.

KEY TERMS

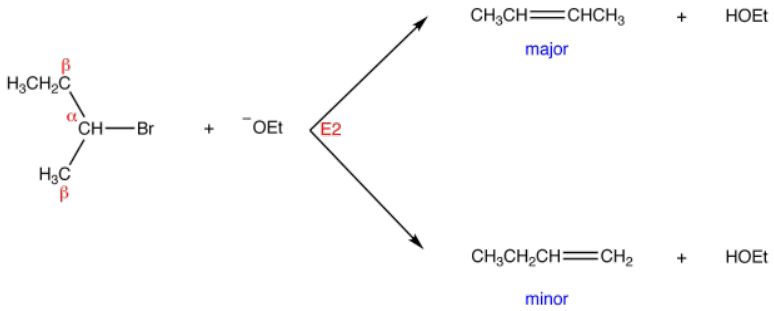
Make certain that you can define, and use in context, the key term below.

Zaitsev's rule

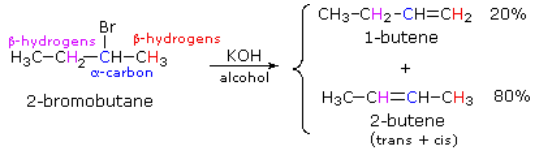
Zaitsev's Rule can be used to predict the regiochemistry of elimination reactions.

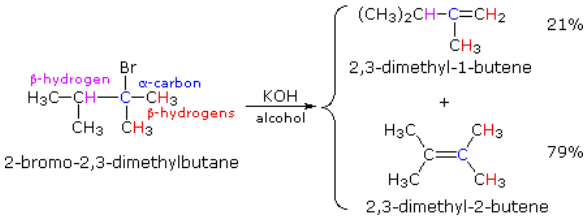
INTRODUCTION

Zaitsev's or Saytzev's (anglicized spelling) rule is an empirical rule used to predict regioselectivity of 1,2-elimination reactions occurring via the E1 or E2 mechanisms. It states that in a regioselective E1 or E2 reaction the major product is the more stable alkene, (i.e., the alkene with the more highly substituted double bond). For example:



If two or more structurally distinct groups of beta-hydrogens are present in a given reactant, then several constitutionally isomeric alkenes may be formed by an E2 elimination. This situation is illustrated by the 2-bromobutane and 2-bromo-2,3-dimethylbutane elimination examples given below.



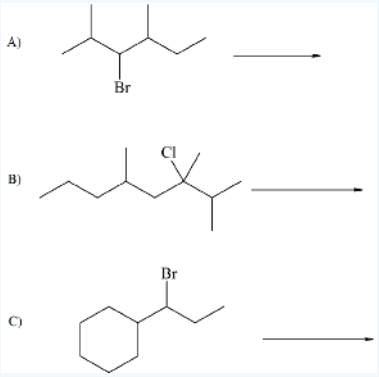


By using the strongly basic hydroxide nucleophile, we direct these reactions toward elimination. In both cases there are two different sets of beta-hydrogens available to the elimination reaction (these are colored red and magenta and the alpha carbon is blue). If the rate of each possible elimination was the same, we might expect the amounts of the isomeric elimination products to reflect the number of hydrogens that could participate in that reaction. For example, since there are three 1º-hydrogens (red) and two 2º-hydrogens (magenta) on beta-carbons in 2-bromobutane, statistics would suggest a 3:2 ratio of 1-butene and 2-butene in the products. This is not observed, and the latter predominates by 4:1. This departure from statistical expectation is even more pronounced in the second example, where there are six 1º-beta-hydrogens compared with one 3º-hydrogen. These results point to a strong regioselectivity favoring the more highly substituted product double bond, an empirical statement generally called the **Zaitsev Rule**.

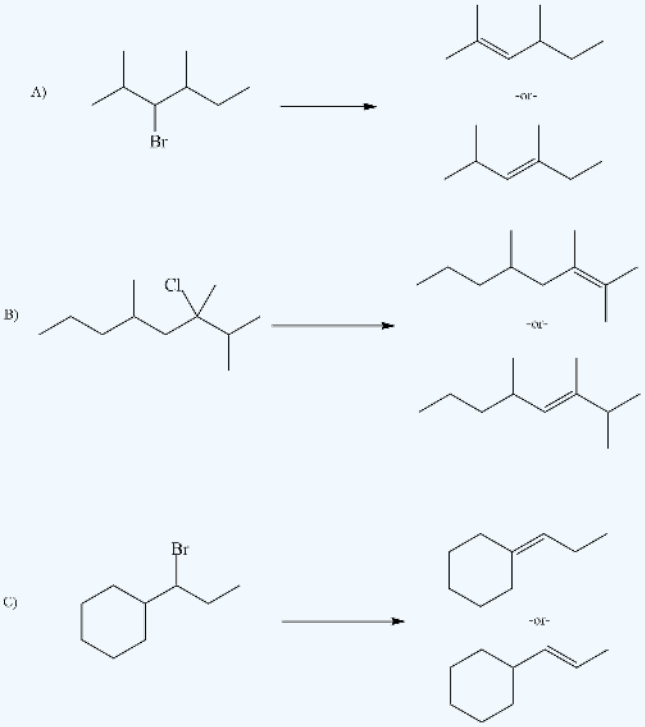
EXERCISES

EXERCISE 11.7.1

Ignoring the alkene stereochemistry show the elimination product(s) of the following compounds:

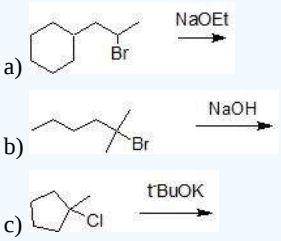


Answer



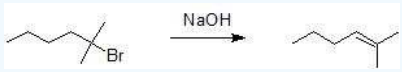
EXERCISE 11.7.2

Predict the major products of the following reactions.



Answer

a) 

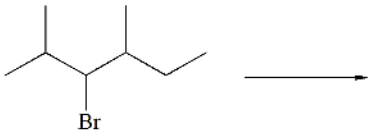
b) 

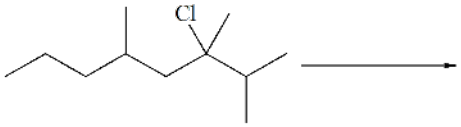
c) 

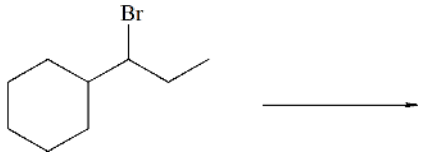
QUESTIONS

Q11.7.1

Ignoring the alkene stereochemistry show the elimination product(s) of the following compounds:

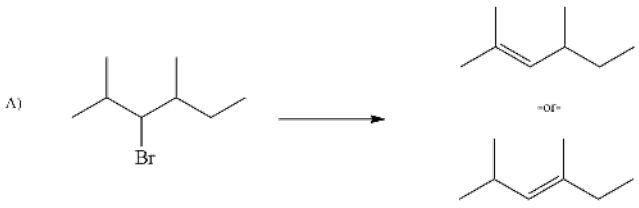
A) 

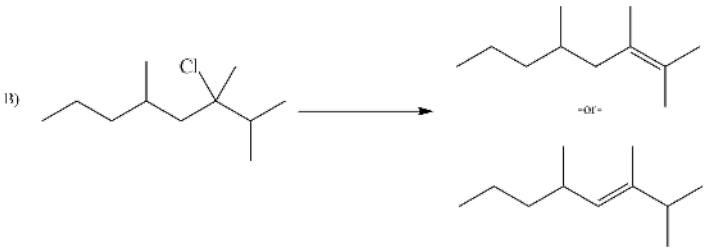
B) 

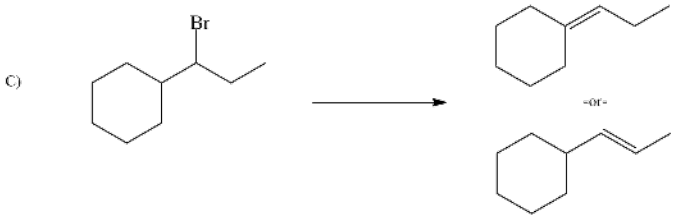
C) 

SOLUTIONS

S11.7.1

A) 

B) 

C) 

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
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11.8: THE E2 REACTION AND THE DEUTERIUM ISOTOPE EFFECT

Objectives

After completing this section, you should be able to

1. write the mechanism of a typical E2 reaction.
2. sketch the transition state of a typical E2 reaction.
3. discuss the kinetic evidence that supports the proposed E2 mechanism.
4. discuss the stereochemistry of an E2 reaction, and explain why the anti periplanar geometry is preferred.
5. determine the structure of the alkene produced from the E2 reaction of a substrate containing two chiral carbon atoms.
6. describe the deuterium isotope effect, and discuss how it can be used to provide evidence in support of the E2 mechanism.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

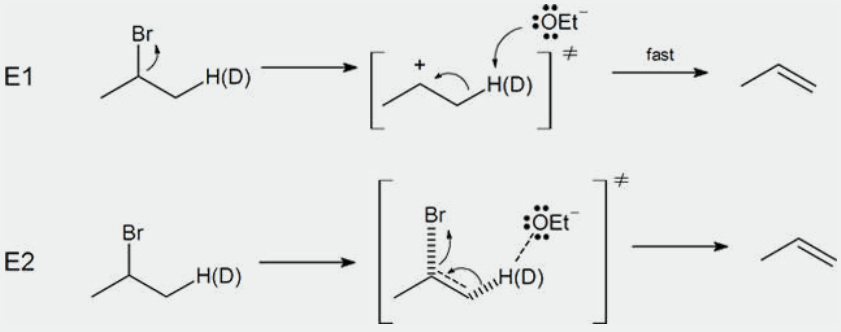
- anti periplanar
- deuterium isotope effect
- E2 reaction
- periplanar
- syn periplanar

STUDY NOTES

An *E2 reaction* is a bimolecular elimination reaction; thus, two molecules are involved in the rate-limiting step. In this section, we are concerned with E2 reactions involving an alkyl halide and a base.

Use molecular models to assist you to understand the difference between syn periplanar and anti periplanar, and to appreciate why E2 eliminations are stereospecific.

Note that when deuterium is used the kinetic isotope effect (KIE) is referred to as the deuterium isotope effect. A $C-H$ bond is about 5 kJ/mol weaker than a $C-D$ bond. So if the rate-limiting step involves a breaking of this bond as it does at the E2 transition state there will be a substantial difference in reaction rates when comparing deuterated and non-deuterated analogues. Indeed, the reaction of 2-bromopropane with sodium ethoxide (NaOEt) is 6.7 times faster than its deuterated counterpart, providing evidence consistent with an E2 mechanism.

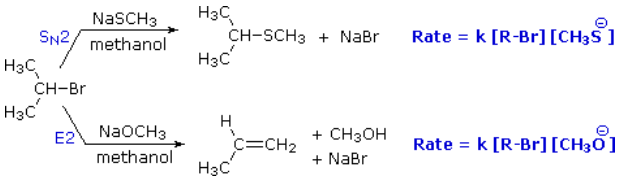


E2, bimolecular elimination, was proposed in the 1920s by British chemist Christopher Kelk Ingold. Unlike E1 reactions, E2 reactions remove two subsituents with the addition of a strong base, resulting in an alkene.

INTRODUCTION

E2 reactions are typically seen with secondary and tertiary alkyl halides, but a hindered base is necessary with a primary halide. The mechanism by which it occurs is a single step **concerted** reaction with one transition state. The rate at which this mechanism occurs is second order kinetics, and depends on both the base and alkyl halide. A good leaving group is required because it is involved in the rate determining step. The leaving groups must be coplanar in order to form a pi bond; carbons go from sp^3 to sp^2 hybridization states.

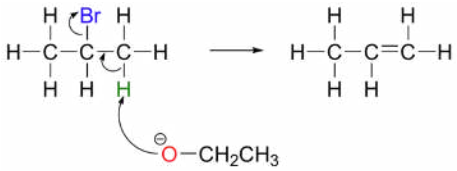
To get a clearer picture of the interplay of these factors involved in a a reaction between a nucleophile/base and an alkyl halide, consider the reaction of a 2º-alkyl halide, isopropyl bromide, with two different nucleophiles. In one pathway, a methanethiolate nucleophile substitutes for bromine in an S_N2 reaction. In the other (bottom) pathway, methoxide ion acts as a base (rather than as a nucleophile) in an elimination reaction. As we will soon see, the mechanism of this reaction is single-step, and is referred to as the E2 mechanism.



GENERAL REACTION

Below is a mechanistic diagram of an elimination reaction by the E2 pathway:

.

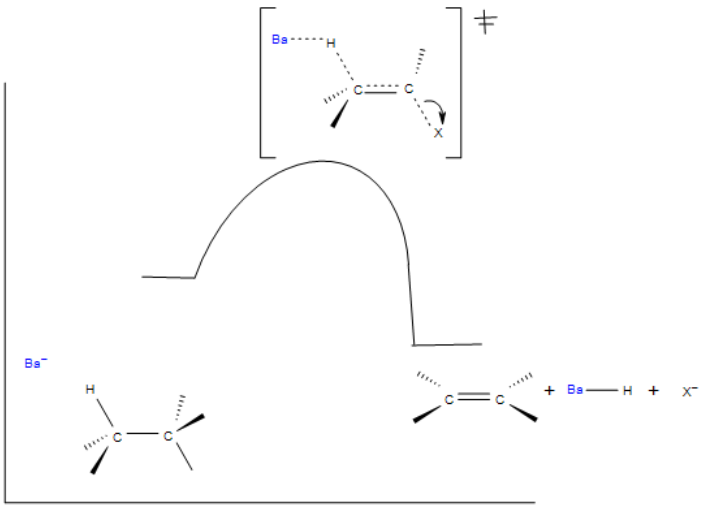


In this reaction Ba represents the base and Br representents a leaving group, typically a halogen. There is one transition state that shows the concerted reaction for the base attracting the hydrogen and the halogen taking the electrons from the bond. The product be both eclipse and staggered depending on the transition states. Eclipsed products have a synperiplanar transition states, while staggered products have antiperiplanar transition states. Staggered conformation is usually the major product because of its lower energy confirmation.

An E2 reaction has certain requirements to proceed:

- A strong base is necessary especially necessary for primary alkyl halides. Secondary and tertirary primary halides will procede with E2 in the precesence of a base (OH-, RO-, R_2N-)
- Both leaving groups should be on the same plane, this allows the double bond to form in the reaction. In the reaction above you can see both leaving groups are in the plane of the carbons.
- Follows Zaitsev's rule, the most substituted alkene is usually the major product.
- Hofmann's Rule, if a sterically hindered base will result in the least substituted product.

E2 REACTION COORDINATE



THE LEAVING GROUP EFFECT IN E2 REACTIONS

As Size Increases, The Ability of the Leaving Group to Leave Increases: Here we revisit the effect size has on basicity. If we move down the periodic table, size increases. With an increase in size, basicity decreases, and the ability of the leaving group to leave increases. The relationship among the following halogens, unlike the previous example, is true to what we will see in upcoming reaction mechanisms.

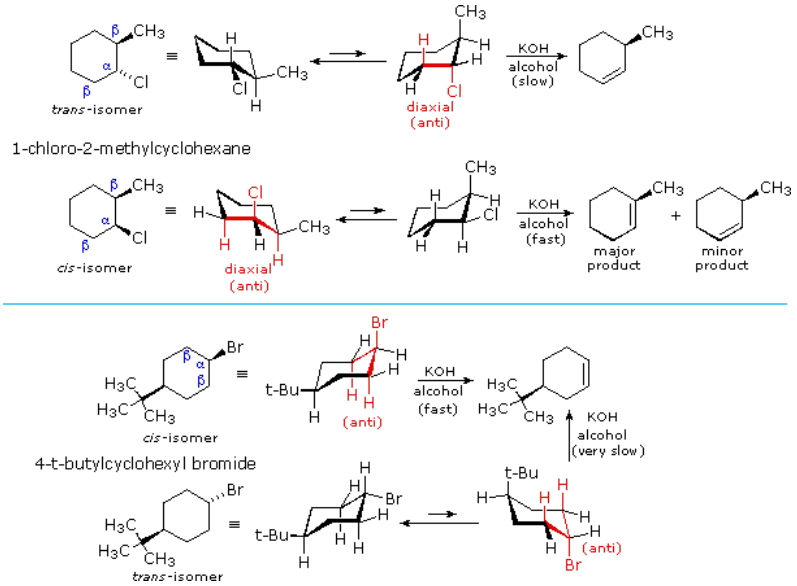
F	<	Cl	<	Br	<	I
Worst		Fair		Good		Excellent

The

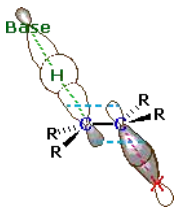
STEREOCHEMISTRY OF THE E2 REACTION EDIT SECTION

E2 elimination reactions of certain isomeric cycloalkyl halides show unusual rates and regioselectivity that are not explained by the principles thus far discussed. For example, trans-2-methyl-1-chlorocyclohexane reacts with alcoholic KOH at a much slower rate than does its cis-isomer. Furthermore, the product from elimination of the trans-isomer is 3-methylcyclohexene (not predicted by the Zaitsev rule), whereas the cis-isomer gives the predicted 1-methylcyclohexene as the chief product. These differences are described by the first two equations in the following diagram.

Unlike open chain structures, cyclic compounds generally restrict the spatial orientation of ring substituents to relatively few arrangements. Consequently, reactions conducted on such substrates often provide us with information about the preferred orientation of reactant species in the transition state. Stereoisomers are particularly suitable in this respect, so the results shown here contain important information about the E2 transition state.



The most sensible interpretation of the elimination reactions of 2- and 4-substituted halocyclohexanes is that this reaction prefers an **anti orientation** of the halogen and the beta-hydrogen which is attacked by the base. These anti orientations are colored in red in the above equations. The compounds used here all have six-membered rings, so the anti orientation of groups requires that they assume a diaxial conformation. The observed differences in rate are the result of a steric preference for equatorial orientation of large substituents, which reduces the effective concentration of conformers having an axial halogen. In the case of the 1-bromo-4-tert-butylcyclohexane isomers, the tert-butyl group is so large that it will always assume an equatorial orientation, leaving the bromine to be axial in the cis-isomer and equatorial in the trans. Because of symmetry, the two axial beta-hydrogens in the cis-isomer react equally with base, resulting in rapid elimination to the same alkene (actually a racemic mixture). This reflects the fixed anti orientation of these hydrogens to the chlorine atom. To assume a conformation having an axial bromine the trans-isomer must tolerate serious crowding distortions. Such conformers are therefore present in extremely low concentration, and the rate of elimination is very slow. Indeed, substitution by hydroxide anion predominates.



A similar analysis of the 1-chloro-2-methylcyclohexane isomers explains both the rate and regioselectivity differences. Both the chlorine and methyl groups may assume an equatorial orientation in a chair conformation of the trans-isomer, as shown in the top equation. The axial chlorine needed for the E2 elimination is present only in the less stable alternative chair conformer, but this structure has only one axial beta-hydrogen (colored red), and the resulting elimination gives 3-methylcyclohexene. In the cis-isomer the smaller chlorine atom assumes an axial position in the more stable chair conformation, and here there are two axial beta hydrogens. The more stable 1-methylcyclohexene is

therefore the predominant product, and the overall rate of elimination is relatively fast.

An orbital drawing of the anti-transition state is shown on the right. Note that the base attacks the alkyl halide from the side opposite the halogen, just as in the S_N2 mechanism. In this drawing the α and β carbon atoms are undergoing a rehybridization from sp^3 to sp^2 and the developing π-bond is drawn as dashed light blue lines. The symbol **R** represents an alkyl group or hydrogen. Since both the base and the alkyl halide are present in this transition state, the reaction is bimolecular and should exhibit second order kinetics. We should note in passing that a syn-transition state would also provide good orbital overlap for elimination, and in some cases where an anti-orientation is prohibited by structural constraints *syn*-elimination has been observed.

Instead, in an E2 reaction, stereochemistry of the double bond -- that is, whether the *E* or *Z* isomer results -- is dictated by the stereochemistry of the starting material, if it is diastereomeric. In other words, if the carbon with the hydrogen and the carbon with the halogen are both chiral, then one diastereomer will lead to one product, and the other diastereomer will lead to the other product.

The following reactions of potassium ethoxide with dibromostilbene (1,2-dibromo-1,2-diphenylethane) both occurred via an E2 mechanism. Two different diastereomers were used. Two different stereoisomers (*E* vs. *Z*) resulted.

KINETIC ISOTOPE EFFECTS

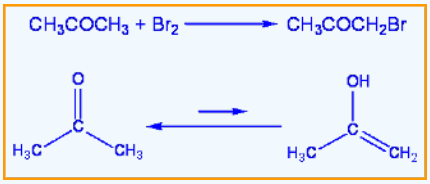
Kinetic Isotope Effects (KIEs) are used to determine reaction mechanisms by determining rate limiting steps and transition states and are commonly measured using NMR to detect isotope location or GC/MS to detect mass changes. In a KIE experiment an atom is replaced by its isotope and the change in rate of the reaction is observed. A very common isotope substitution is when hydrogen is replaced by deuterium. This is known as a deuterium effect and is expressed by the ratio k_H/k_D (as explained above). Normal KIEs for the deuterium effect are around 1 to 7 or 8. Large effects are seen because the percentage mass change between hydrogen and deuterium is great. Heavy atom isotope effects involve the substitution of carbon, oxygen, nitrogen, sulfur, and bromine, with effects that are much smaller and are usually between 1.02 and 1.10. The difference in KIE magnitude is directly related to the percentage change in mass. Large effects are seen when hydrogen is replaced with deuterium because the percentage mass change is very large (mass is being doubled) while smaller percent mass changes are present when an atom like sulfur is replaced with its isotope (increased by two mass units).

PRIMARY KIES

Primary kinetic isotope effects are rate changes due to isotopic substitution at a site of bond breaking in the rate determining step of a reaction.

✔ EXAMPLE

Consider the bromination of acetone: kinetic studies have been performed that show the rate of this reaction is independent of the concentration of bromine. To determine the rate determining step and mechanism of this reaction the substitution of a deuterium for a hydrogen can be made.

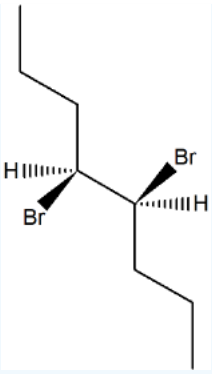


When hydrogen was replaced with deuterium in this reaction a $\frac{k_H}{k_D}$ of 7 was found. Therefore the rate determining step is the tautomerization of acetone and involves the breaking of a C-H bond. Since the breaking of a C-H bond is involved, a substantial isotope effect is expected.

EXERCISE

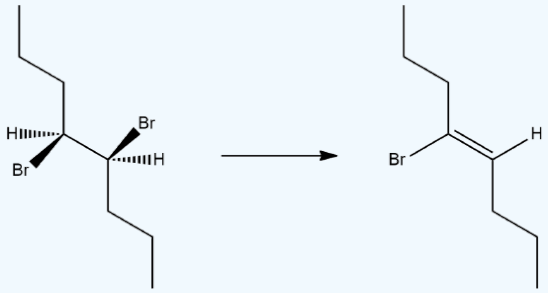
? EXERCISE \PageIndex1

1) What is the product of the following molecule in an E2 reaction? What is the stereochemistry?



Answer

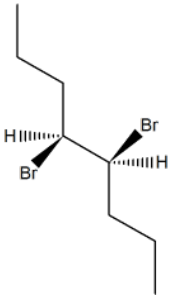
The stereochemistry is (*Z*) for the reaction.



QUESTIONS

Q11.8.1

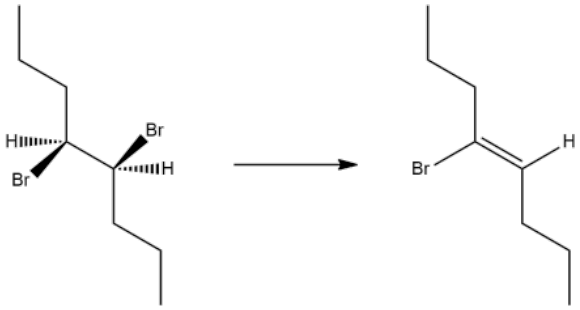
What is the product of the following molecule in an E2 reaction? What is the stereochemistry?



SOLUTIONS

S11.8.1

The stereochemistry is (*Z*) for the reaction.



CONTRIBUTORS AND ATTRIBUTIONS

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- Prof. Steven Farmer (Sonoma State University)

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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11.9: THE E2 REACTION AND CYCLOHEXANE CONFORMATION

Objectives

After completing this section, you should be able to

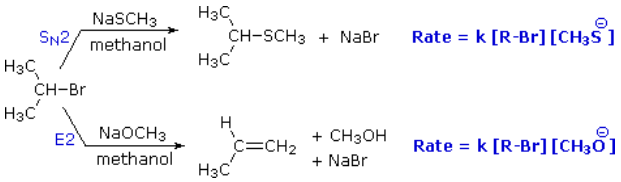
1. identify anti periplanar arrangements of atoms in substituted cyclohexanes.
2. determine which cyclohexane conformation will generate a specific anti periplanar arrangement.

E2, bimolecular elimination, was proposed in the 1920s by British chemist Christopher Kelk Ingold. Unlike E1 reactions, E2 reactions remove two subsituents with the addition of a strong base, resulting in an alkene.

INTRODUCTION

E2 reactions are typically seen with secondary and tertiary alkyl halides, but a hindered base is necessary with a primary halide. The mechanism by which it occurs is a single step **concerted** reaction with one transition state. The rate at which this mechanism occurs is second order kinetics, and depends on both the base and alkyl halide. A good leaving group is required because it is involved in the rate determining step. The leaving groups must be coplanar in order to form a pi bond; carbons go from sp^3 to sp^2 hybridization states.

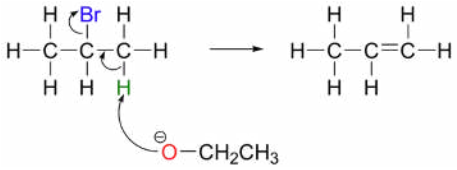
To get a clearer picture of the interplay of these factors involved in a a reaction between a nucleophile/base and an alkyl halide, consider the reaction of a 2º-alkyl halide, isopropyl bromide, with two different nucleophiles. In one pathway, a methanethiolate nucleophile substitutes for bromine in an S_N2 reaction. In the other (bottom) pathway, methoxide ion acts as a base (rather than as a nucleophile) in an elimination reaction. As we will soon see, the mechanism of this reaction is single-step, and is referred to as the E2 mechanism.



GENERAL REACTION

Below is a mechanistic diagram of an elimination reaction by the E2 pathway:

.



In this reaction Ba represents the base and Br representents a leaving group, typically a halogen. There is one transition state that shows the concerted reaction for the base attracting the hydrogen and the halogen taking the electrons from the bond. The product be both eclipse and staggered depending on the transition states. Eclipsed products have a synperiplanar transition states, while staggered products have antiperiplanar transition states. Staggered conformation is usually the major product because of its lower energy confirmation.

An E2 reaction has certain requirements to proceed:

- A strong base is necessary especially necessary for primary alkyl halides. Secondary and tertirary primary halides will procede with E2 in the precesence of a base (OH-, RO-, R_2N-)
- Both leaving groups should be on the same plane, this allows the double bond to form in the reaction. In the reaction above you can see both leaving groups are in the plane of the carbons.
- Follows Zaitsev's rule, the most substituted alkene is usually the major product.
- Hoffman Rule, if a strically hindered base will result in the least substituted product.

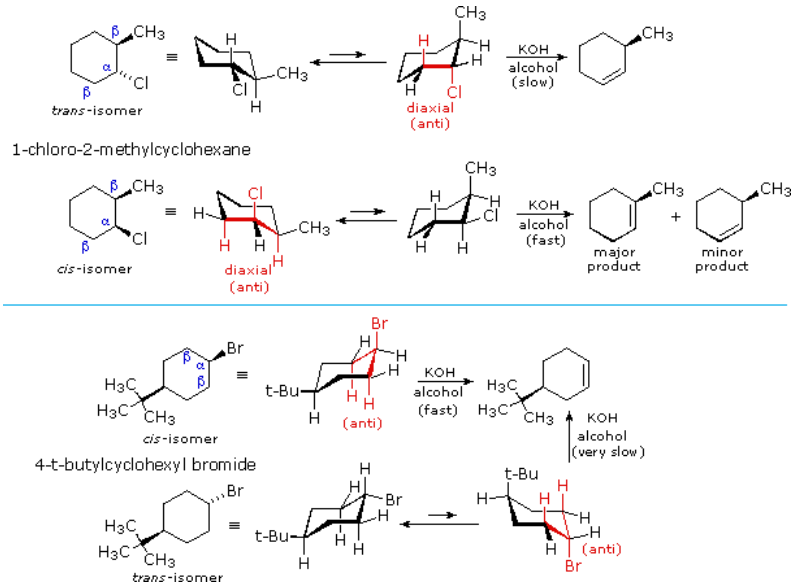
STEREOCHEMISTRY OF THE E2 REACTION

EDIT SECTION

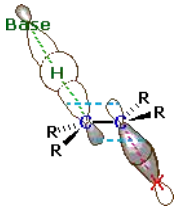
E2 elimination reactions of certain isomeric cycloalkyl halides show unusual rates and regioselectivity that are not explained by the principles thus far discussed. For example, trans-2-methyl-1-chlorocyclohexane reacts with alcoholic KOH at a much slower rate than does

its cis-isomer. Furthermore, the product from elimination of the trans-isomer is 3-methylcyclohexene (not predicted by the Zaitsev rule), whereas the cis-isomer gives the predicted 1-methylcyclohexene as the chief product. These differences are described by the first two equations in the following diagram.

Unlike open chain structures, cyclic compounds generally restrict the spatial orientation of ring substituents to relatively few arrangements. Consequently, reactions conducted on such substrates often provide us with information about the preferred orientation of reactant species in the transition state. Stereoisomers are particularly suitable in this respect, so the results shown here contain important information about the E2 transition state.



The most sensible interpretation of the elimination reactions of 2- and 4-substituted halocyclohexanes is that this reaction prefers an **anti orientation** of the halogen and the beta-hydrogen which is attacked by the base. These anti orientations are colored in red in the above equations. The compounds used here all have six-membered rings, so the anti orientation of groups requires that they assume a diaxial conformation. The observed differences in rate are the result of a steric preference for equatorial orientation of large substituents, which reduces the effective concentration of conformers having an axial halogen. In the case of the 1-bromo-4-tert-butylcyclohexane isomers, the tert-butyl group is so large that it will always assume an equatorial orientation, leaving the bromine to be axial in the cis-isomer and equatorial in the trans. Because of symmetry, the two axial beta-hydrogens in the cis-isomer react equally with base, resulting in rapid elimination to the same alkene (actually a racemic mixture). This reflects the fixed anti orientation of these hydrogens to the chlorine atom. To assume a conformation having an axial bromine the trans-isomer must tolerate serious crowding distortions. Such conformers are therefore present in extremely low concentration, and the rate of elimination is very slow. Indeed, substitution by hydroxide anion predominates.



A similar analysis of the 1-chloro-2-methylcyclohexane isomers explains both the rate and regioselectivity differences. Both the chlorine and methyl groups may assume an equatorial orientation in a chair conformation of the trans-isomer, as shown in the top equation. The axial chlorine needed for the E2 elimination is present only in the less stable alternative chair conformer, but this structure has only one axial beta-hydrogen (colored red), and the resulting elimination gives 3-methylcyclohexene. In the cis-isomer the smaller chlorine atom assumes an axial position in the more stable chair conformation, and here there are two axial beta hydrogens. The more stable 1-methylcyclohexene is therefore the predominant product, and the overall rate of elimination is relatively fast.

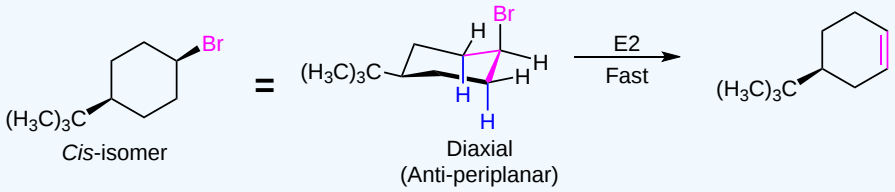
An orbital drawing of the anti-transition state is shown on the right. Note that the base attacks the alkyl halide from the side opposite the halogen, just as in the S_N2 mechanism. In this drawing the α and β carbon atoms are undergoing a rehybridization from sp^3 to sp^2 and the developing π-bond is drawn as dashed light blue lines. The symbol **R** represents an alkyl group or hydrogen. Since both the base and the alkyl halide are present in this transition state, the reaction is bimolecular and should exhibit second order kinetics. We should note in passing that a syn-transition state would also provide good orbital overlap for elimination, and in some cases where an anti-orientation is prohibited by structural constraints *syn*-elimination has been observed.

WORKED EXERCISE11.9.1

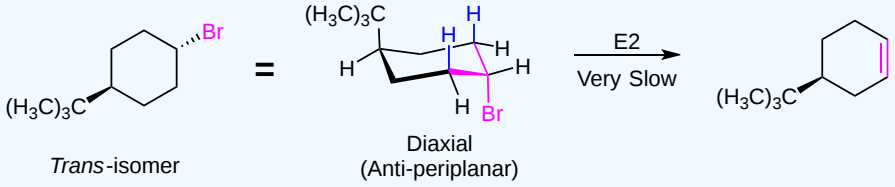
Which isomer would be expected to undergo E2 elimination quicker cis or trans-1-bromo-4-tert-butylcyclohexane? Explain your answer.

Answer

In the case of the 1-bromo-4-tert-butylcyclohexane isomers, the tert-butyl group is so large that it will always assume an equatorial orientation, leaving the bromine to be axial in the *cis*-isomer and equatorial in the *trans*-isomer. Because of symmetry, the two axial adjacent hydrogens in the *cis*-isomer react equally with base, resulting in rapid elimination to the same alkene (actually a racemic mixture). This reflects the fixed anti orientation of these hydrogens to the bromine atom. To assume a conformation having an axial bromine, the *trans*-isomer must tolerate serious crowding distortions. Such conformers are therefore present in extremely low concentration, and the rate of elimination is very slow. Indeed, substitution by hydroxide anion predominates in this situation.



1-Bromo-4-*t*-butylcyclohexane



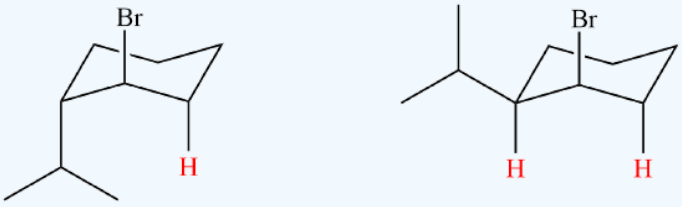
EXERCISE

EXERCISE 11.9.1

Which of the following compounds will react faster in an E2 reaction; *trans*-1-bromo-2-isopropylcyclohexane or *cis*-1-bromo-2-isopropylcyclohexane?

Answer

The *cis* isomer will react faster than the *trans*. The *cis* isomer has two possible perpendicular hydrogen in which it can eliminate from.



trans cis

QUESTIONS

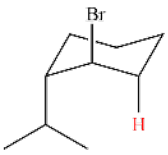
Q11.9.1

Which of the following compounds will react faster in an E2 reaction; *trans*-1-bromo-2-isopropylcyclohexane or *cis*-1-bromo-2-isopropylcyclohexane?

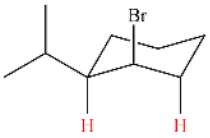
SOLUTIONS

S11.9.1

The *cis* isomer will react faster than the *trans*. The *cis* isomer has two possible perpendicular hydrogen in which it can eliminate from.



trans



cis

CONTRIBUTORS AND ATTRIBUTIONS

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- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
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11.10: THE E1 AND E1CB REACTIONS

Objectives

After completing this section, you should be able to

1. write the mechanism for a typical E1 reaction.
2. explain why E1 elimination often accompanies S_N1 substitution.
3. write an equation to describe the kinetics of an E1 reaction.
4. discuss the stereochemistry of E1 reactions.
5. account for the lack of a deuterium isotope effect in E1 reactions.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- E1 reaction
- E1cB reaction

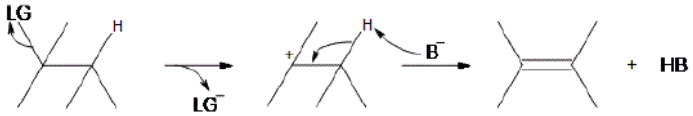
STUDY NOTES

The abbreviation E1 stands for “unimolecular elimination”; that is, an E1 reaction is an elimination reaction in which only one species is involved in the rate-limiting step.

Unimolecular Elimination (E1) is a reaction in which the removal of an HX substituent results in the formation of a double bond. It is similar to a unimolecular nucleophilic substitution reaction (S_N1) in various ways. One being the formation of a carbocation intermediate. Also, the only rate determining (slow) step is the dissociation of the leaving group to form a carbocation, hence the name unimolecular. Thus, since these two reactions behave similarly, they compete against each other. Many times, both these reactions will occur simultaneously to form different products from a single reaction. However, one can be favored over another through thermodynamic control. Although Elimination entails two types of reactions, E1 and E2, we will focus mainly on E1 reactions with some reference to E2.

GENERAL E1 REACTION

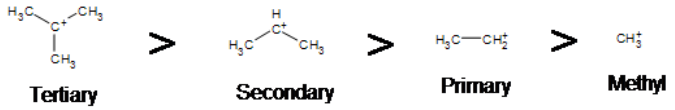
An E1 reaction involves the deprotonation of a hydrogen nearby (usually one carbon away, or the beta position) the carbocation resulting in the formation of an alkene product. In order to accomplish this, a Lewis base is required. For a simplified model, we’ll take B to be a Lewis base, and LG to be a halogen leaving group.



As can be seen above, the preliminary step is the leaving group (LG) leaving on its own. Because it takes the electrons in the bond along with it, the carbon that was attached to it loses its electron, making it a carbocation. Once it becomes a carbocation, a Lewis Base (B^-) deprotonates the intermediate carbocation at the beta position, which then donates its electrons to the neighboring C-C bond, forming a double bond. Unlike E2 reactions, which require the proton to be *anti* to the leaving group, E1 reactions only require a neighboring hydrogen. This is due to the fact that the leaving group has already left the molecule. The final product is an alkene along with the HB byproduct.

REACTIVITY

Due to the fact that E1 reactions create a carbocation intermediate, rules present in S_N1 reactions still apply.



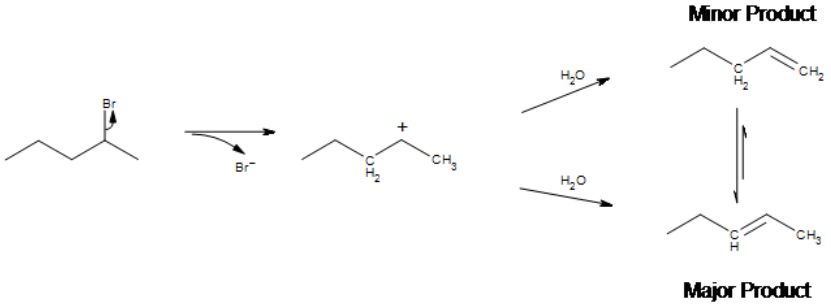
As expected, tertiary carbocations are favored over secondary, primary and methyl's. This is due to the phenomena of hyperconjugation, which essentially allows a nearby C-C or C-H bond to interact with the p orbital of the carbon to bring the electrons down to a lower energy state. Thus, this has a stabilizing effect on the molecule as a whole. In general, primary and methyl carbocations do not proceed through the E1 pathway for this reason, unless there is a means of carbocation rearrangement to move the positive charge to a nearby carbon. Secondary and Tertiary carbons form more stable carbocations, thus this formation occurs quite rapidly.

Secondary carbocations can be subject to the E2 reaction pathway, but this generally occurs in the presence of a good / strong base. Adding a weak base to the reaction disfavors E2, essentially pushing towards the E1 pathway. In many instances, solvolysis occurs rather than using a base to deprotonate. This means heat is added to the solution, and the solvent itself deprotonates a hydrogen. The medium can effect the pathway of the reaction as well. Polar protic solvents may be used to hinder nucleophiles, thus disfavoring E2 / S_n2 from occurring.

HOW ARE REGIOCHEMISTRY & STEREOCHEMISTRY INVOLVED?

In terms of regiochemistry, Zaitsev's rule states that although more than one product can be formed during alkene synthesis, the more substituted alkene is the major product. This infers that the hydrogen on the most substituted carbon is the most probable to be deprotonated, thus allowing for the most substituted alkene to be formed.

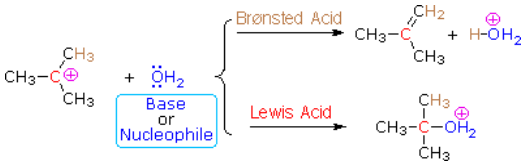
Unlike E2 reactions, E1 is not stereospecific. Thus, a hydrogen is not required to be anti-periplanar to the leaving group.



In this mechanism, we can see two possible pathways for the reaction. One in which the methyl on the right is deprotonated, and another in which the CH_2 on the left is deprotonated. Either one leads to a plausible resultant product, however, only one forms a major product. As stated by **Zaitsev's rule**, deprotonation of the most substituted carbon results in the most substituted alkene. This then becomes the most stable product due to hyperconjugation, and is also more common than the minor product.

THE CONNECTION BETWEEN S_N1 AND E1

The E1 mechanism is nearly identical to the S_N1 mechanism, differing only in the course of reaction taken by the carbocation intermediate. As shown by the following equations, a carbocation bearing beta-hydrogens may function either as a Lewis acid (electrophile), as it does in the S_N1 reaction, or a Brønsted acid, as in the E1 reaction.



Thus, hydrolysis of tert-butyl chloride in a mixed solvent of water and acetonitrile gives a mixture of 2-methyl-2-propanol (60%) and 2-methylpropene (40%) at a rate independent of the water concentration. The alcohol is the product of an S_N1 reaction and the alkene is the product of the E1 reaction. The characteristics of these two reaction mechanisms are similar, as expected. They both show first order kinetics; neither is much influenced by a change in the nucleophile/base; and both are relatively non-stereospecific.

$$(CH_3)_3C–Cl + H_2O \longrightarrow [\ (CH_3)_3C(+)\ ] + Cl^{(-)} + H_2O \longrightarrow (CH_3)_3C–OH + (CH_3)_2C{=}CH_2 + HCl + H_2O$$

To summarize, when carbocation intermediates are formed one can expect them to react further by one or more of the following modes:

1. The cation may bond to a nucleophile to give a substitution product.
2. The cation may transfer a beta-proton to a base, giving an alkene product.
3. The cation may rearrange to a more stable carbocation, and then react by mode #1 or #2.

Since the S_N1 and E1 reactions proceed via the same carbocation intermediate, the product ratios are difficult to control and both substitution and elimination usually take place.

Having discussed the many factors that influence nucleophilic substitution and elimination reactions of alkyl halides, we must now consider the practical problem of predicting the most likely outcome when a given alkyl halide is reacted with a given nucleophile. As we noted earlier, several variables must be considered, **the most important being the structure of the alkyl group and the nature of the nucleophilic reactant**. The nature of the halogen substituent on the alkyl halide is usually not very significant if it is Cl, Br or I. In cases where both S_N2 and E2 reactions compete, chlorides generally give more elimination than do iodides, since the greater electronegativity of chlorine increases the acidity of beta-hydrogens. Indeed, although alkyl fluorides are relatively unreactive, when reactions with basic nucleophiles are forced, elimination occurs (note the high electronegativity of fluorine).

THE E1CB REACTION

Although E1 reactions typically involves a carbocation intermediate, the E1cB reactoin utilizes a carbanion intermediate. This reaction is generally utilized when a poor leaving group, such an and alcohol, is involved. This poor leaving group makes the direct E1 or E2 reactions difficult. This reaction is used later in a reaction called an aldol condensation.

The product of this ***β*-elimination** reaction is an α,β-unsaturated aldehyde or ketone. Base-catalyzed elimination occurs with heating. The additional stability provided by the conjugated carbonyl system of the product makes some aldol reactions thermodynamically and mixtures of stereoisomers (E & Z) are obtained from some reactions.

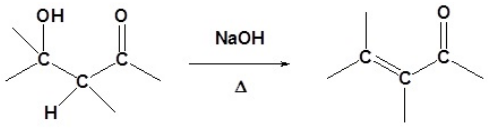
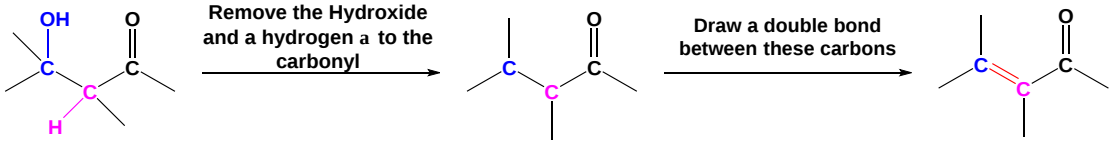
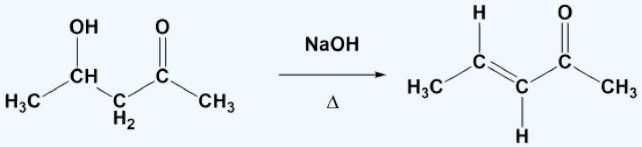


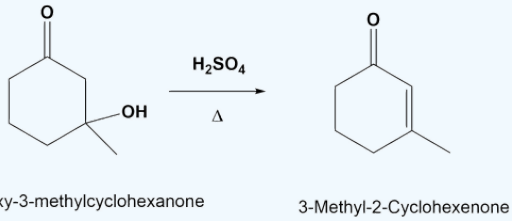
***Figure**: General reaction for an E1cB condensation*

Going from reactants to products simply



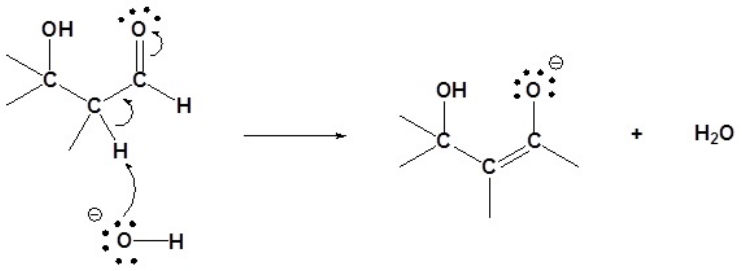
EXAMPLE 11.10.1



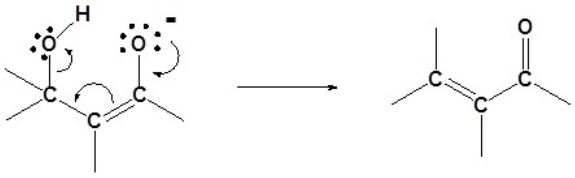


E1CB MECHANISM

1) Form resonance stabilized anion



2) Form for conjugated alkene

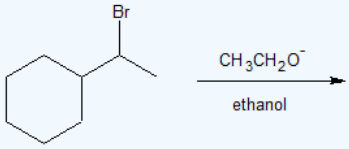


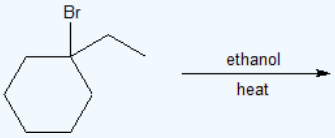
Note! The double bond always forms in conjugation with the carbonyl.

EXERCISES

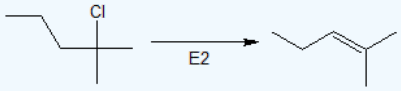
? EXERCISE 11.10.1

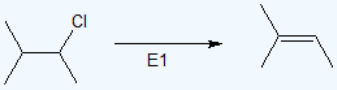
1. Predict the dominant elimination mechanism (E1 or E2) for each reaction below. Explain your reasoning.

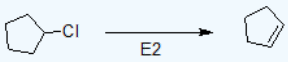
a) 

b) 

2) Specify the reaction conditions to favor the indicated elimination mechanism.

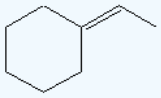
a) 

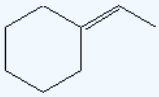
b) 

c) 

Answer

1)

a)  E2 reaction b/c secondary alkyl halide with a strong base.

b)  E1 reaction b/c tertiary alkyl halide with a weak base.

2)

a) strong base, such as hydroxide, an alkoxide, or equivalent

b) water or alcohol or equivalent weak base with heat

c) strong base, such as hydroxide, an alkoxide, or equivalent

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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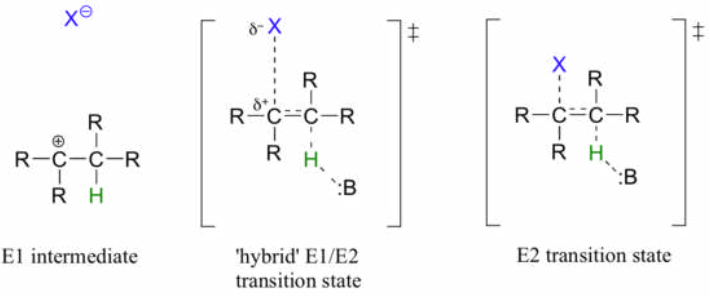
11.11: BIOLOGICAL ELIMINATION REACTIONS

Objective

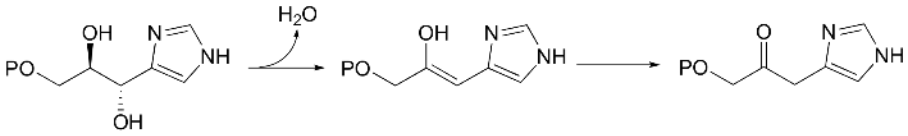
After completing this section, you should have an appreciation that E1, E2 and E1cB mechanisms exist and are well-known in biological chemistry.

ENZYMATIC E1 AND E2 REACTIONS

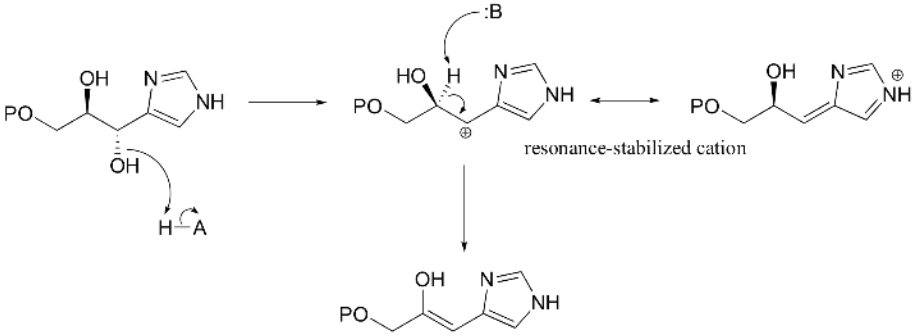
While most biochemical b-elimination reactions are of the E1cb type, some enzymatic E2 and E1 reactions are known. Like the enzymatic S_N2 and S_N1 substitution mechanisms discussed in chapters 8 and 9, the E2 and E1 models represent two possible mechanistic extremes, and actual enzymatic elimination reactions may fall somewhere in between. In an E1/E2 hybrid elimination, for example, C_β-X bond cleavage may be quite advanced (but not complete) before proton abstraction takes place - this would lead to the build-up of transient *partial* positive charge on C_β, but a discreet carbocation intermediate would not form. The extent to which partial positive charge builds up determines whether we refer to the mechanism as 'E1-like' or 'E2-like'.



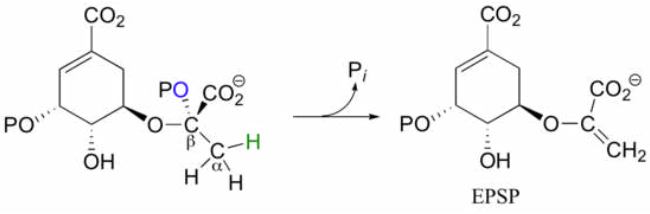
A reaction in the histidine biosynthetic pathway provides a good example of a biological E1-like elimination step (we're looking specifically here at the first, enol-forming step in the reaction below - the second step is simply a tautomerization from the enol to the ketone product (section 13.1A)).



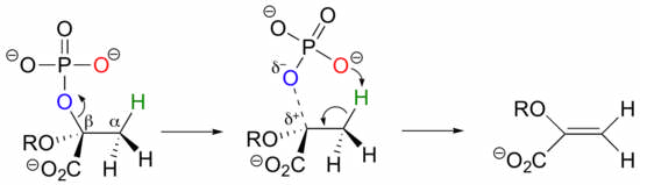
Notice in this mechanism that an E1cb elimination is not possible - there is no electron-withdrawing group (like a carbonyl) to stabilize the carbanion intermediate that would form if the proton were abstracted first. There is, however, an electron-*donating* group (the lone pair on a nitrogen) that can stabilize a positively-charged intermediate that forms when the water leaves.



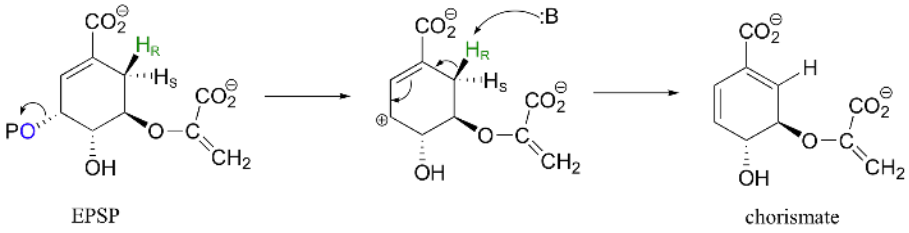
Another good example of a biological E1-like reaction is the elimination of phosphate in the formation of 5-enolpyruvylshikimate-3-phosphate (EPSP), an intermediate in the synthesis of aromatic amino acids.



Experimental evidence indicates that significant positive charge probably builds up on C_β of the starting compound, implying that C-O bond cleavage is advanced before proton abstraction occurs (notice the parallels to the Cope elimination in the previous section):

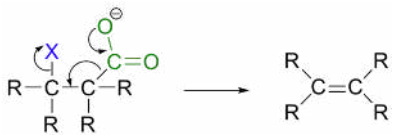


The very next step in the aromatic acid biosynthesis pathway is also an elimination, this time a 1,6-conjugated elimination rather than a simple beta-elimination.

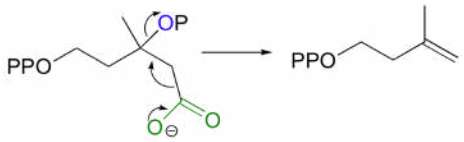


An E1-like mechanism (as illustrated above) has been proposed for this step, but other evidence suggests that a free-radical mechanism may be involved.

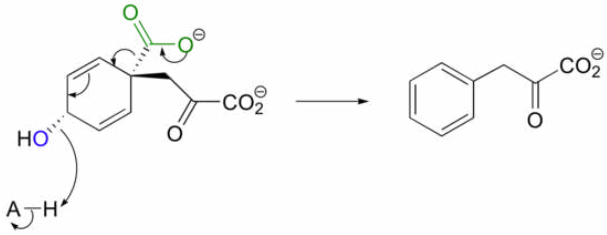
While most E1 and E2 reactions involve proton abstraction, eliminations can also incorporate a decarboxylation step.



Isopentenyl diphosphate, the 'building block' for all isoprenoid compounds, is formed from a decarboxylation-elimination reaction.



Phenylpyruvate, a precursor in the biosynthesis of phenylalanine, results from a conjugated 1,6 decarboxylation-elimination.



Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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11.12: A SUMMARY OF REACTIVITY - SN1, SN2, E1, E1CB, AND E2

Objectives

After completing this section, you should be able to

1. determine whether a specified substrate is most likely to undergo an E1, E2, S_N1 or S_N2 reaction under a given set of conditions.
2. describe the conditions under which a given substrate is most likely to react by a specified mechanism (E1, E2, S_N1 or S_N2).

STUDY NOTES

This section summarizes much of what has been discussed in the chapter. It focuses on how a given substrate will behave under certain conditions, but does not deal with the stereochemistry of the products.

CONTENT

Having discussed the many factors that influence nucleophilic substitution and elimination reactions of alkyl halides, we must now consider the practical problem of predicting the most likely outcome when a given alkyl halide is reacted with a given nucleophile. As we noted earlier, several variables must be considered, **the most important being the structure of the alkyl group and the nature of the nucleophilic reactant**.In general, in order for an SN1 or E1 reaction to occur, the relevant carbocation intermediate must be relatively stable. Strong nucleophile favor substitution, and strong bases, especially strong hindered bases (such as tert-butoxide) favor elimination.

The nature of the halogen substituent on the alkyl halide is usually not very significant if it is Cl, Br or I. In cases where both S_N2 and E2 reactions compete, chlorides generally give more elimination than do iodides, since the greater electronegativity of chlorine increases the acidity of beta-hydrogens. Indeed, although alkyl fluorides are relatively unreactive, when reactions with basic nucleophiles are forced, elimination occurs (note the high electronegativity of fluorine).

The following table summarizes the expected outcome of alkyl halide reactions with nucleophiles. It is assumed that the alkyl halides have one or more beta-hydrogens, making elimination possible; and that low dielectric solvents (e.g. acetone, ethanol, tetrahydrofuran & ethyl acetate) are used. When a high dielectric solvent would significantly influence the reaction this is noted in red. **Note that halogens bonded to sp^2 or sp hybridized carbon atoms do not normally undergo substitution or elimination reactions with nucleophilic reagents**.

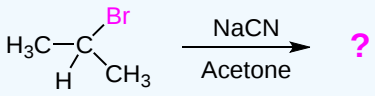
Nucleophile	**Anionic Nucleophiles** (Weak Bases: I^-, Br^-, SCN^-, N_3^-, $CH_3CO_2^-$, RS^-, CN^- etc.) pK_a's from -9 to 10 (left to right)	**Anionic Nucleophiles** (Strong Bases: HO^-, RO^-) pK_a's > 15	**Neutral Nucleophiles** (H_2O, ROH, RSH, R_3N) pK_a's ranging from -2 to 11
Alkyl Group			
Primary RCH_2–	Rapid S_N2 substitution. The rate may be reduced by substitution of β-carbons, as in the case of neopentyl.	Rapid S_N2 substitution. E2 elimination may also occur. *e.g.* $ClCH_2CH_2Cl$ + KOH ⟶ CH_2=CHCl	S_N2 substitution. (N ≈ S >>O)
Secondary R_2CH–	S_N2 substitution and / or E2 elimination (depending on the basicity of the nucleophile). Bases weaker than acetate (pK_a = 4.8) give less elimination. The rate of substitution may be reduced by branching at the β-carbons, and this will increase elimination.	E2 elimination will dominate.	S_N2 substitution. (N ≈ S >>O) In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, S_N1 and E1 products may be formed slowly.
Tertiary R_3C–	E2 elimination will dominate with most nucleophiles (even if they are weak bases). No S_N2 substitution due to steric hindrance. In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, S_N1 and E1 products may be expected.	E2 elimination will dominate. No S_N2 substitution will occur. In high dielectric ionizing solvents S_N1 and E1 products may be formed.	E2 elimination with nitrogen nucleophiles (they are bases). No S_N2 substitution. In high dielectric ionizing solvents S_N1 and E1 products may be formed.
Allyl H_2C=$CHCH_2$–	Rapid S_N2 substitution for 1º and 2º-halides. For 3º-halides a very slow S_N2 substitution or, if the nucleophile is moderately basic, E2 elimination. In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, S_N1 and E1 products may be observed.	Rapid S_N2 substitution for 1º halides. E2 elimination will compete with substitution in 2º-halides, and dominate in the case of 3º-halides. In high dielectric ionizing solvents S_N1	Nitrogen and sulfur nucleophiles will give S_N2 substitution in the case of 1º and 2º-halides. 3º-halides will probably give E2 elimination with nitrogen nucleophiles (they are bases). In

		and E1 products may be formed.	high dielectric ionizing solvents S_N1 and E1 products may be formed. Water hydrolysis will be favorable for 2º & 3º-halides.
Benzyl $C_6H_5CH_2$–	Rapid S_N2 substitution for 1º and 2º-halides. For 3º-halides a very slow S_N2 substitution or, if the nucleophile is moderately basic, E2 elimination. In high dielectric ionizing solvents, such as water, dimethyl sulfoxide & acetonitrile, S_N1 and E1 products may be observed.	Rapid S_N2 substitution for 1º halides (note there are no β hydrogens). E2 elimination will compete with substitution in 2º-halides, and dominate in the case of 3º-halides. In high dielectric ionizing solvents S_N1 and E1 products may be formed.	Nitrogen and sulfur nucleophiles will give S_N2 substitution in the case of 1º and 2º-halides. 3º-halides will probably give E2 elimination with nitrogen nucleophiles (they are bases). In high dielectric ionizing solvents S_N1 and E1 products may be formed. Water hydrolysis will be favorable for 2º & 3º-halides.

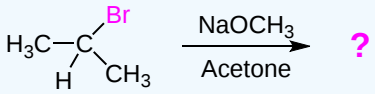
? WORKED EXAMPLE 11.12.1

1) For the following, please determine what kind of reaction is occurring and predict the product(s).

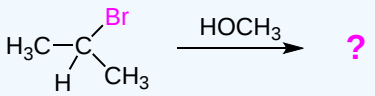
a)



b)

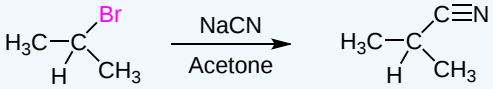


c)

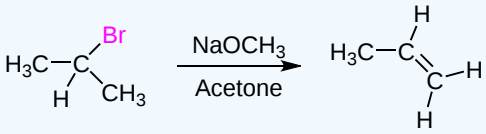


Answer

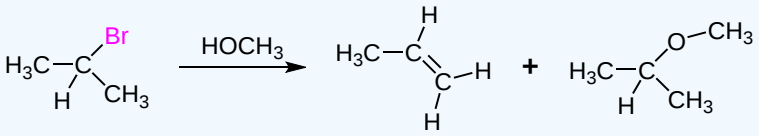
a) The substrate is a secondary halide so the product is determined by the nature of the nucleophile used in the reaction. Cyanide ($^-$CN) is a good nucleophile which is a weak base. The fact that the nucleophile is a weak base means that an E2 reaction is not favored. Also, the fact that cyanide is a good nucleophile means that S_N2 substitutions are favored over S_N1. When a secondary halide is reacted with a good nucleophile which is a weak base, the preferred reaction is S_N2. After S_N2 substitution the product is a nitrile.



b) The substrate is a secondary halide so the product is determined by the nature of the nucleophile used in the reaction. Methoxide ($^-OCH_3$) is a strong base so it could prefer to remove a hydrogen from the substrate. This makes an E2 elimination the preferred reaction and an alkene the product.



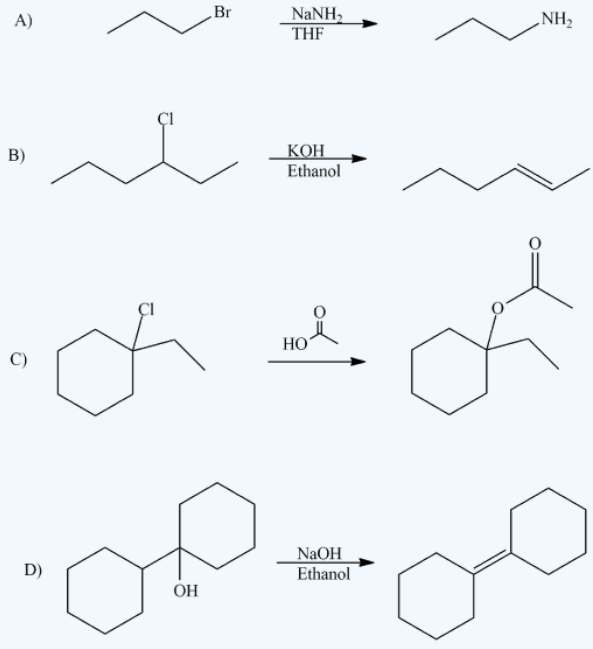
c) The substrate is a secondary halide so the product is determined by the nature of the nucleophile used in the reaction. Methanol ($HOCH_3$) is a weak nucleophile that is a weak base. Being a weak base means that methanol is not capable of actively removing a hydrogen to cause an E2 reaction. Also, because methanol is a weak nucleophile is not capable of attacking the substrate and causing an S_N2 reaction. For the methanol nucleophile to react the substrate must first eject it leaving group to form the highly reactive carbocation intermediate. Formation of the carbocation is the rate determine step for both the S_N1 and E1 reactions so they each form a separate product.



EXERCISES

? EXERCISE 11.12.1

Identify the dominant reaction mechanism (S_N1, S_N2, E1, or E2) for the following reactions.



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Answer

A) S_N2

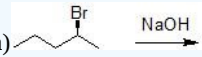
B) E1

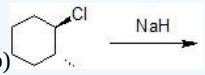
C) S_N1

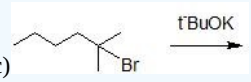
D) E2

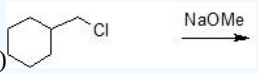
EXERCISES 11.12.2

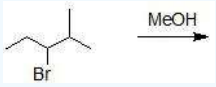
Identify all the products of the following reactions and specify the major product.

a) 

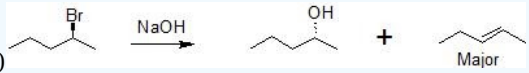
b) 

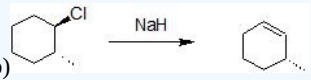
c) 

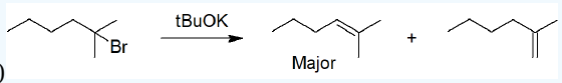
d) 

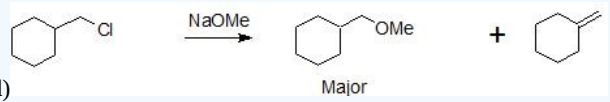
e) 

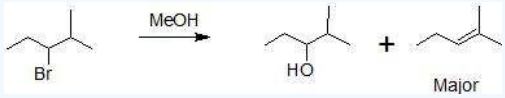
Answer

a) 

b) 

c) 

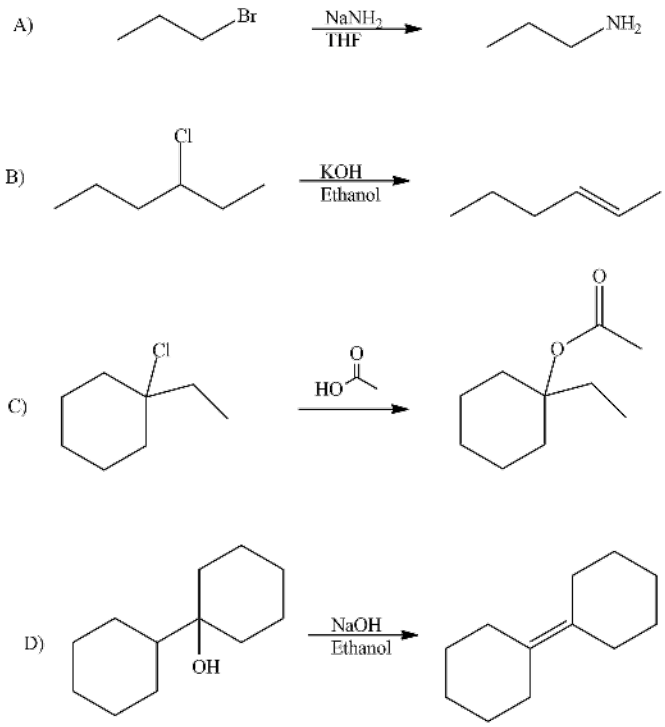
d) 

e) 

QUESTIONS

Q11.12.1

Label the following reactions as S_N1, S_N2, E1, or E2.



SOLUTIONS

S11.12.1

A – S_N2

B – E1

C – S_N1

D – E2

CONTRIBUTORS AND ATTRIBUTIONS

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

11.12: A Summary of Reactivity - SN1, SN2, E1, E1cB, and E2 is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

11.S: REACTIONS OF ALKYL HALIDES - NUCLEOPHILIC SUBSTITUTIONS AND ELIMINATIONS (SUMMARY)

CONCEPTS & VOCABULARY

11.1 Introduction

- Alkyl halides react as electrophiles and undergo nucleophilic substitution and elimination reactions.

11.2 The Discovery of Nucleophilic Substitution Reactions

- Some nucleophilic substitution reactions invert stereochemistry at the reactive carbon.

11.3 The S_N2 Reaction

- Reaction steps with two molecules involved in the rate determining step are called bimolecular.
- A substitution mechanism that has the nucleophile entering at the same time the leaving group leaves, in a concerted step, is called S_N2 - substitution nucleophilic bimolecular.
- Concerted substitution mechanisms (S_N2) occur via backside attack, which causes inversion of the carbon where the reaction occurs.
- Rates of S_N2 reactions depend on concentration of nucleophile and alkyl halide.

11.4 Characteristics of the S_N2 Reaction

- S_N2 reactions are concerted.
- Sterically hindered substrates reduce S_N2 reaction rate.
- A **transition state** in a reaction mechanism is the highest energy point on a pathway from reactants to an intermediate or products.
- Larger groups (such as alkyl vs. hydrogen) cause greater steric repulsion in S_N2 **transition states**, reducing rates of S_N2 reactions.
- Groups that have electron-rich atoms are typically good nucleophiles.
- In general, stronger bases are better nucleophiles.
- Polar aprotic solvents increase rates of S_N2 reactions.
- Polar protic solvents decrease rates of S_N2 reactions.
- As basicity of leaving groups decreases, their ability to leave increases.

11.5 The S_N1 Reaction

- A substitution mechanism that occurs with the leaving group leaving in the first step, creating a carbocation intermediate, followed by the nucleophile entering is called S_N1 - substitution nucleophilic unimolecular.
- S_N1 reactions occur through a stepwise mechanism.
- The first step (dissociation) of an S_N1 mechanism is rate limiting.
- In S_N1 reactions the nucleophile is not involved in the rate limiting step, therefore nucleophile strength or concentration do not affect the rate.
- The intermediate for S_N1 mechanisms contains a planar carbocation. The nucleophile can then enter from either side of the molecule giving racemic products with no additional stereocenters in the molecule.

11.6 Characteristics of the S_N1 Reaction

- Polar solvents increase rates of S_N1 reactions.
- Better leaving groups increase rates of S_N1 and S_N2 reactions.
- Predicting whether a reaction will follow an S_N1 or S_N2 mechanism requires analysis of:
  - Electrophile - primary favor S_N2, tertiary (and allyl or benzyl) favor S_N1, secondary depends on other factors
  - Nucleophile - strong favor S_N2, weak favor S_N1
  - Solvent - polar aprotic favor S_N2, polar protic favor S_N1

11.7 Biological Substitution Reactions

- When biological substitution reactions occur, the electrophiles are often different though the mechanisms are primarily the same.

11.8 Elimination Reactions - Zaitsev's Rule

- The major product of Elimination reactions is the product with the more substituted double bond. This is known as Zaitsev's rule.

11.9 The E2 Reaction and Deuterium Isotope Effect

- The E2 mechanism is concerted with the base removing a proton and the leaving group leaving at the same time.
- Since E2 mechanisms are concerted, both the base and the electrophile are present in the rate equation.

- E2 reactions require strong bases and polar aprotic solvents.
- Kinetic Isotope Effects can provide evidence for E2 mechanisms since they can show when breaking of the C-H bond is part of the rate-determining step.

11.10 The E2 Reaction and Cyclohexane Conformation

- E2 reactions of cyclic structures show necessity for anti orientation of the proton being removed and the leaving group.

11.11 The E1 and E1cB Reactions

- E1 mechanisms begin with a leaving group leaving which forms a carbocation intermediate, which is then deprotonated in a second step.
- E1 mechanisms are step-wise.
- More substituted electrophiles are more reactive in E1 reactions.
- Zaitsev products are preferred, similarly to E2 reactions.
- E1 and S_N1 proceed via the same carbocation intermediate and the same rate-determining step so typically happen concurrently.
- E1cB reactions begin with deprotonation (usually resulting in a resonance stabilized carbanion), followed by loss of the leaving group in the second step.

11.12 Biological Elimination Reactions

- There are many important examples of biological elimination reactions.

11.13 A Summary of Reactivity - S_N1, S_N2, E1, E1CcB, and E2

SKILLS TO MASTER

- Skill 11.1 Draw S_N1/S_N2 mechanisms showing appropriate stereochemistry.
- Skill 11.2 Explain when S_N1/S_N2 mechanisms are likely to occur.
- Skill 11.3 Describe/draw the intermediate for an S_N1 mechanism and transition state(s) for S_N1/S_N2 mechanisms.
- Skill 11.4 Write out rate laws for S_N1/S_N2 mechanisms.
- Skill 11.5 Differentiate between which mechanism is more likely between S_N1/S_N2.
- Skill 11.6 Draw reaction coordinate diagrams for S_N1/S_N2 mechanisms.
- Skill 11.7 Explain how the electrophile, nucleophile, leaving group, and solvent affect S_N1/S_N2 mechanisms.
- Skill 11.8 Recognize use of nucleophilic substitution and elimination reactions in biological systems.
- Skill 11.9 Draw E1/E2 mechanisms showing appropriate stereochemistry.
- Skill 11.10 Explain when E1/E2 mechanisms are likely to occur.
- Skill 11.11Describe/draw the intermediate for an E1 mechanism and transition state(s) for E1/E2mechanisms.
- Skill 11.12 Write out rate laws for E1/E2 mechanisms.
- Skill 11.13 Differentiate between which mechanism is more likely between E1/E2.
- Skill 11.14 Draw reaction coordinate diagrams for E1/E2 mechanisms.
- Skill 11.15 Explain how kinetic isotope effects can be used to support or refute a proposed mechanism.
- Skill 11.16 Draw an E1cB mechanism and explain when it is a viable option.
- Skill 11.17 Differentiate between which mechanism is more likely between S_N1/S_N2 and E1/E2.

MEMORIZATION TASKS (MT)

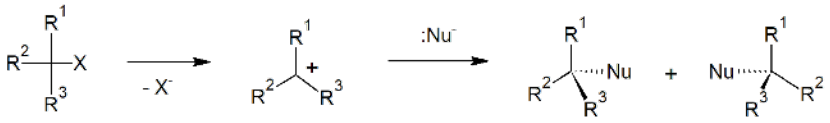
MT 11.1 Memorize the order of good leaving groups.

MT 11.2 Memorize which solvents are polar protic and polar aprotic.

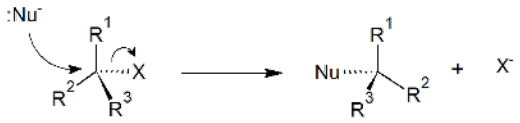
MT 11.3 Memorize the stability order of carbocations.

SUMMARY OF REACTIONS

Nucleophilic Substitutions

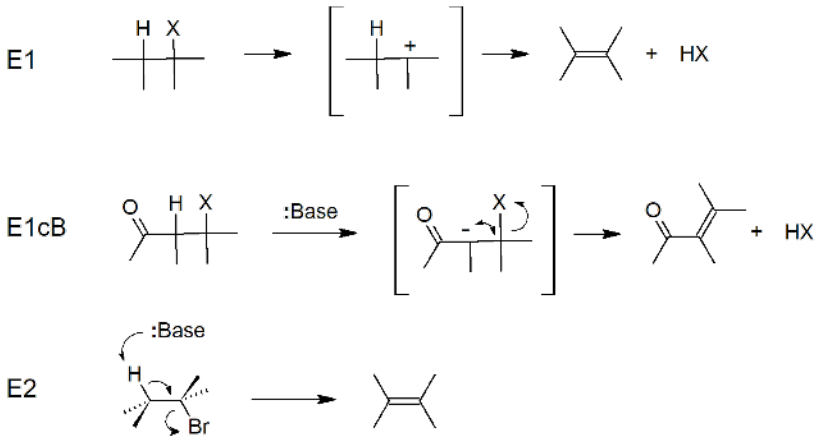


S_N1 (racemic mix of *R* and *S* products)



S_N2 (inverted product)

Eliminations



CONTRIBUTORS

- Layne Morsch (University of Illinois Springfield)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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CHAPTER OVERVIEW

12: STRUCTURE DETERMINATION- MASS SPECTROMETRY AND INFRARED SPECTROSCOPY

LEARNING OBJECTIVES

After you have completed Chapter 12, you should be able to

1. fulfil all of the detailed objectives listed under each individual section.
2. solve road-map problems that include mass spectral data, infrared data, or both.
3. define, and use in context, the key terms introduced.

The processes of identifying and characterizing organic compounds are of great importance to the working organic chemist. With the use of modern instrumental techniques, these tasks can now be accomplished much more readily than in the past. In this chapter, you will learn about two spectroscopic techniques (mass spectroscopy and infrared spectroscopy) that are used to identify organic compounds.

12.0: Introduction

12.1: Mass Spectrometry of Small Molecules - Magnetic-Sector Instruments

12.2: Interpreting Mass Spectra

12.3: Mass Spectrometry of Some Common Functional Groups

12.4: Mass Spectrometry in Biological- Time-of-flight (TOF) Instruments

12.5: Spectroscopy and the Electromagnetic Spectrum

12.6: Infrared Spectroscopy

12.7: Interpreting Infrared Spectra

12.8: Infrared Spectra of Some Common Functional Groups

12.S: Structure Determination - Mass Spectrometry and Infrared Spectroscopy (Summary)

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12.0: INTRODUCTION

Objective

After completing this section, you should be able to recognize the various spectroscopic techniques used to identify and characterize organic compounds.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- spectroscopy

STUDY NOTES

The term spectroscopy is used to describe a number of techniques used by chemists to obtain information about the structure and bonding of chemical compounds. Four types of spectroscopy are described in the course:

1. mass spectroscopy (also called mass spectrometry, Chapter 12).
2. infrared spectroscopy (often simply called IR, Chapter 12).
3. nuclear magnetic resonance spectroscopy (usually referred to as NMR, Chapter 13).
4. ultraviolet spectroscopy (abbreviated UV, Chapter 14).

Of these four techniques, we shall spend the least time on ultraviolet spectroscopy, as it is much less powerful than the other three. If you do any reading on chemistry outside of the course materials, you will almost certainly see references to other spectroscopic techniques, such as Raman spectroscopy, electron spin resonance (ESR) spectroscopy, and atomic absorption (AA) spectroscopy. Even a description of these techniques and the information they can provide is beyond the scope of this course.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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12.1: MASS SPECTROMETRY OF SMALL MOLECULES - MAGNETIC-SECTOR INSTRUMENTS

Objectives

After completing this section, you should be able to

1. describe, briefly, how a mass spectrometer works.
2. sketch a simple diagram to show the essential features of a mass spectrometer.
3. identify peaks in a simple mass spectrum, and explain how they arise.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- base peak
- parent peak (molecular ion peak)
- cation radical
- relative abundance
- mass spectrometer
- mass spectroscopy
- mass spectrum
- molecular ion ($M^{+\cdot}$)
- mass-to-charge ratio (m/z)

STUDY NOTES

You may remember from general first-year chemistry how mass spectroscopy has been used to establish the atomic mass and abundance of isotopes.

Mass spectrometers are large and expensive, and usually operated only by fully trained personnel, so you will not have the opportunity to use such an instrument as part of this course. Research chemists often rely quite heavily on mass spectra to assist them in the identification of compounds, and you will be required to interpret simple mass spectra both in assignments and on examinations. Note that in most attempts to identify an unknown compound, chemists do not rely exclusively on the results obtained from a single spectroscopic technique. A combination of chemical and physical properties and spectral evidence is usually employed.

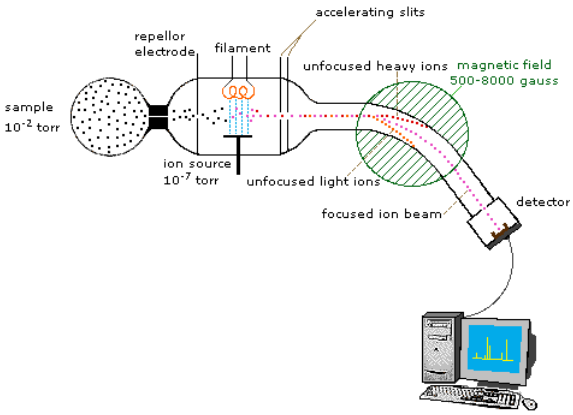
THE MASS SPECTROMETER

In order to measure the characteristics of individual molecules, a mass spectrometer converts them to ions so that they can be moved about and manipulated by external electric and magnetic fields. The three essential functions of a mass spectrometer, and the associated components, are:

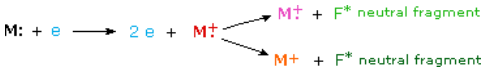
1. A small sample is ionized, usually to cations by loss of an electron. **The Ion Source**
2. The ions are sorted and separated according to their mass and charge. **The Mass Analyzer**
3. The separated ions are then measured, and the results displayed on a chart. **The Detector**

Because ions are very reactive and short-lived, their formation and manipulation must be conducted in a vacuum. Atmospheric pressure is around 760 torr (mm of mercury). The pressure under which ions may be handled is roughly 10^{-5} to 10^{-8} torr (less than a billionth of an atmosphere). Each of the three tasks listed above may be accomplished in different ways. In one common procedure, ionization is effected by a high energy beam of electrons, and ion separation is achieved by accelerating and focusing the ions in a beam, which is then bent by an external magnetic field. The ions are then detected electronically and the resulting information is stored and analyzed in a computer. A mass spectrometer operating in this fashion is outlined in the following diagram. The heart of the spectrometer is the **ion source**. Here molecules of the sample (black dots) are bombarded by electrons (light blue lines) issuing from a heated filament. This is called an **EI** (electron-impact) source. Gases and volatile liquid samples are allowed to leak into the ion source from a reservoir (as shown). Non-volatile solids and liquids may be introduced directly. Cations formed by the electron bombardment (red dots) are pushed away by a charged repellor plate (anions are attracted to it), and accelerated toward other electrodes, having slits through which the ions pass as a beam. Some of these ions fragment into smaller cations and neutral fragments. A perpendicular magnetic field deflects the ion beam in an arc whose radius is

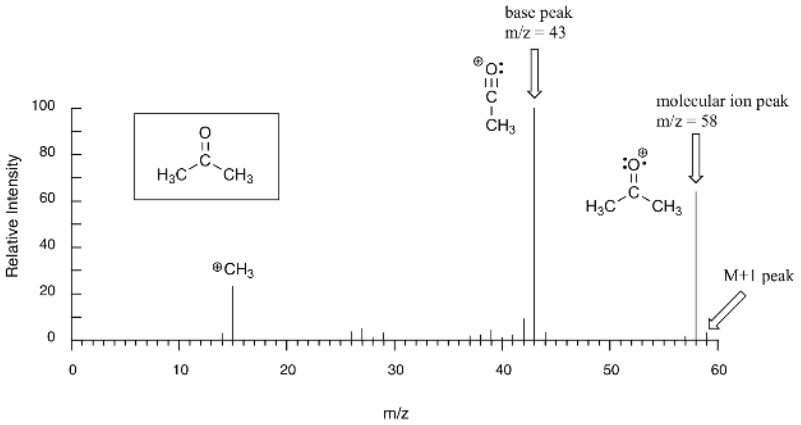
inversely proportional to the mass of each ion. Lighter ions are deflected more than heavier ions. By varying the strength of the magnetic field, ions of different mass can be focused progressively on a detector fixed at the end of a curved tube (also under a high vacuum).



When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind a **molecular ion** (colored red in the following diagram). Residual energy from the collision may cause the molecular ion to fragment into neutral pieces (colored green) and smaller **fragment ions** (colored pink and orange). The molecular ion is a radical cation, but the fragment ions may either be radical cations (pink) or carbocations (orange), depending on the nature of the neutral fragment. An animated display of this ionization process will appear if you click on the ion source of the mass spectrometer diagram.



Below is typical output for an electron-ionization MS experiment (MS data below is derived from the Spectral Database for Organic Compounds, a free, web-based service provided by AIST in Japan.



The sample is acetone. On the horizontal axis is the value for m/z (as we stated above, the charge z is almost always +1, so in practice this is the same as mass). On the vertical axis is the relative abundance of each ion detected. On this scale, the most abundant ion, called the **base peak**, is set to 100%, and all other peaks are recorded relative to this value. For acetone, the base peak corresponds to a fragment with m/z = 43 - . The molecular weight of acetone is 58, so we can identify the peak at m/z = 58 as that corresponding to the **molecular ion peak**, or **parent peak**. Notice that there is a small peak at m/z = 59: this is referred to as the **M+1 peak**. How can there be an ion that has a greater mass than the molecular ion? Simple: a small fraction - about 1.1% - of all carbon atoms in nature are actually the ^{13}C rather than the ^{12}C isotope. The ^{13}C isotope is, of course, heavier than ^{12}C by 1 mass unit. In addition, about 0.015% of all hydrogen atoms are actually deuterium, the ^{2}H isotope. So the M+1 peak represents those few acetone molecules in the sample which contained either a ^{13}C or ^{2}H.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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12.2: INTERPRETING MASS SPECTRA

Objectives

After completing this section, you should be able to

1. suggest possible molecular formulas for a compound, given the *m/z* value for the molecular ion, or a mass spectrum from which this value can be obtained.
2. predict the relative heights of the $M^{+\cdot}$, $(M + 1)^{+\cdot}$, etc., peaks in the mass spectrum of a compound, given the natural abundance of the isotopes of carbon and the other elements present in the compound.
3. interpret the fragmentation pattern of the mass spectrum of a relatively simple, known compound (e.g., hexane).
4. use the fragmentation pattern in a given mass spectrum to assist in the identification of a relatively simple, unknown compound (e.g., an unknown alkane).

STUDY NOTES

When interpreting fragmentation patterns, you may find it helpful to know that, as you might expect, the weakest carbon-carbon bonds are the ones most likely to break. You might wish to refer to the table of bond dissociation energies when attempting problems involving the interpretation of mass spectra.

This page looks at how fragmentation patterns are formed when organic molecules are fed into a mass spectrometer, and how you can get information from the mass spectrum.

THE ORIGIN OF FRAGMENTATION PATTERNS

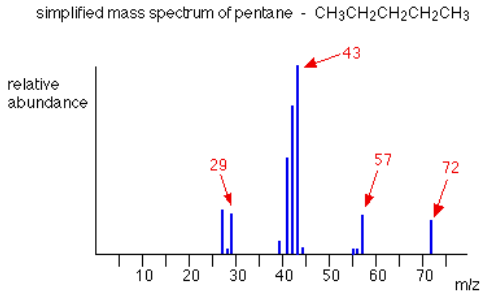
When the vaporized organic sample passes into the ionization chamber of a mass spectrometer, it is bombarded by a stream of electrons. These electrons have a high enough energy to knock an electron off an organic molecule to form a positive ion. This ion is called the **molecular ion - or sometimes the parent ion** and is often given the symbol M^+ or $M^{+\cdot}$. The dot in this second version represents the fact that somewhere in the ion there will be a single unpaired electron. That's one half of what was originally a pair of electrons - the other half is the electron which was removed in the ionization process.

The molecular ions are energetically unstable, and some of them will break up into smaller pieces. The simplest case is that a molecular ion breaks into two parts - one of which is another positive ion, and the other is an uncharged free radical.



The uncharged free radical will **not** produce a line on the mass spectrum. Only charged particles will be accelerated, deflected and detected by the mass spectrometer. These uncharged particles will simply get lost in the machine - eventually, they get removed by the vacuum pump.

The ion, X^+, will travel through the mass spectrometer just like any other positive ion - and will produce a line on the stick diagram. All sorts of fragmentations of the original molecular ion are possible - and that means that you will get a whole host of lines in the mass spectrum. For example, the mass spectrum of pentane looks like this:



NOTE

The pattern of lines in the mass spectrum of an *organic compound* tells you something quite different from the pattern of lines in the mass spectrum of an *element*. With an element, each line represents a different isotope of that element. With a compound, each line represents a different fragment produced when the molecular ion breaks up.

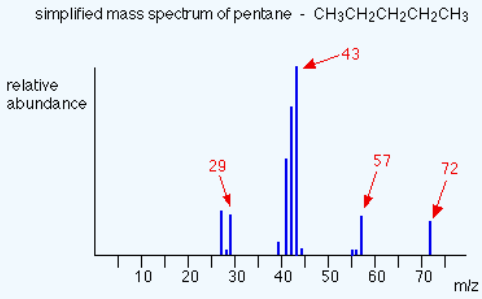
In the stick diagram showing the mass spectrum of pentane, the line produced by the heaviest ion passing through the machine (at m/z = 72) is due to the molecular ion. The tallest line in the stick diagram (in this case at m/z = 43) is called the **base peak**. This is usually given an arbitrary height of 100, and the height of everything else is measured relative to this. The base peak is the tallest peak because it represents the commonest fragment ion to be formed - either because there are several ways in which it could be produced during fragmentation of the parent ion, or because it is a particularly stable ion.

USING FRAGMENTATION PATTERNS

This section will ignore the information you can get from the molecular ion (or ions). That is covered in three other pages which you can get at via the mass spectrometry menu. You will find a link at the bottom of the page.

EXAMPLE 12.2.1: PENTANE

Let's have another look at the mass spectrum for pentane:



What causes the line at m/z = 57?

How many carbon atoms are there in this ion? There cannot be 5 because 5 x 12 = 60. What about 4? 4 x 12 = 48. That leaves 9 to make up a total of 57. How about $C_4H_9^+$ then?

$C_4H_9^+$ would be $[CH_3CH_2CH_2CH_2]^+$, and this would be produced by the following fragmentation:

$$[CH_3CH_2CH_2CH_2CH_3]^{\ddagger} \longrightarrow [CH_3CH_2CH_2CH_2]^+ + \bullet CH_3$$

The methyl radical produced will simply get lost in the machine.

The line at m/z = 43 can be worked out similarly. If you play around with the numbers, you will find that this corresponds to a break producing a 3-carbon ion:

$$[CH_3CH_2CH_2CH_2CH_3]^{\ddagger} \longrightarrow [CH_3CH_2CH_2]^+ + \bullet CH_2CH_3$$

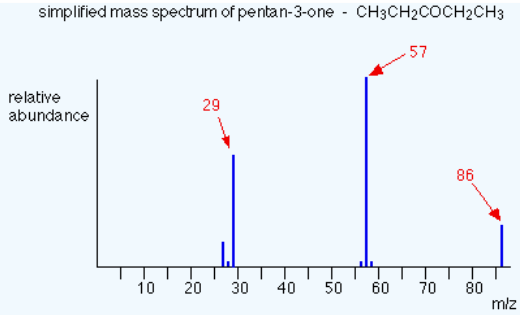
The line at m/z = 29 is typical of an ethyl ion, $[CH_3CH_2]^+$:

$$[CH_3CH_2CH_2CH_2CH_3]^{\ddagger} \longrightarrow [CH_3CH_2]^+ + \bullet CH_2CH_2CH_3$$

The other lines in the mass spectrum are more difficult to explain. For example, lines with m/z values 1 or 2 less than one of the easy lines are often due to loss of one or more hydrogen atoms during the fragmentation process.

EXAMPLE 12.2.2: PENTAN-3-ONE

This time the base peak (the tallest peak - and so the commonest fragment ion) is at m/z = 57. But this is not produced by the same ion as the same m/z value peak in pentane.



If you remember, the m/z = 57 peak in pentane was produced by $[CH_3CH_2CH_2CH_2]^+$. If you look at the structure of pentan-3-one, it's impossible to get that particular fragment from it.

Work along the molecule mentally chopping bits off until you come up with something that adds up to 57. With a small amount of patience, you'll eventually find $[CH_3CH_2CO]^+$ - which is produced by this fragmentation:

$$[CH_3CH_2COCH_2CH_3]^{\ddagger} \longrightarrow [CH_3CH_2CO]^+ + \bullet CH_2CH_3$$

You would get exactly the same products whichever side of the CO group you split the molecular ion. The m/z = 29 peak is produced by the ethyl ion - which once again could be formed by splitting the molecular ion either side of the CO group.

$$[CH_3CH_2COCH_2CH_3]^{\ddagger} \longrightarrow [CH_3CH_2]^+ + \bullet COCH_2CH_3$$

PEAK HEIGHTS AND STABILITY

The more stable an ion is, the more likely it is to form. The more of a particular sort of ion that's formed, the higher its peak height will be. We'll look at two common examples of this.

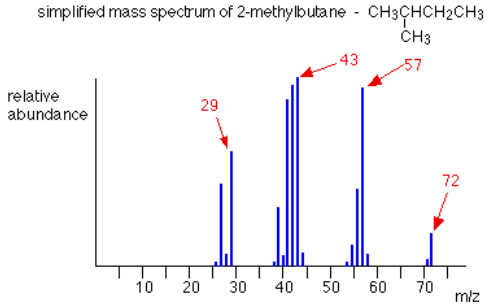
CARBOCATIONS (CARBONIUM IONS)

Summarizing the most important conclusion from the page on carbocations:

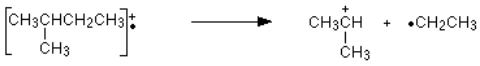
Order of stability of carbocations

primary < secondary < tertiary

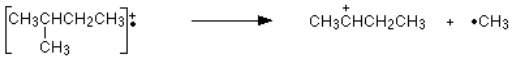
Applying the logic of this to fragmentation patterns, it means that a split which produces a secondary carbocation is going to be more successful than one producing a primary one. A split producing a tertiary carbocation will be more successful still. Let's look at the mass spectrum of 2-methylbutane. 2-methylbutane is an isomer of pentane - isomers are molecules with the same molecular formula, but a different spatial arrangement of the atoms.



Look first at the very strong peak at m/z = 43. This is caused by a different ion than the corresponding peak in the pentane mass spectrum. This peak in 2-methylbutane is caused by:



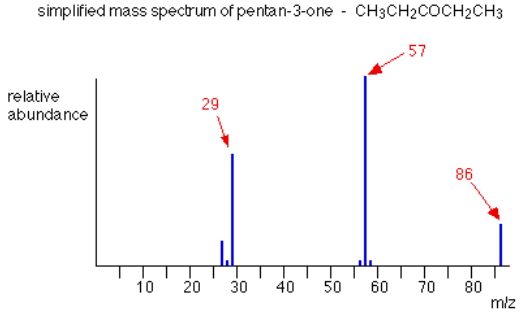
The ion formed is a secondary carbocation - it has two alkyl groups attached to the carbon with the positive charge. As such, it is relatively stable. The peak at m/z = 57 is much taller than the corresponding line in pentane. Again a secondary carbocation is formed - this time, by:



You would get the same ion, of course, if the left-hand CH_3 group broke off instead of the bottom one as we've drawn it. In these two spectra, this is probably the most dramatic example of the extra stability of a secondary carbocation.

ACYLIUM IONS, $[RCO]^+$

Ions with the positive charge on the carbon of a carbonyl group, C=O, are also relatively stable. This is fairly clearly seen in the mass spectra of ketones like pentan-3-one.



The base peak, at m/z=57, is due to the $[CH_3CH_2CO]^+$ ion. We've already discussed the fragmentation that produces this.

> **NOTE**
>
> The more stable an ion is, the more likely it is to form. The more of a particular ion that is formed, the higher will be its peak height.

USING MASS SPECTRA TO DISTINGUISH BETWEEN COMPOUNDS

Suppose you had to suggest a way of distinguishing between pentan-2-one and pentan-3-one using their mass spectra.

pentan-2-one	$CH_3COCH_2CH_2CH_3$
pentan-3-one	$CH_3CH_2COCH_2CH_3$

Each of these is likely to split to produce ions with a positive charge on the CO group. In the pentan-2-one case, there are two different ions like this:

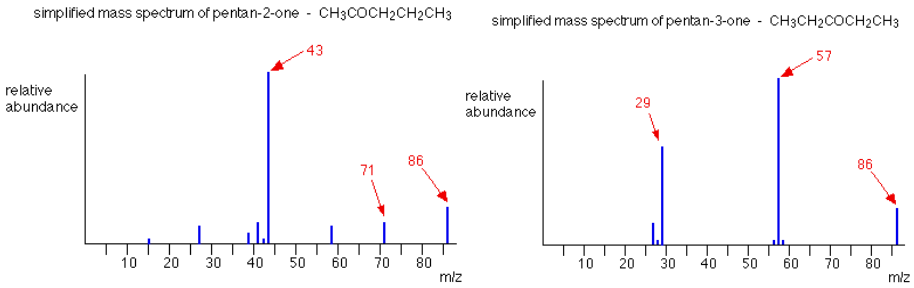
- $[CH_3CO]^+$
- $[COCH_2CH_2CH_3]^+$

That would give you strong lines at m/z = 43 and 71. With pentan-3-one, you would only get one ion of this kind:

- $[CH_3CH_2CO]^+$

In that case, you would get a strong line at 57. You don't need to worry about the other lines in the spectra - the 43, 57 and 71 lines give you plenty of difference between the two. The 43 and 71 lines are missing from the pentan-3-one spectrum, and the 57 line is missing from the pentan-2-one one.

The two mass spectra look like this:



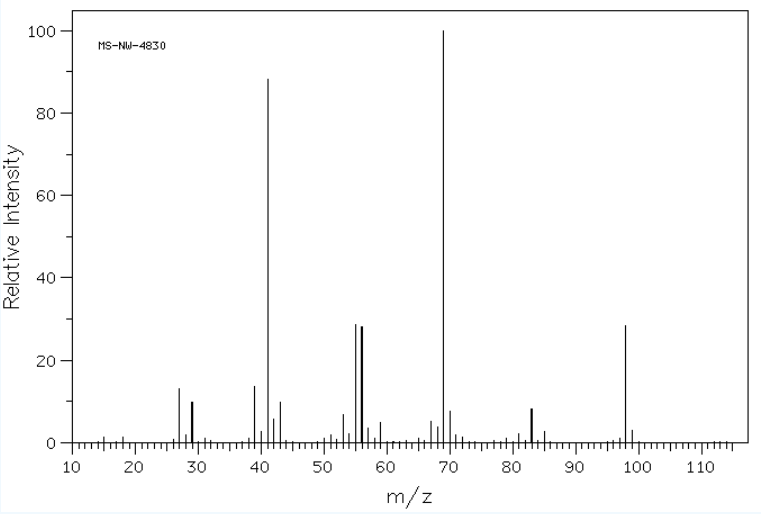
As you've seen, the mass spectrum of even very similar organic compounds will be quite different because of the different fragmentation patterns that can occur. Provided you have a computer data base of mass spectra, any unknown spectrum can be computer analyzed and simply matched against the data base.

EXERCISE

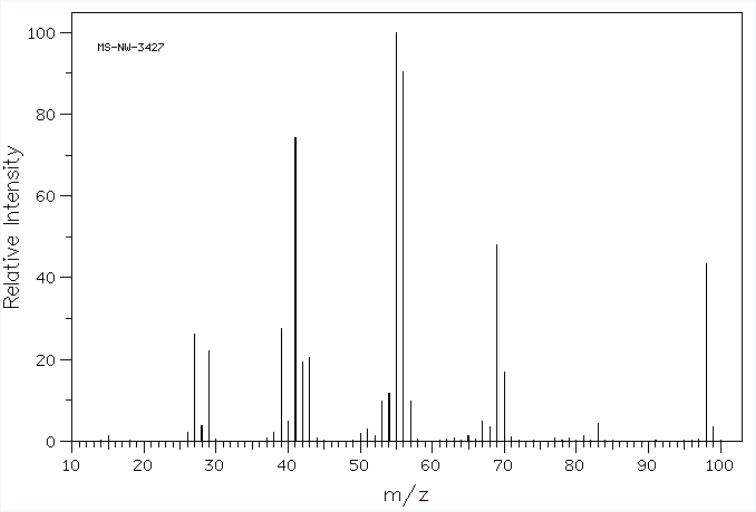
EXERCISE 12.2.1

The following are the spectrum for 2-methyl-2-hexene and 2-heptene, which spectra belongs to the correct molecule. Explain.

A



B



Answer

Spectrum A is the 2-methyl-2-hexene and the Spectrum B is is 2-heptene.

Looking at A the peak at 68 *m/z* is the fractioned molecule with just the tri-substituted alkene present. While B has a strong peak around the 56 *m/z*, which in this case is the di-substituted alkene left behind from the linear heptene.

QUESTIONS

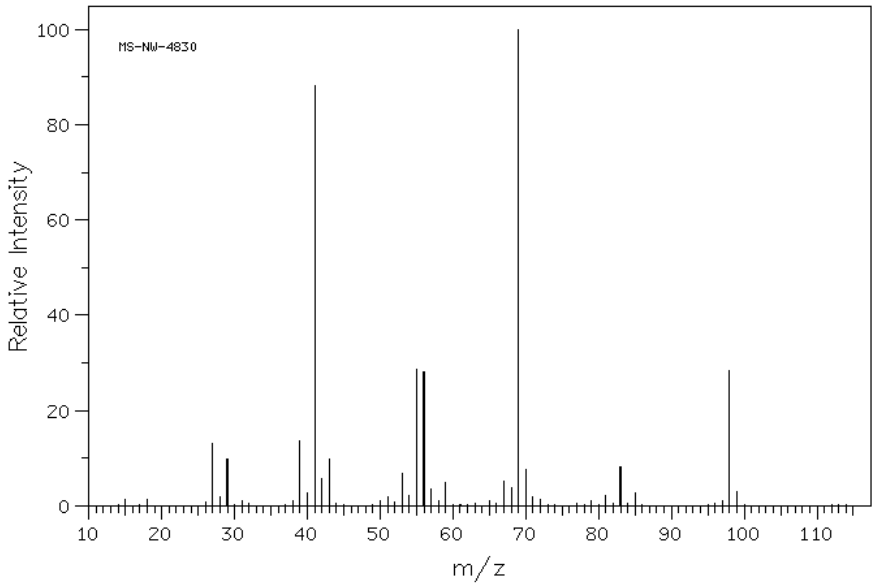
Q12.2.1

Caffeine has a mass of 194.19 amu, determined by mass spectrometry, and contains C, N, H, O. What is a molecular formula for this molecule?

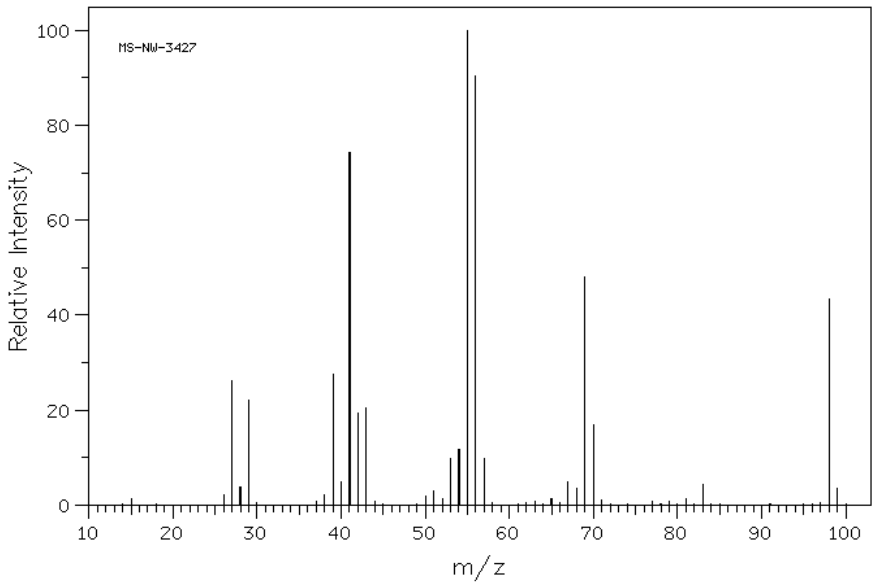
Q12.2.2

The following are the spectra for 2-methyl-2-hexene and 2-heptene, which spectra belongs to the correct molecule. Explain.

A:



B:



Source: SDBSWeb : http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 2 December 2016)

SOLUTIONS

S12.2.1

$C_8H_{10}N_4O_2$

C = 12 × 8 = 96

https://chem.libretexts.org/@go/page/67278

N = 14 × 4 = 56

H = 1 × 10 = 10

O = 2 × 16 = 32

96+56+10+32 = 194 g/mol

S12.2.2

The (A) spectrum is 2-methyl-2-hexene and the (B) spectrum is 2-heptene. Looking at (A) the peak at 68 *m/z* is the fractioned molecule with just the tri-substituted alkene present. While (B) has a strong peak around the 56 *m/z*, which in this case is the di-substituted alkene left behind from the linear heptene.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)

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12.3: MASS SPECTROMETRY OF SOME COMMON FUNCTIONAL GROUPS

Objective

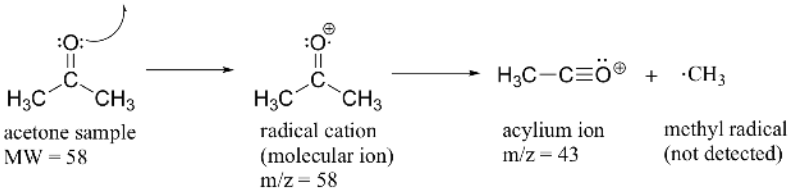
After completing this section, you should be able to predict the expected fragmentation for common functional groups, such as alcohols, amines, and carbonyl compounds.

KEY TERMS

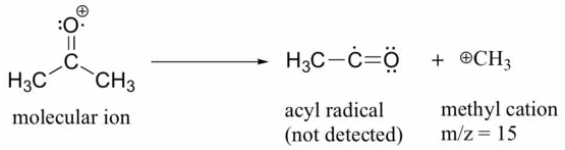
Make certain that you can define, and use in context, the key terms below.

- alpha (α) cleavage
- McLafferty rearrangement

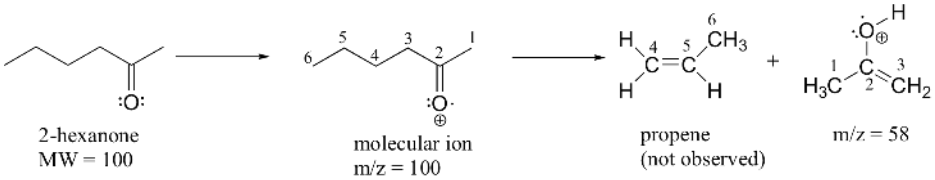
Much of the utility in electron-ionization MS comes from the fact that the radical cations generated in the electron-bombardment process tend to fragment in predictable ways. Detailed analysis of the typical fragmentation patterns of different functional groups is beyond the scope of this text, but it is worthwhile to see a few representative examples, even if we don't attempt to understand the exact process by which the fragmentation occurs. We saw, for example, that the base peak in the mass spectrum of acetone is m/z = 43. This is the result of cleavage at the 'alpha' position - in other words, at the carbon-carbon bond adjacent to the carbonyl. Alpha cleavage results in the formation of an acylium ion (which accounts for the base peak at m/z = 43) and a methyl radical, which is neutral and therefore not detected.



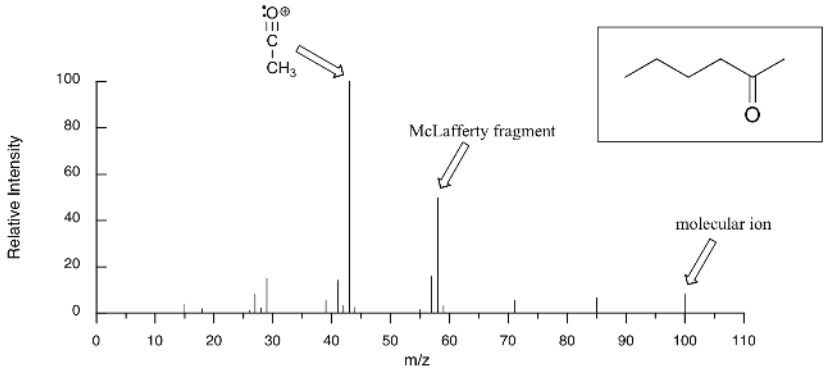
After the parent peak and the base peak, the next largest peak, at a relative abundance of 23%, is at m/z = 15. This, as you might expect, is the result of formation of a methyl cation, in addition to an acyl radical (which is neutral and not detected).



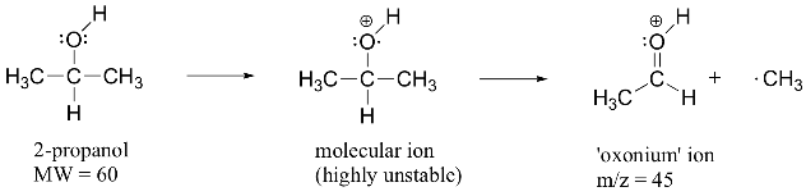
A common fragmentation pattern for larger carbonyl compounds is called the **McLafferty rearrangement**:

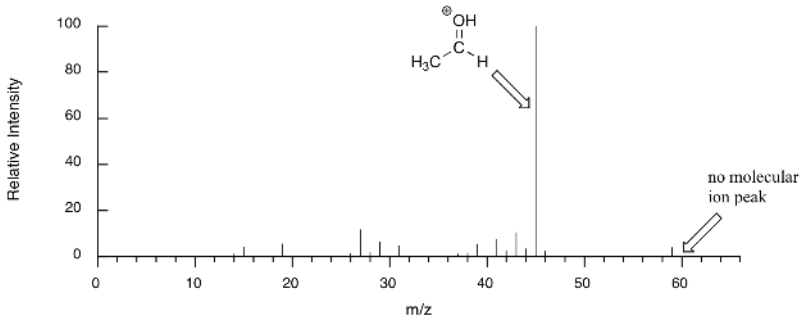


The mass spectrum of 2-hexanone shows a 'McLafferty fragment' at m/z = 58, while the propene fragment is not observed because it is a neutral species (remember, only cationic fragments are observed in MS). The base peak in this spectrum is again an acylium ion.



When alcohols are subjected to electron ionization MS, the molecular ion is highly unstable and thus a parent peak is often not detected. Often the base peak is from an 'oxonium' ion.





Other functional groups have predictable fragmentation patterns as well. By carefully analyzing the fragmentation information that a mass spectrum provides, a knowledgeable spectrometrist can often 'put the puzzle together' and make some very confident predictions about the structure of the starting sample.

Click here for examples of compounds listed by functional group, which demonstrate patterns which can be seen in mass spectra of compounds ionized by electron impact ionization.

EXAMPLE 12.3.1

The mass spectrum of an aldehyde gives prominent peaks at *m/z* = 59 (12%, highest value of *m/z* in the spectrum), 58 (85%), and 29 (100%), as well as others. Propose a structure, and identify the three species whose *m/z* values were listed.

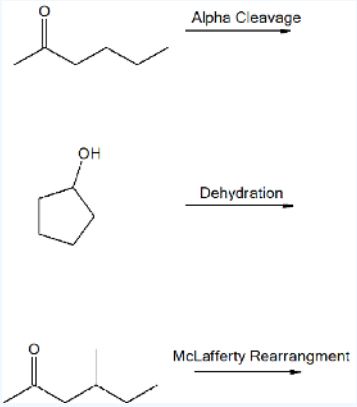
Solution

The mass spectrum fits that of propanal. The most abundant fragment (the base peak) is the acylium ion containing the aldehyde hydrogen.

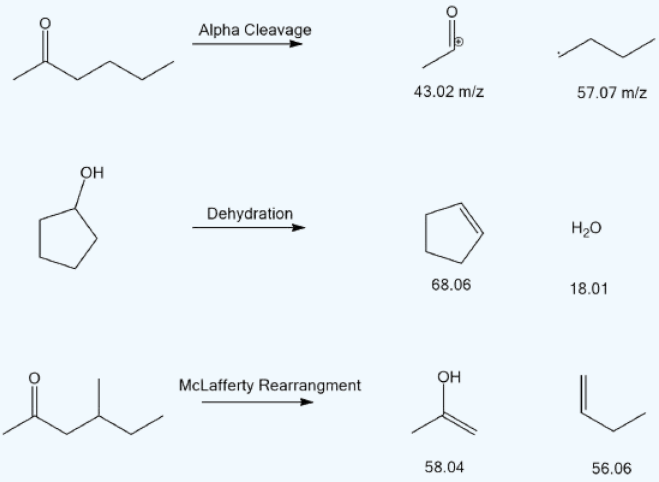
EXERCISES

EXERCISE 12.3.1

What are the masses of the following fragments in the following fragmentations?



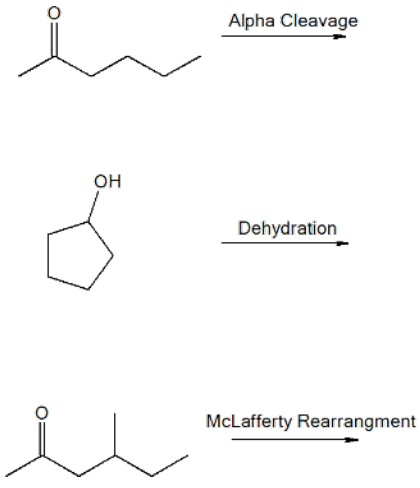
Answer



QUESTIONS

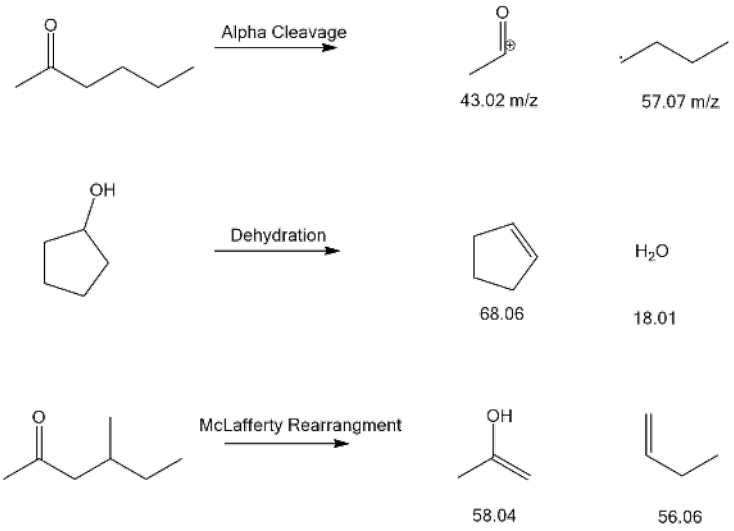
Q12.3.1

What are the masses of all the components in the following fragmentations?



SOLUTIONS

S12.3.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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12.4: MASS SPECTROMETRY IN BIOLOGICAL- TIME-OF-FLIGHT (TOF) INSTRUMENTS

Objective

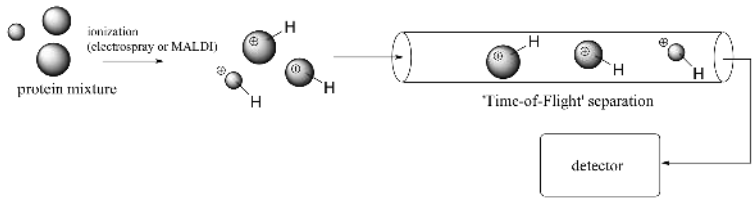
This section is intended only to demonstrate that mass spectrometry can be useful for the investigation of some very large molecules present in biological systems.

MASS SPECTROMETRY OF PROTEINS - APPLICATIONS IN PROTEOMICS EDIT SECTION

Mass spectrometry has become in recent years an increasingly important tool in the field of **proteomics**. Traditionally, protein biochemists tend to study the structure and function of individual proteins. Proteomics researchers, in contrast, want to learn more about how large numbers of proteins in a living system interact with each other, and how they respond to changes in the state of the organism. One very important subfield of proteomics is the search for protein **biomarkers** for human disease. These can be proteins which are present in greater quantities in a sick person than in a healthy person, and their detection and identification can provide medical researchers with valuable information about possible causes or treatments. Detection in a healthy person of a known biomarker for a disease such as diabetes or cancer could also provide doctors with an early warning that the patient may be especially susceptible, so that preventive measures could be taken to prevent or delay onset of the disease.

New developments in MS technology have made it easier to detect and identify proteins that are present in very small quantities in biological samples. Mass spectrometrists who study proteins often use instrumentation that is somewhat different from the electron-ionization, magnetic deflection system described earlier. When proteins are being analyzed, the object is often to ionize the proteins *without* causing fragmentation, so 'softer' ionization methods are required. In one such method, called **electrospray ionization**, the protein sample, in solution, is sprayed into a tube and the molecules are induced by an electric field to pick up extra protons from the solvent. Another common 'soft ionization' method is 'matrix-assisted laser desorption ionization' (**MALDI**). Here, the protein sample is adsorbed onto a solid matrix, and protonation is achieved with a laser.

Typically, both electrospray ionization and MALDI are used in conjunction with a time-of-flight (TOF) mass analyzer component.



The ionized proteins are accelerated by an electrode through a column, and separation is achieved because lighter ions travel at greater velocity than heavier ions with the same overall charge. In this way, the many proteins in a complex biological sample (such as blood plasma, urine, etc.) can be separated and their individual masses determined very accurately. Modern protein MS is extremely sensitive – very recently, scientists were even able to obtain a mass spectrum of *Tyrannosaurus rex* protein from fossilized bone! (Science **2007**, 316, 277).

In one recent study, MALDI-TOF mass spectrometry was used to compare fluid samples from lung transplant recipients who had suffered from tissue rejection to control samples from recipients who had not suffered rejection. Three peptides (short proteins) were found to be present at elevated levels specifically in the tissue rejection samples. It is hoped that these peptides might serve as biomarkers to identify patients who are at increased risk of rejecting their transplanted lungs (Proteomics **2005**, 5, 1705).

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12.5: SPECTROSCOPY AND THE ELECTROMAGNETIC SPECTRUM

Objectives

After completing this section, you should be able to

1. write a brief paragraph discussing the nature of electromagnetic radiation.
2. write the equations that relate energy to frequency, frequency to wavelength and energy to wavelength, and perform calculations using these relationships.
3. describe, in general terms, how absorption spectra are obtained.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- electromagnetic radiation
- electromagnetic spectrum
- hertz (Hz)
- infrared spectroscopy
- photon
- quantum

STUDY NOTES

From your studies in general chemistry or physics, you should be familiar with the idea that electromagnetic radiation is a form of energy that possesses wave character and travels through space at a speed of $3.00 \times 10^8 \text{m} \cdot \text{s}^{-1}$. However, such radiation also displays some of the properties of particles, and on occasion it is more convenient to think of electromagnetic radiation as consisting of a stream of particles called *photons*.

In spectroscopy, the frequency of the electromagnetic radiation being used is usually expressed in *hertz* (*Hz*), that is, cycles per second. Note that $1 \text{ Hz} = \text{s}^{-1}$.

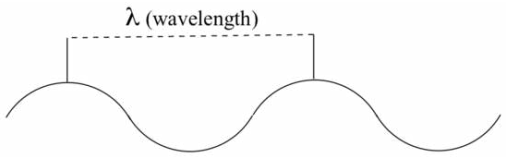
A *quantum* is a small, definite quantity of electromagnetic radiation whose energy is directly proportional to its frequency. (The plural is "quanta.") If you wish, you can read about the properties of electromagnetic radiation and the relationships among wavelength, frequency and energy, or refer to your general chemistry textbook if you still have it.

Note also that in SI units, Planck's constant is $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$.

THE ELECTROMAGNETIC SPECTRUM

Electromagnetic radiation, as you may recall from a previous chemistry or physics class, is composed of electrical and magnetic waves which oscillate on perpendicular planes. Visible light is electromagnetic radiation. So are the gamma rays that are emitted by spent nuclear fuel, the x-rays that a doctor uses to visualize your bones, the ultraviolet light that causes a painful sunburn when you forget to apply sun block, the infrared light that the army uses in night-vision goggles, the microwaves that you use to heat up your frozen burritos, and the radio-frequency waves that bring music to anybody who is old-fashioned enough to still listen to FM or AM radio.

Just like ocean waves, electromagnetic waves travel in a defined direction. While the speed of ocean waves can vary, however, the speed of electromagnetic waves – commonly referred to as the speed of light – is essentially a constant, approximately 300 million meters per second. This is true whether we are talking about gamma radiation or visible light. Obviously, there is a big difference between these two types of waves – we are surrounded by the latter for more than half of our time on earth, whereas we hopefully never become exposed to the former to any significant degree. The different properties of the various types of electromagnetic radiation are due to differences in their wavelengths, and the corresponding differences in their energies: *shorter wavelengths correspond to higher energy.*



High-energy radiation (such as gamma- and x-rays) is composed of very short waves – as short as 10^{-16} meter from crest to crest. Longer waves are far less energetic, and thus are less dangerous to living things. Visible light waves are in the range of 400 – 700 nm (nanometers, or 10^{-9} m), while radio waves can be several hundred meters in length.

The notion that electromagnetic radiation contains a quantifiable amount of energy can perhaps be better understood if we talk about light as a stream of *particles*, called **photons**, rather than as a wave. (Recall the concept known as 'wave-particle duality': at the quantum level, wave behavior and particle behavior become indistinguishable, and very small particles have an observable 'wavelength'). If we describe light as a stream of photons, the energy of a particular wavelength can be expressed as:

$$E = \frac{hc}{\lambda} \tag{12.5.1}$$

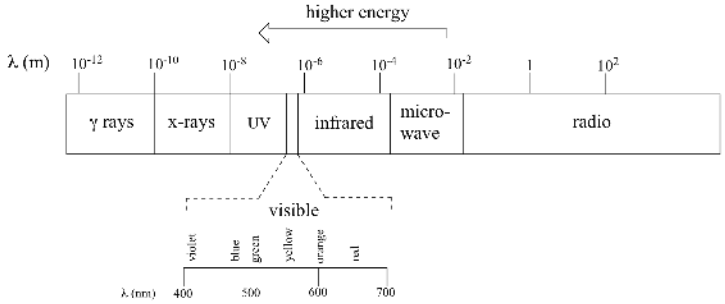
where E is energy in J, **λ** (the Greek letter *lambda*) is wavelength in meters, *c* is 3.00 x 10^8 m/s (the speed of light), and *h* is 6.626×10^{-34} J · s, a number known as Planck's constant.

Because electromagnetic radiation travels at a constant speed, each wavelength corresponds to a given frequency, which is the number of times per second that a crest passes a given point. Longer waves have lower frequencies, and shorter waves have higher frequencies. Frequency is commonly reported in hertz (Hz), meaning 'cycles per second', or 'waves per second'. The standard unit for frequency is s^{-1}.

When talking about electromagnetic waves, we can refer either to wavelength or to frequency - the two values are interconverted using the simple expression:

$$\lambda\nu = c \tag{12.5.2}$$

where **ν** (the Greek letter '*nu*') is frequency in s^{-1}. Visible red light with a wavelength of 700 nm, for example, has a frequency of 4.29 x 10^{14} Hz, and an energy of 2.84 x 10^{-19} J per photon or 171 kJ per mole of photons (remember Avogadro's number = 6.02×10^{23} mol^{-1}). The full range of electromagnetic radiation wavelengths is referred to as the **electromagnetic spectrum**.



Notice in the figure above that visible light takes up just a narrow band of the full spectrum. White light from the sun or a light bulb is a mixture of all of the visible wavelengths. You see the visible region of the electromagnetic spectrum divided into its different wavelengths every time you see a rainbow: violet light has the shortest wavelength, and red light has the longest.

EXAMPLE 12.5.1

Visible light has a wavelength range of about 400-700 nm. What is the corresponding frequency range? What is the corresponding energy range, in kJ mol^{-1} of photons?

Answer

Add texts here. Do not delete this text firstFor light with a wavelength of 400 nm, the frequency is 7.50×10^{14} Hz:

$$\nu = \frac{3 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}} = 7.50 \times 10^{14} \text{ s}^{-1}$$

In the same way, we calculate that light with a wavelength of 700 nm has a frequency of 4.29×10^{14} Hz.

To calculate corresponding energies using *hc*/λ. We find for light at 400 nm:

$$E = \frac{(6.626 \times 10^{-34}\ \text{J s mol}^{-1})(3.00 \times 10^{8}\ \text{m s}^{-1})}{400 \times 10^{-9}\ \text{m}}$$

$$= 4.97 \times 10^{-19}\ \text{J per photon}$$

$$E\ (\text{one mole}) = E \times N$$

$$= (4.97 \times 10^{-19}\ \text{J})(6.02 \times 10^{23}\ \text{mol}^{-1})$$

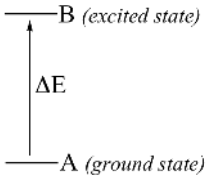
$$= 299\ \text{kJ mol}^{-1}$$

Using the same equation, we find that light at 700 nm corresponds to 171 kJ mol^{-1}.

MOLECULAR SPECTROSCOPY – THE BASIC IDEA

In a spectroscopy experiment, electromagnetic radiation of a specified range of wavelengths is allowed to pass through a sample containing a compound of interest. The sample molecules absorb energy from some of the wavelengths, and as a result jump from a low energy 'ground state' to some higher energy 'excited state'. Other wavelengths are *not* absorbed by the sample molecule, so they pass on through. A detector on the other side of the sample records which wavelengths were absorbed, and to what extent they were absorbed.

Here is the key to molecular spectroscopy: *a given molecule will specifically absorb only those wavelengths which have energies that correspond to the energy difference of the transition that is occurring.* Thus, if the transition involves the molecule jumping from ground state A to excited state B, with an energy difference of **ΔE**, the molecule will specifically absorb radiation with wavelength that corresponds to **ΔE**, while allowing other wavelengths to pass through unabsorbed.



By observing which wavelengths a molecule absorbs, and to what extent it absorbs them, we can gain information about the nature of the energetic transitions that a molecule is able to undergo, and thus information about its structure.

These generalized ideas may all sound quite confusing at this point, but things will become much clearer as we begin to discuss specific examples.

EXERCISES

? EXERCISE 12.5.1

Which of the following frequencies/wavelengths are higher energy

A. $\lambda = 2.0 \times 10^{-6}$ m or $\lambda = 3.0 \times 10^{-9}$ m

B. $\upsilon = 3.0 \times 10^{9}$ Hz or $\upsilon = 3.0 \times 10^{-6}$ Hz

Answer

A. $\lambda = 3.0 \times 10^{-9}$ m

B. $\upsilon = 3.0 \times 10^{9}$ Hz

? EXERCISE 12.5.2

Calculate the energies (J) for the following;

A – Gamma Ray $\lambda = 4.0 \times 10^{-11}$ m

B – X-Ray $\lambda = 4.0 \times 10^{-9}$ m

C – UV light $\upsilon = 5.0 \times 10^{15}$ Hz

D – Infrared Radiation $\lambda = 3.0 \times 10^{-5}$ m

E – Microwave Radiation $\upsilon = 3.0 \times 10^{11}$ Hz

Answer

The following are in joules.

A – 4.96×10^{-15}

B – 4.96×10^{-17}

C – 3.31×10^{-18}

D – 6.62×10^{-21}

E – 1.99×10^{-22}

QUESTIONS

Q12.5.1

Which of the following frequencies/wavelengths are higher energy

A. $\lambda = 2.0 \times 10^{-6}$ m or $\lambda = 3.0 \times 10^{-9}$ m

B. $\upsilon = 3.0 \times 10^{9}$ Hz or $\upsilon = 3.0 \times 10^{-6}$ Hz

Q12.5.2

Calculate the energies for the following;

A. Gamma Ray $\lambda = 4.0 \times 10^{-11}$ m

B. X-Ray $\lambda = 4.0 \times 10^{-9}$ m

C. UV light $\upsilon = 5.0 \times 10^{15}$ Hz

D. Infrared Radiation $\lambda = 3.0 \times 10^{-5}$ m

E. Microwave Radiation $\upsilon = 3.0 \times 10^{11}$ Hz

SOLUTIONS

S12.5.1

A. $\lambda = 3.0 \times 10^{-9}$ m

B. $\upsilon = 3.0 \times 10^{9}$ Hz

S12.5.2

A. 4.965×10^{-15} J

B. 4.965×10^{-17} J

C. 3.31×10^{-18} J

D. 6.62×10^{-21} J

E. 1.99×10^{-22} J

Contributors and Attributions

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- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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12.6: INFRARED SPECTROSCOPY

Objectives

After completing this section, you should be able to

1. identify (by wavelength, wavenumber, or both) the region of the electromagnetic spectrum which is used in infrared (IR) spectroscopy.
2. interconvert between wavelength and wavenumber.
3. discuss, in general terms, the effect that the absorption of infrared radiation can have on a molecule.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- infrared spectrum
- wavenumber (reciprocal centimetres)

STUDY NOTES

Notice that the scale at the bottom of the infrared spectrum for 2-hexanone shown is calibrated in wavenumbers (cm^{-1}). A wavenumber is the reciprocal of a wavelength (1/λ); thus, a wavenumber of 1600 cm^{-1} corresponds to a wavelength of

$$\frac{1}{1600\,cm^{-1}} = 6.25 \times 10^{-4} cm \text{ or } 6.25\,\mu m$$

Organic chemists find it more convenient to deal with wavenumbers rather than wavelengths when discussing infrared spectra.

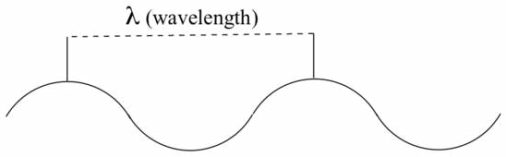
You will obtain infrared spectra for a number of the compounds you will synthesize in the laboratory component of this course.

The inverted peaks observed in the spectra correspond to molecular stretching and bending vibrations that only occur at certain quantized frequencies. When infrared radiation matching these frequencies falls on the molecule, the molecule absorbs energy and becomes excited. Eventually the molecule returns to its original (ground) state, and the energy which was absorbed is released as heat.

THE ELECTROMAGNETIC SPECTRUM

Electromagnetic radiation, as you may recall from a previous chemistry or physics class, is composed of electrical and magnetic waves which oscillate on perpendicular planes. Visible light is electromagnetic radiation. So are the gamma rays that are emitted by spent nuclear fuel, the x-rays that a doctor uses to visualize your bones, the ultraviolet light that causes a painful sunburn when you forget to apply sun block, the infrared light that the army uses in night-vision goggles, the microwaves that you use to heat up your frozen burritos, and the radio-frequency waves that bring music to anybody who is old-fashioned enough to still listen to FM or AM radio.

Just like ocean waves, electromagnetic waves travel in a defined direction. While the speed of ocean waves can vary, however, the speed of electromagnetic waves – commonly referred to as the speed of light – is essentially a constant, approximately 300 million meters per second. This is true whether we are talking about gamma radiation or visible light. Obviously, there is a big difference between these two types of waves – we are surrounded by the latter for more than half of our time on earth, whereas we hopefully never become exposed to the former to any significant degree. The different properties of the various types of electromagnetic radiation are due to differences in their wavelengths, and the corresponding differences in their energies: *shorter wavelengths correspond to higher energy.*



High-energy radiation (such as gamma- and x-rays) is composed of very short waves – as short as 10^{-16} meter from crest to crest. Longer waves are far less energetic, and thus are less dangerous to living things. Visible light waves are in the range of 400 – 700 nm (nanometers, or 10^{-9} m), while radio waves can be several hundred meters in length.

The notion that electromagnetic radiation contains a quantifiable amount of energy can perhaps be better understood if we talk about light as a stream of *particles*, called **photons**, rather than as a wave. (Recall the concept known as 'wave-particle duality': at the quantum level,

wave behavior and particle behavior become indistinguishable, and very small particles have an observable 'wavelength'). If we describe light as a stream of photons, the energy of a particular wavelength can be expressed as:

$E = hc/\lambda$

where E is energy in kcal/mol, **λ** (the Greek letter *lambda*) is wavelength in meters, *c* is 3.00 x 10^8 m/s (the speed of light), and *h* is 9.537 x 10^{-14} kcal·s·mol^{-1}, a number known as Planck's constant.

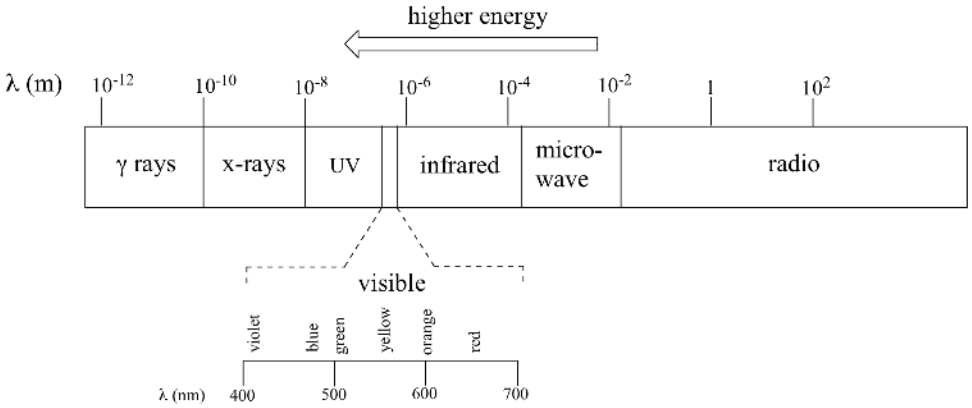
Because electromagnetic radiation travels at a constant speed, each wavelength corresponds to a given frequency, which is the number of times per second that a crest passes a given point. Longer waves have lower frequencies, and shorter waves have higher frequencies. Frequency is commonly reported in hertz (Hz), meaning 'cycles per second', or 'waves per second'. The standard unit for frequency is s^{-1}.

When talking about electromagnetic waves, we can refer either to wavelength or to frequency - the two values are interconverted using the simple expression:

$\lambda\nu = c$

where **ν** (the Greek letter '*nu*') is frequency in s^{-1}. Visible red light with a wavelength of 700 nm, for example, has a frequency of 4.29 x 10^{14} Hz, and an energy of 40.9 kcal per mole of photons.

The full range of electromagnetic radiation wavelengths is referred to as the **electromagnetic spectrum**.



Notice in the figure above that visible light takes up just a narrow band of the full spectrum. White light from the sun or a light bulb is a mixture of all of the visible wavelengths. You see the visible region of the electromagnetic spectrum divided into its different wavelengths every time you see a rainbow: violet light has the shortest wavelength, and red light has the longest.

? EXERCISE \PageIndex1

Visible light has a wavelength range of about 400-700 nm. What is the corresponding frequency range? What is the corresponding energy range, in kcal/mol of photons?

Answer

Using $\lambda\nu = c$, we first rearrange to $\nu = c/\lambda$ to solve for frequency.

For light with a wavelength of 400 nm, the frequency is 7.50×10^{14} Hz:

$$\nu = \frac{3 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}} = 7.50 \times 10^{14} \text{ s}^{-1}$$

In the same way, we calculate that light with a wavelength of 700 nm has a frequency of 4.29×10^{14} Hz.

To calculate corresponding energies using hc/λ. We find for light at 400 nm:

$$E = \frac{(6.626 \times 10^{-34}\ \text{J s mol}^{-1})(3.00 \times 10^{8}\ \text{m s}^{-1})}{400 \times 10^{-9}\ \text{m}}$$

$$= 4.97 \times 10^{-19}\ \text{J per photon}$$

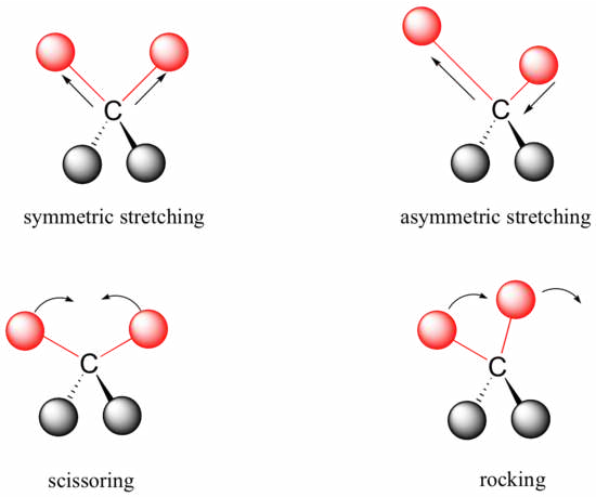
$$E\ (\text{one mole}) = E \times N$$

$$= (4.97 \times 10^{-19}\ \text{J})(6.02 \times 10^{23}\ \text{mol}^{-1})$$

$$= 299\ \text{kJ mol}^{-1}$$

Using the same equation, we find that light at 700 nm corresponds to 171 kJ mol^{-1}

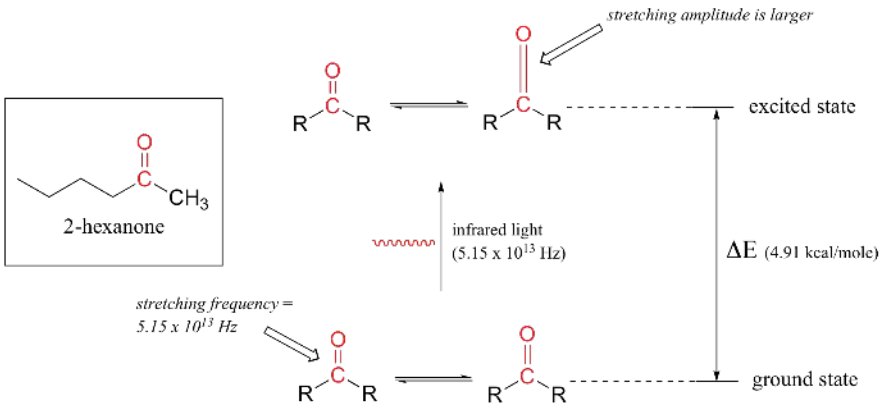
Covalent bonds in organic molecules are not rigid sticks – rather, they behave more like springs. At room temperature, organic molecules are always in motion, as their bonds stretch, bend, and twist. These complex vibrations can be broken down mathematically into individual **vibrational modes**, a few of which are illustrated below.



The energy of molecular vibration is *quantized* rather than continuous, meaning that a molecule can only stretch and bend at certain 'allowed' frequencies. If a molecule is exposed to electromagnetic radiation that matches the frequency of one of its vibrational modes, it will in most cases absorb energy from the radiation and jump to a higher vibrational energy state - what this means is that the *amplitude* of the vibration will increase, but the vibrational *frequency* will remain the same. The difference in energy between the two vibrational states is equal to the energy associated with the wavelength of radiation that was absorbed. It turns out that it is the *infrared* region of the electromagnetic spectrum which contains frequencies corresponding to the vibrational frequencies of organic bonds.

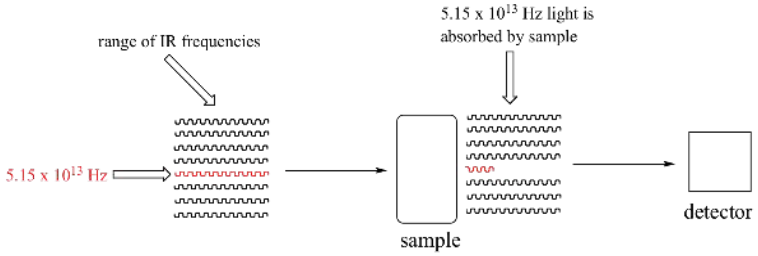
Let's take 2-hexanone as an example. Picture the carbonyl bond of the ketone group as a spring. This spring is constantly bouncing back and forth, stretching and compressing, pushing the carbon and oxygen atoms further apart and then pulling them together. This is the **stretching mode** of the carbonyl bond. In the space of one second, the spring 'bounces' back and forth 5.15 x 10^{13} times - in other words, the ground-state frequency of carbonyl stretching for a the ketone group is about 5.15 x 10^{13} Hz.

If our ketone sample is irradiated with infrared light, the carbonyl bond will specifically absorb light with this same frequency, which by equations 4.1 and 4.2 corresponds to a wavelength of 5.83 x 10^{-6} m and an energy of 4.91 kcal/mol. When the carbonyl bond absorbs this energy, it jumps up to an excited vibrational state.



The value of **ΔE** - the energy difference between the low energy (ground) and high energy (excited) vibrational states - is equal to 4.91 kcal/mol, the same as the energy associated with the absorbed light frequency. The molecule does not remain in its excited vibrational state for very long, but quickly releases energy to the surrounding environment in form of heat, and returns to the ground state.

With an instrument called an infrared spectrophotometer, we can 'see' this vibrational transition. In the spectrophotometer, infrared light with frequencies ranging from about 10^{13} to 10^{14} Hz is passed though our sample of cyclohexane. Most frequencies pass right through the sample and are recorded by a detector on the other side.



Our 5.15 x 10^{13} Hz carbonyl stretching frequency, however, is absorbed by the 2-hexanone sample, and so the detector records that the intensity of this frequency, after having passed through the sample, is something less than 100% of its initial intensity.

The vibrations of a 2-hexanone molecule are not, of course, limited to the simple stretching of the carbonyl bond. The various carbon-carbon bonds also stretch and bend, as do the carbon-hydrogen bonds, and all of these vibrational modes also absorb different frequencies of infrared light.

The power of infrared spectroscopy arises from the observation that *different functional groups have different characteristic absorption frequencies*. The carbonyl bond in a ketone, as we saw with our 2-hexanone example, typically absorbs in the range of 5.11 - 5.18 x 10^{13} Hz, depending on the molecule. The carbon-carbon triple bond of an alkyne, on the other hand, absorbs in the range 6.30 - 6.80 x 10^{13} Hz. The technique is therefore very useful as a means of identifying which functional groups are present in a molecule of interest. If we pass infrared light through an unknown sample and find that it absorbs in the carbonyl frequency range but not in the alkyne range, we can infer that the molecule contains a carbonyl group but not an alkyne.

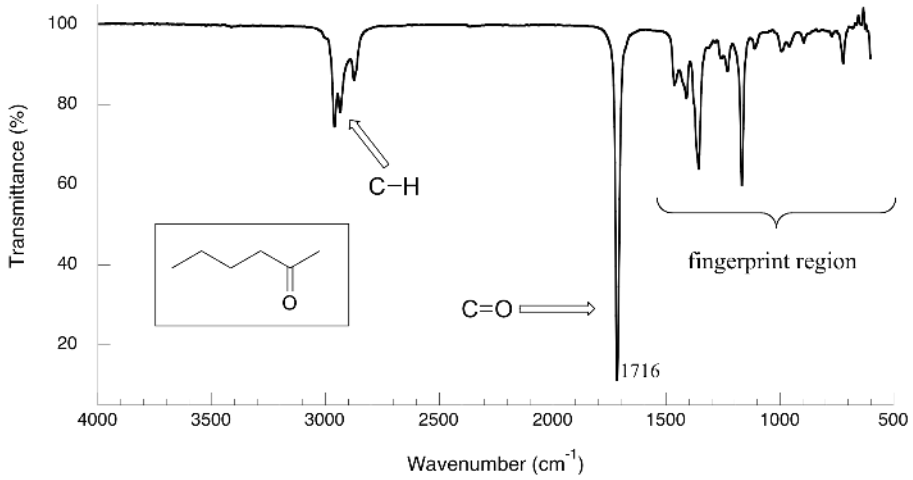
Some bonds absorb infrared light more strongly than others, and some bonds do not absorb at all. *In order for a vibrational mode to absorb infrared light, it must result in a periodic change in the dipole moment of the molecule*. Such vibrations are said to be **infrared active**. In general, the greater the polarity of the bond, the stronger its IR absorption. The carbonyl bond is very polar, and absorbs very strongly. The carbon-carbon triple bond in most alkynes, in contrast, is much less polar, and thus a stretching vibration does not result in a large change in the overall dipole moment of the molecule. Alkyne groups absorb rather weakly compared to carbonyls.

Some kinds of vibrations are **infrared inactive**. The stretching vibrations of completely symmetrical double and triple bonds, for example, do not result in a change in dipole moment, and therefore do not result in any absorption of light (but other bonds and vibrational modes in these molecules *do* absorb IR light).



infrared-inactive double and triple bonds

Now, let's look at some actual output from IR spectroscopy experiments. Below is the IR spectrum for 2-hexanone.



There are a number of things that need to be explained in order for you to understand what it is that we are looking at. On the horizontal axis we see IR wavelengths expressed in terms of a unit called **wavenumber** (cm^{-1}), which tells us how many waves fit into one centimeter. On the vertical axis we see '**% transmittance**', which tells us how strongly light was absorbed at each frequency (100% transmittance means no absorption occurred at that frequency). The solid line traces the values of % transmittance for every wavelength – the 'peaks' (which are actually pointing down) show regions of strong absorption. For some reason, it is typical in IR spectroscopy to report wavenumber values rather than wavelength (in meters) or frequency (in Hz). The 'upside down' vertical axis, with absorbance peaks pointing down rather than up, is also a curious convention in IR spectroscopy. We wouldn't want to make things too easy for you!

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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12.7: INTERPRETING INFRARED SPECTRA

Objectives

After completing this section, you should be able to

1. describe how the so-called “fingerprint region” of an infrared spectrum can assist in the identification of an unknown compound.
2. identify the functional group or groups present in a compound, given a list of the most prominent absorptions in the infrared spectrum and a table of characteristic absorption frequencies.
3. identify the broad regions of the infrared spectrum in which occur absorptions caused by
   a. N−H, C−H, and O−H
   b. C≡C and C≡N
   c. C=O, C=N, and C=C

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- fingerprint region

STUDY NOTES

When answering assignment questions, you may use this IR table to find the characteristic infrared absorptions of the various functional groups. However, you should be able to indicate in broad terms where certain characteristic absorptions occur. You can achieve this objective by memorizing the following table.

Region of Spectrum (cm^{-1})	Absorption
2500-4000	N − H, O − H, C − H
2000-2500	C≡C, C≡N
1500-2000	C=O, C=N, C=C
below 1500	Fingerprint region

THE ORIGIN OF GROUP FREQUENCIES

An important observation made by early researchers is that many functional group absorb infrared radiation at about the same wavenumber, regardless of the structure of the rest of the molecule. For example, C-H stretching vibrations usually appear between 3200 and 2800cm^{-1} and carbonyl(C=O) stretching vibrations usually appear between 1800 and 1600cm^{-1}. This makes these bands diagnostic markers for the presence of a functional group in a sample. These types of infrared bands are called group frequencies because they tell us about the presence or absence of specific functional groups in a sample.

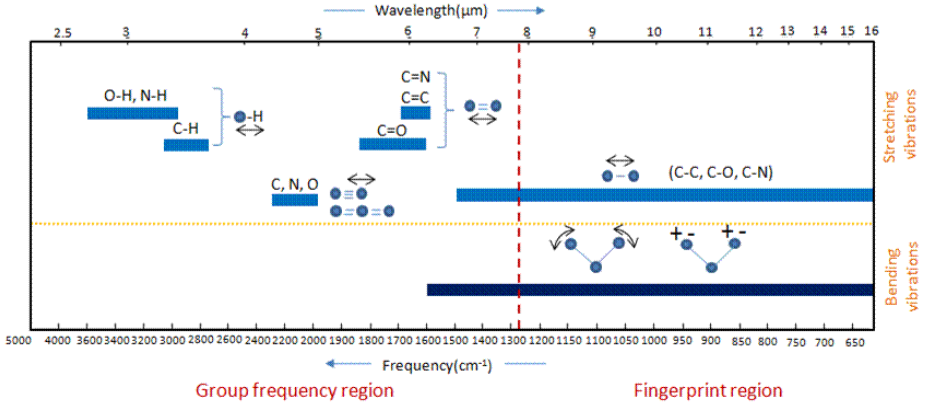
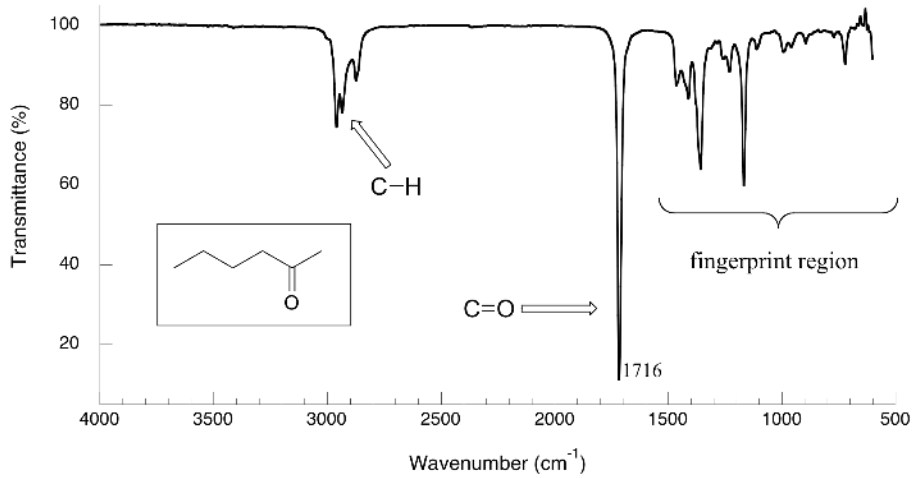


Figure 2. Group frequency and fingerprint regions of the mid-infrared spectrum

The region of the infrared spectrum from 1200 to 700 cm^{-1} is called the fingerprint region. This region is notable for the large number of infrared bands that are found there. Many different vibrations, including C-O, C-C and C-N single bond stretches, C-H bending vibrations, and some bands due to benzene rings are found in this region. The fingerprint region is often the most complex and confusing region to interpret, and is usually the last section of a spectrum to be interpreted. However, the utility of the fingerprint region is that the many bands there provide a fingerprint for a molecule.

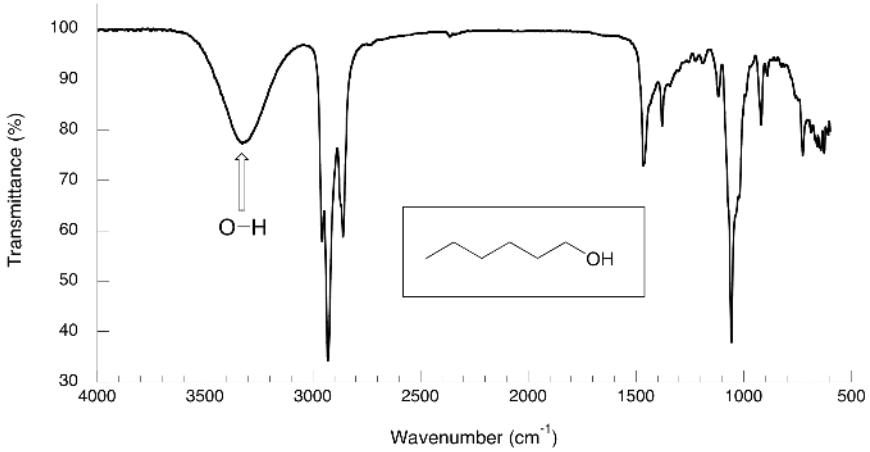


The key absorption peak in this spectrum is that from the carbonyl double bond, at 1716 cm^{-1} (corresponding to a wavelength of 5.86 mm, a frequency of 5.15 x 10^{13} Hz, and a **Δ**E value of 4.91 kcal/mol). Notice how strong this peak is, relative to the others on the spectrum: *a strong peak in the 1650-1750 cm^{-1} region is a dead giveaway for the presence of a carbonyl group*. Within that range, carboxylic acids, esters, ketones, and aldehydes tend to absorb in the shorter wavelength end (1700-1750 cm-1), while conjugated unsaturated ketones and amides tend to absorb on the longer wavelength end (1650-1700 cm^{-1}).

The jagged peak at approximately 2900-3000 cm^{-1} is characteristic of tetrahedral carbon-hydrogen bonds. This peak is not terribly useful, as just about every organic molecule that you will have occasion to analyze has these bonds. Nevertheless, it can serve as a familiar reference point to orient yourself in a spectrum.

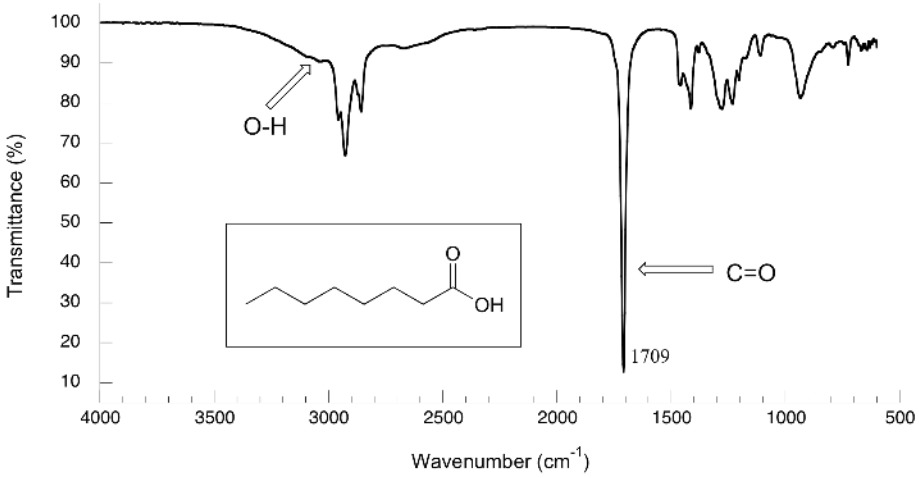
You will notice that there are many additional peaks in this spectrum in the longer-wavelength 400 -1400 cm^{-1} region. This part of the spectrum is called the **fingerprint region**. While it is usually very difficult to pick out any specific functional group identifications from this region, it does, nevertheless, contain valuable information. The reason for this is suggested by the name: just like a human fingerprint, the pattern of absorbance peaks in the fingerprint region is unique to every molecule, meaning that the data from an unknown sample can be compared to the IR spectra of known standards in order to make a positive identification. In the mid-1990's, for example, several paintings were identified as forgeries because scientists were able to identify the IR footprint region of red and yellow pigment compounds that would not have been available to the artist who supposedly created the painting (for more details see Chemical and Engineering News, Sept 10, 2007, p. 28).

Now, let's take a look at the IR spectrum for 1-hexanol.



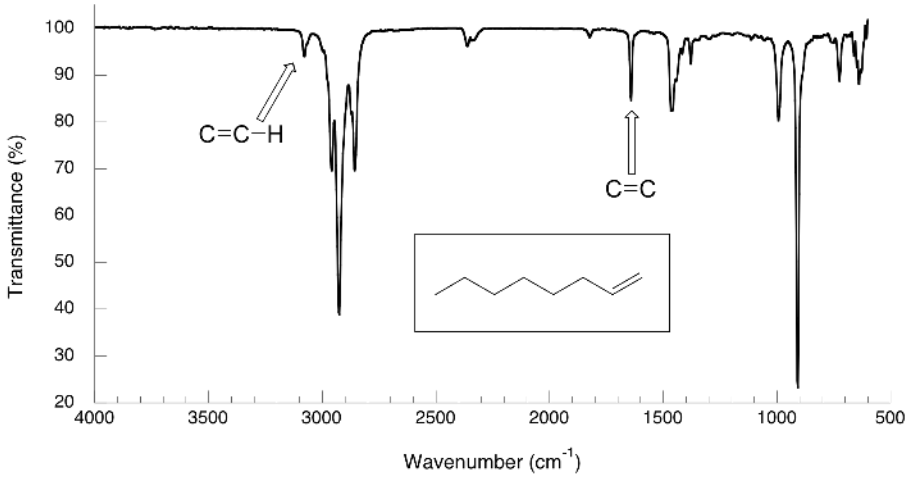
As you can see, the carbonyl peak is gone, and in its place is a very broad 'mountain' centered at about 3400 cm^{-1}. This signal is characteristic of the O-H stretching mode of alcohols, and is a dead giveaway for the presence of an alcohol group. The breadth of this signal is a consequence of hydrogen bonding between molecules.

In the spectrum of octanoic acid we see, as expected, the characteristic carbonyl peak, this time at 1709 cm^{-1}.



We also see a low, broad absorbance band that looks like an alcohol, except that it is displaced slightly to the right (long-wavelength) side of the spectrum, causing it to overlap to some degree with the C-H region. This is the characteristic carboxylic acid O-H single bond stretching absorbance.

The spectrum for 1-octene shows two peaks that are characteristic of alkenes: the one at 1642 cm^{-1} is due to stretching of the carbon-carbon double bond, and the one at 3079 cm-1 is due to stretching of the s bond between the alkene carbons and their attached hydrogens.



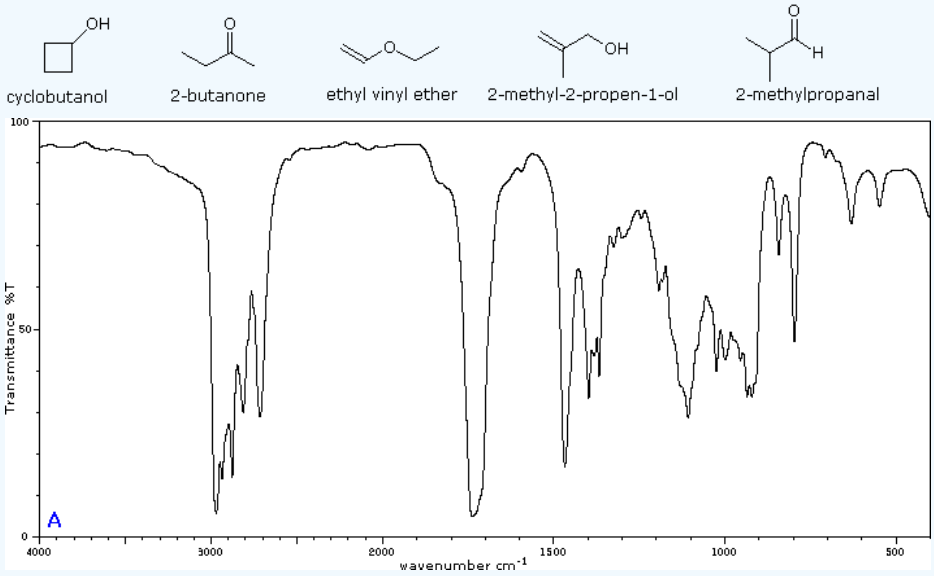
Alkynes have characteristic IR absorbance peaks in the range of 2100-2250 cm^{-1} due to stretching of the carbon-carbon triple bond, and terminal alkenes can be identified by their absorbance at about 3300 cm-1, due to stretching of the bond between the sp-hybridized carbon and the terminal hydrogen.

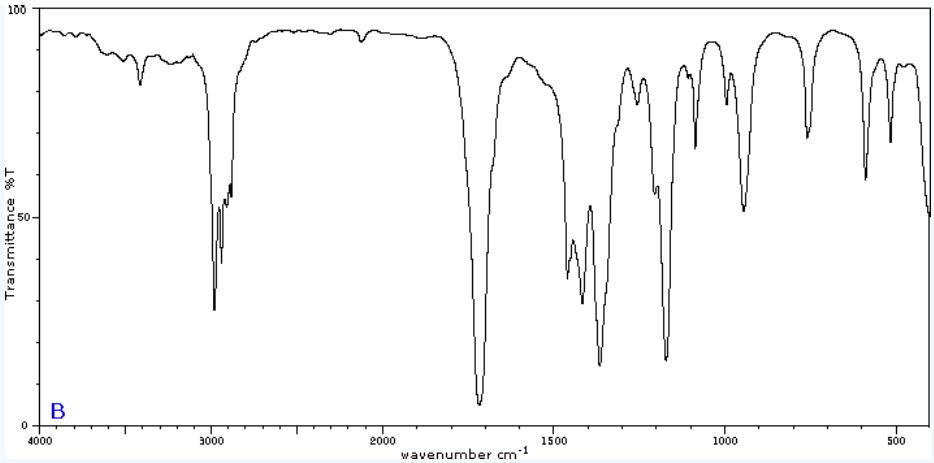
It is possible to identify other functional groups such as amines and ethers, but the characteristic peaks for these groups are considerably more subtle and/or variable, and often are overlapped with peaks from the fingerprint region. For this reason, we will limit our discussion here to the most easily recognized functional groups, which are summarized in this table.

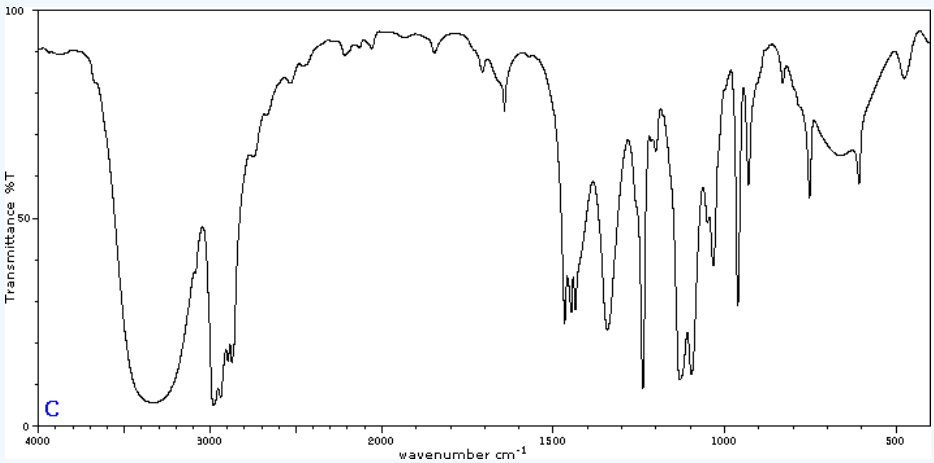
As you can imagine, obtaining an IR spectrum for a compound will not allow us to figure out the complete structure of even a simple molecule, unless we happen to have a reference spectrum for comparison. In conjunction with other analytical methods, however, IR spectroscopy can prove to be a very valuable tool, given the information it provides about the presence or absence of key functional groups. IR can also be a quick and convenient way for a chemist to check to see if a reaction has proceeded as planned. If we were to run a reaction in which we wished to convert cyclohexanone to cyclohexanol, for example, a quick comparison of the IR spectra of starting compound and product would tell us if we had successfully converted the ketone group to an alcohol.

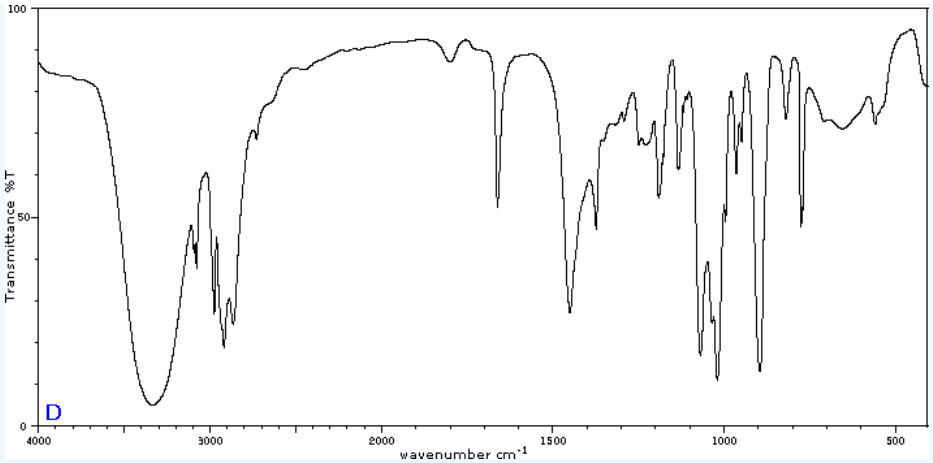
✔ EXAMPLE \PageIndex1

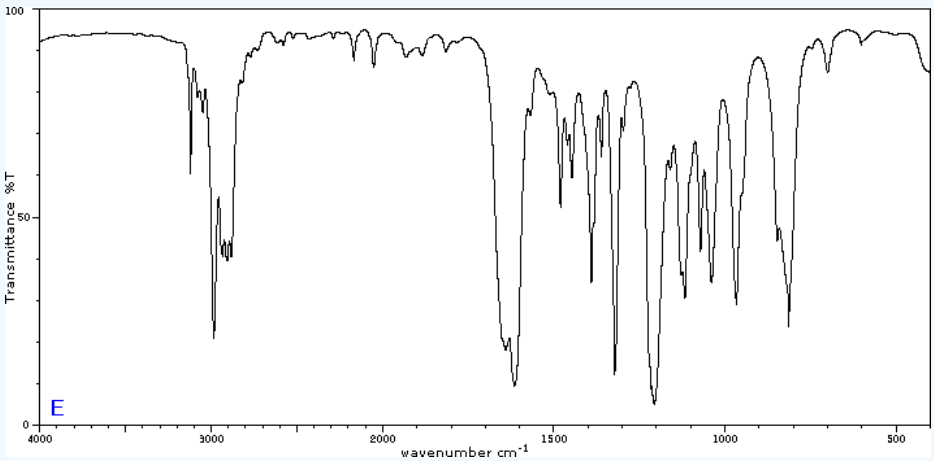
To illustrate the usefulness of infrared absorption spectra, examples for five C_4H_8O isomers are presented below their corresponding structural formulas. Try to associate each spectrum with one of the isomers in the row above it.




100
50
0
Transmittance %T
B
4000
3000
2000
1500
1000
500
wavenumber cm-1

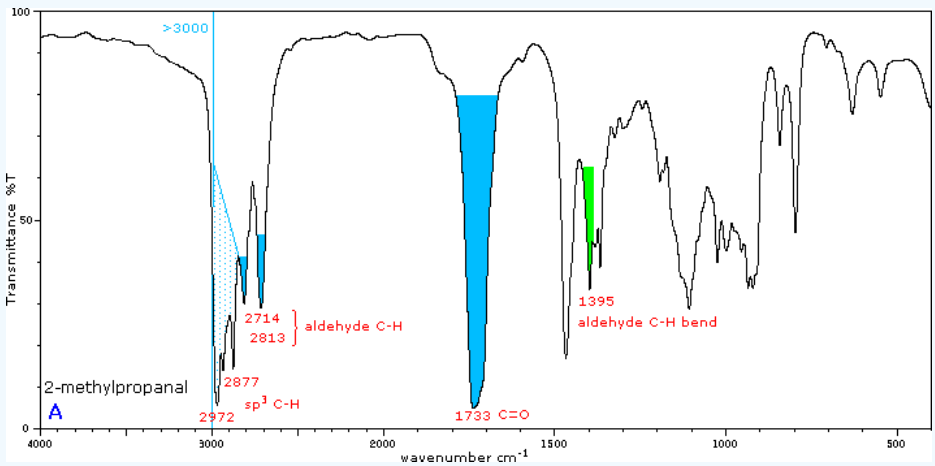

100
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0
Transmittance %T
C
4000
3000
2000
1500
1000
500
wavenumber cm-1

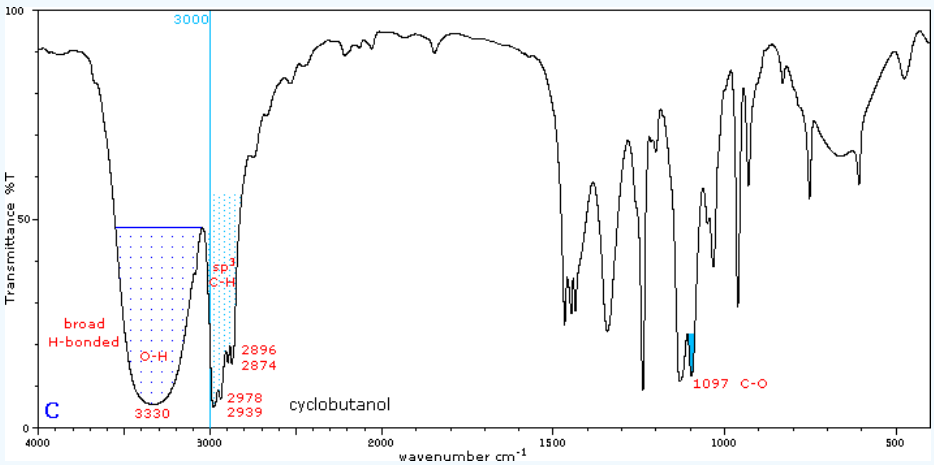




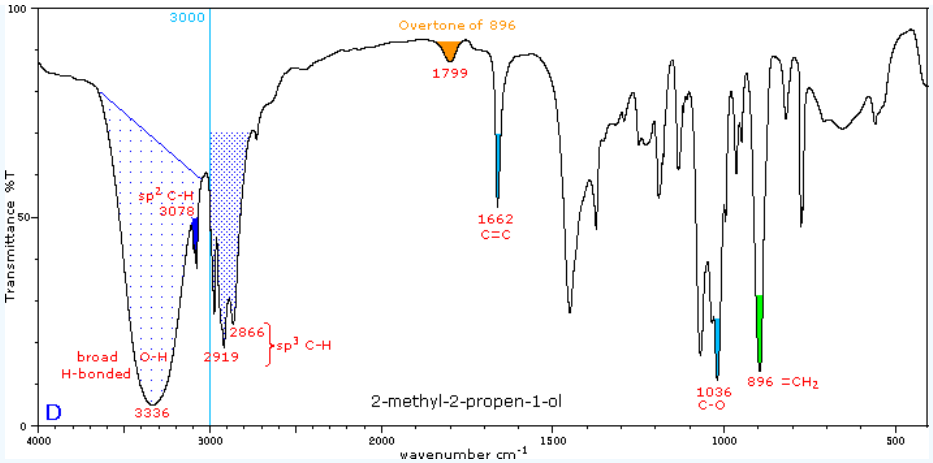
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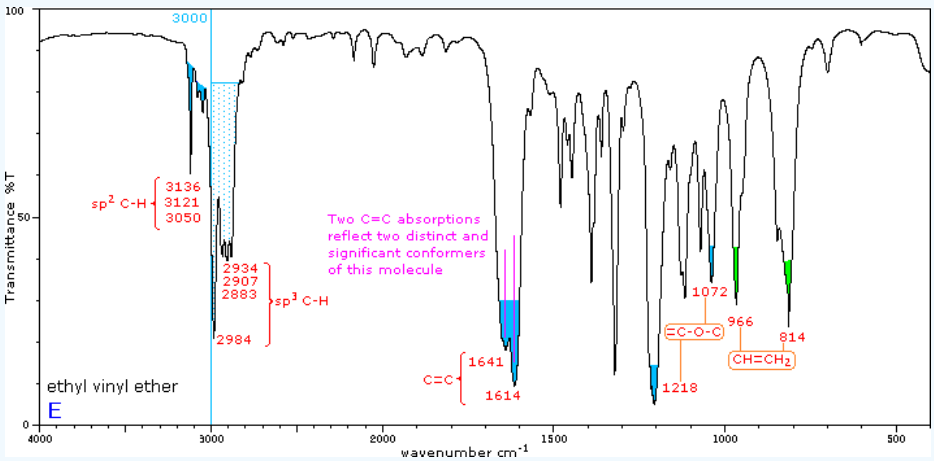
Solution





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EXERCISES

? EXERCISE \PageIndex1

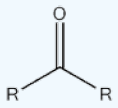
What functional groups give the following signals in an IR spectrum?

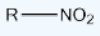
A – 1700 cm^{-1}

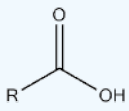
B – 1550 cm^{-1}

C – 1700 cm^{-1} and 2510-3000 cm^{-1}

Answer

A)  Carbonyl

B)  Nitro

C)  Carboxylic Acid

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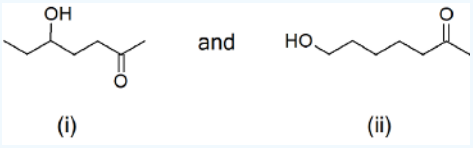
? EXERCISE \PageIndex2

How can you distinguish the following pairs of compounds through IR analysis?

A) CH_3OH (methanol) and $CH_3CH_2OCH_2CH_3$ (diethylether)

B) Cyclopentane and 1-pentene.

C)



Answer

A) A OH peak will be present around 3300 cm^{-1} for methanol and will be absent in the ether.

B) 1-pentene will have a alkene peak around 1650 cm^{-1} for the C=C and there will be another peak around 3100 cm^{-1} for the sp^2 C-H group on the alkene

C) Cannot distinguish these two isomers. They both have the same functional groups and therefore would have the same peaks on an IR spectra.

QUESTIONS

Q12.7.1

What functional groups give the following signals in an IR spectrum?

A) 1700 cm^{-1}

B) 1550 cm^{-1}

C) 1700 cm^{-1} and 2510-3000 cm^{-1}

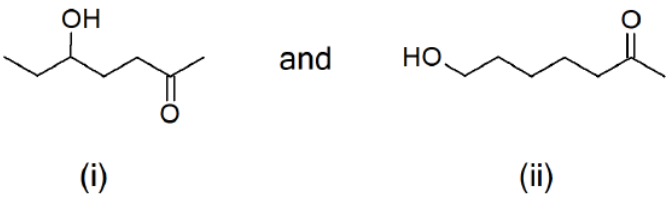
Q12.7.2

How can you distinguish the following pairs of compounds through IR analysis?

A) CH_3OH (Methanol) and $CH_3CH_2OCH_2CH_3$ (Diethylether)

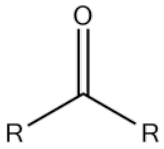
B) Cyclopentane and 1-pentene.

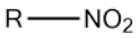
C)

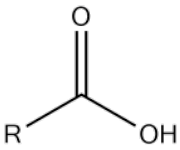


SOLUTIONS

S12.7.1

A)  Carbonyl

B)  Nitro

C)  Carboxylic Acid

S12.7.2

A) A OH peak will be present around 3300 cm^{-1} for methanol and will be absent in the ether.

B) 1-pentene will have a alkene peak around 1650 cm^{-1} for the C=C and there will be another peak around 3100 cm^{-1} for the sp^2 C-H group on the alkene

C) Cannot distinguish these two isomers. They both have the same functional groups and therefore would have the same peaks on an IR spectra.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- **Organic Chemistry With a Biological Emphasis** by Tim Soderberg (University of Minnesota, Morris)

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12.8: INFRARED SPECTRA OF SOME COMMON FUNCTIONAL GROUPS

Objective

After completing this section, you should be able to use an infrared spectrum to determine the presence of functional groups, such as alcohols, amines and carbonyl groups, in an unknown compound, given a list of infrared absorption frequencies.

STUDY NOTES

In Chapter 12.7, you should have learned, in broad terms, where a few key absorptions occur. Otherwise, to find the characteristic infrared absorptions of the various functional groups, refer to this IR table.

SPECTRAL INTERPRETATION BY APPLICATION OF GROUP FREQUENCIES

One of the most common application of infrared spectroscopy is to the identification of organic compounds. The major classes of organic molecules are shown in this category and also linked on the bottom page for the number of collections of spectral information regarding organic molecules.

HYDROCARBONS

Hydrocarbons compounds contain only C-H and C-C bonds, but there is plenty of information to be obtained from the infrared spectra arising from C-H stretching and C-H bending.

In alkanes, which have very few bands, each band in the spectrum can be assigned:

- C–H stretch from 3000–2850 cm^{-1}
- C–H bend or scissoring from 1470-1450 cm^{-1}
- C–H rock, methyl from 1370-1350 cm^{-1}
- C–H rock, methyl, seen only in long chain alkanes, from 725-720 cm^{-1}

Figure 3. shows the IR spectrum of octane. Since most organic compounds have these features, these C-H vibrations are usually not noted when interpreting a routine IR spectrum. Note that the change in dipole moment with respect to distance for the C-H stretching is greater than that for others shown, which is why the C-H stretch band is the more intense.

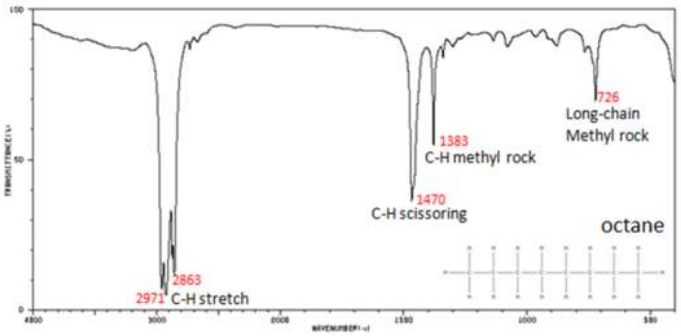


Figure 3. Infrared Spectrum of Octane

In alkenes compounds, each band in the spectrum can be assigned:

- C=C stretch from 1680-1640 cm^{-1}
- =C–H stretch from 3100-3000 cm^{-1}
- =C–H bend from 1000-650 cm^{-1}

Figure 4. shows the IR spectrum of 1-octene. As alkanes compounds, these bands are not specific and are generally not noted because they are present in almost all organic molecules.

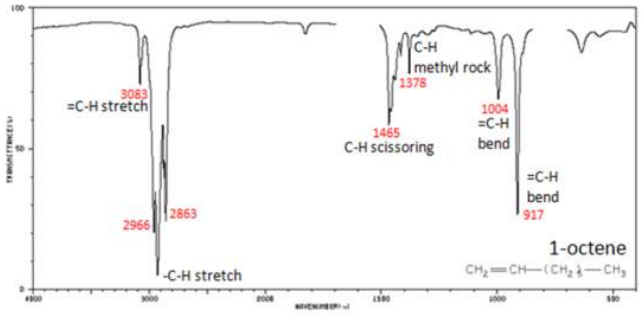


Figure 4. Infrared Spectrum of 1-Octene

In alkynes, each band in the spectrum can be assigned:

- –C≡C– stretch from 2260-2100 cm^{-1}
- –C≡C–H: C–H stretch from 3330-3270 cm^{-1}
- –C≡C–H: C–H bend from 700-610 cm^{-1}

The spectrum of 1-hexyne, a terminal alkyne, is shown below.

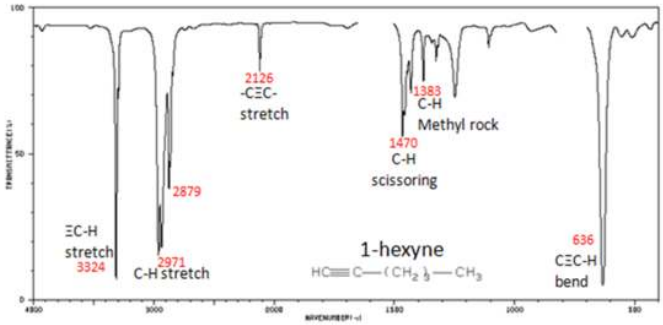


Figure 5. Infrared Spectrum of 1-Hexyne

In aromatic compounds, each band in the spectrum can be assigned:

- C–H stretch from 3100-3000 cm^{-1}
- overtones, weak, from 2000-1665 cm^{-1}
- C–C stretch (in-ring) from 1600-1585 cm^{-1}
- C–C stretch (in-ring) from 1500-1400 cm^{-1}
- C–H "oop" from 900-675 cm^{-1}

Note that this is at slightly higher frequency than is the –C–H stretch in alkanes. This is a very useful tool for interpreting IR spectra. Only alkenes and aromatics show a C–H stretch slightly higher than 3000 cm^{-1}.

Figure 6. shows the spectrum of toluene.

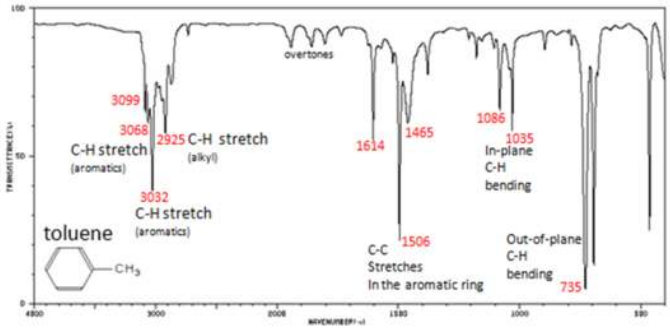


Figure 6. Infrared Spectrum of Toluene

Alcohols have IR absorptions associated with both the O-H and the C-O stretching vibrations.

- O–H stretch, hydrogen bonded 3500-3200 cm^{-1}
- C–O stretch 1260-1050 cm^{-1} (s)

Figure 7. shows the spectrum of ethanol. Note the very broad, strong band of the O–H stretch.

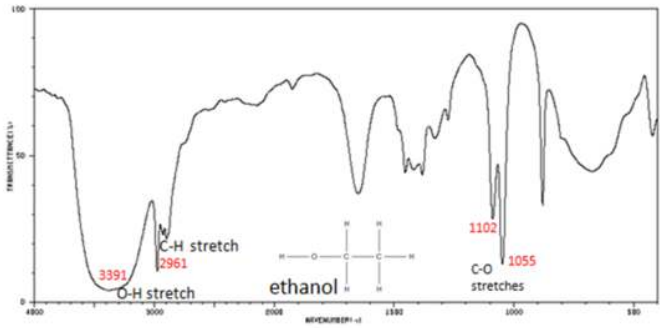


Figure 7. Infrared Spectrum of Ethanol

The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears:

- C=O stretch - aliphatic ketones 1715 cm^{-1}
- α, β -unsaturated ketones 1685-1666 cm^{-1}

Figure 8. shows the spectrum of 2-butanone. This is a saturated ketone, and the C=O band appears at 1715.

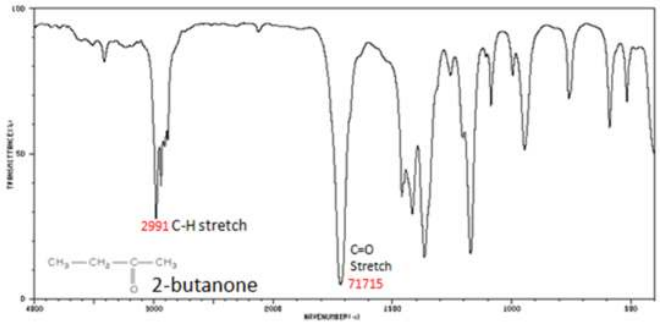


Figure 8. Infrared Spectrum of 2-Butanone

If a compound is suspected to be an aldehyde, a peak always appears around 2720 cm^{-1} which often appears as a shoulder-type peak just to the right of the alkyl C–H stretches.

- H–C=O stretch 2830-2695 cm^{-1}
- C=O stretch:
  - aliphatic aldehydes 1740-1720 cm^{-1}
  - α, β-unsaturated aldehydes 1710-1685 cm^{-1}

Figure 9. shows the spectrum of butyraldehyde.

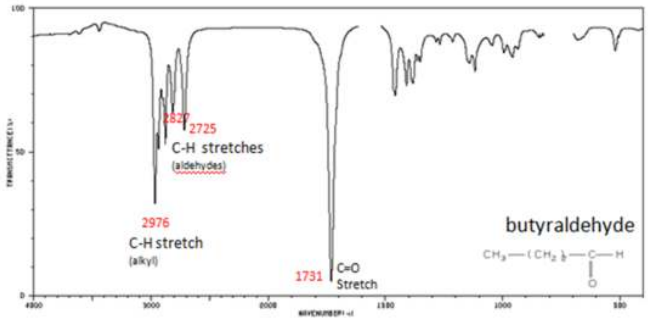


Figure 9. Infrared Spectrum of Butyraldehyde

The carbonyl stretch C=O of esters appears:

- C=O stretch
  - aliphatic from 1750-1735 cm^{-1}
  - α, β -unsaturated from 1730-1715 cm^{-1}
- C–O stretch from 1300-1000 cm^{-1}

Figure 10. shows the spectrum of ethyl benzoate.

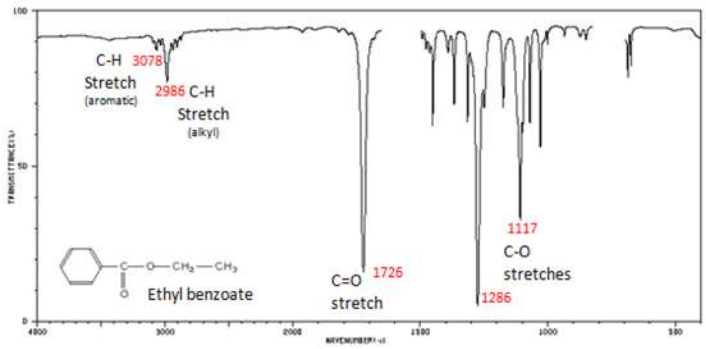


Figure 10. Infrared Spectrum of Ethyl benzoate

The carbonyl stretch C=O of a carboxylic acid appears as an intense band from 1760-1690 cm^{-1}. The exact position of this broad band depends on whether the carboxylic acid is saturated or unsaturated, dimerized, or has internal hydrogen bonding.

- O–H stretch from 3300-2500 cm^{-1}
- C=O stretch from 1760-1690 cm^{-1}
- C–O stretch from 1320-1210 cm^{-1}
- O–H bend from 1440-1395 and 950-910 cm^{-1}

Figure 11. shows the spectrum of hexanoic acid.

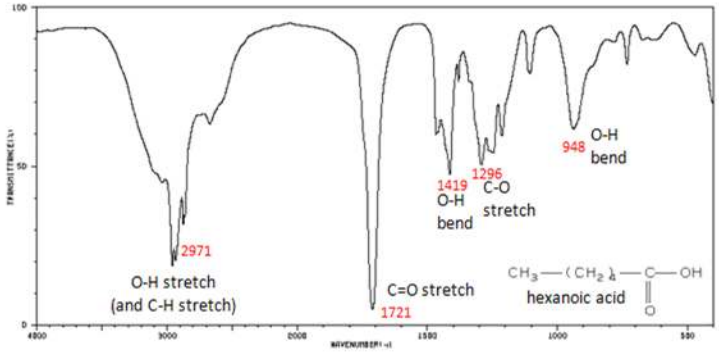


Figure 11. Infrared Spectrum of Hexanoic acid

ORGANIC NITROGEN COMPOUNDS

- N–O asymmetric stretch from 1550-1475 cm^{-1}
- N–O symmetric stretch from 1360-1290 cm^{-1}

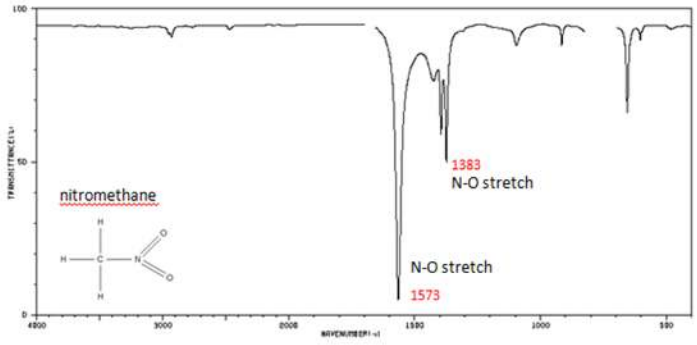


Figure 12. Infrared Spectrum of Nitomethane

ORGANIC COMPOUNDS CONTAINING HALOGENS

Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorene, or iodine.

- C–H wag (-CH_2X) from 1300-1150 cm^{-1}
- C–X stretches (general) from 850-515 cm^{-1}
  - C–Cl stretch 850-550 cm^{-1}
  - C–Br stretch 690-515 cm^{-1}

The spectrum of 1-chloro-2-methylpropane are shown below.

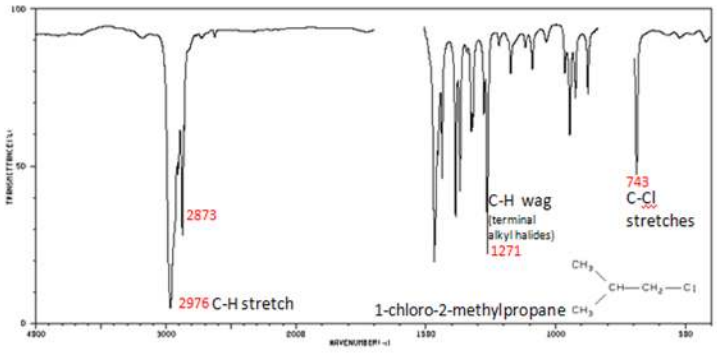


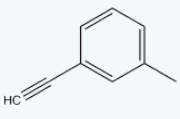
Figure 13. Infrared Spectrum of 1-chloro-2-methylpropane

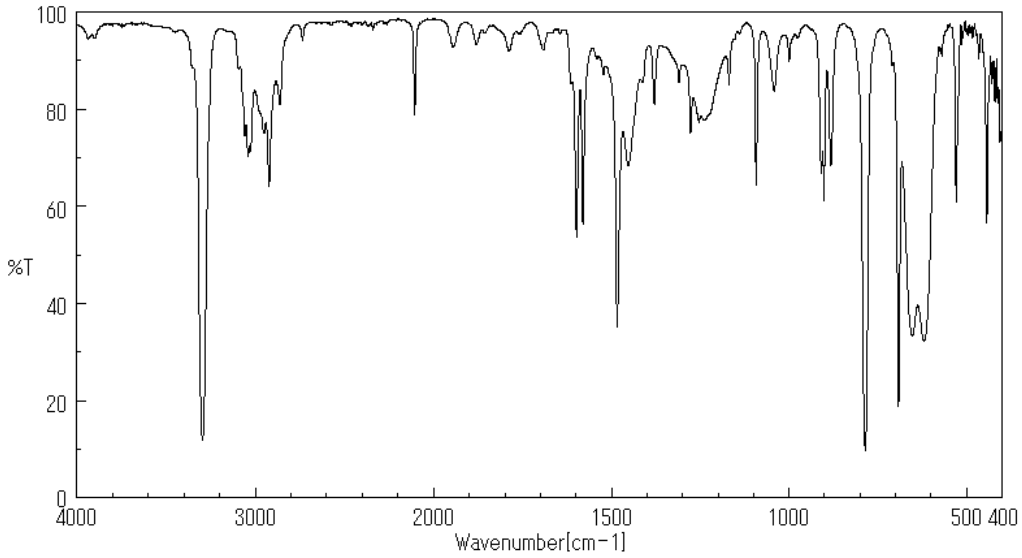
For more Infrared spectra Spectral database of organic molecules is introduced to use free database. Also, the infrared spectroscopy correlation table is linked on bottom of page to find other assigned IR peaks.

EXERCISES

? EXERCISE 12.8.1

The following spectrum is for the accompanying compound. What are the peaks that you can identify?





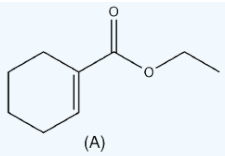
Answer

Frequency (cm^{-1})	Functional Group
3200	C≡C-H
2900-3000	C-C-H, C=C-H
2100	C≡C
1610	C=C

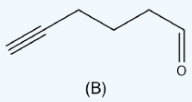
(There is also an aromatic undertone region between 2000-1600 which describes the substitution on the phenyl ring.)

? EXERCISE 12.8.2

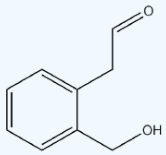
What absorptions would the following compounds have in an IR spectra?



(A)



(B)



(C)

Answer

A

Frequency (cm^{-1})	**Functional Group**
2900-3000	C-C-H, C=C-H
1710	C=O
1610	C=C
1100	C-O

B

Frequency (cm^{-1})	**Functional Group**
3200	C≡C-H
2900-3000	C-C-H, C=C-H

2100	C≡C
1710	C=O

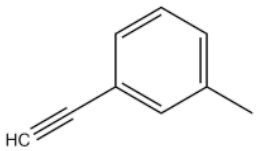
C

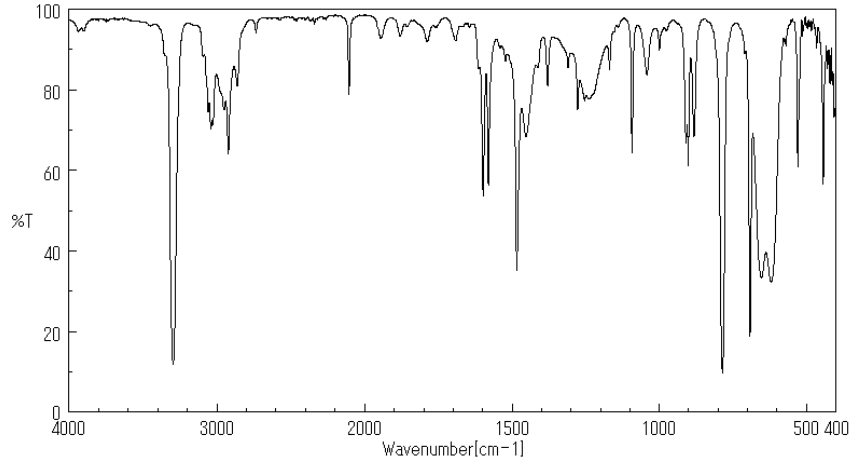
Frequency (cm^{-1})	**Functional Group**
3300 (broad)	O-H
2900-3000	C-C-H, C=C-H
2000-1800	Aromatic Overtones
1710	C=O
1610	C=C

QUESTIONS

Q12.8.1

The following spectra is for the accompanying compound. What are the peaks that you can I identify in the spectrum?

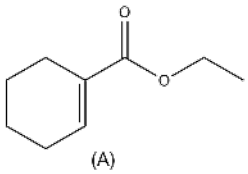




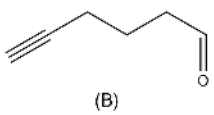
Source: SDBSWeb : http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 2 December 2016)

Q12.8.2

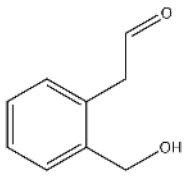
What absorptions would the following compounds have in an IR spectra?



(A)



(B)



(C)

SOLUTIONS

S12.8.1

Frequency (cm-1) Functional Group

3200 C≡C-H

2900-3000 C-C-H, C=C-H

2100 C≡C

1610 C=C

(There is also an aromatic undertone region between 2000-1600 which describes the substitution on the phenyl ring.)

S12.8.2

A)

Frequency (cm-1) Functional Group

2900-3000 C-C-H, C=C-H

1710 C=O

1610 C=C

1100 C-O

B)

Frequency (cm-1) Functional Group

3200 C≡C-H

2900-3000 C-C-H, C=C-H

2100 C≡C

1710 C=O

C)

Frequency (cm-1) Functional Group

3300 (broad) O-H

2900-3000 C-C-H, C=C-H

2000-1800 Aromatic Overtones

1710 C=O

1610 C=C

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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12.S: STRUCTURE DETERMINATION - MASS SPECTROMETRY AND INFRARED SPECTROSCOPY (SUMMARY)

CONCEPTS & VOCABULARY

12.1 Introduction

- Spectroscopy describes several techniques used by chemists to understand chemical structures and bonds.

12.2 Mass Spectrometry of Small Molecules - Magnetic Sector Instruments

- Mass spectrometers consist of an **ion source**, **mass analyzer** and detector.
- There are several common **ion sources** including **electron ionization** and **chemical ionization**.
- Upon ionization, a molecular ion is formed (the molecule after losing a single electron) which will break into smaller pieces (fragments).
- Fragments that are charged will appear in the mass spectrum and are helpful in identifying the parent molecule.
- The most abundant ion in a mass spectrum is called the **base peak**.
- The ion with the same mass as the parent molecule is called the **molecular ion**.
- Isotopes of carbon and hydrogen lead to common M+1 peaks.
- The x-axis of a mass spectrum is **m/z -** the mass to charge ratio, which in practice equals the mass of the ion.

12.3 Interpreting Mass Spectra

- Uncharged particles do not appear in mass spectra.
- The y-axis of a mass spectrum is the relative abundance, with the base peak set at 100 as the most abundant ion.
- Abundance of ions is related to their stability.

12.4 Mass Spectrometry of Some Common Functional Groups

12.5 Mass Spectrometry in Biological - Time-of-flight (TOF) Instruments

12.6 Spectroscopy and the Electromagnetic Spectrum

- Electromagnetic radiation is composed of waves where shorter wavelengths correspond to higher energy radiation.
- Electromagnetic radiation can also be thought of as a stream of particles called **photons**.
- The electromagnetic spectrum is made up of many types of radiation including infrared, ultraviolet, and visible lights as well as x-rays, gamma rays, microwaves, and radio waves.
- Molecular spectroscopy works by exposing a chemical sample to electromagnetic radiation. It will only absorb radiation with energy that corresponds to some excited state, while all other energies will pass through unabsorbed.

12.7 Infrared Spectroscopy

- When infrared radiation is absorbed, molecules will move to a higher vibrational energy state.
- Examples of molecular vibrations include bending and stretching of bonds. These vibrations can be symmetric or asymmetric.
- In general, more polar bonds have stronger IR absorption.
- IR spectra typically use wavenumbers (cm^{-1}) as units for the x-axis.
- The y-axis for IR spectra is usually % transmittance, with 100% at the top of the spectrum and absorbances looking like valleys (or downward peaks).

12.8 Interpreting Infrared Spectra

- Functional groups have standard regions within the IR spectrum where they absorb.
- The general regions include hydrogen bonding (O-H and N-H), carbon-hydrogen bonds, triple bonds, carbonyls, alkenes, and fingerprint region.

12.9 Infrared Spectra of Some Common Functional Groups

SKILLS TO MASTER

- Skill 12.1 Determine specific atoms from mass spectra based on molecular ion and M+2 peaks (N, Cl, Br).
- Skill 12.2 Interpret mass spectra fragments - recognizing common fragments.
- Skill 12.3 Interpret infrared spectra to determine functional groups that are present or absent.

MEMORIZATION TASKS (MT)

MT 12.1 Memorize common mass spectra fragments.

MT 12.2 Memorize common functional group regions in infrared spectroscopy.

CONTRIBUTORS

- Layne Morsch (University of Illinois Springfield)

12.S: Structure Determination - Mass Spectrometry and Infrared Spectroscopy (Summary) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

13: STRUCTURE DETERMINATION- NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

LEARNING OBJECTIVES

After you have completed Chapter 13, you should be able to

1. fulfill all of the detailed objectives listed under each individual section.
2. solve road-map problems which may require the interpretation of ^{1}H NMR spectra in addition to other spectral data.
3. define, and use in context, the key terms introduced.

In Chapter 12, you learned how an organic chemist could use two spectroscopic techniques, mass spectroscopy and infrared spectroscopy, to assist in determining the structure of an unknown compound. This chapter introduces a third technique, nuclear magnetic resonance (NMR). The two most common forms of NMR spectroscopy, ^{1}H NMR and ^{13}C NMR, will be discussed, the former in much more detail than the latter. Nuclear magnetic resonance spectroscopy is a very powerful tool, particularly when used in combination with other spectroscopic techniques.

13.0: Prelude
13.1: Nuclear Magnetic Resonance Spectroscopy
13.2: The Nature of NMR Absorptions
13.3: Chemical Shifts
13.4: ^{13}C NMR Spectroscopy- Signal Averaging and FT-NMR
13.5: Characteristics of ^{13}C NMR Spectroscopy
13.6: DEPT ^{13}C NMR Spectroscopy
13.7: Uses of ^{13}C NMR Spectroscopy
13.8: ^{1}H NMR Spectroscopy and Proton Equivalence
13.9: Chemical Shifts in ^{1}H NMR Spectroscopy
13.10: Integration of ^{1}H NMR Absorptions- Proton Counting
13.11: Spin-Spin Splitting in ^{1}H NMR Spectra
13.12: More Complex Spin-Spin Splitting Patterns
13.13: Uses of ^{1}H NMR Spectroscopy
13.S: Structure Determination - Nuclear Magnetic Resonance Spectroscopy (Summary)

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13.1: NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Objectives

After completing this section, you should be able to

1. discuss the principles of NMR spectroscopy.
2. identify the two magnetic nuclei that are most important to an organic chemist.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- resonance

STUDY NOTES

Notice that the word “resonance” has a different meaning when we are discussing nuclear magnetic resonance spectroscopy than it does when discussing molecular structures.

INTRODUCTION

Some types of atomic nuclei act as though they spin on their axis similar to the Earth. Since they are positively charged they generate an electromagnetic field just as the Earth does. So, in effect, they will act as tiny bar magnetics. Not all nuclei act this way, but fortunately both ^{1}H and ^{13}C do have nuclear spins and will respond to this technique.



NMR Spectrometer

In the absence of an external magnetic field the direction of the spin of the nuclei will be randomly oriented (see figure below left). However, when a sample of these nuclei is place in an external magnetic field, the nuclear spins will adopt specific orientations much as a compass needle responses to the Earth’s magnetic field and aligns with it. Two possible orientations are possible, with the external field (*i.e.* parallel to and in the same direction as the external field) or against the field (*i.e.* antiparallel to the external field). See figure below right.

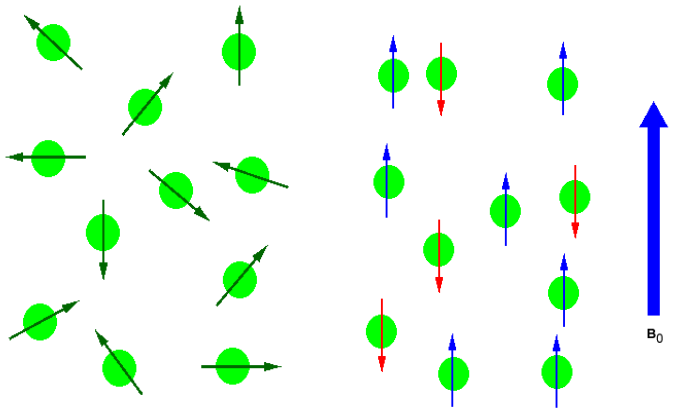
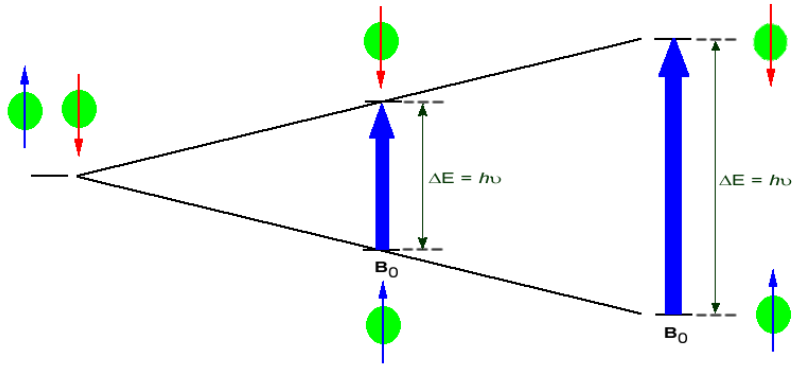


Figure 1: (Left) Random nuclear spin without an external magnetic field. (Right) Ordered nuclear spin in an external magnetic field

If the ordered nuclei are now subjected to EM radiation of the proper frequency the nuclei aligned with the field will absorb energy and "spin-flip" to align themselves against the field, a higher energy state. When this spin-flip occurs the nuclei are said to be in "resonance" with the field, hence the name for the technique, **N**uclear **M**agentic **R**esonance or NMR.

The amount of energy, and hence the exact frequency of EM radiation required for resonance to occur is dependent on both the strength of the magnetic field applied and the type of the nuclei being studied. As the strength of the magnetic field increases the energy difference between the two spin states increases and a higher frequency (more energy) EM radiation needs to be applied to achieve a spin-flip (see image below).



Superconducting magnets can be used to produce very strong magnetic field, on the order of 21 tesla (T). Lower field strengths can also be used, in the range of 4 - 7 T. At these levels the energy required to bring the nuclei into resonance is in the MHz range and corresponds to radio wavelength energies, *i.e.* at a field strength of 4.7 T 200 MHz bring ^{1}H nuclei into resonance and 50 MHz bring ^{13}C into resonance. This is considerably less energy then is required for IR spectroscopy, ~10^{-4} kJ/mol versus ~5 - ~50 kJ/mol.

^{1}H and ^{13}C are not unique in their ability to undergo NMR. All nuclei with an odd number of protons (^{1}H, ^{2}H, ^{14}N, ^{19}F, ^{31}P ...) or nuclei with an odd number of neutrons (*i.e.* ^{13}C) show the magnetic properties required for NMR. Only nuclei with even number of both protons and neutrons (^{12}C and ^{16}O) do not have the required magnetic properties.

EXERCISES

? EXERCISE 13.1.1

If in a field strength of 4.7 T, H^{1} requires 200 MHz of energy to maintain resonance. If atom X requires 150 MHz, calculate the amount of energy required to spin flip atom X's nucleus. Is this amount greater than the energy required for hydrogen?

Answer

$E = h\upsilon$

$E = (6.62 \times 10^{-34})(150\ \text{MHz})$

$E = 9.93 \times 10^{-26}$ J

The energy is equal to 9.93 x 10^{-26} J. This value is smaller than the energy required for hydrogen (1.324×10^{-25} J).

EXERCISE 13.1.2

Calculate the energy required to spin flip at 400 MHz. Does changing the frequency to 500 MHz decrease or increase the energy required? What about 300 MHz.

Answer

Add

$E = h\upsilon$

$E = (6.62 \times 10^{-34})(400\ \text{MHz})$

$E = 2.648 \times 10^{-25}$ J

The energy would increase if the frequency would increase to 500 MHz, and decrease if the frequency would decrease to 300 MHz.

QUESTIONS

Q13.1.1

If in a field strength of 4.7 T, H^1 requires 200 MHz of energy to maintain resonance. If atom X requires 150 MHz, calculate the amount of energy required to spin flip atom X's nucleus. Is this amount greater than the energy required for hydrogen?

Q13.1.2

Calculate the energy required to spin flip at 400 MHz. Does changing the frequency to 500 MHz decrease or increase the energy required? What about 300 MHz.

SOLUTIONS

S13.1.1

$E = h\upsilon$

$E = (6.62 \times 10^{-34})(150\ \text{MHz})$

$E = 9.93 \times 10^{-26}$ J

The energy is equal to 9.93x10^{-26} J. This value is smaller than the energy required for hydrogen (1.324×10^{-25} J).

S13.1.2

$E = h\upsilon$

$E = (6.62 \times 10^{-34})(400\ \text{MHz})$

$E = 2.648 \times 10^{-25}$ J

The energy would increase if the frequency would increase to 500 MHz, and decrease if the frequency would decrease to 300 MHz.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

Dr. Richard Spinney (The Ohio State University)

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13.2: THE NATURE OF NMR ABSORPTIONS

Objectives

After completing this section, you should be able to

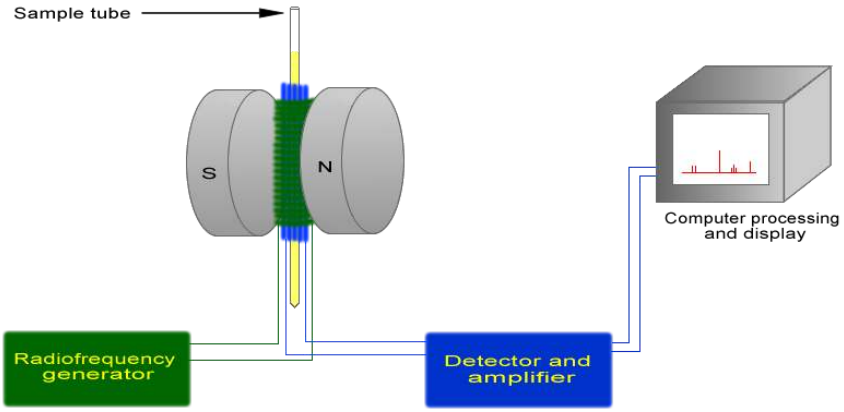
1. explain, in general terms, the origin of shielding effects in NMR spectroscopy.
2. explain the number of peaks occurring in the ^{1}H or ^{13}C NMR spectrum of a simple compound, such as methyl acetate.
3. describe, and sketch a diagram of, a simple NMR spectrometer.
4. explain the difference in time scales of NMR and infrared spectroscopy.
5. predict the number of peaks expected in the ^{1}H or ^{13}C NMR spectrum of a given compound.

STUDY NOTES

Before you go on, make sure that you understand that each signal in the ^{1}H NMR spectrum shown for methyl acetate is due to a different proton environment. The three protons on the same methyl group are equivalent and appear in the spectrum as one signal. However, the two methyl groups are in two different environments (one is more deshielded) and so we see two signals in the whole spectrum (aside from the TMS reference peak).

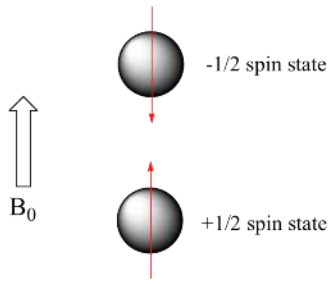
Methyl acetate has a very simple ^{1}H NMR spectrum, because there is no proton-proton coupling, and therefore no splitting of the signals. In later sections, we discuss splitting patterns in ^{1}H NMR spectra and how they help a chemist determine the structure of organic compounds.

The basic arrangement of an NMR spectrometer is displayed below. A sample (in a small glass tube) is placed between the poles of a strong magnetic. A radio frequency generator pulses the sample and excites the nuclei causing a spin-flip. The spin flip is detected by the detector and the signal sent to a computer where it is processed.



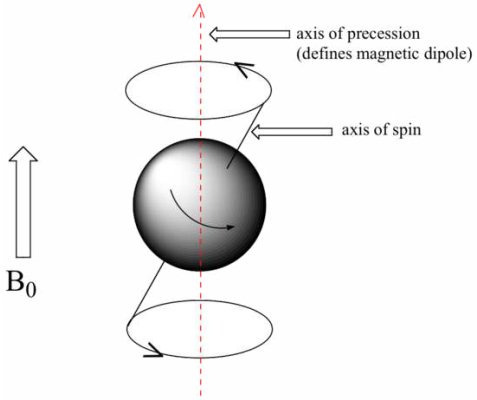
NUCLEAR PRECESSION, SPIN STATES, AND THE RESONANCE CONDITION

When a sample of an organic compound is sitting in a flask on a laboratory benchtop, the magnetic moments of its hydrogen atoms are randomly oriented. When the same sample is placed within the field of a very strong magnet in an NMR instrument (this field is referred to by NMR spectroscopists as the **applied field**, abbreviated $\mathbf{B_0}$) each hydrogen will assume one of two possible **spin states**. In what is referred to as the +½ spin state, the hydrogen's magnetic moment is aligned *with* the direction of B_0, while in the -½ spin state it is aligned *opposed to* the direction of B_0.



Because the +½ spin state is slightly lower in energy, in a large population of organic molecules slightly more than half of the hydrogen atoms will occupy this state, while slightly less than half will occupy the –½ state. *The difference in energy between the two spin states increases with increasing strength of B_0.*This last statement is in italics because it is one of the key ideas in NMR spectroscopy, as we shall soon see.

At this point, we need to look a little more closely at how a proton spins in an applied magnetic field. You may recall playing with spinning tops as a child. When a top slows down a little and the spin axis is no longer completely vertical, it begins to exhibit **precessional motion**, as the spin axis rotates slowly around the vertical. In the same way, hydrogen atoms spinning in an applied magnetic field also exhibit precessional motion about a vertical axis. It is this axis (which is either parallel or antiparallel to B_0) that defines the proton's magnetic moment. In the figure below, the proton is in the +1/2 spin state.

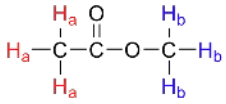


The **frequency of precession** (also called the **Larmour frequency,** abbreviated $\boldsymbol{\omega_L}$) is simply the number of times per second that the proton precesses in a complete circle. A proton`s precessional frequency increases with the strength of B_0.

If a proton that is precessing in an applied magnetic field is exposed to electromagnetic radiation of a frequency ν that matches its precessional frequency ω_L, we have a condition called **resonance**. *In the resonance condition, a proton in the lower-energy +½ spin state (aligned with B_0) will transition (flip) to the higher energy –½ spin state (opposed to B_0). In doing so, it will absorb radiation at this resonance frequency* $\boldsymbol{\nu} = \boldsymbol{\omega_L}$. This frequency, as you might have already guessed, corresponds to the energy difference between the proton's two spin states. With the strong magnetic fields generated by the superconducting magnets used in modern NMR instruments, the resonance frequency for protons falls within the radio-wave range, anywhere from 100 MHz to 800 MHz depending on the strength of the magnet.

THE BASICS OF AN NMR EXPERIMENT

Given that chemically nonequivalent protons have different resonance frequencies in the same applied magnetic field, we can see how NMR spectroscopy can provide us with useful information about the structure of an organic molecule. A full explanation of how a modern NMR instrument functions is beyond the scope of this text, but in very simple terms, here is what happens. First, a sample compound (we'll use methyl acetate) is placed inside a very strong applied magnetic field (B_0).

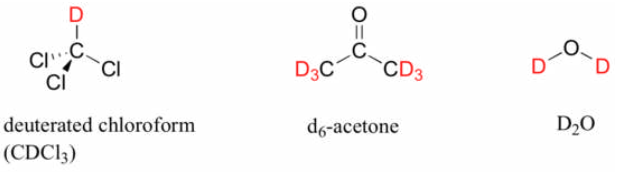


methyl acetate

All of the protons begin to precess: the H_a protons at precessional frequency ω_a, the H_b protons at ω_b.At first, the magnetic moments of (slightly more than) half of the protons are aligned with B_0, and half are aligned against B_0. Then, the sample is hit with electromagnetic radiation in the radio frequency range. The two specific frequencies which match $\omega_a$andω_b(i.e. the resonance frequencies) cause those H_a

and H_b protons which are aligned *with* B_0 to 'flip' so that they are now aligned *against* B_0. In doing so, the protons absorb radiation at the two resonance frequencies. The NMR instrument records which frequencies were absorbed, as well as the intensity of each absorbance.

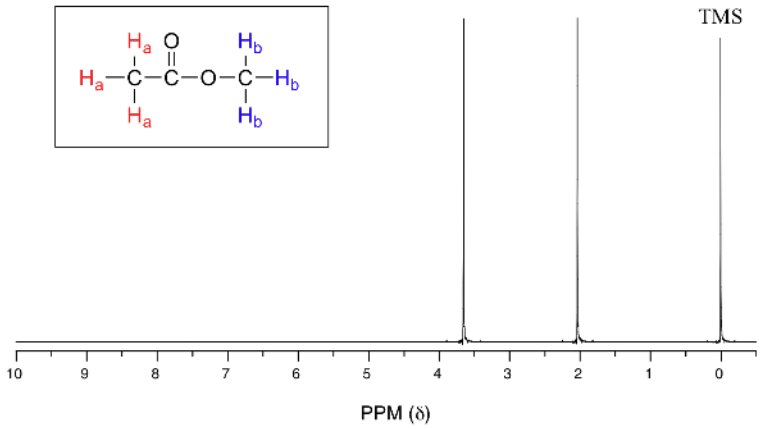
In most cases, a sample being analyzed by NMR is in solution. If we use a common laboratory solvent (diethyl ether, acetone, dichloromethane, ethanol, water, etc.) to dissolve our NMR sample, however, we run into a problem – there many more solvent protons in solution than there are sample protons, so the signals from the sample protons will be overwhelmed. To get around this problem, we use special NMR solvents in which all protons have been replaced by deuterium. Recall that deuterium is NMR-active, but its resonance frequency is very different from that of protons, and thus it is `invisible` in ^{1}H-NMR. Some common NMR solvents are shown below.



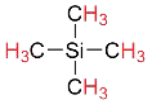
deuterated chloroform ($CDCl_3$) | d_6-acetone | D_2O

THE CHEMICAL SHIFT

Let's look at an actual ^{1}H-NMR plot for methyl acetate. Just as in IR and UV-vis spectroscopy, the vertical axis corresponds to intensity of absorbance, the horizontal axis to frequency (typically the vertical axis is not shown in an NMR spectrum).



We see three absorbance signals: two of these correspond to H_a and H_b, while the peak at the far right of the spectrum corresponds to the 12 chemically equivalent protons in tetramethylsilane (TMS), a standard reference compound that was added to our sample.



tetramethylsilane (TMS)

You may be wondering about a few things at this point - why is TMS necessary, and what is the meaning of the `ppm (δ)` label on the horizontal axis? Shouldn't the frequency units be in Hz? Keep in mind that NMR instruments of many different applied field strengths are used in organic chemistry laboratories, and that the proton's resonance frequency range depends on the strength of the applied field. The spectrum above was generated on an instrument with an applied field of approximately 7.1 Tesla, at which strength protons resonate in the neighborhood of 300 million Hz (chemists refer to this as a 300 MHz instrument). If our colleague in another lab takes the NMR spectrum of the same molecule using an instrument with a 2.4 Tesla magnet, the protons will resonate at around 100 million Hz (so we'd call this a 100 MHz instrument). It would be inconvenient and confusing to always have to convert NMR data according to the field strength of the instrument used. Therefore, chemists report resonance frequencies not as absolute values in Hz, but rather as values *relative to a common standard*, generally the signal generated by the protons in TMS. This is where the ppm – parts per million – term comes in. Regardless of the magnetic field strength of the instrument being used, the resonance frequency of the 12 equivalent protons in TMS is defined as a zero point. The resonance frequencies of protons in the sample molecule are then reported in terms of how much higher they are, in ppm, relative to the TMS signal (almost all protons in organic molecules have a higher resonance frequency than those in TMS, for reasons we shall explore quite soon).

The two proton groups in our methyl acetate sample are recorded as resonating at frequencies 2.05 and 3.67 ppm higher than TMS. One-millionth (1.0 ppm) of 300 MHz is 300 Hz. Thus 2.05 ppm, on this instrument, corresponds to 615 Hz, and 3.67 ppm corresponds to 1101 Hz. If the TMS protons observed by our 7.1 Tesla instrument resonate at exactly 300,000,000 Hz, this means that the protons in our ethyl acetate samples are resonating at 300,000,615 and 300,001,101 Hz, respectively. Likewise, if the TMS protons in our colleague's 2.4 Tesla instrument resonate at exactly 100 MHz, the methyl acetate protons in her sample resonate at 100,000,205 and 100,000,367 Hz (on the 100 MHz instrument, 1.0 ppm corresponds to 100 Hz). The absolute frequency values in each case are not very useful – they will vary according to the instrument used – but the *difference* in resonance frequency from the TMS standard, expressed in parts per million, should be the same regardless of the instrument.

Expressed this way, the resonance frequency for a given proton in a molecule is called its **chemical shift**. A frequently used symbolic designation for chemical shift in ppm is the lower-case Greek letter *delta* (δ). Most protons in organic compounds have chemical shift values between 0 and 12 ppm from TMS, although values below zero and above 12 are occasionally observed. By convention, the left-hand side of an NMR spectrum (higher chemical shift) is called **downfield**, and the right-hand direction is called **upfield**.

In our methyl acetate example we included for illustrative purposes a small amount of TMS standard directly in the sample, as was the common procedure for determining the zero point with older NMR instruments. That practice is generally no longer necessary, as modern NMR instruments are designed to use the deuterium signal from the solvent as a standard reference point, then to extrapolate the 0 ppm baseline that corresponds to the TMS proton signal (in an applied field of 7.1 Tesla, the deuterium atom in $CDCl_3$ resonates at 32 MHz, compared to 300 MHz for the protons in TMS). In the remaining NMR spectra that we will see in this text we will not see an actual TMS signal, but we can always assume that the 0 ppm point corresponds to where the TMS protons *would* resonate if they were present.

EXAMPLE

A proton has a chemical shift (relative to TMS) of 4.56 ppm.

a. a) What is its chemical shift, expressed in Hz, in a 300 MHz instrument? On a 200 MHz instrument?
b. b) What is its resonance frequency, expressed in Hz, in a 300 MHz instrument? On a 200 MHz instrument?

(Assume that in these instruments, the TMS protons resonate at exactly 300 or 200 MHz, respectively)

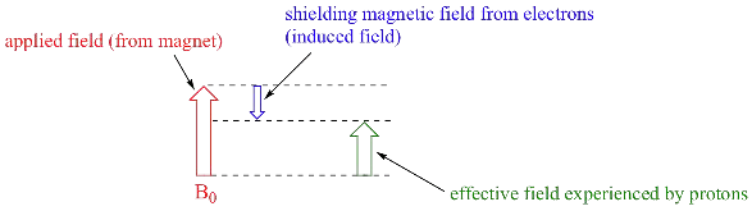
Answer

a) 1 ppm = 300 Hz, so 4.56 ppm corresponds to 1368 Hz on the 300 MHz instrument. On the 200 MHz instrument, the chemical shift is 912 Hz.

b) 300 MHz instrument: 300,001,368 Hz. 200 MHz instrument: 200,000,912 Hz.

DIAMAGNETIC SHIELDING AND DESHIELDING

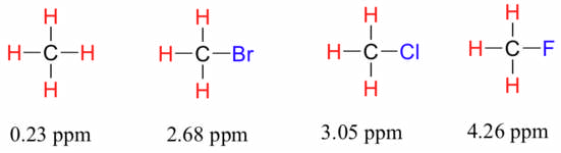
We come now to the question of *why* nonequivalent protons have different chemical shifts. The chemical shift of a given proton is determined primarily by its immediate electronic environment. Consider the methane molecule (CH_4), in which the protons have a chemical shift of 0.23 ppm. The valence electrons around the methyl carbon, when subjected to B_0, are induced to circulate and thus generate their own very small magnetic field that *opposes* B_0. This **induced field**, to a small but significant degree, *shields* the nearby protons from experiencing the full force of B_0, an effect known as **local diamagnetic shielding**. The methane protons therefore do not experience the full force of B_0 - what they experience is called B_{eff}, or the **effective field**, which is slightly *weaker* than B_0.



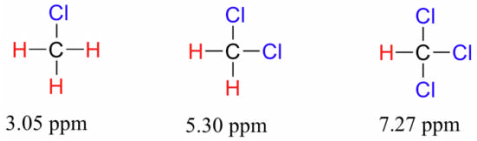
Therefore, their resonance frequency is slightly lower than what it would be if they did not have electrons nearby to shield them.

Now consider methyl fluoride, CH_3F, in which the protons have a chemical shift of 4.26 ppm, significantly higher than that of methane. This is caused by something called the **deshielding effect**. Because fluorine is more electronegative than carbon, it pulls valence electrons away from the carbon, effectively *decreasing* the electron density around each of the protons. For the protons, lower electron density means less diamagnetic shielding, which in turn means a greater overall exposure to B_0, a stronger B_{eff}, and a higher resonance frequency. Put another way, the fluorine, by pulling electron density away from the protons, is *deshielding* them, leaving them more exposed to B_0. As the electronegativity of the substituent increases, so does the extent of deshielding, and so does the chemical shift. This is evident when we look

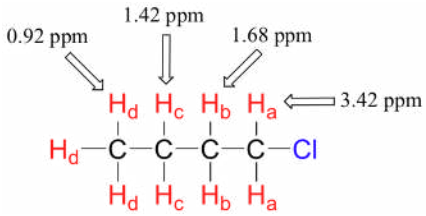
at the chemical shifts of methane and three halomethane compounds (remember that electronegativity increases as we move up a column in the periodic table).



To a large extent, then, we can predict trends in chemical shift by considering how much deshielding is taking place near a proton. The chemical shift of trichloromethane is, as expected, higher than that of dichloromethane, which is in turn higher than that of chloromethane.



The deshielding effect of an electronegative substituent diminishes sharply with increasing distance:



The presence of an electronegative oxygen, nitrogen, sulfur, or sp^2-hybridized carbon also tends to shift the NMR signals of nearby protons slightly downfield:

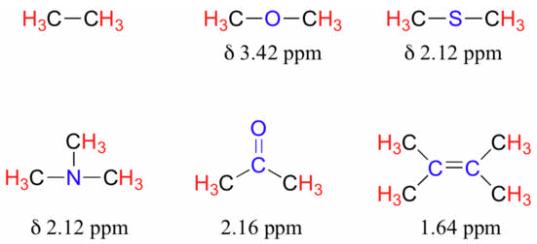
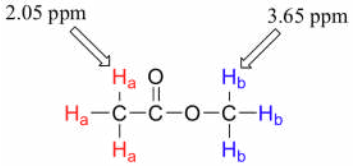
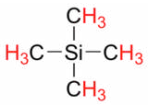


Table 2 lists typical chemical shift values for protons in different chemical environments.

Armed with this information, we can finally assign the two peaks in the the ^{1}H-NMR spectrum of methyl acetate that we saw a few pages back. The signal at 3.65 ppm corresponds to the methyl ester protons (H_b), which are deshielded by the adjacent oxygen atom. The upfield signal at 2.05 ppm corresponds to the acetate protons (H_a), which is deshielded - but to a lesser extent - by the adjacent carbonyl group.



Finally, a note on the use of TMS as a standard in NMR spectroscopy: one of the main reasons why the TMS proton signal was chosen as a zero-point is that the TMS protons are highly shielded: silicon is slightly *less* electronegative than carbon, and therefore *donates* some additional shielding electron density. Very few organic molecules contain protons with chemical shifts that are negative relative to TMS.

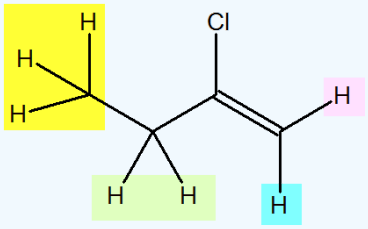


EXERCISE

? EXERCISE 13.2.1

2-cholorobutene shows 4 different hydrogen signals. Explain why this is.

Answer



The same colors represent the same signal. 4 different colors for 4 different signals of hydrogens in 4 different magnetic environments. The hydrogen on the alkene would give two different signals.

13.2 EXERCISES

QUESTIONS

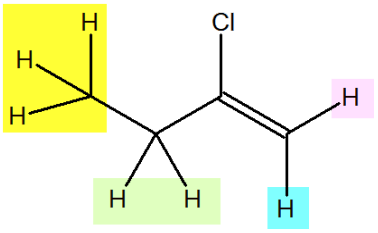
Q13.2.1

2-cholorobutene shows 4 different hydrogen signals. Explain why this is.

SOLUTIONS

S13.2.1

The same colors represent the same signal. 4 different colors for 4 different signals. The hydrogen on the alkene would give two different signals.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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13.3: CHEMICAL SHIFTS

Objectives

After completing this section, you should be able to

1. describe the delta scale used in NMR spectroscopy.
2. perform calculations based on the relationship between the delta value (in ppm), the observed chemical shift (in Hz), and the operating frequency of an NMR spectrometer (in Hz).

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- chemical shift
- delta scale
- upfield/downfield

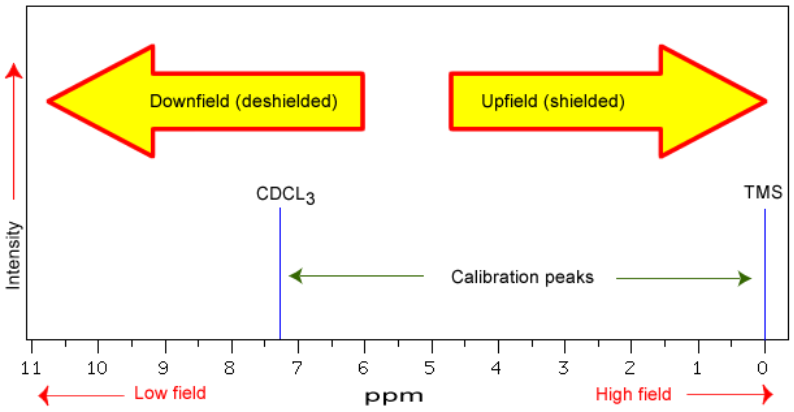
STUDY NOTES

Although the calculations described in this section will help you understand the principles of NMR, it is the actual delta values, not the calculations, which are of greatest importance to the beginning organic chemist. Thus, we shall try to focus on the interpretation of NMR spectra, not the mathematical aspects of the technique.

In Section 13.9 we discuss ^{1}H NMR chemical shifts in more detail. Although you will eventually be expected to associate the approximate region of a ^{1}H NMR spectrum with a particular type of proton, you are expected to use a general table of ^{1}H NMR chemical shifts such as the one shown in Section 13.9.

CHEMICAL SHIFTS

The NMR spectra is displayed as a plot of the applied radio frequency versus the absorption. The applied frequency increases from left to right, thus the left side of the plot is the low field, downfield or deshielded side and the right side of the plot is the high field, upfield or shielded side (see the figure below). The concept of shielding will be explained shortly.



The position on the plot at which the nuclei absorbs is called the **chemical shift**. Since this has an arbitrary value a standard reference point must be used. The two most common standards are TMS (tetramethylsilane, $(Si(CH_3)_4)$ which has been assigned a chemical shift of zero, and $CDCl_3$ (deuterochloroform) which has a chemical shift of 7.26 for ^{1}H NMR and 77 for ^{13}C NMR.

The scale is commonly expressed as parts per million (ppm) which is independent of the spectrometer frequency. The scale is the **delta (δ) scale**.

$$\delta = \frac{\text{frequency of signal - frequency of standard}}{\text{spectrometer frequency}} \times 10^{6}$$

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The range at which most NMR absorptions occur is quite narrow. Almost all ^{1}H absorptions occur downfield within 10 ppm of TMS. For ^{13}C NMR almost all absorptions occurs within 220 ppm downfield of the C atom in TMS.

SHIELDING IN NMR

Structural features of the molecule will have an effect on the exact magnitude of the magnetic field experienced by a particular nucleus. This means that H atoms which have different chemical environments will have different chemical shifts. This is what makes NMR so useful for structure determination in organic chemistry. There are three main features that will affect the shielding of the nucleus, electronegativity, magnetic anisotropy of π systems and hydrogen bonding.

ELECTRONEGATIVITY

The electrons that surround the nucleus are in motion so they created their own electromagnetic field. This field opposes the the applied magnetic field and so reduces the field experienced by the nucleus. Thus the electrons are said to **shield** the nucleus. Since the magnetic field experienced at the nucleus defines the energy difference between spin states it also defines what the chemical shift will be for that nucleus. Electron with-drawing groups can decrease the electron density at the nucleus, deshielding the nucleus and result in a larger chemical shift. Compare the data in the table below.

Compound, CH_3X	**CH_3F**	**CH_3OH**	**CH_3Cl**	**CH_3Br**	**CH_3I**	**CH_4**	**$(CH_3)_4Si$**
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift δ (ppm)	4.26	3.4	3.05	2.68	2.16	0.23	0

As can be seen from the data, as the electronegativity of X increases the chemical shift, δ increases. This is an effect of the halide atom pulling the electron density away from the methyl group. This exposes the nuclei of both the C and H atoms, "deshielding" the nuclei and shifting the peak downfield.

The effects are cumulative so the presence of more electron withdrawing groups will produce a greater deshielding and therefore a larger chemical shift, *i.e.*

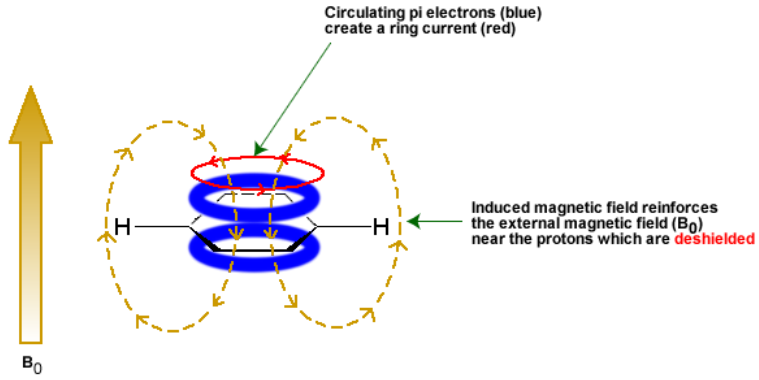
Compound	**CH_4**	**CH_3Cl**	**CH_2Cl_2**	**$CHCl_3$**
δ (ppm)	0.23	3.05	5.30	7.27

These **inductive effects** are not only felt by the immediately adjacent atoms, but the deshielding can occur further down the chain, *i.e.*

NMR signal	$-CH_2-CH_2-CH_2Br$
δ (ppm)	1.25 1.69 3.30

MAGNETIC ANISOTROPY: Π ELECTRON EFFECTS

The π electrons in a compound, when placed in a magnetic field, will move and generate their own magnetic field. The new magnetic field will have an effect on the shielding of atoms within the field. The best example of this is benzene (see the figure below).

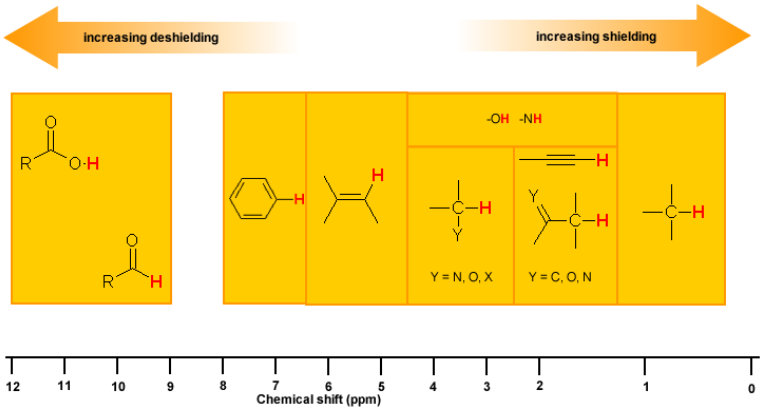


This effect is common for any atoms near a π bond, *i.e.*

Proton Type	Effect	Chemical shift (ppm)
C_6H_5-H	highly deshielded	6.5 - 8
C=C-H	deshielded	4.5 - 6
C≡C-H	shielded*	~2.5
O=C-H	very highly deshielded	9 - 10
* the acetylene H is shielded due to its location relative to the π system		

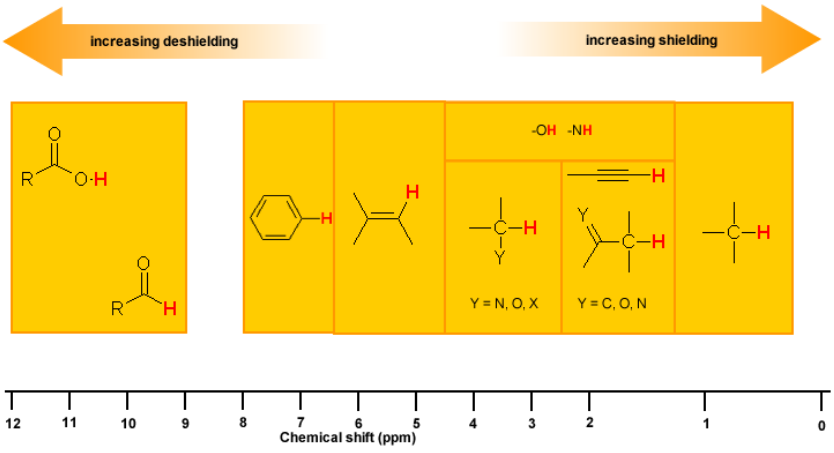
HYDROGEN BONDING

Protons that are involved in hydrogen bonding (*i.e.*-OH or -NH) are usually observed over a wide range of chemical shifts. This is due to the deshielding that occurs in the hydrogen bond. Since hydrogen bonds are dynamic, constantly forming, breaking and forming again, there will be a wide range of hydrogen bonds strengths and consequently a wide range of deshielding. This as well as solvation effects, acidity, concentration and temperature make it very difficult to predict the chemical shifts for these atoms.



Experimentally -OH and -NH can be identified by carrying out a simple D_2O exchange experiment since these protons are exchangeable.

- run the normal H-NMR experiment on your sample
- add a few drops of D_2O
- re-run the H-NMR experiment
- compare the two spectra and look for peaks that have "disappeared"



EXERCISES

? EXERCISE 13.3.1

The following peaks were from a H^1 NMR spectra from a 400 MHz spectrometer. Convert to δ units

A. $CHCl_3$ 1415 Hz

B. CH_3Cl 610 Hz

C. CH_3OH 693 Hz

D. CH_2Cl_2 1060 Hz

Answer

A. 3.627 ppm

B. 1.525 ppm

C. 1.732 ppm

D. 2.65 ppm

? EXERCISE 13.3.2

Butan-2-one shows a chemical shit around 2.1 on a 300 MHz spectrometer in the H^1 NMR spectrum.

A. How far downfield is this peak from TMS in Hz?

B. If the spectrum was done with a 400 MHz instrument, would a different chemical shift be seen?

C. On this new 400 MHz spectrum, what would be the difference in Hz from the chemical shift and TMS?

Answer

A. Since TMS is at 0 δ = 0 Hz for reference, the difference between the two would be 630 Hz

B. No not a different chemical shift, but a different frequency would be seen, 840 Hz

C. 840 Hz

QUESTIONS

Q13.3.1

The following peaks were from a H^1 NMR spectra from a 400 MHz spectrometer. Convert to δ units

A. $CHCl_3$ 1451 Hz

B. CH_3Cl 610 Hz

C. CH_3OH 693 Hz

D. CH_2Cl_2 1060 Hz

Q13.3.2

Butan-2-one shows a chemical shift around 2.1 on a 300 MHz spectrometer in the H^1 NMR spectrum.

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C. On this new 400 MHz spectrum, what would be the difference in Hz from the chemical shift and TMS?

SOLUTIONS

S13.3.1

A. 3.627 ppm

B. 1.525 ppm

C. 1.732 ppm

D. 2.65 ppm

S13.3.2

A. Since TMS is at 0 δ = 0 Hz for reference, the difference between the two would be 630 Hz

B. No not a different chemical shift, but a different frequency would be seen, 840 Hz

C. 840 Hz

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Dr. Richard Spinney (The Ohio State University)

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13.4: ^{13}C NMR SPECTROSCOPY- SIGNAL AVERAGING AND FT-NMR

The ^{12}C isotope of carbon - which accounts for up about 99% of the carbons in organic molecules - does not have a nuclear magnetic moment, and thus is NMR-inactive. Fortunately for organic chemists, however, the ^{13}C isotope, which accounts for most of the remaining 1% of carbon atoms in nature, has a magnetic moment just like protons. Most of what we have learned about ^{1}H-NMR spectroscopy also applies to ^{13}C-NMR, although there are several important differences.

THE BASICS OF ^{13}C-NMR SPECTROSCOPY

The magnetic moment of a ^{13}C nucleus is much weaker than that of a proton, meaning that NMR signals from ^{13}C nuclei are inherently much weaker than proton signals. This, combined with the low natural abundance of ^{13}C, means that it is much more difficult to observe carbon signals: more sample is required, and often the data from hundreds of scans must be averaged in order to bring the signal-to-noise ratio down to acceptable levels. Unlike ^{1}H-NMR signals, the area under a ^{13}C-NMR signal cannot be used to determine the number of carbons to which it corresponds. This is because the signals for some types of carbons are inherently weaker than for other types – peaks corresponding to carbonyl carbons, for example, are much smaller than those for methyl or methylene (CH_2) peaks. Peak integration is generally not useful in ^{13}C-NMR spectroscopy, except when investigating molecules that have been enriched with ^{13}C isotope (see section 5.6B).

The resonance frequencies of ^{13}C nuclei are lower than those of protons in the same applied field - in a 7.05 Tesla instrument, protons resonate at about 300 MHz, while carbons resonate at about 75 MHz. This is fortunate, as it allows us to look at ^{13}C signals using a completely separate 'window' of radio frequencies. Just like in ^{1}H-NMR, the standard used in ^{13}C-NMR experiments to define the 0 ppm point is tetramethylsilane (TMS), although of course in ^{13}C-NMR it is the signal from the four equivalent *carbons* in TMS that serves as the standard. Chemical shifts for ^{13}C nuclei in organic molecules are spread out over a much wider range than for protons – up to 200 ppm for ^{13}C compared to 12 ppm for protons (see Table 3 for a list of typical ^{13}C-NMR chemical shifts). This is also fortunate, because it means that the signal from each carbon in a compound can almost always be seen as a distinct peak, without the overlapping that often plagues ^{1}H-NMR spectra. The chemical shift of a ^{13}C nucleus is influenced by essentially the same factors that influence a proton's chemical shift: bonds to electronegative atoms and diamagnetic anisotropy effects tend to shift signals downfield (higher resonance frequency). In addition, sp^2 hybridization results in a large downfield shift. The ^{13}C-NMR signals for carbonyl carbons are generally the furthest downfield (170-220 ppm), due to both sp^2 hybridization and to the double bond to oxygen.

✔ EXAMPLE 13.4.1

How many sets of non-equivalent carbons are there in each of the molecules shown in exercise 5.1?

Solution

✔ EXAMPLE 13.4.2

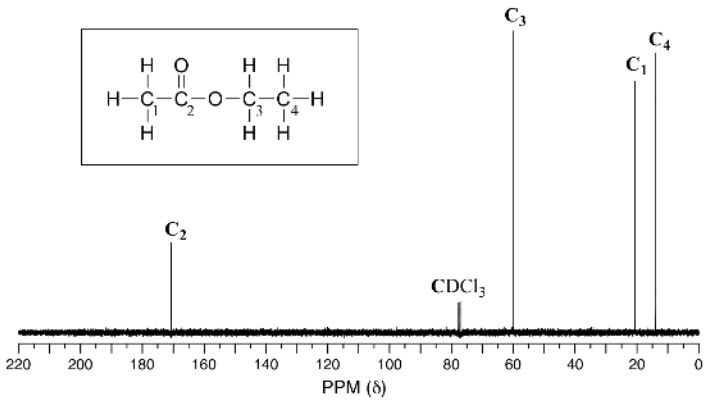
How many sets of non-equivalent carbons are there in:

a. toluene
b. 2-pentanone
c. para-xylene
d. triclosan

(all structures are shown earlier in this chapter)

Solution

Because of the low natural abundance of ^{13}C nuclei, it is very unlikely to find two ^{13}C atoms near each other in the same molecule, and thus *we do not see spin-spin coupling between neighboring carbons in a ^{13}C-NMR spectrum*. There is, however, **heteronuclear coupling** between ^{13}C carbons and the hydrogens to which they are bound. Carbon-proton coupling constants are very large, on the order of 100 – 250 Hz. For clarity, chemists generally use a technique called **broadband decoupling**, which essentially 'turns off' C-H coupling, resulting in a spectrum in which all carbon signals are singlets. Below is the proton-decoupled^{13}C-NMR spectrum of ethyl acetate, showing the expected four signals, one for each of the carbons.



While broadband decoupling results in a much simpler spectrum, useful information about the presence of neighboring protons is lost. However, another modern NMR technique called DEPT (Distortionless Enhancement by Polarization Transfer) allows us to determine how many hydrogens are bound to each carbon. For example, a DEPT experiment tells us that the signal at 171 ppm in the ethyl acetate spectrum is a quaternary carbon (no hydrogens bound, in this case a carbonyl carbon), that the 61 ppm signal is from a methylene (CH_2) carbon, and that the 21 ppm and 14 ppm signals are both methyl (CH_3) carbons. The details of the DEPT experiment are beyond the scope of this text, but DEPT information will often be provided along with ^{13}C spectral data in examples and problems.

CONTRIBUTORS AND ATTRIBUTIONS

- Prof. Steven Farmer (Sonoma State University)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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13.5: CHARACTERISTICS OF ^{13}C NMR SPECTROSCOPY

The ^{12}C isotope of carbon - which accounts for up about 99% of the carbons in organic molecules - does not have a nuclear magnetic moment, and thus is NMR-inactive. Fortunately for organic chemists, however, the ^{13}C isotope, which accounts for most of the remaining 1% of carbon atoms in nature, has a magnetic moment just like protons. Most of what we have learned about ^{1}H-NMR spectroscopy also applies to ^{13}C-NMR, although there are several important differences.

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The resonance frequencies of ^{13}C nuclei are lower than those of protons in the same applied field - in a 7.05 Tesla instrument, protons resonate at about 300 MHz, while carbons resonate at about 75 MHz. This is fortunate, as it allows us to look at ^{13}C signals using a completely separate 'window' of radio frequencies. Just like in ^{1}H-NMR, the standard used in ^{13}C-NMR experiments to define the 0 ppm point is tetramethylsilane (TMS), although of course in ^{13}C-NMR it is the signal from the four equivalent *carbons* in TMS that serves as the standard. Chemical shifts for ^{13}C nuclei in organic molecules are spread out over a much wider range than for protons – up to 200 ppm for ^{13}C compared to 12 ppm for protons (see Table 3 for a list of typical ^{13}C-NMR chemical shifts). This is also fortunate, because it means that the signal from each carbon in a compound can almost always be seen as a distinct peak, without the overlapping that often plagues ^{1}H-NMR spectra. The chemical shift of a ^{13}C nucleus is influenced by essentially the same factors that influence a proton's chemical shift: bonds to electronegative atoms and diamagnetic anisotropy effects tend to shift signals downfield (higher resonance frequency). In addition, sp^2 hybridization results in a large downfield shift. The ^{13}C-NMR signals for carbonyl carbons are generally the furthest downfield (170-220 ppm), due to both sp^2 hybridization and to the double bond to oxygen.

✔ EXAMPLE 13.5.1

Exercise 5.11: How many sets of non-equivalent carbons are there in each of the molecules shown in exercise 5.1?

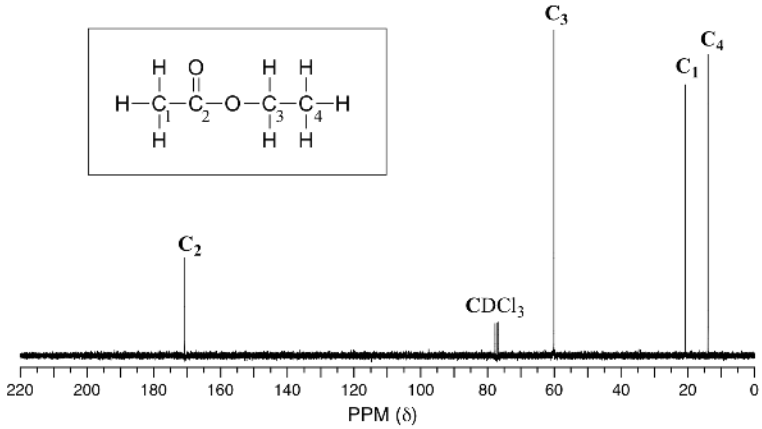
Exercise 5.12: How many sets of non-equivalent carbons are there in:

a. toluene
b. 2-pentanone
c. para-xylene
d. triclosan

(all structures are shown earlier in this chapter)

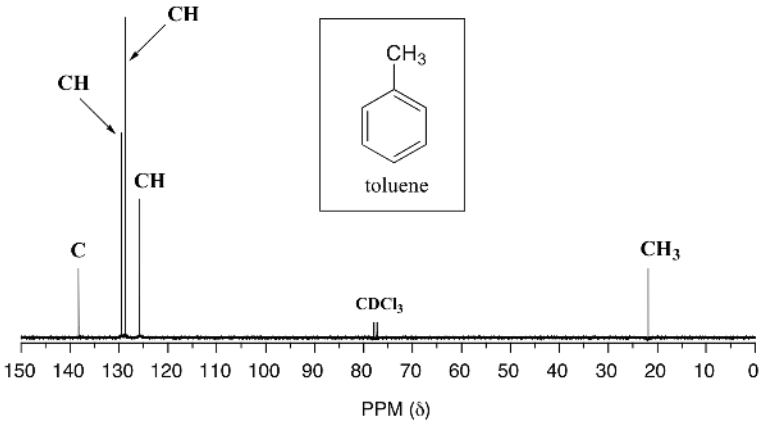
Solution

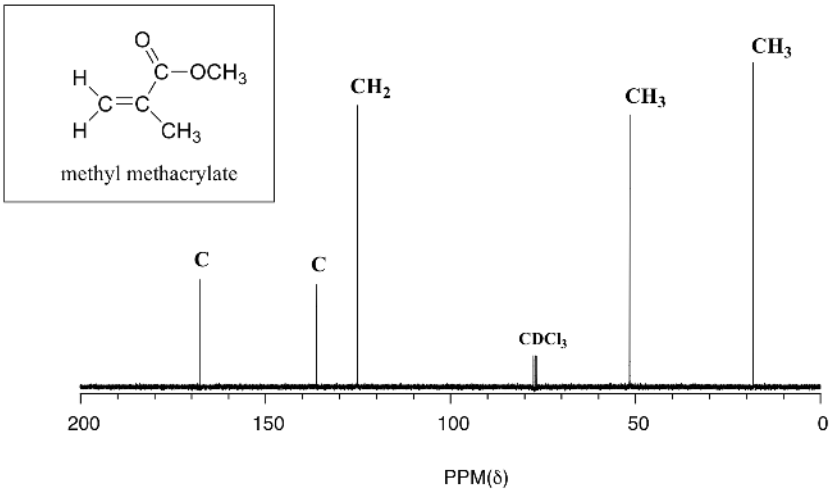
Because of the low natural abundance of ^{13}C nuclei, it is very unlikely to find two ^{13}C atoms near each other in the same molecule, and thus *we do not see spin-spin coupling between neighboring carbons in a ^{13}C-NMR spectrum*. There is, however, **heteronuclear coupling** between ^{13}C carbons and the hydrogens to which they are bound. Carbon-proton coupling constants are very large, on the order of 100 – 250 Hz. For clarity, chemists generally use a technique called **broadband decoupling**, which essentially 'turns off' C-H coupling, resulting in a spectrum in which all carbon signals are singlets. Below is the proton-decoupled^{13}C-NMR spectrum of ethyl acetate, showing the expected four signals, one for each of the carbons.



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Below are two more examples of ^{13}C NMR spectra of simple organic molecules, along with DEPT information.



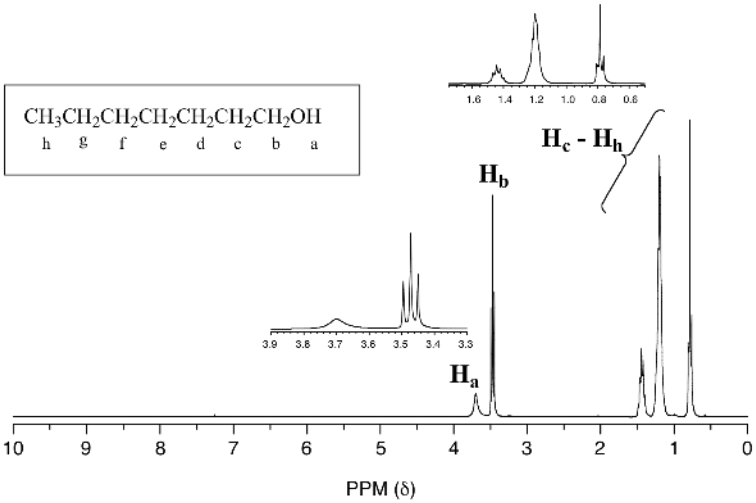


EXAMPLE 13.5.2

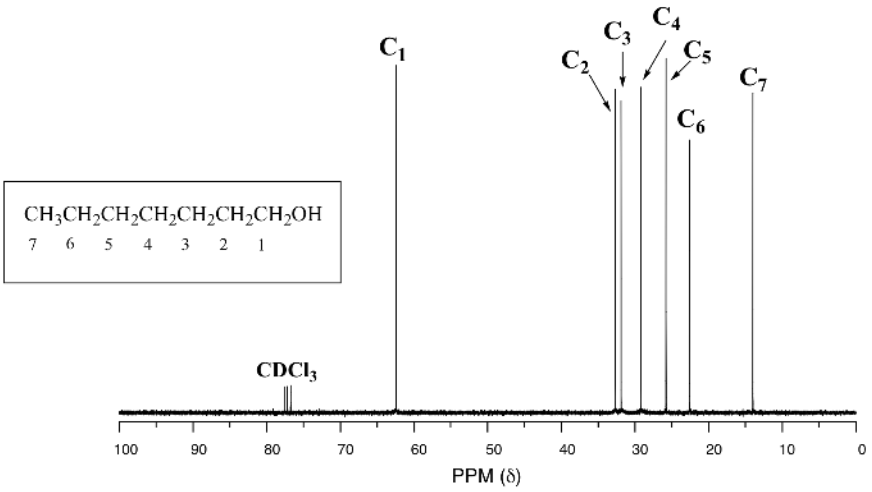
Give peak assignments for the ^{13}C-NMR spectrum of methyl methacrylate, shown above.

Solution

One of the greatest advantages of ^{13}C-NMR compared to ^{1}H-NMR is the breadth of the spectrum - recall that carbons resonate from 0-220 ppm relative to the TMS standard, as opposed to only 0-12 ppm for protons. Because of this, ^{13}C signals rarely overlap, and we can almost always distinguish separate peaks for each carbon, even in a relatively large compound containing carbons in very similar environments. In the proton spectrum of 1-heptanol, for example, only the signals for the alcohol proton (H_a) and the two protons on the adjacent carbon (H_b) are easily analyzed. The other proton signals overlap, making analysis difficult.



In the ^{13}C spectrum of the same molecule, however, we can easily distinguish each carbon signal, and we know from this data that our sample has seven non-equivalent carbons. (Notice also that, as we would expect, the chemical shifts of the carbons get progressively smaller as they get farther away from the deshielding oxygen.)



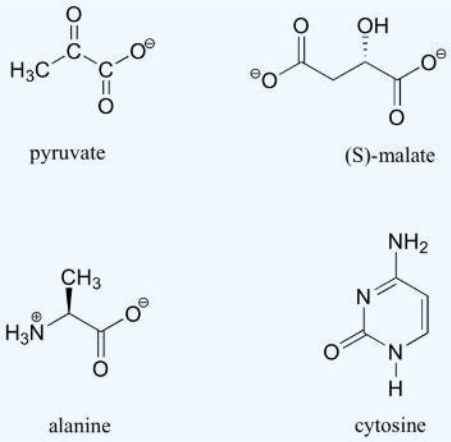
This property of ^{13}C-NMR makes it very helpful in the elucidation of larger, more complex structures.

EXAMPLE 13.5.3

^{13}C-NMR (and DEPT) data for some common biomolecules are shown below (data is from the Aldrich Library of ^{1}H and ^{13}C NMR). Match the NMR data to the correct structure, and make complete peak assignments.

- spectrum a: 168.10 ppm (C), 159.91 ppm (C), 144.05 ppm (CH), 95.79 ppm (CH)
- spectrum b: 207.85 ppm (C), 172.69 ppm (C), 29.29 ppm (CH_3)

- spectrum c: 178.54 ppm (C), 53.25 ppm (CH), 18.95 ppm (CH_3)
- spectrum d: 183.81 ppm (C), 182. 63 ppm (C), 73.06 ppm (CH), 45.35 ppm (CH_2)



Solution

^{13}C NMR CHEMICAL SHIFTS

The Carbon NMR is used for determining functional groups using characteristic shift values. ^{13}C chemical shifts are greatly affected by electronegative effects. If a H atom in an alkane is replaced by substituent X, electronegative atoms (O, N, halogen), ^{13}C signals for nearby carbons shift downfield (left; increase in ppm) with the effect diminishing with distance from the electron withdrawing group. Figure 13.5.1 shows typical ^{13}C chemical shift regions of the major chemical class.

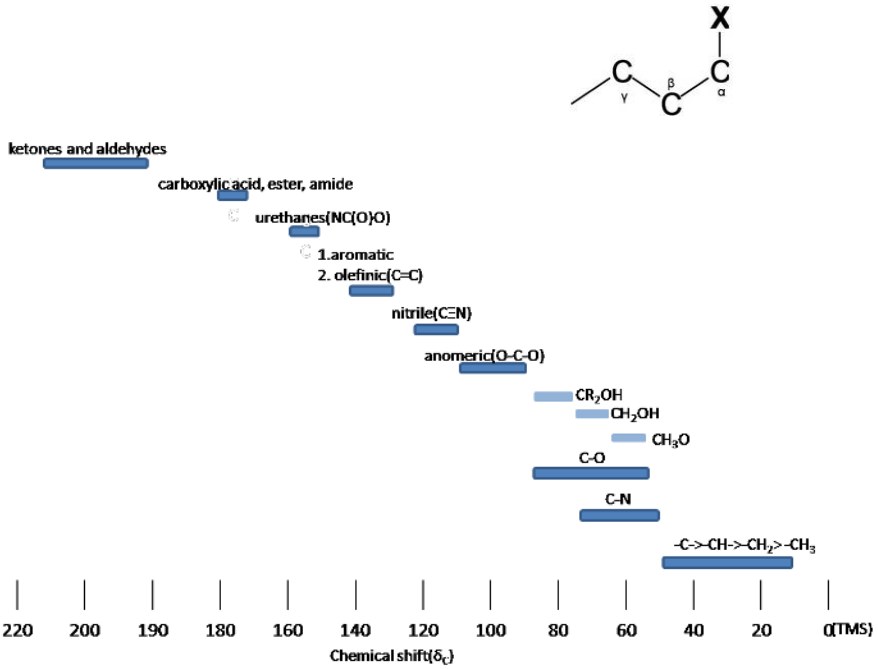


Figure 13.5.1: ^{13}C Chemical shift range for organic compound

SPIN-SPIN SPLITTING

Comparing the ^{1}H NMR, there is a big difference thing in the ^{13}C NMR. The ^{13}C-^{13}Cspin-spin splitting rarely exit between adjacent carbons because ^{13}C is naturally lower abundant (1.1%)

- **^{13}C-^{1}H Spin coupling**: ^{13}C-^{1}H Spin coupling provides useful information about the number of protons attached a carbon atom. In case of one bond coupling ($^{1}J_{CH}$), -CH, -CH_2, and CH_3 have respectively doublet, triplet, quartets for the ^{13}C resonances in the spectrum. However, ^{13}C-^{1}H Spin coupling has an disadvantage for ^{13}C spectrum interpretation. ^{13}C-^{1}H Spin coupling is hard to analyze and reveal structure due to a forest of overlapping peaks that result from 100% abundance of ^{1}H.

- **Decoupling**: Decoupling is the process of removing ^{13}C-^{1}H coupling interaction to simplify a spectrum and identify which pair of nuclei is involved in the J coupling. The decoupling ^{13}C spectra shows only one peak(singlet) for each unique carbon in the molecule (Figure 13.5.2). Decoupling is performed by irradiating at the frequency of one proton with continuous low-power RF.

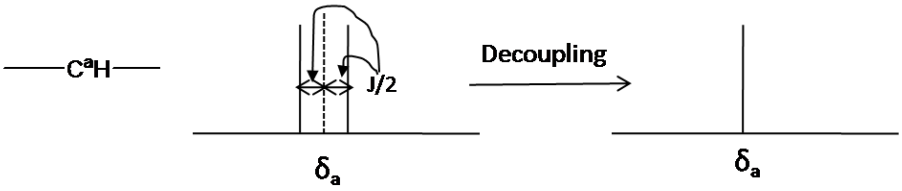


Figure 13.5.2. Decoupling in the ^{13}C NMR

CONTRIBUTORS AND ATTRIBUTIONS

- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

13.5: Characteristics of ^{13}C NMR Spectroscopy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

13.6: DEPT ^{13}C NMR SPECTROSCOPY

DISTORTIONS ENHANCEMENT BY POLARIZATION TRANSFER (DEPT)

DEPT is used for distinguishing between a CH_3 group, a CH_2 group, and a CH group. The proton pulse is set at 45°, 90°, or 135° in the three separate experiments. The different pulses depend on the number of protons attached to a carbon atom. Fig 13.6.1. is an example about DEPT spectrum.

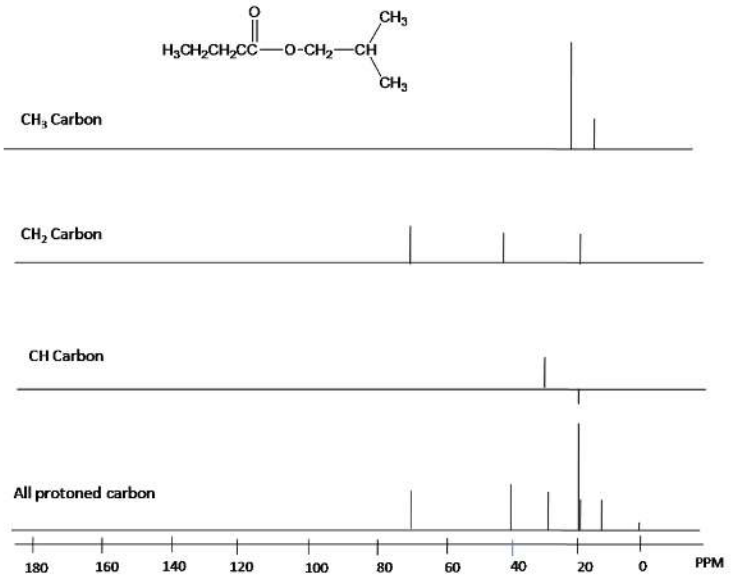
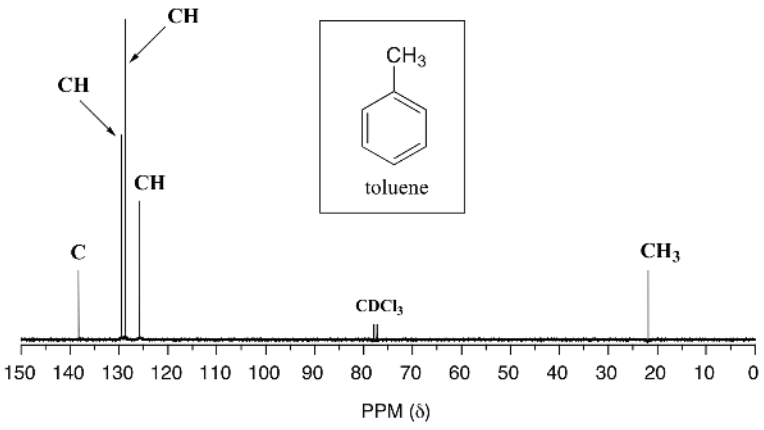


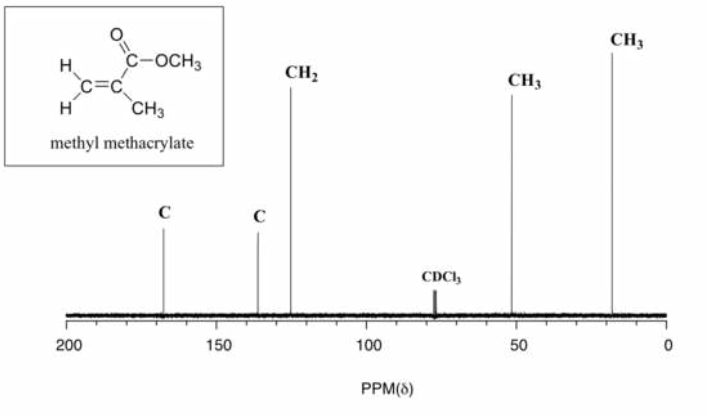
Fig 13.6.1. *DEPT spectrum of n-isobutlybutrate*

While broadband decoupling results in a much simpler spectrum, useful information about the presence of neighboring protons is lost. However, another modern NMR technique called DEPT (Distortionless Enhancement by Polarization Transfer) allows us to determine how many hydrogens are bound to each carbon. For example, a DEPT experiment tells us that the signal at 171 ppm in the ethyl acetate spectrum is a quaternary carbon (no hydrogens bound, in this case a carbonyl carbon), that the 61 ppm signal is from a methylene (CH_2) carbon, and that the 21 ppm and 14 ppm signals are both methyl (CH_3) carbons. The details of the DEPT experiment are beyond the scope of this text, but DEPT information will often be provided along with ^{13}C spectral data in examples and problems.

Below are two more examples of ^{13}C NMR spectra of simple organic molecules, along with DEPT information.



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13.7: USES OF ^{13}C NMR SPECTROSCOPY

The interpretation of ^{13}C NMR spectra does not form a part of Chemistry 350; hence, you may omit Section 13.7. Interested students may wish to read this section for enrichment purposes.

FEATURES OF A C-13 NMR SPECTRUM EDIT SECTION

Butane shows two different peaks in the ^{13}C NMR spectrum, below. Note that: the chemical shifts of these peaks are not very different from methane. The carbons in butane are in a similar environment to the one in methane.

- there are two distinct carbons in butane: the methyl, or CH_3, carbon, and the methylene, or CH_2, carbon.
- the methyl carbon absorbs slightly upfield, or at lower shift, around 10 ppm.
- the methylene carbon absorbs at slightly downfield, or at higher shift, around 20 ppm.
- other factors being equal, methylene carbons show up at slightly higher shift than methyl carbons.



***Figure NMR2**. Simulated ^{13}C NMR spectrum of butane (showing only the upfield portion of the spectrum).*

In the ^{13}C NMR spectrum of pentane (below), you can see three different peaks, even though pentane just contains methyl carbons and methylene carbons like butane. As far as the NMR spectrometer is concerned, pentane contains three different kinds of carbon, in three different environments. That result comes from symmetry.



***Figure NMR3**.^{13}C NMR spectrum of pentane. Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)*

Symmetry is an important factor in spectroscopy. Nature says:

- atoms that are symmetry-inequivalent can absorb at different shifts.
- atoms that are symmetry-equivalent must absorb at the same shift.

To learn about symmetry, take a model of pentane and do the following:

- make sure the model is twisted into the most symmetric shape possible: a nice "W".
- choose one of the methyl carbons to focus on.
- rotate the model 180 degrees so that you are looking at the same "W" but from the other side.
- note that the methyl you were focusing on has simply switched places with the other methyl group. These two carbons are symmetry-equivalent via two-fold rotation.

Animation NMR1. A three-dimensional model of pentane. Grab the model with the mouse and rotate it so that you are convinced that the second and fourth carbons are symmetry-equivalent, but the third carbon is not.

By the same process, you can see that the second and fourth carbons along the chain are also symmetry-equivalent. However, the middle carbon is not; it never switches places with the other carbons if you rotate the model. There are three different sets of inequivalent carbons; these three groups are not the same as each other according to symmetry.

✔ EXAMPLE 13.7.1

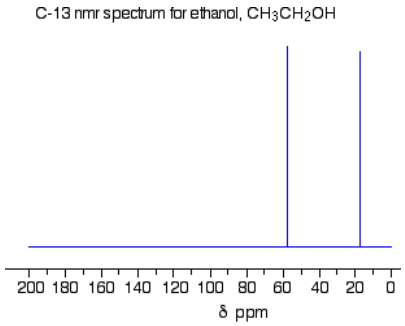
Determine how many inequivalent carbons there are in each of the following compounds. How many peaks do you expect in each ^{13}C NMR spectrum?



Practically speaking, there is only so much room in the spectrum from one end to the other. At some point, peaks can get so crowded together that you can't distinguish one from another. You might expect to see ten different peaks in eicosane, a twenty-carbon alkane chain, but when you look at the spectrum you can only see seven different peaks. That may be frustrating, because the experiment does not seem to agree with your expectation. However, you will be using a number of methods together to minimize the problem of misleading data.

THE C-13 NMR SPECTRUM FOR ETHANOL EDIT SECTION

This is a simple example of a C-13 NMR spectrum. Don't worry about the scale for now - we'll look at that in a minute.



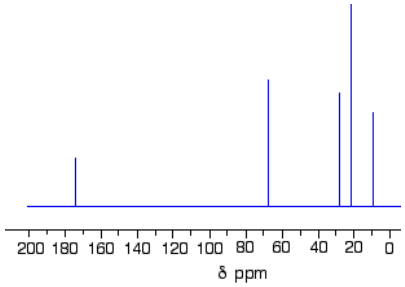
NOTE

Note: The NMR spectra on this page have been produced from graphs taken from the Spectral Data Base System for Organic Compounds (SDBS) at the National Institute of Materials and Chemical Research in Japan.

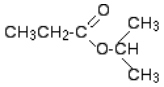
There are two peaks because there are two different environments for the carbons. The carbon in the CH_3 group is attached to 3 hydrogens and a carbon. The carbon in the CH_2 group is attached to 2 hydrogens, a carbon and an oxygen. The two lines are in different places in the NMR spectrum because they need different external magnetic fields to bring them in to resonance at a particular radio frequency.

THE C-13 NMR SPECTRUM FOR A MORE COMPLICATED COMPOUND

This is the C-13 NMR spectrum for 1-methylethyl propanoate (also known as isopropyl propanoate or isopropyl propionate).



This time there are 5 lines in the spectrum. That means that there must be 5 different environments for the carbon atoms in the compound. Is that reasonable from the structure?



Well - if you count the carbon atoms, there are 6 of them. So why only 5 lines? In this case, two of the carbons are in exactly the same environment. They are attached to exactly the same things. Look at the two CH_3 groups on the right-hand side of the molecule.

You might reasonably ask why the carbon in the CH_3 on the left is not also in the same environment. Just like the ones on the right, the carbon is attached to 3 hydrogens and another carbon. But the similarity is not exact - you have to chase the similarity along the rest of the molecule as well to be sure.

The carbon in the left-hand CH_3 group is attached to a carbon atom which in turn is attached to a carbon with two oxygens on it - and so on down the molecule. That's not exactly the same environment as the carbons in the right-hand CH_3 groups. They are attached to a carbon which is attached to a single oxygen - and so on down the molecule. We'll look at this spectrum again in detail on the next page - and look at some more similar examples as well. This all gets easier the more examples you look at.

For now, all you need to realize is that each line in a C-13 NMR spectrum recognizes a carbon atom in one particular environment in the compound. If two (or more) carbon atoms in a compound have exactly the same environment, they will be represented by a single line.

NOTE

You might wonder why all this works, since only about 1% of carbon atoms are C-13. These are the only ones picked up by this form of NMR. If you had a single molecule of ethanol, then the chances are only about 1 in 50 of there being one C-13 atom in it, and only about 1 in 10,000 of both being C-13.

> But you have got to remember that you will be working with a sample containing huge numbers of molecules. The instrument can pick up the magnetic effect of the C-13 nuclei in the carbon of the CH_3 group and the carbon of the CH_2 group even if they are in separate molecules. There's no need for them to be in the same one.

CONTRIBUTORS AND ATTRIBUTIONS

- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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13.8: ^{1}H NMR SPECTROSCOPY AND PROTON EQUIVALENCE

Objectives

After completing this section, you should be able to

1. identify those protons which are equivalent in a given chemical structure.
2. use the ^{1}H NMR spectrum of a simple organic compound to determine the number of equivalent sets of protons present.

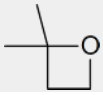
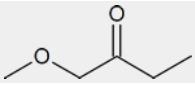
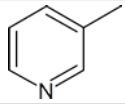
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

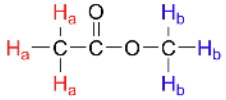
- diastereotopic
- enantiotopic
- homotopic

STUDY NOTES

It is important at this stage to be able to identify equivalent protons in any organic compound given the structure of that compound. Once you know the number of different groups of equivalent protons in a compound, you can predict the number (before coupling) and relative strength of signals. Look at the following examples and make sure you understand how the number and intensity ratio of signals are derived from the structure shown.

Structure	Number of Signals	Ratio of Signals	
$CH_3OCH_2CH_2Br$	3	A : B : C	3 : 2 : 2
	1		
	3	A : B : C	2 : 2 : 6 (or 1 : 1 : 3)
	3	A : B : C	2 : 4 : 2 (or 1 : 2 : 1)
	4	A : B : C : D	3 : 2 : 2 : 3
	5	A : B : C : D : E	3 : 1 : 1 : 1 : 1

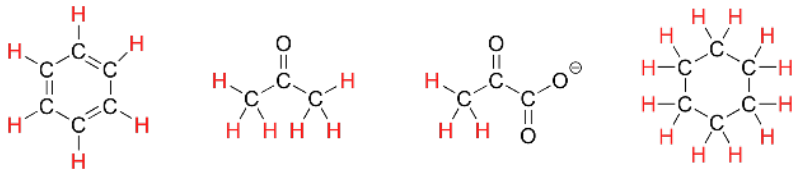
If all protons in all organic molecules had the same resonance frequency in an external magnetic field of a given strength, the information in the previous paragraph would be interesting from a theoretical standpoint, but would not be terribly useful to organic chemists. Fortunately for us, however, resonance frequencies are not uniform for all protons in a molecule. *In an external magnetic field of a given strength, protons in different locations in a molecule have different resonance frequencies, because they are in non-identical electronic environments.* In methyl acetate, for example, there are two 'sets' of protons. The three protons labeled H_a have a different - and easily distinguishable – resonance frequency than the three H_b protons, because the two sets of protons are in non-identical environments: they are, in other words, chemically nonequivalent.



On the other hand, the three H_a protons are all in the same electronic environment, and are chemically equivalent to one another. They have identical resonance frequencies. The same can be said for the three H_b protons.

The ability to recognize chemical equivalency and nonequivalency among atoms in a molecule will be central to understanding NMR. In each of the molecules below, all protons are chemically equivalent, and therefore will have the same resonance frequency in an NMR

experiment.



benzene acetone pyruvate cyclohexane

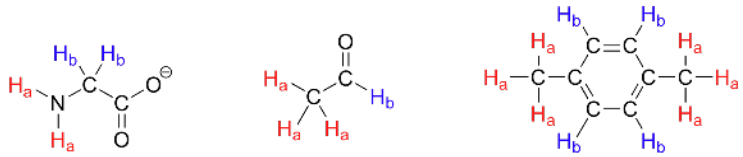
You might expect that the equitorial and axial hydrogens in cyclohexane would be non-equivalent, and would have different resonance frequencies. In fact, an axial hydrogen *is* in a different electronic environment than an equitorial hydrogen. Remember, though, that the molecule rotates rapidly between its two chair conformations, meaning that any given hydrogen is rapidly moving back and forth between equitorial and axial positions. It turns out that, except at extremely low temperatures, this rotational motion occurs on a time scale that is much faster than the time scale of an NMR experiment.



ring-flip process is *fast* compared to the NMR time-scale

In this sense, NMR is like a camera that takes photographs of a rapidly moving object with a slow shutter speed - the result is a blurred image. In NMR terms, this means that all 12 protons in cyclohexane are equivalent.

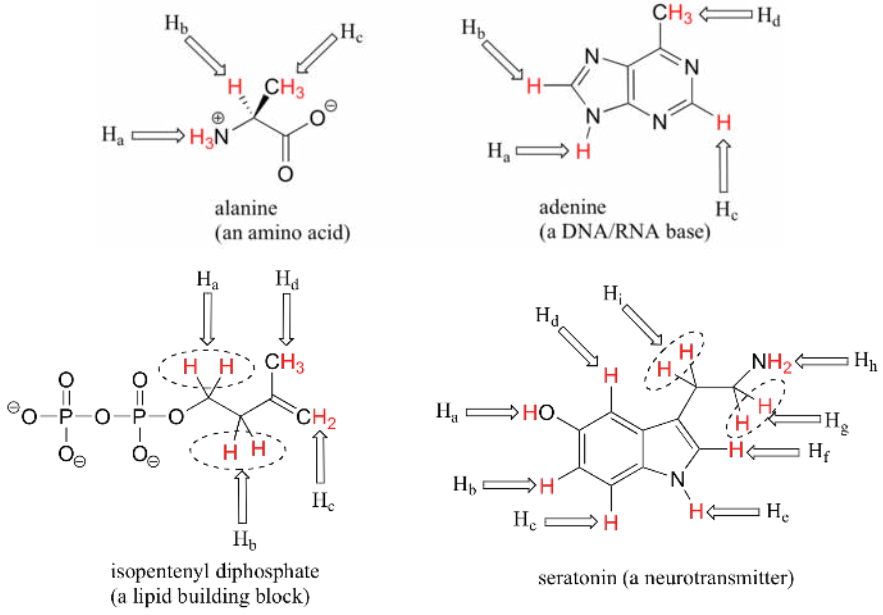
Each the molecules in the next figure contains *two* sets of protons, just like our previous example of methyl acetate, and again in each case the resonance frequency of the H_a protons will be different from that of the H_b protons.



glycine acetaldehyde *para*-xylene

Notice how the symmetry of *para*-xylene results in there being only two different sets of protons.

Most organic molecules have several sets of protons in different chemical environments, and each set, in theory, will have a different resonance frequency in ^{1}H-NMR spectroscopy.

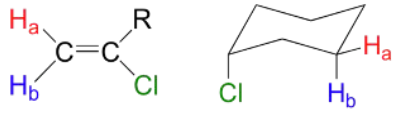


alanine (an amino acid) adenine (a DNA/RNA base)

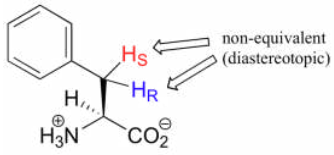
isopentenyl diphosphate (a lipid building block) seratonin (a neurotransmitter)

When stereochemistry is taken into account, the issue of equivalence vs nonequivalence in NMR starts to get a little more complicated. It should be fairly intuitive that hydrogens on different sides of asymmetric ring structures and double bonds are in different electronic

environments, and thus are non-equivalent and have different resonance frequencies. In the alkene and cyclohexene structures below, for example, H_a is *trans* to the chlorine substituent, while H_b is *cis* to chlorine.

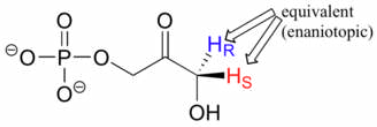


What is not so intuitive is that diastereotopic hydrogens (section 3.10) on chiral molecules are also non-equivalent:

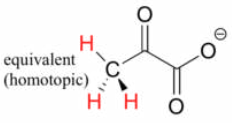


phenylalanine

However, enantiotopic and homotopic hydrogens are chemically equivalent.



dihydroxyacetone phosphate

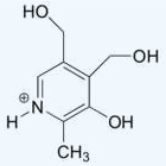


pyruvate

EXAMPLE 13.8.1

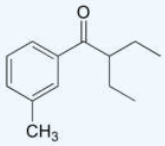
How many different sets of protons do the following molecules contain? (count diastereotopic protons as non-equivalent).

a)



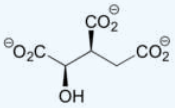
pyridoxine (vitamin B_6)

b)



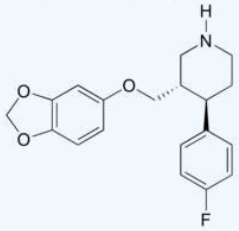
DEET (an insect repellent)

c)



isocitrate (a citric acid cycle intermediate)

d)



paroxetine (an antianxietry drug, trade name Paxil)

Solution

a) 8 b) 8 c) 5 d) 18

EXERCISE

EXERCISE \PageIndex1

How many non-equivalent hydrogen are in the following molecules; how many different signals will you see in a H^1 NMR spectrum.

A. $CH_3CH_2CH_2Br$

B. $CH_3OCH_2C(CH_3)_3$

C. Ethyl Benzene

D. 2-methyl-1-hexene

Answer

A. 3

B. 3

C. 5

D. 7

QUESTIONS

Q13.8.1

How many non-equivalent hydrogen are in the following molecules; how many different signals will you see in a H^1 NMR spectrum.

A. $CH_3CH_2CH_2Br$

B. $CH_3OCH_2C(CH_3)_3$

C. Ethyl Benzene

D. 2-methyl-1-hexene

SOLUTIONS

S13.8.1

A. 3; B. 3; C. 5; D. 7

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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13.9: CHEMICAL SHIFTS IN ^{1}H NMR SPECTROSCOPY

Objectives

After completing this section, you should be able to

1. state the approximate chemical shift (δ) for the following types of protons:
   a. aromatic.
   b. vinylic.
   c. those bonded to carbon atoms which are in turn bonded to a highly electronegative element.
   d. those bonded to carbons which are next to unsaturated centres.
   e. those bonded to carbons which are part of a saturated system.
2. predict the approximate chemical shifts of each of the protons in an organic compound, given its structure and a table of chemical shift correlations.

STUDY NOTES

You should not attempt to memorize the chemical shifts listed in the table of this section, although it is probable that you will need to refer to it quite frequently throughout the remainder of this course. To fulfil Objective 1, above, you should be familiar with the information presented in the figure of chemical shift ranges for organic compounds. If you have an approximate idea of the chemical shifts of some of the most common types of protons, you will find the interpretation of ^{1}H NMR spectra less arduous than it might otherwise be. Notice that we shall not try to understand why aromatic protons are deshielded or why alkynyl protons are not deshielded as much as vinylic protons. These phenonomena can be explained, but the focus is on the interpretation of ^{1}H NMR spectra, not on the underlying theory.

^{1}H NMR CHEMICAL SHIFTS

Chemical shift is associated with the Larmor frequency of a nuclear spin to its chemical environment. Tetramethylsilan[TMS;$(CH_3)_4Si$] is generally used for standard to determine chemical shift of compounds: δ_{TMS}=0ppm. In other words, frequencies for chemicals are measured for a ^{1}H or ^{13}C nucleus of a sample from the ^{1}H or ^{13}C resonance of TMS. It is important to understand trend of chemical shift in terms of NMR interpretation. The proton NMR chemical shift is affect by nearness to electronegative atoms (O, N, halogen.) and unsaturated groups (C=C,C=O, aromatic). Electronegative groups move to the down field (left; increase in ppm). Unsaturated groups shift to downfield (left) when affecting nucleus is in the plane of the unsaturation, but reverse shift takes place in the regions above and below this plane. ^{1}H chemical shift play a role in identifying many functional groups. Figure 1. indicates important example to figure out the functional groups.

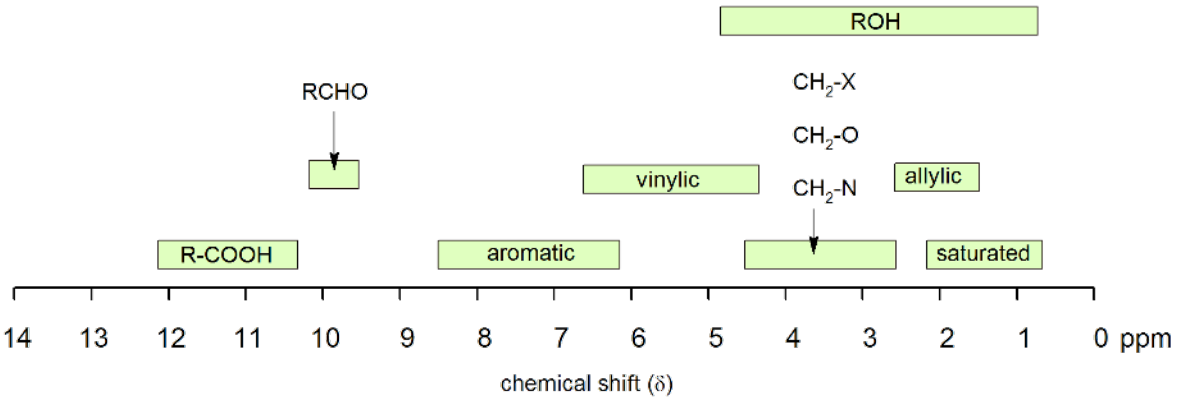
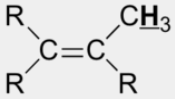
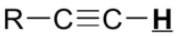
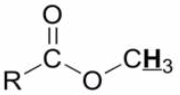
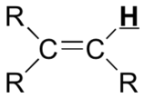
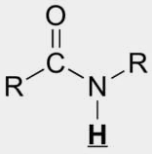
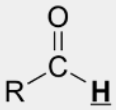
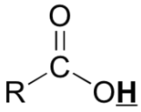


***Figure 1**. 1H chemical shift ranges for organic compounds*

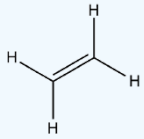
Chemical shift values are in parts per million (ppm) relative to tetramethylsilane.

Hydrogen type	Chemical shift (ppm)
$RC\underline{H}_3$	0.9 - 1.0
$RC\underline{H}_2R$	1.2 - 1.7
$R_3C\underline{H}$	1.5 – 2.0
	2.0 – 2.3
	1.5 – 1.8
$RN\underline{H}_2$	1 - 3
$ArC\underline{H}_3$	2.2 – 2.4
	2.3 – 3.0
$ROC\underline{H}_3$	3.7 – 3.9
	3.7 – 3.9
$RO\underline{H}$	1 - 5
	3.7 – 6.5
	5 - 9
$Ar\underline{H}$	6.0 – 8.7
	9.5 – 10.0
	10 - 13

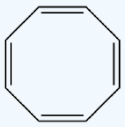
EXERCISES

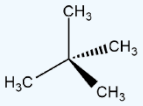
EXERCISE 13.9.1

The following have one H^1 NMR peak. Predict where these peaks would be in a spectra. (MAY not be exact, but will be close)

A) 

B) 

C) 

D) 

Answer

A. 5.20 δ

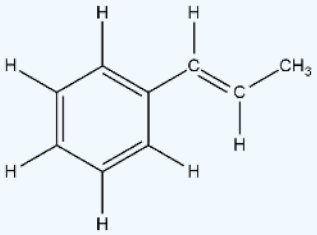
B. 1.50 δ

C. 6.40 δ

D. 1.00 δ

EXERCISE 13.9.2

Identify the different protons in the following molecule and predict where they would be on a chemical spectrum.



Answer

There are 6 different protons in this molecule

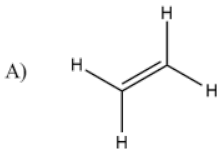
The shifts are (close) to the following: a. 2 δ; b. 6 δ; c. 6.5 δ; d. 7 δ; e. 7.5 δ; f. 7 δ

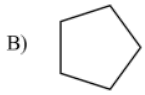
QUESTIONS

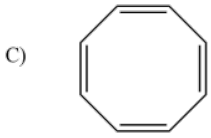
Q13.9.1

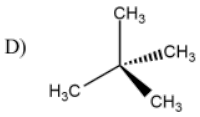
The following have one H^1 NMR peak. In each case predict approximately where this peak would be in a spectra.

https://chem.libretexts.org/@go/page/67295



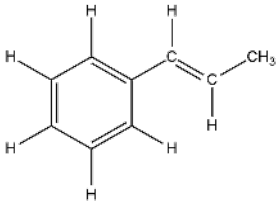






Q13.9.2

Identify the different equivalent protons in the following molecule and predict their expected chemical shift.



SOLUTIONS

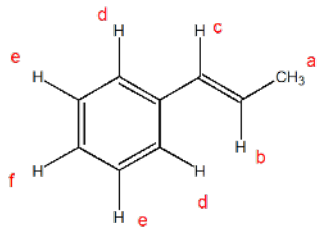
S13.9.1

A. 5.20 δ; B. 1.50 δ; C. 6.40 δ; D. 1.00 δ

S13.9.2

There are 6 different protons in this molecule

The shifts are (close) to the following: (a) 2 δ; (b) 6 δ; (c) 6.5 δ; (d) 7 δ; (e) 7.5 δ; (f) 7 δ



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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13.10: INTEGRATION OF ^{1}H NMR ABSORPTIONS- PROTON COUNTING

Objectives

After completing this section, you should be able to

1. explain what information can be obtained from an integrated ^{1}H NMR spectrum, and use this information in the interpretation of such a spectrum.
2. use an integrated ^{1}H NMR spectrum to determine the ratio of the different types of protons present in an organic compound.

STUDY NOTES

The concept of peak integration is that the area of a given peak in a 1H NMR spectrum is proportional to the number of (equivalent) protons giving rise to the peak. Thus, a peak which is caused by a single, unique proton has an area which measures one third of the area of a peak resulting from a methyl (CH_3) group in the same spectrum.

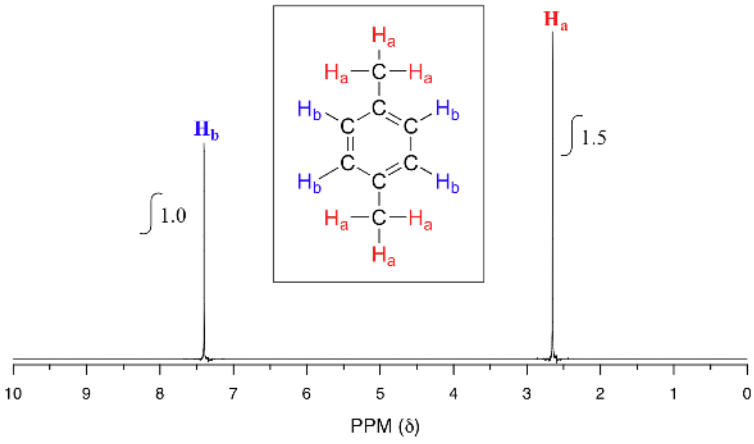
In practice, we do not have to measure these areas ourselves: it is all done electronically by the spectrometer, and an integration curve is superimposed on the rest of the spectrum. The integration curve appears as a series of steps, with the height of each step being proportional to the area of the corresponding absorption peak, and consequently, to the number of protons responsible for the absorption.

As it can be difficult to decide precisely where to start and stop when measuring integrations, you should not expect your ratios to be exact whole numbers.

SIGNAL INTEGRATION

The computer in an NMR instrument can be instructed to automatically integrate the area under a signal or group of signals. This is very useful, because *in ^{1}H-NMR spectroscopy the area under a signal is proportional to the number of hydrogens to which the peak corresponds*. The two signals in the methyl acetate spectrum, for example, integrate to approximately the same area, because they both correspond to a set of three equivalent protons.

Take a look next at the spectrum of *para*-xylene (IUPAC name 1,4-dimethylbenzene):



This molecule has two sets of protons: the six methyl (H_a) protons and the four aromatic (H_b) protons. When we instruct the instrument to integrate the areas under the two signals, we find that the area under the peak at 2.6 ppm is 1.5 times greater than the area under the peak at 7.4 ppm. This (along with the actual chemical shift values, which we'll discuss soon) tells us which set of protons corresponds to which NMR signal.

The integration function can also be used to determine the relative amounts of two or more compounds in a *mixed* sample. If we have a sample that is a 50:50 (mole/mole) mixture of benzene and acetone, for example, the acetone signal should integrate to the same value as the benzene sample, because both signals represent six equivalent protons. If we have a 50:50 mixture of acetone and cyclopentane, on the other hand, the ratio of the acetone peak area to the cylopentane peak area will be 3:5 (or 6:10), because the cyclopentane signal represents ten protons.

EXAMPLE 13.10.1

You take a ^{1}H-NMR spectrum of a mixed sample of acetone ($CH_3(CO)CH_3$) and dichloromethane (CH_2Cl_2). The integral ratio of the two signals (acetone : dichloromethane) is 2.3 to 1. What is the molar ratio of the two compounds in the sample?.

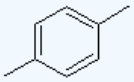
Solution

The acetone:dichloromethane molar ratio is 0.76:1. If the molar ratio was a 1:1 ratio, the signal integration ratio would be 3:1 because acetone has 6 protons while dichloromethane has 2. So, you need to divide the 2.3 integral value by a factor of 3 to get 0.76.

EXAMPLE 13.10.2

You take the ^{1}H-NMR spectrum of a mixed sample of 36% *para*-xylene and 64% acetone in $CDCl_3$ solvent. How many peaks do you expect to see?

What is the expected ratio of integration values for these peaks? (set the acetone peak integration equal to 1.0)





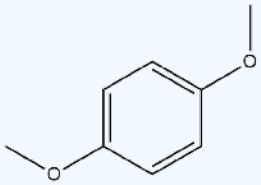
Solution

There are three peaks: two from *para*-xylene and one from acetone. The acetone peak and the *para*-xylene methyl peak both represent six protons, so the ratio of their integration values is simply 64 to 36 or 1 to 0.56. The ratio of the *para*-xylene methyl peak to the *para*-xylene aromatic peak is 6 to 4, or 0.56 to 0.37. So the final integral ratio of acetone:methyl:aromatic signals should be 1 to 0.56 to 0.37.

EXERCISE

EXERCISE 13.10.1

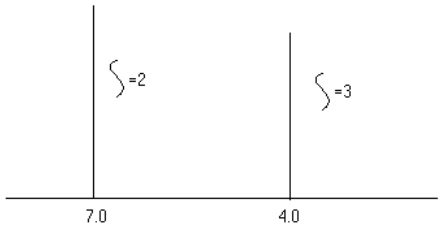
Predict how many signals the following molecule would have? Sketch the spectra and estimate the integration of the peaks.



Answer

There will be two peaks in a ratio (integration) of 2 to 3 of benzene to methyl protons.

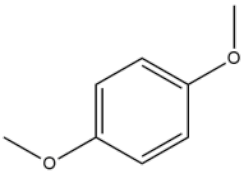
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QUESTIONS

Q13.10.1

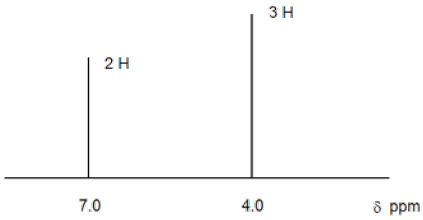
Predict how many signals the following molecule would have? Sketch the spectra and estimate the integration of the peaks.



SOLUTIONS

S13.10.1

There will be two peaks. Ideal general spectrum shown with integration.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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13.11: SPIN-SPIN SPLITTING IN ^{1}H NMR SPECTRA

Objectives

After completing this section, you should be able to

1. explain the spin-spin splitting pattern observed in the ^{1}H NMR spectrum of a simple organic compound, such as chloroethane or 2-bromopropane.
2. interpret the splitting pattern of a given ^{1}H NMR spectrum.
3. determine the structure of a relatively simple organic compound, given its ^{1}H NMR spectrum and other relevant information.
4. use coupling constants to determine which groups of protons are coupling with one another in a ^{1}H NMR spectrum.
5. predict the splitting pattern which should be observed in the ^{1}H NMR spectrum of a given organic compound.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- coupling constant
- multiplet
- quartet
- triplet
- doublet

STUDY NOTES

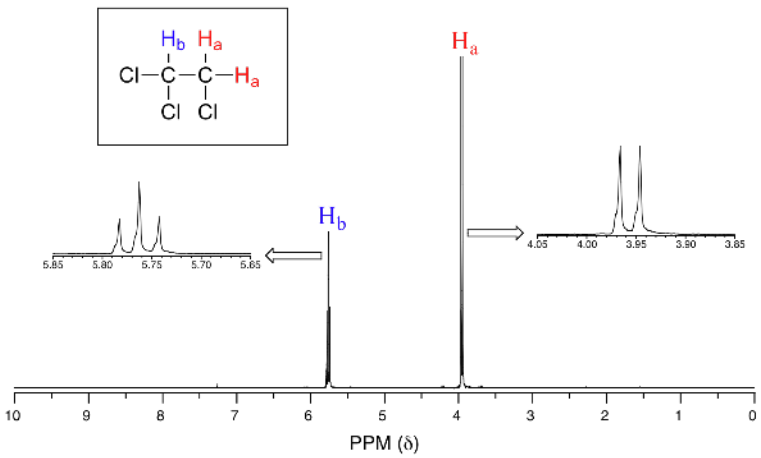
From what we have learned about ^{1}H NMR spectra so far, we might predict that the spectrum of 1,1,2-trichloroethane, $CHCl_2CH_2Cl$, would consist of two peaks—one, at about 2.5-4.0 δ, expected for CH_2-halogen compounds and one shifted downfield because of the presence of an additional electronegative chlorine atom on the second carbon. However, when we look at the spectrum it appears to be much more complex. True, we see absorptions in the regions we predicted, but these absorptions appear as a group of two peaks (a *doublet*) and a group of three peaks (a *triplet*). This complication, which may be disturbing to a student who longs for the simple life, is in fact very useful to the organic chemist, and adds greatly to the power of NMR spectroscopy as a tool for the elucidation of chemical structures. The split peaks (*multiplets*) arise because the magnetic field experienced by the protons of one group is influenced by the spin arrangements of the protons in an adjacent group.

Spin-spin coupling is often one of the more challenging topics for organic chemistry students to master. Remember the $n + 1$ rule and the associated coupling patterns.

THE SOURCE OF SPIN-SPIN COUPLING

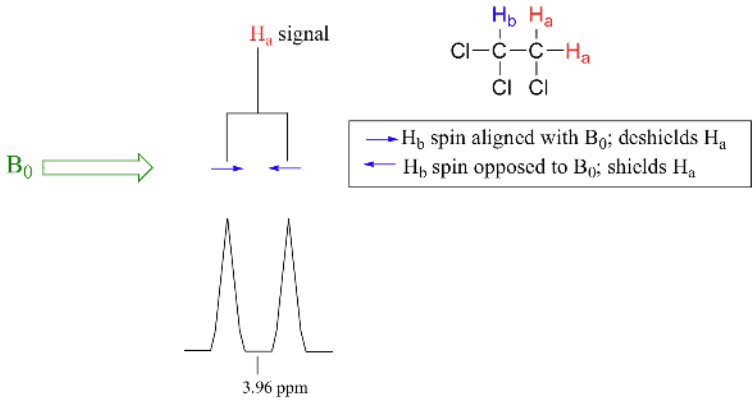
The ^{1}H-NMR spectra that we have seen so far (of methyl acetate and *para*-xylene) are somewhat unusual in the sense that in both of these molecules, each set of protons generates a single NMR signal. In fact, the ^{1}H-NMR spectra of most organic molecules contain proton signals that are 'split' into two or more sub-peaks. Rather than being a complication, however, this splitting behavior actually provides us with more information about our sample molecule.

Consider the spectrum for 1,1,2-trichloroethane. In this and in many spectra to follow, we show enlargements of individual signals so that the signal splitting patterns are recognizable.

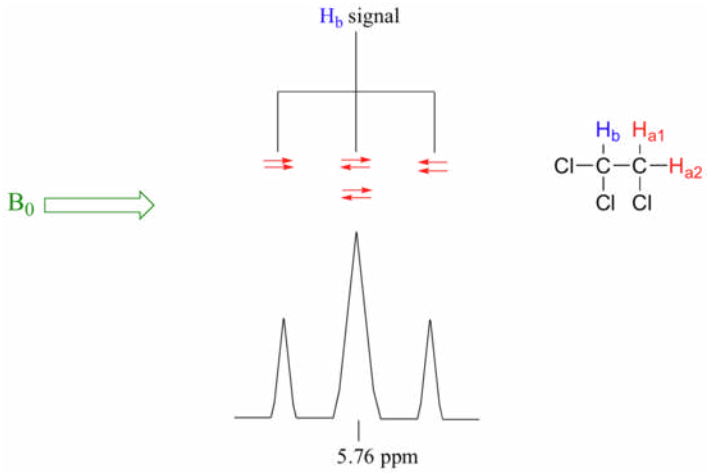


The signal at 3.96 ppm, corresponding to the two H_a protons, is split into two subpeaks of equal height (and area) – this is referred to as a **doublet**. The H_b signal at 5.76 ppm, on the other hand, is split into three sub-peaks, with the middle peak higher than the two outside peaks - if we were to integrate each subpeak, we would see that the area under the middle peak is twice that of each of the outside peaks. This is called a **triplet**.

The source of signal splitting is a phenomenon called **spin-spin coupling**, a term that describes the magnetic interactions between neighboring, non-equivalent NMR-active nuclei. In our 1,1,2 trichloromethane example, the H_a and H_b protons are spin-coupled to each other. Here's how it works, looking first at the H_a signal: in addition to being shielded by nearby valence electrons, each of the H_a protons is also influenced by the small magnetic field generated by H_b next door (remember, each spinning proton is like a tiny magnet). The magnetic moment of H_b will be aligned *with* B_0 in (slightly more than) half of the molecules in the sample, while in the remaining half of the molecules it will be opposed to B_0. The B_{eff} 'felt' by H_a is a slightly weaker if H_b is aligned against B_0, or slightly stronger if H_b is aligned with B_0. In other words, in half of the molecules H_a is *shielded* by H_b (thus the NMR signal is shifted slightly upfield) and in the other half H_a is *deshielded* by H_b(and the NMR signal shifted slightly downfield). What would otherwise be a single H_a peak has been split into two sub-peaks (a doublet), one upfield and one downfield of the original signal. These ideas an be illustrated by a **splitting diagram**, as shown below.

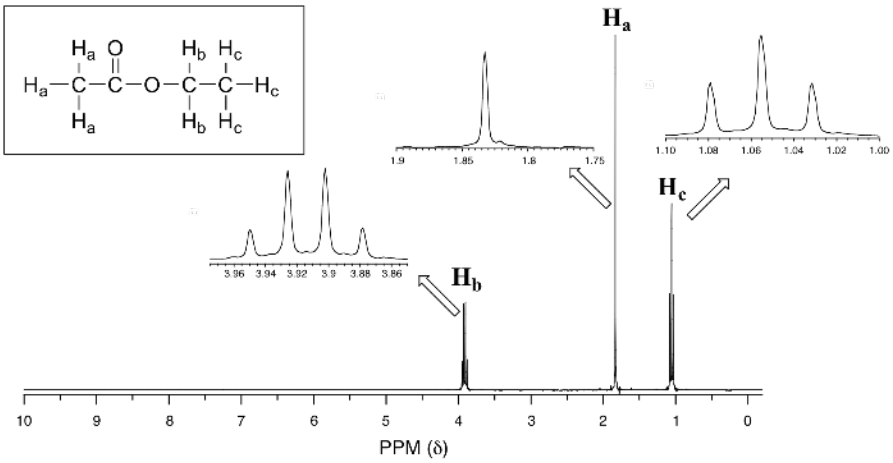


Now, let's think about the $H_b$signal. The magnetic environment experienced by H_b is influenced by the fields of both neighboring H_a protons, which we will call H_{a1} and H_{a2}. There are four possibilities here, each of which is equally probable. First, the magnetic fields of both H_{a1} and H_{a2} could be aligned with B_0, which would deshield H_b, shifting its NMR signal slightly downfield. Second, both the H_{a1} and H_{a2} magnetic fields could be aligned opposed to B_0, which would shield H_b, shifting its resonance signal slightly upfield. Third and fourth, H_{a1} could be with B_0 and H_{a2} opposed, or H_{a1}opposed to B_0 and H_{a2} with B_0. In each of the last two cases, the shielding effect of one H_a proton would cancel the deshielding effect of the other, and the chemical shift of H_b would be unchanged.



So in the end, the signal for H_b is a **triplet**, with the middle peak twice as large as the two outer peaks because there are *two* ways that H_{a1} and H_{a2} can cancel each other out.

Now, consider the spectrum for ethyl acetate:



We see an unsplit '**singlet**' peak at 1.833 ppm that corresponds to the acetyl (H_a) hydrogens – this is similar to the signal for the acetate hydrogens in methyl acetate that we considered earlier. This signal is unsplit because there are no adjacent hydrogens on the molecule. The signal at 1.055 ppm for the H_c hydrogens is split into a triplet by the two H_b hydrogens next door. The explanation here is the same as the explanation for the triplet peak we saw previously for 1,1,2-trichloroethane.

The $H_b$hydrogens give rise to a **quartet** signal at 3.915 ppm – notice that the two middle peaks are taller then the two outside peaks. This splitting pattern results from the spin-coupling effect of the *three* H_c hydrogens next door, and can be explained by an analysis similar to that which we used to explain the doublet and triplet patterns.

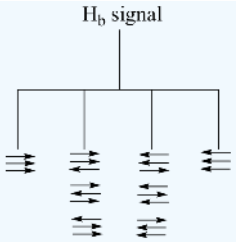
EXAMPLE 13.11.1

a. Explain, using left and right arrows to illustrate the possible combinations of nuclear spin states for the H_c hydrogens, why the H_b signal in ethyl acetate is split into a quartet.

b. The integration ratio of doublets is 1:1, and of triplets is 1:2:1. What is the integration ratio of the H_b quartet in ethyl acetate? (Hint – use the illustration that you drew in part a to answer this question.)

Answer

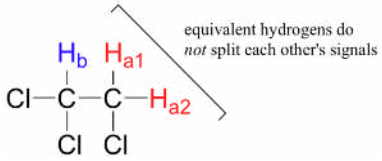
a)



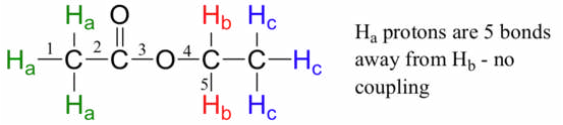
b) The figure above demonstrates that the quartet subpeaks integrate to 1:3:3:1 (eg., there are three ways for two spins to be aligned with B_0 and one against B_0). As an analogy, if you flip three coins at once, you have a 1 in eight chance of getting all heads, 1 in 8 chance of all tails, a 3 in 8 chance of two heads and a tail, and a 3 in 8 chance of two tails and a head.

By now, you probably have recognized the pattern which is usually referred to as the ***n* + 1 rule**: if a set of hydrogens has *n* neighboring, non-equivalent hydrogens, it will be split into *n* + 1 subpeaks. Thus the two H_b hydrogens in ethyl acetate split the H_c signal into a triplet, and the three H_c hydrogens split the H_b signal into a quartet. This is very useful information if we are trying to determine the structure of an unknown molecule: if we see a triplet signal, we know that the corresponding hydrogen or set of hydrogens has two `neighbors`. When we begin to determine structures of unknown compounds using ^{1}H-NMR spectral data, it will become more apparent how this kind of information can be used.

Three important points need to be emphasized here. First, signal splitting only occurs between non-equivalent hydrogens – in other words, H_{a1} in 1,1,2-trichloroethane is *not* split by H_{a2}, and vice-versa.

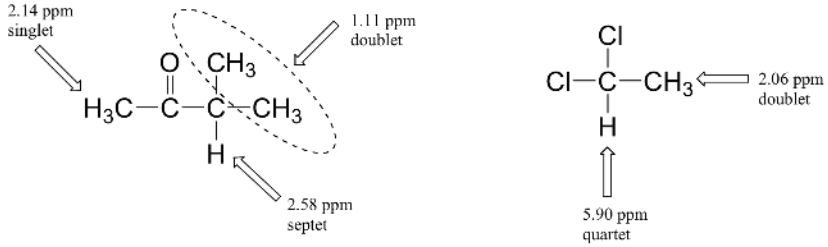


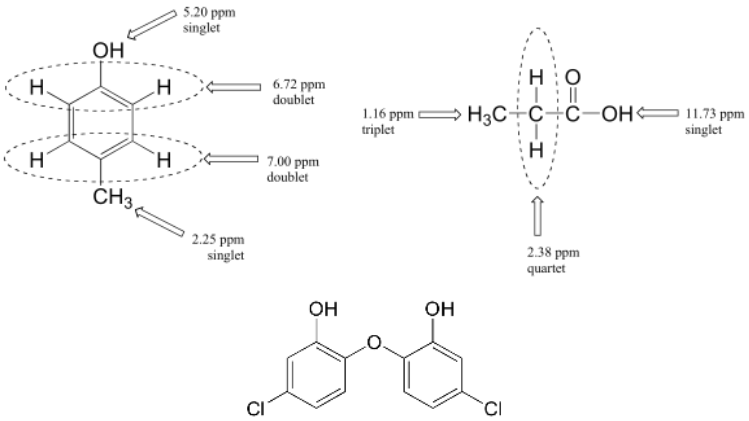
Second, splitting occurs primarily between hydrogens that are separated by three bonds. This is why the H_a hydrogens in ethyl acetate form a singlet– the nearest hydrogen neighbors are five bonds away, too far for coupling to occur.



Occasionally we will see four-bond and even 5-bond splitting, but in these cases the magnetic influence of one set of hydrogens on the other set is much more subtle than what we typically see in three-bond splitting (more details about how we quantify coupling interactions is provided in section 5.5B). Finally, splitting is most noticeable with hydrogens bonded to carbon. Hydrogens that are bonded to heteroatoms (alcohol or amino hydrogens, for example) are coupled weakly - or not at all - to their neighbors. This has to do with the fact that these protons exchange rapidly with solvent or other sample molecules.

Below are a few more examples of chemical shift and splitting pattern information for some relatively simple organic molecules.





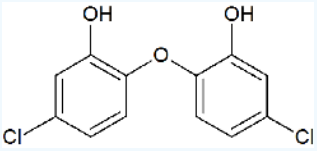
MULTIPLICITY IN PROTON NMR

The number of lines in a peak is always one more (n+1) than the number of hydrogens on the neighboring carbon. This table summarizes coupling patterns that arise when protons have different numbers of neighbors.

# of lines	ratio of lines	term for peak	# of neighbors
1	-	singlet	0
2	1:1	doublet	1
3	1:2:1	triplet	2
4	1:3:3:1	quartet	3
5	1:4:6:4:1	quintet	4
6	1:5:10:10:5:1	sextet	5
7	1:6:15:20:15:6:1	septet	6
8	1:7:21:35:35:21:7:1	octet	7
9	1:8:28:56:70:56:28:8:1	nonet	8

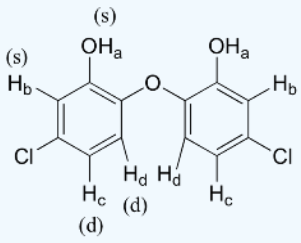
EXAMPLE 13.11.2

How many proton signals would you expect to see in the ^{1}H-NMR spectrum of the structure shown below? For each of the proton signals, predict the splitting pattern. Assume that you see only 3-bond coupling.



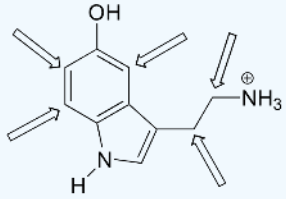
Answer

Because of the symmetry in the molecule, there are only four proton signals. Predicted splitting is indicated.

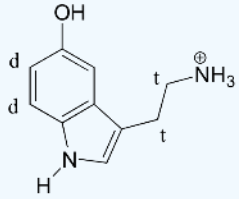


EXAMPLE 13.11.3

Predict the splitting pattern for the ^{1}H-NMR signals corresponding to the protons at the locations indicated by arrows (the structure is that of the neurotransmitter serotonin).



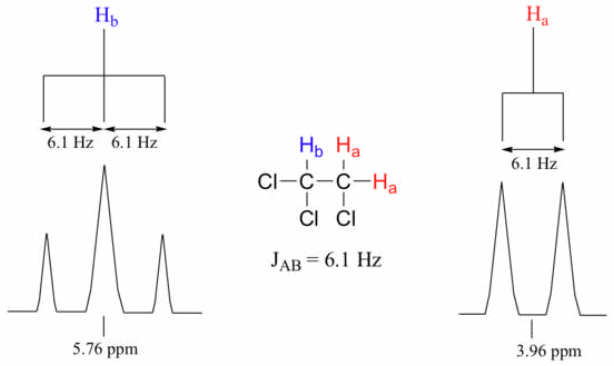
Answer



(recall that splitting is generally not seen with protons on heteroatoms)

COUPLING CONSTANTS

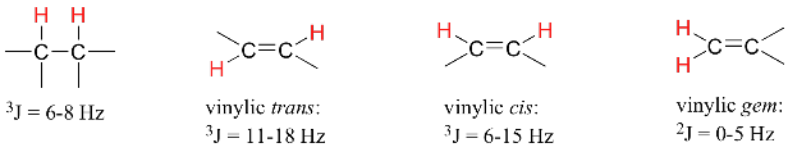
Chemists quantify the spin-spin coupling effect using something called the **coupling constant**, which is abbreviated with the capital letter *J*. The coupling constant is simply the difference, expressed in Hz, between two adjacent sub-peaks in a split signal. For our doublet in the 1,1,2-trichloroethane spectrum, for example, the two subpeaks are separated by 6.1 Hz, and thus we write $^3J_{a\text{-}b}$ = 6.1 Hz.



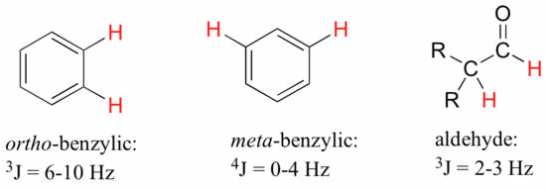
The superscript 3 tells us that this is a three-bond coupling interaction, and the a-b subscript tells us that we are talking about coupling between H_a and H_b. Unlike the chemical shift value, *the coupling constant, expressed in Hz, is the same regardless of the applied field strength of the NMR magnet*. This is because the strength of the magnetic moment of a neighboring proton, which is the source of the spin-spin coupling phenomenon, does *not* depend on the applied field strength.

When we look closely at the triplet signal in 1,1,2-trichloroethane, we see that the coupling constant - the `gap` between subpeaks - is 6.1 Hz, the same as for the doublet. This is an important concept! The coupling constant $^3J_{a\text{-}b}$ quantifies the magnetic interaction between the H_a and H_b hydrogen sets, and *this interaction is of the same magnitude in either direction*. In other words, H_a influences H_b to the same extent that H_b influences H_a. When looking at more complex NMR spectra, this idea of **reciprocal coupling constants** can be very helpful in identifying the coupling relationships between proton sets.

Coupling constants between proton sets on neighboring sp^3-hybridized carbons is typically in the region of 6-8 Hz. With protons bound to sp^2-hybridized carbons, coupling constants can range from 0 Hz (no coupling at all) to 18 Hz, depending on the bonding arrangement.



For vinylic hydrogens in a *trans* configuration, we see coupling constants in the range of ^3J = 11-18 Hz, while *cis* hydrogens couple in the ^3J = 6-15 Hz range. The 2-bond coupling between hydrogens bound to the same alkene carbon (referred to as geminal hydrogens) is very fine, generally 5 Hz or lower. *Ortho* hydrogens on a benzene ring couple at 6-10 Hz, while 4-bond coupling of up to 4 Hz is sometimes seen between *meta* hydrogens.

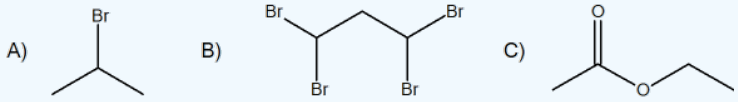


Fine (2-3 Hz) coupling is often seen between an aldehyde proton and a three-bond neighbor. Table 4 lists typical constant values.

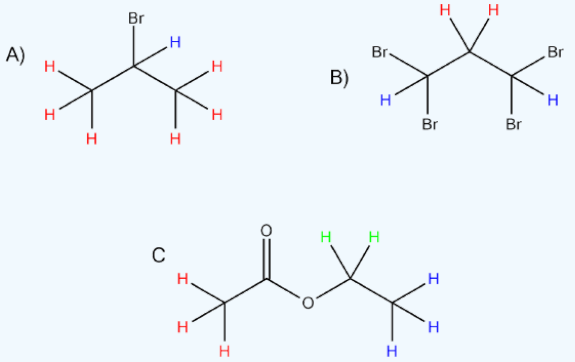
EXERCISES

EXERCISE 13.11.1

Predict the splitting patterns of the following molecules.



Answer



A. H: Doublet. H: Septet

B. H: Triplet, H: Triplet

C. H: Singlet, H: Quartet, H: Triplet

EXERCISE 13.11.2

Draw the following according to the criteria given.

A. C_3H5O; two triplet, 1 doublet

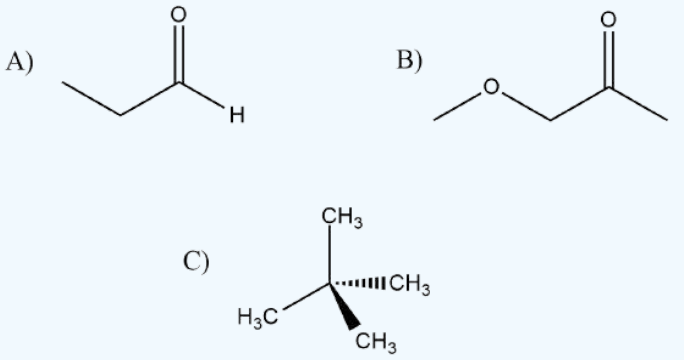
https://chem.libretexts.org/@go/page/67297

B. $C_4H_8O_2$; three singlets

C. C_5H_{12}; one singlet

Answer

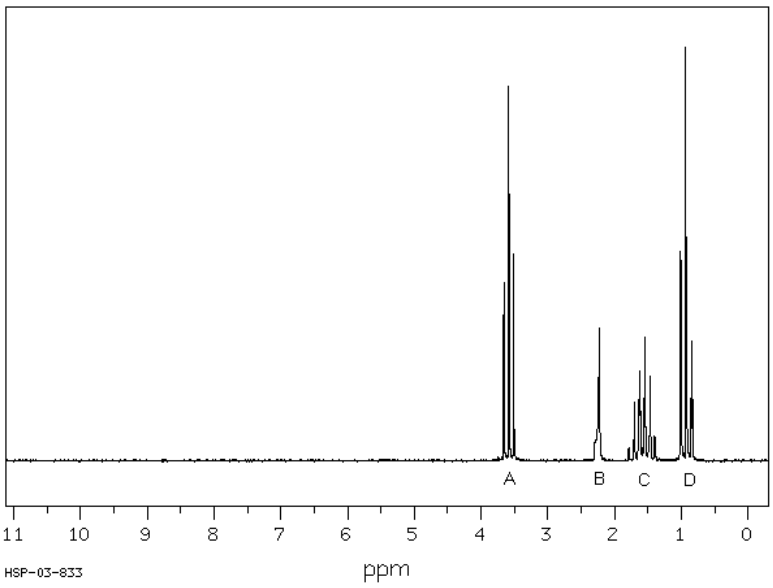
These are just some drawings, more may be possible.



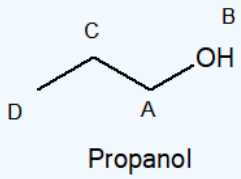
EXERCISE 13.11.3

The following spectrum is for C_3H_8O. Determine the structure.

A; triplet, B; Singlet, C; Sextet, D; Triplet



Answer



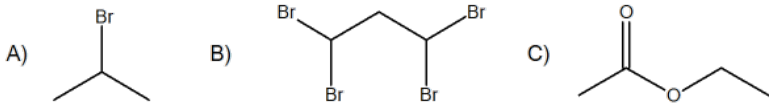
Propanol

Note: Remember, chemically equivalent protons do not couple with one another to give spin-spin splitting.

QUESTIONS

Q13.11.1

Predict the splitting patterns of the following molecules:



Q13.11.2

Draw the following according to the criteria given.

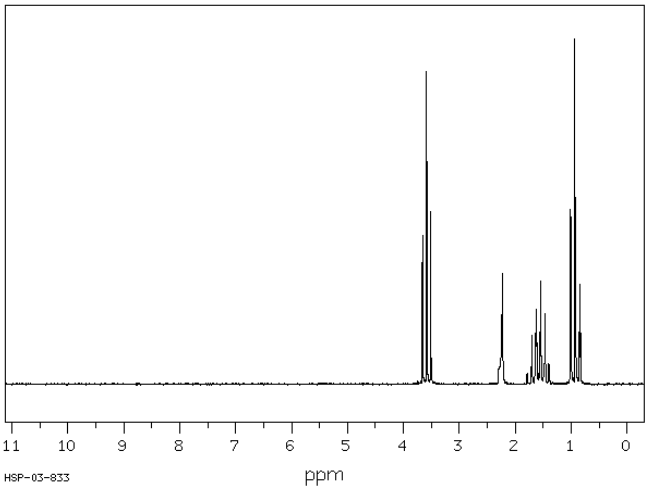
A. C_3H_5O; two triplet, 1 doublet

B. $C_4H_8O_2$; three singlets

C. C_5H_{12}; one singlet

Q13.11.3

The following spectrum is for C_3H_8O. Determine the structure.



A triplet; B singlet; C sextet; D triplet

Source: SDBSWeb : http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 3 December 2016)

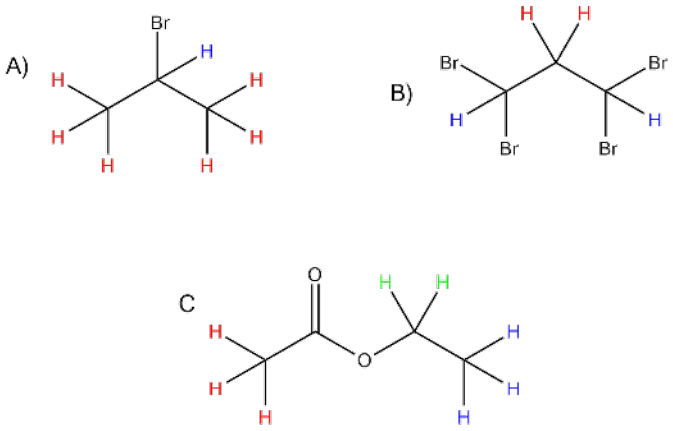
SOLUTIONS

S13.11.1

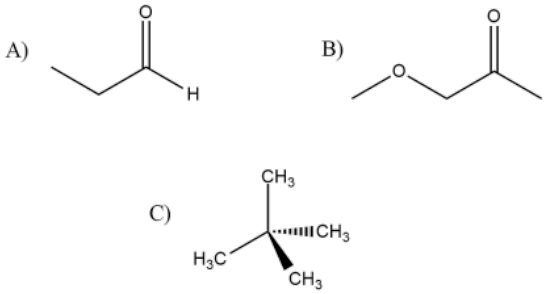
A. H: Doublet. H: Septet

B. H: Doublet, H: Triplet

C. H: Singlet, H: Quartet, H: Triplet

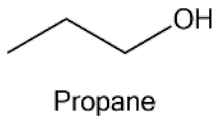


S13.11.2



These are just some drawings, more may be possible.

S13.11.3



Propane

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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13.12: MORE COMPLEX SPIN-SPIN SPLITTING PATTERNS

Objectives

After completing this section, you should be able to

1. explain how multiple coupling can give rise to complex-looking ^{1}H NMR spectra.
2. predict the splitting pattern expected in the ^{1}H NMR spectrum of an organic compound in which multiple coupling is possible.
3. interpret ^{1}H NMR spectra in which multiple coupling is evident.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

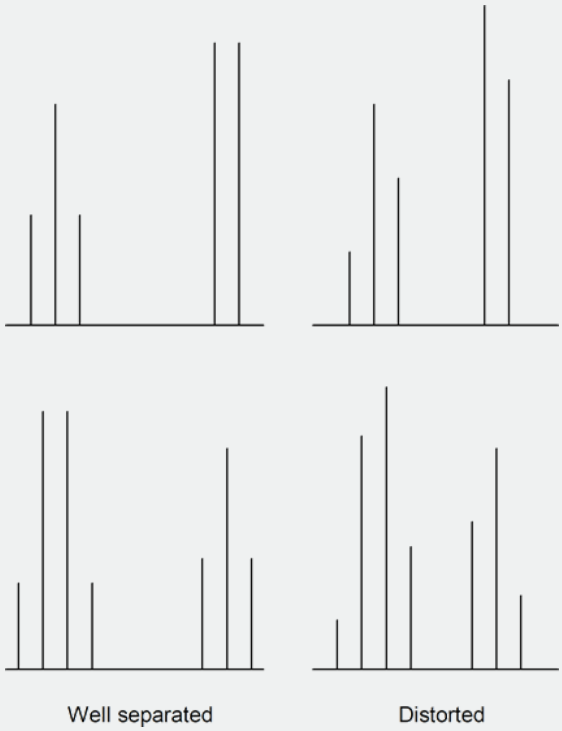
- tree diagram

STUDY NOTES

We saw the effects of spin-spin coupling on the appearance of a ^{1}H NMR signal. These effects can be further complicated when that signal is coupled to several different protons. For example, $BrCH_2CH_2CH_2Cl$ would produce three signals. The hydrogens at C_1 and C_3 would each be triplets because of coupling to the two hydrogens on C_2. However, the hydrogen on C_2 "sees" two different sets of neighbouring hydrogens, and would therefore produce a triplet of triplets.

Another effect that can complicate a spectrum is the "closeness" of signals. If signals accidently overlap they can be difficult to identify. In the example above, we expected a triplet of triplets. However, if the coupling is identical (or almost identical) between the hydrogens on C_2 and the hydrogens on both C_1 and C_3, one would observe a quintet in the ^{1}H NMR spectrum. [You can try this yourself by drawing a tree diagram of a triplet of triplets assuming, first, different coupling constants, and then, identical coupling constants.] Keep this point in mind when interpreting real ^{1}H NMR spectra.

Also, when multiplets are well separated, they form patterns. However, when multiplets approach each other in the spectrum they sometimes become distorted. Usually, the inner peaks become larger than the outer peaks. Note the following examples:



Aromatic ring protons quite commonly have overlapping signals and multiplet distortions. Sometimes you cannot distinguish between individual signals, and one or more messy multiplets often appear in the aromatic region.

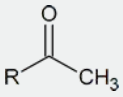
It is much easier to rationalize the observed ^{1}H NMR spectrum of a known compound than it is to determine the structure of an unknown compound from its ^{1}H NMR spectrum. However, rationalizations can be a useful learning technique as you try to improve your proficiency in spectral interpretation. Remember that when a chemist tries to interpret the ^{1}H NMR spectrum of an unknown compound, he or she usually has additional information available to make the task easier. For example, the chemist will almost certainly have an infrared spectrum of the compound and possibly a mass spectrum too. Details of how the compound was synthesized may be available, together with some indication of its chemical properties, its physical properties, or both.

In examinations, you will be given a range of information (IR, MS, UV data and empirical formulae) to aid you with your structural determination using ^{1}H NMR spectroscopy. For example, you may be asked to determine the structure of $C_6H_{12}O$ given the following spectra:

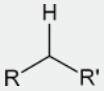
Infrared spectrum: 3000 cm^{-1} and 1720 cm^{-1} absorptions are both strong

^{1}H NMR	δ (ppm)	Protons	Multiplicity
	0.87	6	doublet
	1.72	1	broad multiplet
	2.00	3	singlet
	2.18	2	doublet

To answer this question, you note that the infrared spectrum of $C_6H_{12}O$ shows $C-H$ stretching (3000 cm^{-1}) and $C-O$ stretching (1720 cm^{-1}). Now you have to piece together the information from the ^{1}H NMR spectrum. Notice the singlet with three protons at 2.00 ppm. This signal indicates a methyl group that is not coupled to other protons. It could possibly mean the presence of a methyl ketone functional group.



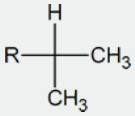
The signal at 1.72 ppm is a broad multiplet, suggesting that a carbon with a single proton is beside carbons with several different protons.



The doublet signal at 2.18 ppm implies that a $-CH_2-$ group is attached to a carbon having only one proton.

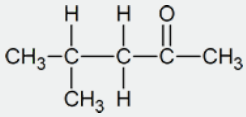


The six protons showing a doublet at 0.87 ppm indicate two equivalent methyl groups attached to a carbon with one proton.



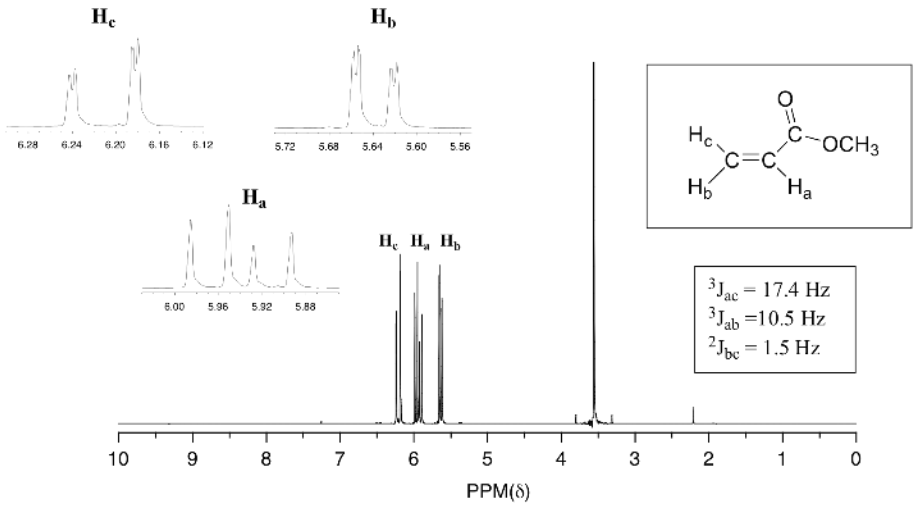
Whenever you see a signal in the 0.7-1.3 ppm range that is a multiplet of three protons (3, 6, 9) it is most likely caused by equivalent methyl groups.

Using trial and error, and with the above observations, you should come up with the correct structure.

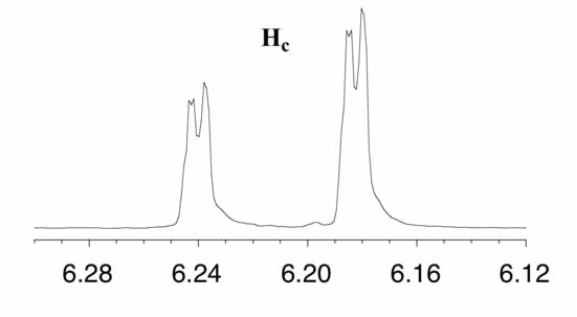


COMPLEX COUPLING

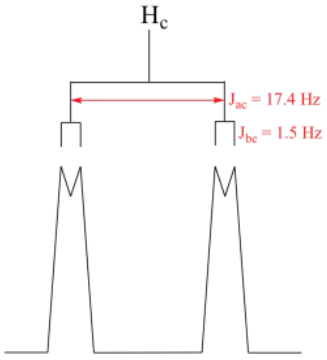
In all of the examples of spin-spin coupling that we have seen so far, the observed splitting has resulted from the coupling of one set of hydrogens to *just one* neighboring set of hydrogens. When a set of hydrogens is coupled to *two or more* sets of nonequivalent neighbors, the result is a phenomenon called **complex coupling**. A good illustration is provided by the ^{1}H-NMR spectrum of methyl acrylate:



First, let's first consider the H_c signal, which is centered at 6.21 ppm. Here is a closer look:

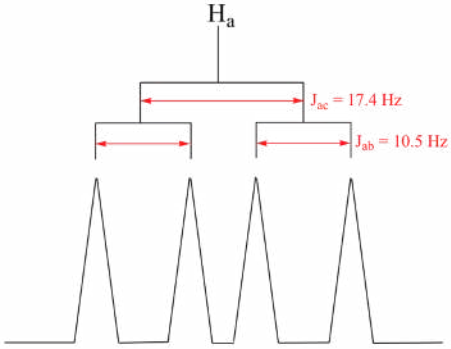


With this enlargement, it becomes evident that the Hc signal is actually composed of four sub-peaks. Why is this? H_c is coupled to both H_a and H_b , but with *two different coupling constants*. Once again, a splitting diagram (or tree diagram) can help us to understand what we are seeing. H_a is *trans* to H_c across the double bond, and splits the H_c signal into a doublet with a coupling constant of $^3J_{ac}$ = 17.4 Hz. In addition, each of these H_c doublet sub-peaks is split again by H_b (*geminal* coupling) into two more doublets, each with a much smaller coupling constant of $^2J_{bc}$ = 1.5 Hz.

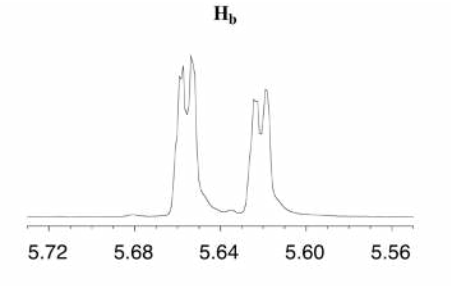


The result of this $doub \leq spli \in g$ is a pattern referred to as a **doublet of doublets**, abbreviated `**dd**`.

The signal for H_a at 5.95 ppm is also a doublet of doublets, with coupling constants $^3J_{ac}$= 17.4 Hz and $^3J_{ab}$ = 10.5 Hz.



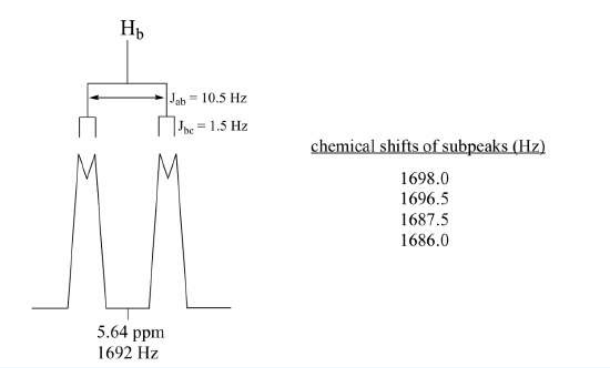
The signal for H_b at 5.64 ppm is split into a doublet by H_a, a *cis* coupling with $^3J_{ab}$ = 10.4 Hz. Each of the resulting sub-peaks is split again by H_c, with the same *geminal* coupling constant $^2J_{bc}$ = 1.5 Hz that we saw previously when we looked at the H_c signal. The overall result is again a doublet of doublets, this time with the two $\subset -doub \leq ts$ spaced slightly closer due to the smaller coupling constant for the *cis* interaction. Here is a blow-up of the actual $H_b$signal:



EXAMPLE \PageIndex1

Construct a splitting diagram for the H_b signal in the ^{1}H-NMR spectrum of methyl acrylate. Show the chemical shift value for each sub-peak, expressed in Hz (assume that the resonance frequency of TMS is exactly 300 MHz).

Solution:

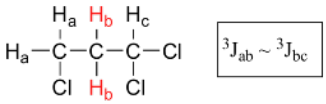


NOTE

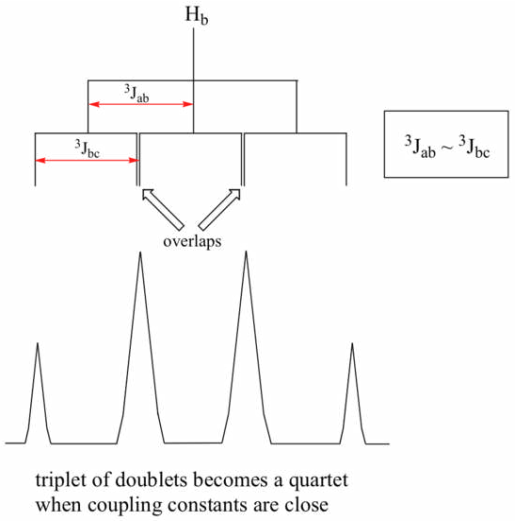
When constructing a splitting diagram to analyze complex coupling patterns, it is usually easier to show the larger splitting first, followed by the finer splitting (although the reverse would give the same end result).

When a proton is coupled to two different neighboring proton sets with identical or very close coupling constants, the splitting pattern that emerges often appears to follow the

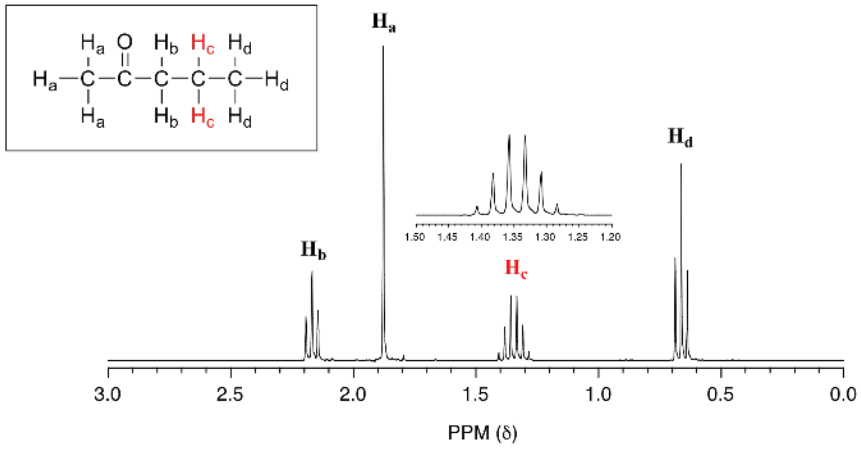
When a proton is coupled to two different neighboring proton sets with identical or very close coupling constants, the splitting pattern that emerges often appears to follow the simple `$n$ + 1 rule` of non-complex splitting. In the spectrum of 1,1,3-trichloropropane, for example, we would expect the signal for H_b to be split into a triplet by H_a, and again into doublets by H_c, resulting in a 'triplet of doublets'.



H_a and H_c are not equivalent (their chemical shifts are different), but it turns out that $^3J_{ab}$ is very close to $^3J_{bc}$. If we perform a splitting diagram analysis for H_b, we see that, due to the overlap of sub-peaks, the signal appears to be a quartet, and for all intents and purposes follows the $n + 1$ rule.

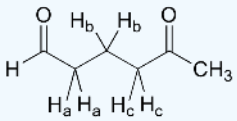


For similar reasons, the H_c peak in the spectrum of 2-pentanone appears as a sextet, split by the five combined H_b and H_d protons. Technically, this 'sextet' could be considered to be a 'triplet of quartets' with overlapping sub-peaks.



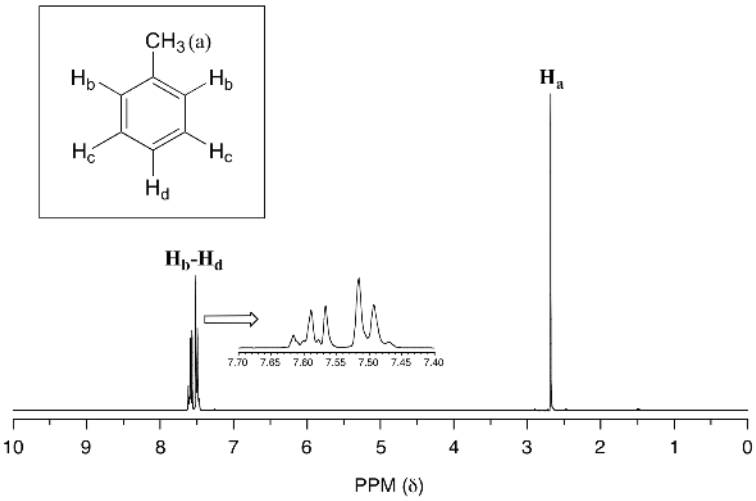
EXAMPLE \PageIndex2

What splitting pattern would you expect for the signal coresponding to H_b in the molecule below? Assume that $J_{ab} \sim J_{bc}$. Draw a splitting diagram for this signal, and determine the relative integration values of each subpeak.



Solution: We can think of this signal as being a triplet of triplets, but because the two coupling constants are very close, what we would actually see is a 1,2,3,2,1 pentet.

In many cases, it is difficult to fully analyze a complex splitting pattern. In the spectrum of toluene, for example, if we consider only 3-bond coupling we would expect the signal for H_b to be a doublet, H_d a triplet, and H_c a triplet.



In practice, however, all three aromatic proton groups have very similar chemical shifts and their signals overlap substantially, making such detailed analysis difficult. In this case, we would refer to the aromatic part of the spectrum as a **multiplet**.

When we start trying to analyze complex splitting patterns in larger molecules, we gain an appreciation for why scientists are willing to pay large sums of money (hundreds of thousands of dollars) for higher-field NMR instruments. Quite simply, the stronger our magnet is, the more resolution we get in our spectrum. In a 100 MHz instrument (with a magnet of approximately 2.4 Tesla field strength), the 12 ppm frequency 'window' in which we can observe proton signals is 1200 Hz wide. In a 500 MHz (~12 Tesla) instrument, however, the window is 6000 Hz - five times wider. In this sense, NMR instruments are like digital cameras and HDTVs: better resolution means more information and clearer pictures (and higher price tags!)

EXERCISES

1. Given the information below, draw the structures of compounds *A* through *D*.

   a. An unknown compound *A* was prepared as follows:

   $$CH_3{=}C(CH_2Cl)_2 \xrightarrow[THF]{Mg} A$$

   Mass spectrum:

   base peak *m*/*e* = 39

   parent peak *m*/*e* = 54

   ^{1}H NMR spectrum:

δ (ppm)	Relative Area	Multiplicity
1.0	2	triplet
5.4	1	quintet

   b. Unknown compound *B* has the molecular formula $C_7H_6O_2$.

   Infrared spectrum:

   3200 cm^{-1} (broad) and 1747 cm^{-1} (strong) absorptions

   ^{1}H NMR spectrum:

δ (ppm)	Protons
6.9	2
7.4	2
9.8	1
10.9	1

Hint: Aromatic ring currents deshield all proton signals just outside the ring.

c. Unknown compound *C* shows no evidence of unsaturation and contains only carbon and hydrogen.

Mass spectrum:

parent peak *m*/*e* = 68

^{1}H NMR spectrum:

δ (ppm)	Relative Area	Multiplicity
1.84	3	triplet
2.45	1	septet

Hint: Think three dimensionally!

d. Unknown compound *D* ($C_{15}H_{14}O$) has the following spectral properties.

Infrared spectrum:

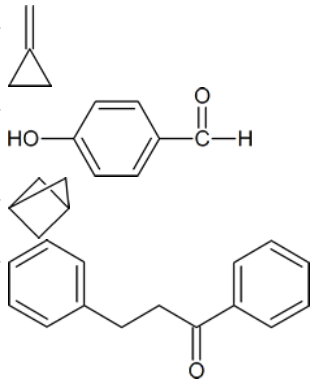
3010 cm^{-1} (medium)
1715 cm^{-1} (strong)
1610 cm^{-1} (strong)
1500 cm^{-1} (strong)

^{1}H NMR spectrum:

δ (ppm)	Relative Area	Multiplicity
3.00	2	triplet
3.07	2	triplet
7.1-7.9	10	Multiplets

Answers

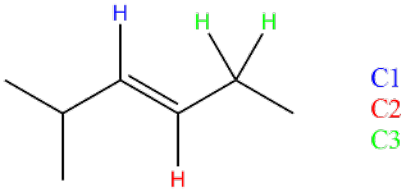
1. a.
   b.
   c.
   d.



QUESTIONS

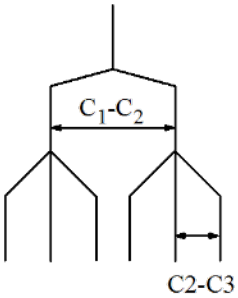
Q13.12.1

In the following molecule, the C2 is coupled with both the vinyl, C1, and the alkyl C3. Draw the splitting tree diagram.



SOLUTIONS

S13.12.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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13.13: USES OF ^{1}H NMR SPECTROSCOPY

Objective

After completing this section, you should be able to use data from ^{1}H NMR spectra to distinguish between two (or more) possible structures for an unknown organic compound.

There will be cases in which you already know what the structure might be. In these cases:

- You should draw attention to pieces of data that most strongly support your expected structure. This approach will demonstrate evaluative understanding of the data; that means you can look at data and decide what parts are more crucial than others.
- You should also draw attention to negative results: that is, peaks that might be there if this spectrum matched another, possible structure, but that are in fact missing.

One of the most complicated problems to deal with is the analysis of a mixture. This situation is not uncommon when students run reactions in lab and analyse the data.

- Sometimes the spectra show a little starting material mixed in with the product.
- Sometimes solvents show up in the spectrum.
- As you might expect, the minor component usually shows up as smaller peaks in the spectrum. If there are fewer molecules present, then there are usually fewer protons to absorb in the spectrum.
- In this case, you should probably make two completely separate sets of data tables for your analysis, one for each compound, or else one for the main compound and one for impurities.

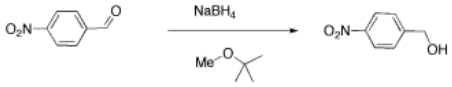
Remember that integration ratios are really only meaningful within a single compound. If your NMR sample contains some benzene (C_6H_6) and some acetone (CH_3COCH_3), and there is a peak at 7.15 that integrates to 1 proton and a peak at 2.10 ppm integrating to 6 protons, it might mean there are 6 protons in acetone and 1 in benzene, but you can tell that isn't true by looking at the structure. There must be six times as many acetone molecules as benzene molecules in the sample.

There are six protons in the benzene, and they should all show up near 7 ppm. There are six protons in acetone, and they should all show up near 2 ppm. Assuming that small integral of 1H for the benzene is really supposed to be 6H, then the large integral of 6H for the acetone must also represent six times as many hydrogens, too. It would be 36 H. There are only six hydrogens in acetone, so it must represent six times as many acetone molecules as there are benzenes.

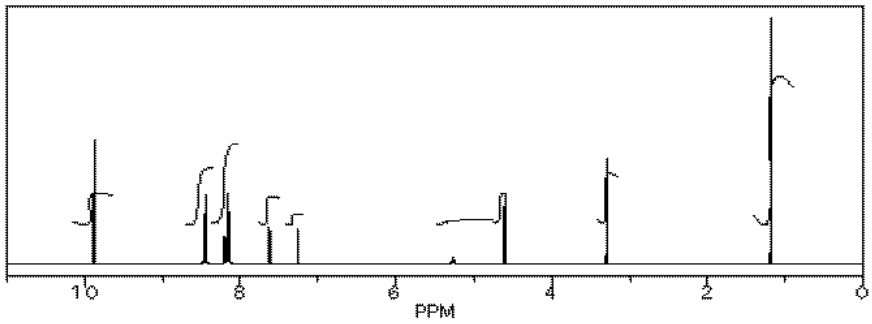
Similarly, if you have decided that you can identify two sets of peaks in the ^{1}H spectrum, analysing them in different tables makes it easy to keep the integration analysis completely separate too ; 1 H in one table will not be the same size integral as 1 H in the other table unless the concentrations of the two compounds in the sample are the same.

However, comparing the ratio of two integrals for two different compounds can give you the ratio of the two compounds in solution, just as we could determine the ratio of benzene to acetone in the mixture described above.

We will look at two examples of sample mixtures that could arise in lab. Results like these are pretty common events in the labIn the first example, a student tried to carry out the following reaction, a borohydride reduction of an aldehyde. The borohydride should give a hydride anion to the C=O carbon; washing with water should then supply a proton to the oxygen, giving an alcohol.

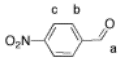
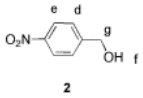
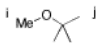


Her reaction produced the following spectrum.



(simulated data)

From this data, she produced the table below.

	shift	integration	int(n)	internal ratio	multiplicity	part structure	assignment
a	9.9 ppm	11 mm	2H	1H	singlet		
b	8.5 ppm	23 mm	4H	2H	doublet		 1
c	8.1 ppm	(20 mm?)	4H	2H	doublet		
d	8.2 ppm	(10 mm?)	2H	2H	doublet		
e	7.6 ppm	9 mm	2H	2H	doublet		 2
f	5.3 ppm	2 mm	0.4H	<1H	singlet	OH	
g	4.7 ppm	12 mm	2H	2H	singlet		
h	7.2 ppm	4 mm	0.8H	1H	singlet	$CHCl_3$	
i	3.3 ppm	8 mm	1.5H	3H	singlet		
j	1.2 ppm	24 mm	4.5H	9H	singlet		
			23.4H total				

Ratio of reactant **1** to product **2** is 2:1 based on peaks at 9.9 and 4.7 ppm (2H / 1H) : (2H / 2H); the reaction is 33% complete [2 / (2+1)]

Ratio of product **2** to TBME is 2:1 based on peaks at 4.7 and 3.3 ppm (2H / 2H) : (1.5H / 3H); the ratio of **1**:**2**:TBME is 2:1:0.5, so the sample is 57% **1** [2/(2+1+0.5)], 29% **2** and 14% TBME.

Notice how she calculated that ratio. She found a peak in molecule 1, the aldehyde, that she was pretty sure corresponded to the aldehydic hydrogen, the H attached to the C=O; in other words, the CH=O. She found another peak from molecule 2, the alcohol, that she was pretty sure represented the two hydrogens on the carbon attached to oxygen, the CH_2-O.

The integrals for those two peaks are equal. They are both 2H in her table. However, she notes that within each molecule, the first integral really represents 1H and the second represents 2H. That means there must be twice as many of molecule 1 as there are molecule 2. That way, there would be 2 x CH=O, and its integral would be the same as the 1 x CH_2-O in the other molecule.

One way to approach this kind of problem is to:

- choose one peak from each of the two compounds you want to compare.
- decide how many hydrogens each peak is supposed to represent in a molecule. Is it supposed to be a CH_2, a CH, a CH_3?
- divide the integral value for that peak by that number of hydrogens it is supposed to represent in a molecule.
- compare the two answers (integral A / ideal # H) vs (integral B / ideal # H).
- the ratio of those two answers is the ratio of the two molecules in the sample.

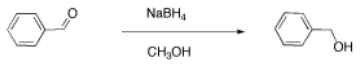
So there is twice as much aldehyde as alcohol in the mixture. In terms of these two compounds alone, she has 33% alcohol and 66% aldehyde. That's (1/(1+2)) x100% for the alcohol, and (2/(1+2)) x100% for the aldehyde. That calculation just represents the amount of individual component divided by the total of the components she wants to compare.

There are a number of things to take note of here.

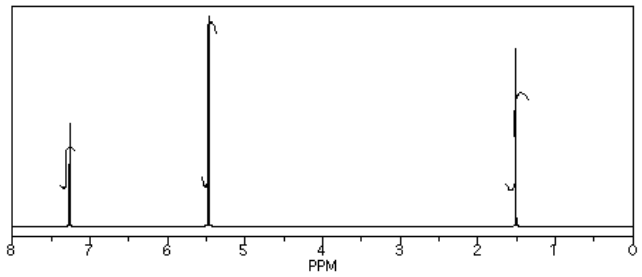
- Her reaction really didn't work very well. She still has majority starting material, not product.
- She will get a good grade on this lab. Although the experiment didn't work well, she has good data, and she has analyzed it very clearly.
- She has separated her data table into different sections for different compounds. Sometimes that makes it easier to analyze things.
- She has noted the actual integral data (she may have measured the integral with a ruler) and also converted it into a more convenient ratio, based on the integral for a peak that she felt certain about.
- She went one step further, and indicated the internal integration ratio within each individual compound.

- She calculated the % completion of the reaction using the integral data for the reactant and product, and she made clear what part of the data she used for that calculation. A similar procedure could be done if a student were just trying to separate two components in a mixture rather than carry out a reaction.
- She also calculated the overall purity of the mixture, including a solvent impurity that she failed to remove.
- However, $CHCl_3$ is not included in her analysis of purity. $CHCl_3$ really isn't part of her sample; it was just present in the NMR solvent, so it doesn't represent anything in the material she ended up with at the end of lab.

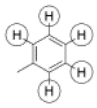
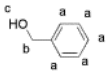
Another student carried out a similar reaction, shown below. He also finished the reaction by washing with water, but because methanol is soluble in water, he had to extract his product out of the water. He chose to use dichloromethane for that purpose.



He obtained the following data.



From this data, he constructed the following table.

	shift	integration	int(n)	multiplicity	partial structure	assignment
a	7.3 ppm	16 mm	5H	singlet		
b	5.4 ppm	64 mm	2H	singlet		
c	1.6 ppm	37 mm	1H	singlet	OH	

There are some things to learn about this table, too.

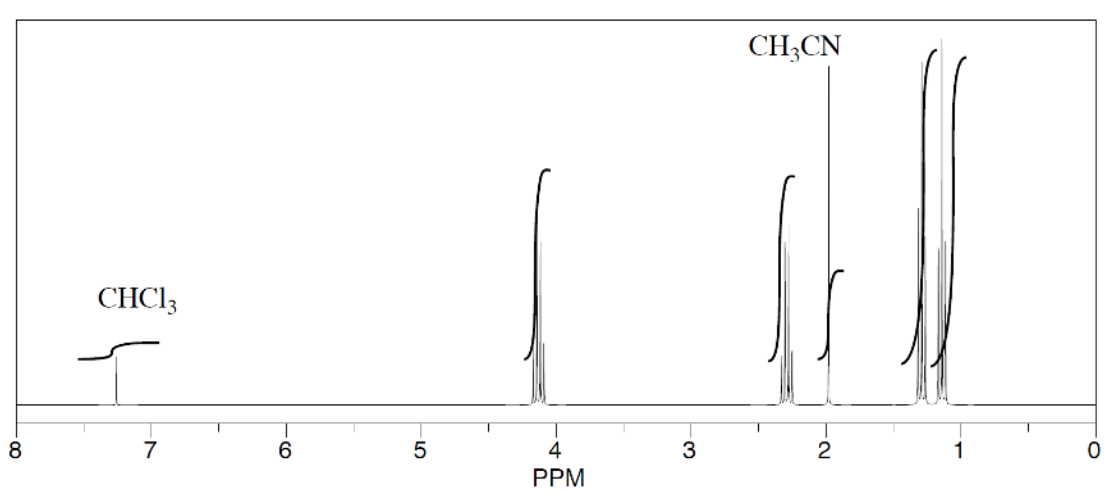
- Does the integration ratio really match the integral data? Or is this just wishful thinking?
- This table might reflect what he wants to see in the data. But what else could be in the data?
- $CHCl_3$ is often seen in NMR spectra if $CDCl_3$ is used for the NMR sample. It's there, at 7.2 ppm.
- "Leftover" or residual solvent is very common in real lab data. There it is, CH_2Cl_2 from the extraction, at 5.4 ppm.
- What about water? Sometimes people don't dry their solutions properly before evaporating the solvent. There is probably water around 1.5 to 1.6 ppm here.

This student might not get a very good grade; the sample does not even show up in the spectrum, so he lost it somewhere. But his analysis is also poor, so he will really get a terrible grade.

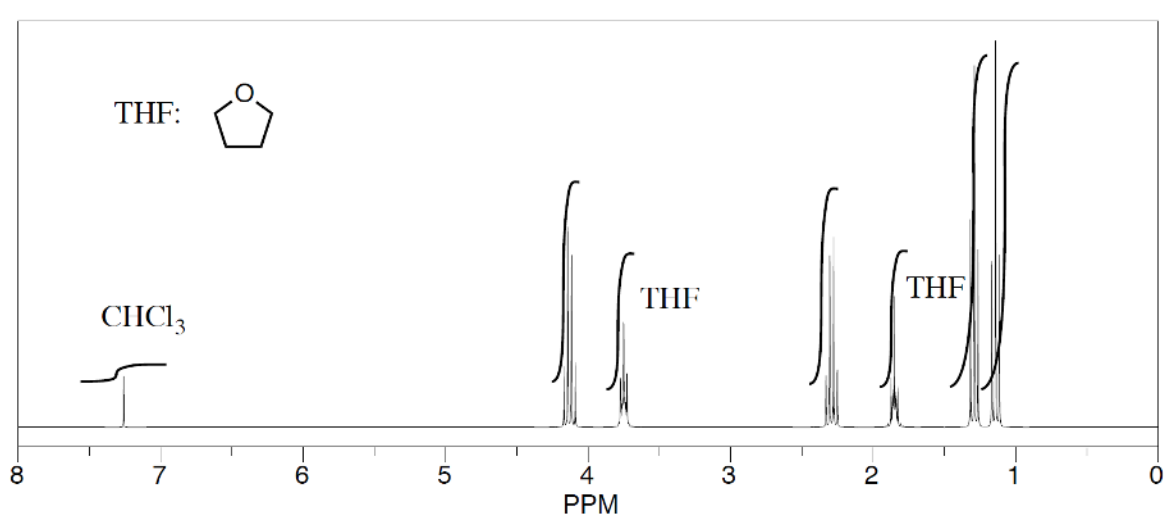
EXAMPLE 13.13.1

Three students performed a synthesis of a fragrant ester, ethyl propanoate, $CH_3CH_2CO_2CH_2CH_3$. During their reactions, they each used a different solvent. The students were able to see peaks in the NMR spectrum for ethyl propanoate, as well as peaks for chloroform ($CHCl_3$, in the $CDCl_3$ they used to make their NMR samples).

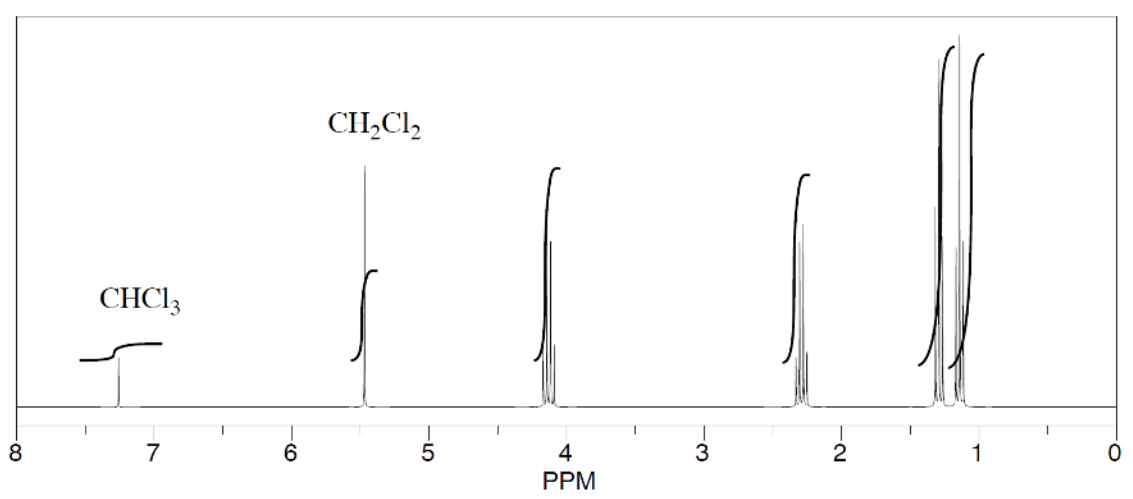
See the first student's spectrum:



See the second student's spectrum:



See the third student's spectrum:



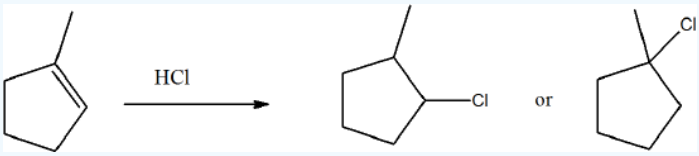
They were also able to determine that they had some leftover solvent in their samples by consulting a useful table of solvent impurities in NMR (which they found in Goldberg et. al., Organometallics 2010, 29, 2176-2179).

1. What is the ratio of leftover solvent to ethyl propanoate in each sample?
2. What is the percent of each sample that is leftover solvent

EXERCISE

? EXERCISE 13.13.1

How can H1 NMR determine products? For example, how can you tell the difference between the products of this reaction?



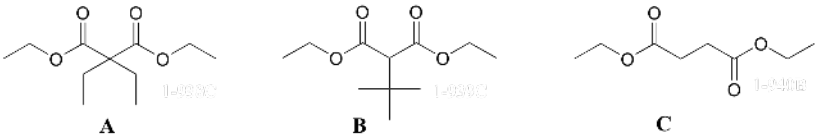
Answer

Yes, you are able to determine the difference in the spectra. For the 2-chloro compound will have multiple quartets while the 1-chloro compound will only have a quintet and a triplet for the signals in the ring.

ADDITIONAL NMR EXAMPLES

Match spectra 1-6 below to their corresponding structures A-F.

Structures:



Spectrum 1

δ	splitting	integration
4.13	q	2
2.45	t	2
1.94	quintet	1
1.27	t	3

Spectrum 2

δ	splitting	integration
3.68	s	3
2.99	t	2
1.95	quintet	1

Spectrum 3

δ	splitting	integration
4.14	q	1
2.62	s	1
1.26	t	1.5

Spectrum 4

δ	splitting	integration
4.14	q	4
3.22	s	1
1.27	t	6
1.13	s	9

Spectrum 5

δ	splitting	integration
4.18	q	1
1.92	q	1
1.23	t	1.5
0.81	t	1.5

Spectrum 6

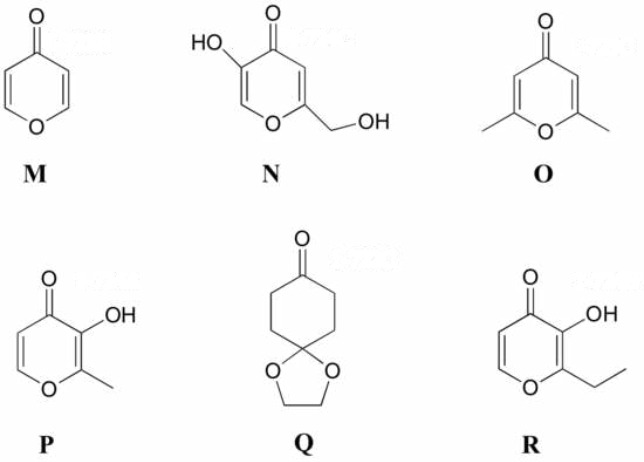
δ	splitting	integration
3.69	s	1.5
2.63	s	1

Solution:

Spectrum 1: structure D
Spectrum 2: structure F
Spectrum 3: structure C
Spectrum 4: structure B
Spectrum 5: structure A
Spectrum 6: structure E

Match the ^{1}H-NMR spectra 13-18 below to their corresponding structures M-R .

Structures:



Spectrum 13

δ	splitting	integration
8.15	d	1
6.33	d	1

Spectrum 14

δ	splitting	integration
6.05	s	1
2.24	s	3

Spectrum 15

δ	splitting	integration
8.57	s (b)	1
7.89	d	1
6.30	d	1
2.28	s	3

Spectrum 16

δ	splitting	integration
9.05	s (b)	1
8.03	s	1
6.34	s	1
5.68	s (b)	1
4.31	s	2

Spectrum 17

δ	splitting	integration
7.76	d	1
7.57	s (b)	1
6.44	d	1
2.78	q	2
1.25	t	3

Spectrum 18

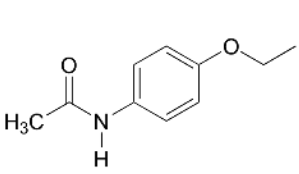
δ	splitting	integration
4.03	s	1
2.51	t	1
2.02	t	1

Solution:

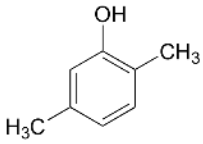
Spectrum 13: structure M
Spectrum 14: structure O
Spectrum 15: structure P
Spectrum 16: structure N
Spectrum 17: structure R
Spectrum 18: structure Q

Match the ^{1}H-NMR spectra 31-36 below to their corresponding structures GG-LL

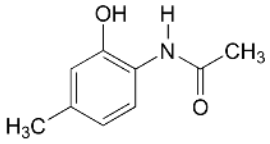
Structures:



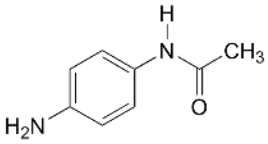
GG



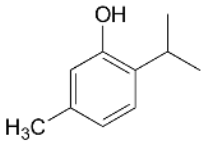
HH



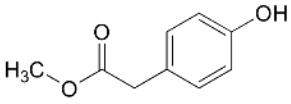
II



JJ



KK



LL

Spectrum 31

δ	splitting	integration
6.98	d	1
6.64	d	1
6.54	s	1
4.95	s	1
2.23	s	3
2.17	s	3

Spectrum 32

δ	splitting	integration
7.08	d	1
6.72	d	1
6.53	s	1
4.81	s	1
3.15	7-tet	1
2.24	s	3
1.22	d	6

Spectrum 33

δ	splitting	integration
7.08	d	2
6.71	d	2
6.54	s	1
3.69	s	3
3.54	s	2

Spectrum 34

δ	splitting	integration
9.63	s	1
7.45	d	2
6.77	d	2
3.95	q	2
2.05	s	3
1.33	t	3

Spectrum 35

δ	splitting	integration
9.49	s	1
7.20	d	2
6.49	d	2
4.82	s	2
1.963	s	3

Spectrum 36

δ	splitting	integration
9.58	s(b)	1
9.31	s	1
7.36	d	1
6.67	s	1
6.55	d	1
2.21	s	3
2.11	s	3

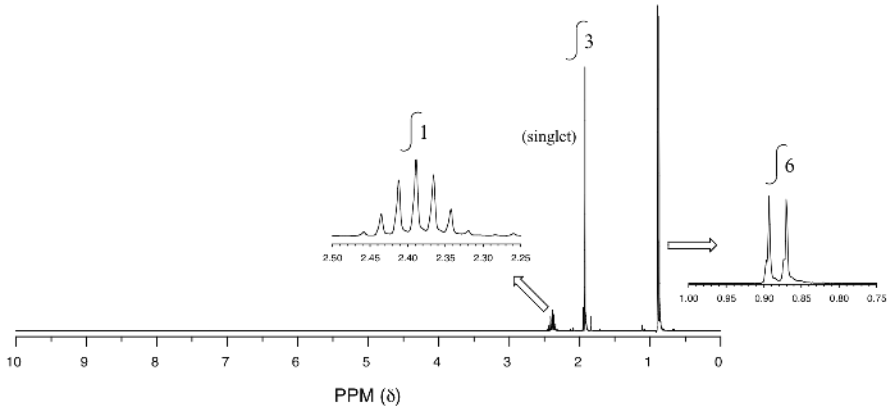
Solution:

Spectrum 31: structure HH
Spectrum 32: structure KK
Spectrum 33: structure LL
Spectrum 34: structure GG
Spectrum 35: structure JJ
Spectrum 36: structure II

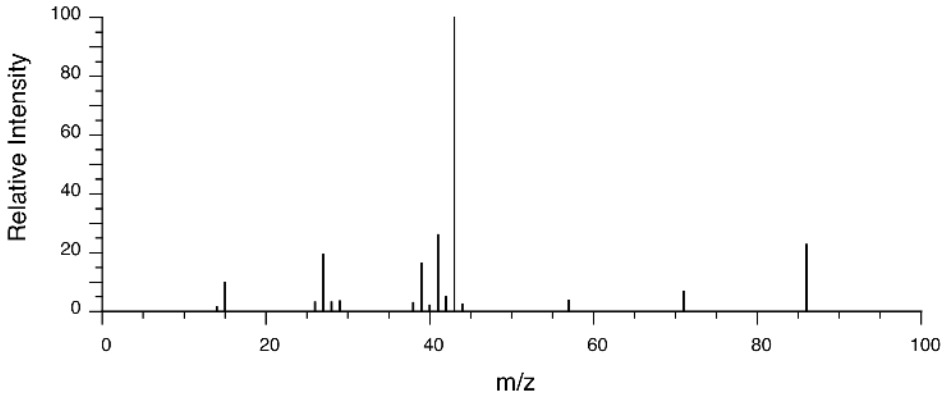
You obtain the following data for an unknown sample. Deduce its structure.

Combustion Analysis: C (69.7%); H (11.7%)

^{1}H-NMR:



Mass Spectrometry:



Solution: The structure is 3-methyl-2-butanone.

You take a ^{1}H-NMR spectrum of a sample that comes from a bottle of 1-bromopropane. However, you suspect that the bottle might be contaminated with 2-bromopropane. The NMR spectrum shows the following peaks:

δ	splitting	integration
4.3	septet	0.0735
3.4	triplet	0.661
1.9	sextet	0.665
1.7	doublet	0.441
1.0	triplet	1.00

How badly is the bottle contaminated? Specifically, what percent of the molecules in the bottle are 2-bromopropane?

Solution:

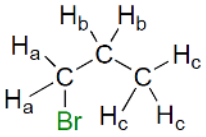
First, assign the peaks.

1-bromopropane: Ha is the triplet at 3.4 ppm, Hb is the sextet at 1.9 ppm, Hc is the triplet at 1.0 ppm.

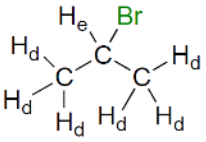
2-bromopropane: Hd is the doublet at 1.7 ppm, He is the septet at 4.3 ppm.

Now, just add up the integrations for each molecule and figure the percentage.
1-bromopropane: 0.661 + 0.665 + 1.00 = 2.326.
2-bromopropane: 0.0735 + 0.441 = 0.5145.
Percent 2-bromopropane is (0.5145)*100 / (0.5145 + 2.326) = 18.1%.

Notice that even if some peaks overlapped, you could still get this number as long as you could integrate one signal on each molecule: you could, for example, do the samecalculation (and get the same result) by comparing integrations of Hc and Hd signals, and just scale based on the fact that the Hc signal represents three protons while the Hd signal represents six protons.



H_c: 1.0 ppm (t)



H_d: 1.7 ppm (d)

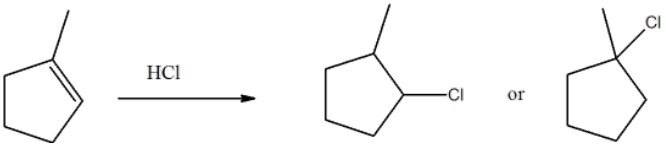
$$\text{integration: } \frac{1.00}{3 \text{ protons}} = 0.33 \qquad \text{integration: } \frac{0.441}{6 \text{ protons}} = 0.0735$$

$$\text{percent 2-bromopropane} = \left(\frac{0.0735}{0.0735 + 0.33}\right) \text{x } 100 = 18.2\ \%$$

QUESTIONS

Q13.13.1

How can H^1 NMR determine products? For example, how can you tell the difference between the products of this reaction?



SOLUTIONS

S13.13.1

Yes, you are able to determine the difference in the spectra. For the 2-chloro compound will have multiple quartets while the 1-chloro compound will only have a quintet and a triplet for the signals in the ring.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

13.13: Uses of ^{1}H NMR Spectroscopy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

13.S: STRUCTURE DETERMINATION - NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (SUMMARY)

CONCEPTS & VOCABULARY

13.1 Nuclear Magnetic Resonance Spectroscopy

- An applied magnetic field orients nuclei from random to aligned with or against the field. The nuclei absorb EM radiation of a frequency with energy that matches this energy gap.

13.2 The Nature of NMR Absorptions

- Nuclei in an applied field can align with the magnetic field (+1/2) or against the magnetic field (-1/2). The difference in the energy of these two states is the resonant frequency of that atom.
- To allow comparison between NMR spectra from instruments of differing field strength, the x-axis is reported as chemical shift, rather than frequency.
- **Chemical shift** is defined as the frequency of absorbance (in Hz) divided by the resonant frequency of the instrument (in MHz), thus the units are PPM (parts per million).
- Tetramethylsilane is used as a standard reference with its **chemical shift** set to 0 PPM (since these protons are highly shielded).
- Higher **chemical shifts** are called downfield, while lower shifts are called upfield.
- Nearby electrons shield the nuclei from the induced magnetic field, thus reducing their chemical shift. Atoms of higher electronegativity pull some of this electron density away from the nuclei causing increased **chemical shift**. This is called **deshielding**.

13.3 The Chemical Shift

- Pi electrons in a compound generate their own magnetic field that influences shielding of nearby atoms. This is most clearly exemplified by benzene protons that are highly unshielded (chemical shifts of 6.5-8 PPM).
- Protons that are involved in hydrogen bonding have variable chemical shifts and often do not absorb at one specific frequency, leading to broader peaks.

13.4 Chemical Shifts in ^{1}H NMR Spectroscopy

- Chemical shifts of protons are shifted upfield (higher ppm) by electronegative groups attached to the same carbon (and to a lesser effect when attached to nearby carbons).
- Aromatic protons appear between 6.5 and 8 ppm.
- Chemical shifts of O-H and N-H bonds vary with temperature and concentration.

13.5 Integration of ^{1}H NMR Absorptions - Proton Counting

- The are under a ^{1}H NMR signal is proportional to the number of hydrogens that caused the signal.

13.6 Spin-Spin Splitting in ^{1}H NMR Spectra

- ^{1}H signals are split into multiple peaks by neighboring H atoms whose spins can add to or subtract from the magnetic field.
- Spin-spin coupling yields n+1 peaks where n is the number of neighboring protons.
- Multiplets formed from spin-spin splitting follow specific symmetry based on the number of neighboring protons.
- The distance between peaks in a signal are called coupling constants.

13.7 ^{1}H NMR Spectroscopy and Proton Equivalence

- Equivalent protons (protons in identical electrical environments) only give 1 signal.
- To determine the number of ^{1}H NMR signals expected, symmetry of a molecule needs to be examined to find equivalent protons.
- Protons with different stereochemistry are not equivalent.
- Protons on chiral molecules that are diastereotopic (would create a diastereomer if replaced) are not equivalent.

13.8 More Complex Spin-Spin Splitting Patterns

- ^{1}H NMR signals can overlap making interpretation more difficult.
- Signals can distort where the peaks are not completely symmetrical in shape.
- When neighboring protons are nonequivalent, the coupling constant can be different leading to complex sets of peaks.
- Some complex multiplets can be identified such as a doublet of doublets, but others cannot and are referred to as multiplets.

13.9 Uses of ^{1}H NMR Spectroscopy

- ^{1}H NMR can help identify components of a mixture or determine which product was formed in a reaction.

SKILLS TO MASTER

- Skill 13.1 Interpretation of ^{1}H NMR Spectra.

MEMORIZATION TASKS (MT)

MT 13.1 Memorize chemical shifts patterns in ^{1}H NMR.

MT 13.2 Memorize spin-spin splitting patterns

CONTRIBUTORS

- Layne Morsch (University of Illinois Springfield)

13.S: Structure Determination - Nuclear Magnetic Resonance Spectroscopy (Summary) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

14: CONJUGATED COMPOUNDS AND ULTRAVIOLET SPECTROSCOPY

LEARNING OBJECTIVES

After you have completed Chapter 14, you should be able to

1. fulfill all of the detailed objectives listed under each individual section.
2. use the reactions discussed, along with those from previous chapters, when designing multi-step syntheses.
3. use the reactions and concepts discussed to solve road-map problems.
4. use ultraviolet-spectral data, in conjunction with other spectral data, to elucidate the structure of an unknown compound.
5. define, and use in context, the key terms introduced.

You have already studied the chemistry of compounds that contain one carbon-carbon double bond. In this chapter, you will focus your attention on compounds that contain two or more such bonds. In particular you will study the properties of those compounds that contain two carbon-carbon double bonds which are separated by one carbon-carbon single bond. These compounds are called “conjugated dienes.”

To understand the properties exhibited by conjugated dienes, you must first examine their bonding in terms of the molecular orbital theory introduced in Section 1.5. Then, you must learn how the products of a reaction are dependent on both thermodynamic and kinetic considerations. Which of these two factors is the most important can sometimes determine which of two possible products will predominate when a reaction is carried out under specific conditions. Although we shall not make extensive use of ultraviolet spectroscopy, this technique can often provide important information when conjugated compounds are being investigated. In general, ultraviolet spectroscopy is less useful than the other spectroscopic techniques introduced earlier.

14.0: Introduction
14.1: Stability of Conjugated Dienes- Molecular Orbital Theory
14.2: Electrophilic Additions to Conjugated Dienes- Allylic Carbocations
14.3: Kinetic vs. Thermodynamic Control of Reactions
14.4: The Diels-Alder Cycloaddition Reaction
14.5: Characteristics of the Diels-Alder Reaction
14.6: Diene Polymers- Natural and Synthetic Rubbers
14.7: Structure Determination in Conjugated Systems- Ultraviolet Spectroscopy
14.8: Interpreting Ultraviolet Spectra- The Effect of Conjugation
14.9: Conjugation, Color, and the Chemistry of Vision
14.S: Conjugated Compounds and Ultraviolet Spectroscopy (Summary)

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14.0: INTRODUCTION

Objective

After completing this section, you should be able to determine whether or not a molecule contains a conjugated system, given its Kekulé, condensed or shorthand formula.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

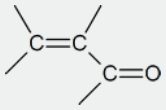
- conjugated diene
- conjugated double bonds
- diene
- enone
- polyene

STUDY NOTES

Conjugated double bonds are double bonds which are separated by one carbon-carbon single bond. Thus the double bonds in butadiene, $CH_2{=}CH{-}CH{=}CH_2$, are conjugated, and this compound is an example of a *conjugated diene*.

Just as the term *diene*indicates the presence of two carbon-carbon double bonds in a compound, so the term *polyene* is used to describe compounds containing many carbon-carbon double bonds.

An *enone* is a compound containing a carbon-carbon double bond (ene) and a carbonyl group (one). A conjugated enone contains the structural unit:



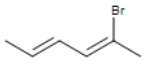
CONJUGATED **DIENES**

A diene is a hydrocarbon chain that has two double bonds that may or may not be adjacent to each other. This section focuses on the delocalization of pi systems by comparing two neighboring double bonds. The arrangements of these double bonds can have varying affects on the compounds reactivity and stability.

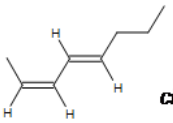
NAMING DIENES

First identify the longest chain containing both carbons with double bonds in the compound. Then give the lowest possible number for the location of the carbons with double bonds and any other functional groups present (remember when naming alkenes that some groups take priority such as alcohols). Do not forget stereochemistry or any other orientation of the double bond such as (E/Z,cis or trans).

Examples:



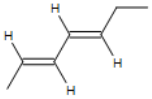
2-Bromo-2,4-hexadiene



cis-2-*trans*-4-octadiene



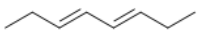
1,3-cyclopentadiene



trans-2,4-heptadiene

CONJUGATED VS. NONCONJUGATED VS. CUMULATED DIENES

Conjugated dienes are two double bonds separated by a single bond



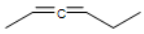
3,5-octadiene

Nonconjugated (Isolated) Dienes are two double bonds are separated by more than one single bond.



2,5-heptadiene

Cumulated Dienes are two double bond connected to a similar atom.



2,3-hexadiene

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Shravan Rao

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14.1: STABILITY OF CONJUGATED DIENES- MOLECULAR ORBITAL THEORY

Objectives

After completing this section, you should be able to

1. write a reaction sequence to show a convenient method for preparing a given conjugated diene from an alkene, allyl halide, alkyl dihalide or alcohol (diol).
2. identify the reagents needed to prepare a given diene from one of the starting materials listed in Objective 1, above.
3. compare the stabilities of conjugated and nonconjugated dienes, using evidence obtained from hydrogenation experiments.
4. discuss the bonding in a conjugated diene, such as 1,3-butadiene, in terms of the hybridization of the carbon atoms involved.
5. discuss the bonding in 1,3-butadiene in terms of the molecular orbital theory, and draw a molecular orbital for this and similar compounds.

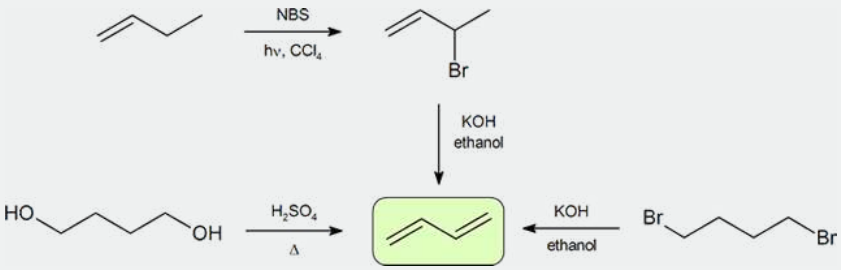
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- delocalized electrons
- node

STUDY NOTES

The two most frequent ways to synthesize conjugated dienes are dehydration of alcohols and dehydrohalogenation of organohalides, which were introduced in the preparation of alkenes (Section 8.1). The following scheme illustrates some of the routes to preparing a conjugated diene.



The formation of synthetic polymers from dienes such as 1,3-butadiene and isoprene is discussed in Section 14.6. Synthetic polymers are large molecules made up of smaller repeating units. You are probably somewhat familiar with a number of these polymers; for example, polyethylene, polypropylene, polystyrene and poly(vinyl chloride).

As the hydrogenation of 1,3-butadiene releases less than the predicted amount of energy, the energy content of 1,3-butadiene must be lower than we might have expected. In other words, 1,3-butadiene is more stable than its formula suggests.

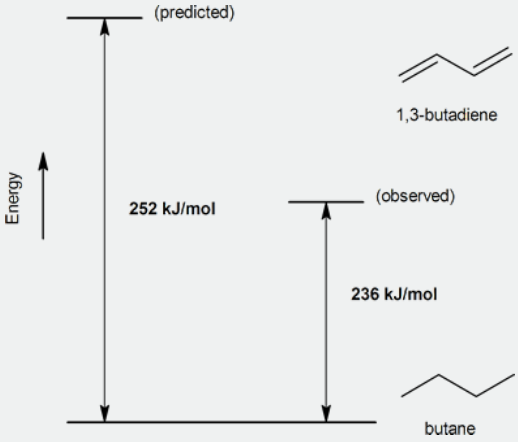
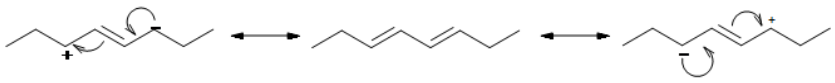


Figure 14.1: Energy diagram for the hydrogenation of 1,3-butadiene (not to scale).

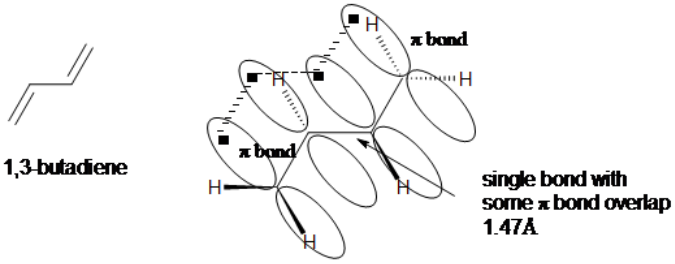
Some university-level general chemistry courses do not introduce the subject of molecular orbitals. If you have taken such a course, or forgotten what is meant by the term “molecular orbital,” combine a review of Section 1.11 with your study of this section.

Conjugated dienes are more stable than non conjugated dienes (both isolated and cumulated) due to factors such as delocalization of charge through resonance and hybridization energy. This can also explain why allylic radicals are much more stable than secondary or even tertiary carbocations. This is all due to the positioning of the pi orbitals and ability for overlap to occur to strengthen the single bond between the two double bonds.

The resonance structure shown below gives a good understanding of how the charge is delocalized across the four carbons in this conjugated diene. This delocalization of charges stablizes the conjugated diene:

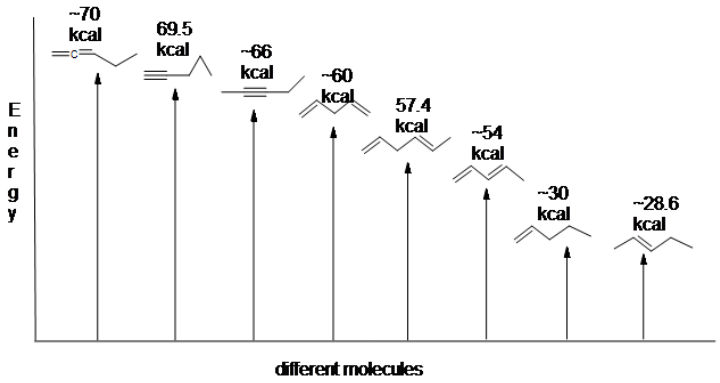


Along with resonance, hybridization energy effect the stability of the compound. For example in 1,3-butadiene the carbons with the single bond are sp2 hybridized unlike in nonconjugated dienes where the carbons with single bonds are sp3 hybridized. This difference in hybridization shows that the conjugated dienes have more 's' character and draw in more of the pi electrons, thus making the single bond stronger and shorter than an ordinary alkane C-C bond (1.54Å).



Another useful resource to consider are the heats of hydrogenation of different arrangements of double bonds. Since the higher the heat of hydrogenation the less stable the compound, it is shown below that conjugated dienes (~54 kcal) have a lower heat of hydrogenation than their isolated (~60 kcal) and cumulated diene (~70 kcal) counterparts.

Here is an energy diagram comparing different types of bonds with their heats of hydrogenation to show relative stability of each molecule:

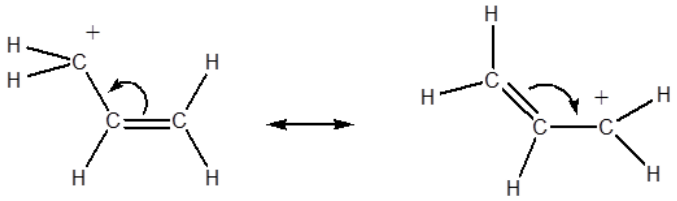


The stabilization of dienes by conjugation is less dramatic than the aromatic stabilization of benzene. Nevertheless, similar resonance and molecular orbital descriptions of conjugation may be written.

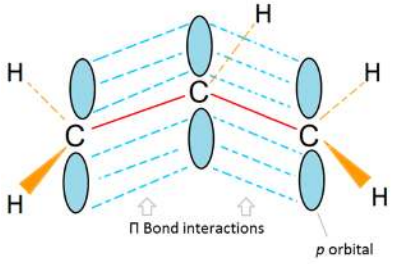
ALLYLIC CARBOCATION

Conjugation occurs when p orbital on three or more adjacent atoms can overlap Conjugation tends to stabilize molecules

Allylic carbocations are a common conjugated system.



The positive charge of a carbocation is contained in a P orbital of a sp^2 hybrizied carbon. This allows for overlap with double bonds. The positive charge is more stable because it is spread over 2 carbons.



MOLECULAR ORBITALS OF AN ALLYLIC CARBOCATION

The stability of the carbocation of propene is due to a conjugated π electron system. A "double bond" doesn't really exist. Instead, it is a group of 3 adjacent, overlapping, non-hybridized *p* orbitals we call a **conjugated π electron system**. You can clearly see the interactions between all three of the *p* orbitals from the three carbons resulting in a really stable cation. It all comes down to where the location of the electron-deficient carbon is.

Molecular orbital descriptions can explain allylic stability in yet another way using 2-propenyl. Fig.6

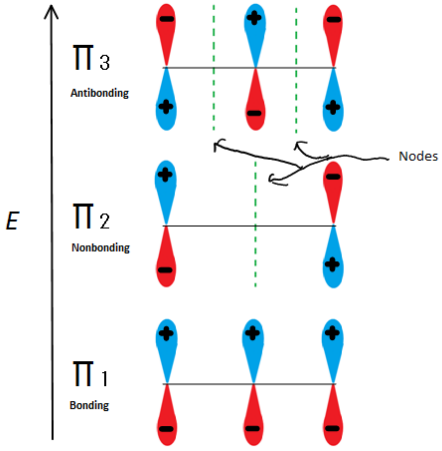


Fig.6 Shows the 3 possible Molecular orbitals of 2-propenyl

If we just take the π molecular orbital and not any of the s, we get three of them. π_1 is bonding with no nodes, π_2 is nonbonding (In other words, the same energy as a regular *p*-orbital) with a node, and π_3 is antibonding with 2 nodes (none of the orbitals are interacting). The first two electrons will go into the π_1 molecular orbital, regardless of whether it is a cation, radical, or anion. If it is a radical or anion, the next electron goes into the π_2 molecular orbital. The last anion electron goes into the nonbonding orbital also. So no matter what kind of carbon center exists, no electron will ever go into the antibonding orbital.

The Bonding orbitals are the lowest energy orbitals and are favorable, which is why they are filled first. Even though the nonbonding orbitals can be filled, the overall energy of the system is still lower and more stable due to the filled bonding molecular orbitals.

This figure also shows that π_2 is the only molecular orbital where the electron differs, and it is also where a single node passes through the middle. Because of this, the charges of the molecule are mainly on the two terminal carbons and not the middle carbon.

This molecular orbital description can also illustrate the stability of allylic carbon centers in figure 7.

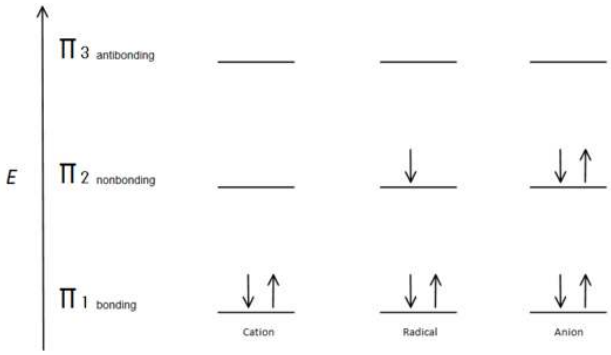
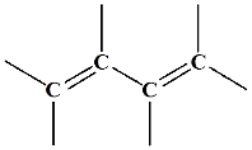


Fig. 7: *diagram showing how the electrons fill based on the Aufbau principle.*

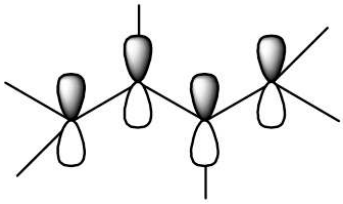
The π bonding orbital is lower in energy than the nonbonding *p* orbital. Since every carbon center shown has two electrons in the lower energy, bonding π orbitals, the energy of each system is lowered overall (and thus more stable), regardless of cation, radical, or anion.

1,3-DIENES

Conjugated double bonds are separated by a single bond. 1,3-dienes are an excellent example of a conjugated system. Each carbon in 1,3 dienes are sp^2 hybridized and therefore have one *p* orbital. The four *p* orbitals in 1,3-butadiene overlap to form a conjugated system.

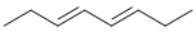


1,3-Diene



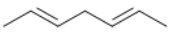
CONJUGATED VS. NONCONJUGATED DIENES

Conjugated dienes are two double bonds separated by a single bond



3,5-octadiene

Nonconjugated (Isolated) Dienes are two double bonds are separated by more than one single bond.



2,5-heptadiene

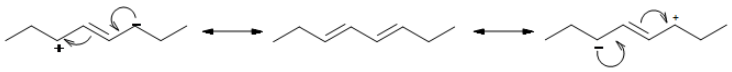
When using electrostatic potential maps, it is observed that the pi electron density overlap is closer together and delocalized in conjugated dienes, while in non conjugated dienes the pi electron density is located differently across the molecule. Since having more electron density delocalized makes the molecule more stable conjugated dienes are more stable than non conjugated

For example in 1,3-butadiene the carbons with the single bond are sp2 hybridized unlike in nonconjugated dienes where the carbons with single bonds are sp3 hybridized. This difference in hybridization shows that the conjugated dienes have more 's' character and draw in more of the pi electrons, thus making the single bond stronger and shorter than an ordinary alkane C-C bond (1.54Å).

STABILITY OF CONJUGATED DIENES

Conjugated dienes are more stable than non conjugated dienes (both isolated and cumulated) due to factors such as delocalization of charge through resonance and hybridization energy. This can also explain why allylic radicals are much more stable than secondary or even tertiary carbocations. This is all due to the positioning of the pi orbitals and ability for overlap to occur to strengthen the single bond between the two double bonds.

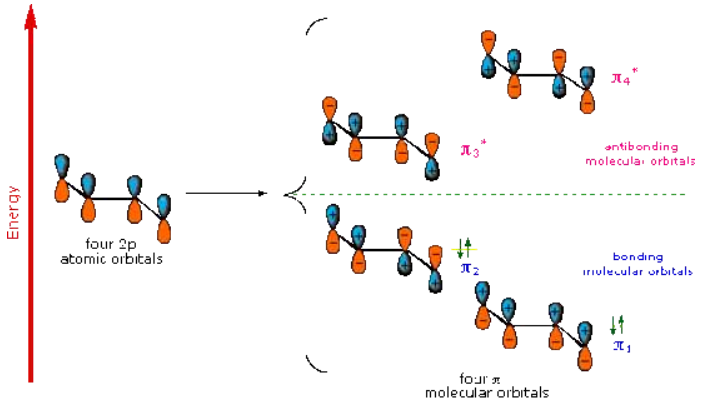
The resonance structure shown below gives a good understanding of how the charge is delocalized across the four carbons in this conjugated diene. This delocalization of charges stabilizes the conjugated diene:



Along with resonance, hybridization energy effect the stability of the compound. For example in 1,3-butadiene the carbons with the single bond are sp2 hybridized unlike in nonconjugated dienes where the carbons with single bonds are sp3 hybridized. This difference in hybridization shows that the conjugated dienes have more 's' character and draw in more of the pi electrons, thus making the single bond stronger and shorter than an ordinary alkane C-C bond (1.54Å).

MOLECULAR ORBITALS OF 1,3 DIENES

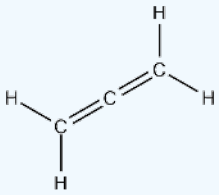
A molecular orbital model for 1,3-butadiene is shown below. Note that the lobes of the four p-orbital components in each pi-orbital are colored differently and carry a plus or minus sign. This distinction refers to different phases, defined by the mathematical wave equations for such orbitals. Regions in which adjacent orbital lobes undergo a phase change are called **nodes**. Orbital electron density is zero in such regions. Thus a single p-orbital has a node at the nucleus, and all the pi-orbitals shown here have a nodal plane that is defined by the atoms of the diene. This is the only nodal surface in the lowest energy pi-orbital, π_1. Higher energy pi-orbitals have an increasing number of nodes.



EXERCISE

? EXERCISE 14.1.1

The heat of hydrogenation for allene is about 300 kJ/mol. Order a conjugated diene, a non-conjugated diene, and allene in increasing stability.



Allene

Answer

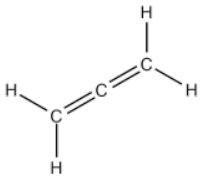
allene < non-conjugated diene < conjugated diene (most stable)

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QUESTIONS

Q14.1.1

The heat of hydrogenation for allene is about 300 kJ/mol. Order a conjugated diene, a non-conjugated diene, and allene in increasing stability.



Allene

SOLUTIONS

S14.1.1

allene < non-conjugated diene < conjugated diene (most stable)

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

14.1: Stability of Conjugated Dienes- Molecular Orbital Theory is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

14.2: ELECTROPHILIC ADDITIONS TO CONJUGATED DIENES- ALLYLIC CARBOCATIONS

Objectives

After completing this section, you should be able to

1. write an equation for the addition of one or two mole equivalents of a halogen or a hydrogen halide to a nonconjugated diene.
2. write an equation for the addition of one or two mole equivalents of a halogen or a hydrogen halide to a conjugated diene.
3. write the mechanism for the addition of one mole equivalent of hydrogen halide to a conjugated diene, and hence account for the formation of 1,2- and 1,4-addition products.
4. explain the stability of allylic carbocations in terms of resonance.
5. draw the resonance contributors for a given allylic carbocation.
6. predict the products formed from the reaction of a given conjugated diene with one mole equivalent of halogen or hydrogen halide.
7. predict which of the possible 1,2- and 1,4-addition products is likely to predominate when one mole equivalent of a hydrogen halide is reacted with a given conjugated diene.
8. use the concept of carbocation stability to explain the ratio of the products obtained when a given conjugated diene is reacted with one mole equivalent of hydrogen halide.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

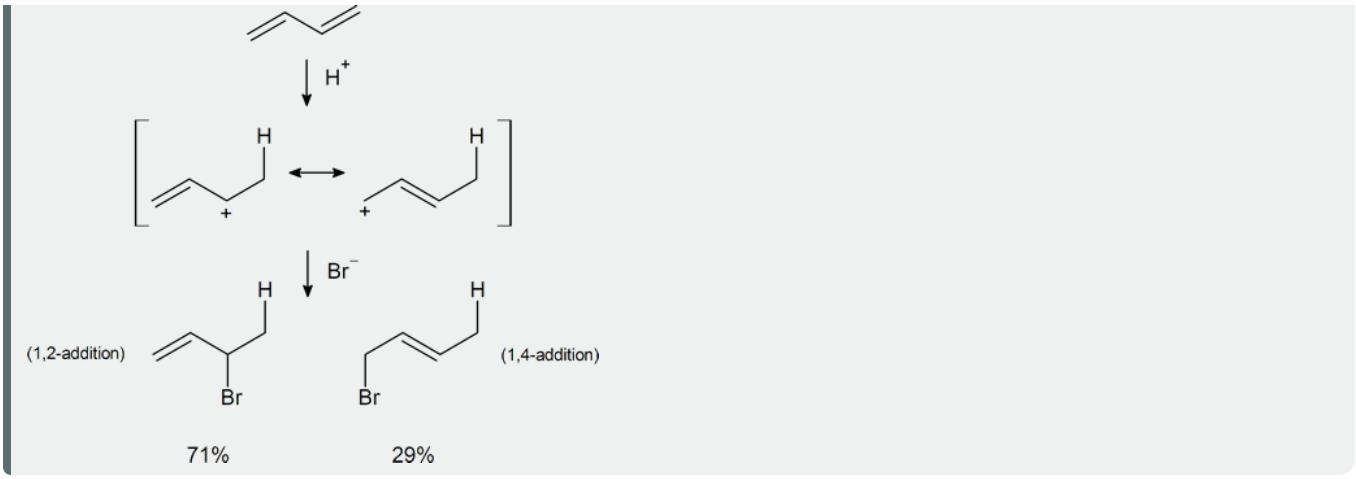
- 1,2-addition
- 1,4-addition

STUDY NOTES

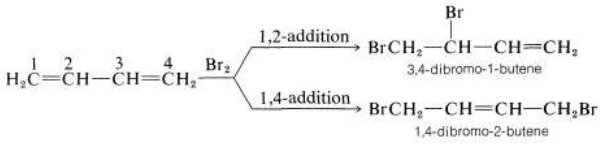
Notice that the numbers used in the expressions 1,2-addition and 1,4-addition do *not* refer to the positions of the carbon atoms in the diene molecule. Here, 1,2 indicates two neighbouring carbon atoms, while 1,4 indicates two carbon atoms which are separated in the carbon chain by two additional carbon atoms. Thus in 1,2- and 1,4-additions to 2,4-hexadiene, the additions actually occur at carbons 2 and 3, and 2 and 5, respectively.

The term “monoadduct” should be interpreted as meaning the product or products formed when one mole of reagent adds to one mole of substrate. In the objectives above, this process is referred to as the addition of one mole equivalent (or one mol equiv).

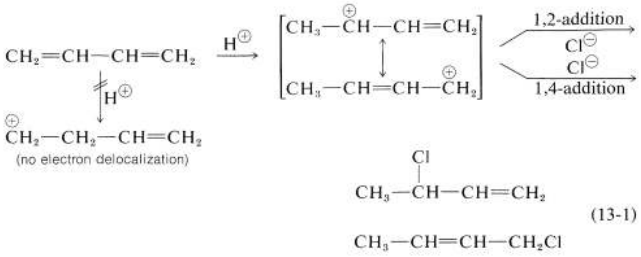
In Section 7.9 we saw that electrophilic addition to a simple alkene would follow Markovnikov’s rule, where the stability of the carbocation intermediate would increase: primary < secondary < tertiary. With conjugated dienes the allylic carbocation intermediately generated has different resonance forms. The following scheme represents the mechanism for the addition of HBr to 1,3-butadiene (at 0°C). Note the resonance contributors for the allylic carbocation intermediate and that the product resulting from the secondary cation is generated in higher yield than from the primary cation as you might expect from our discussions until now. However, in the next section you will see that the resulting product ratio can be drastically affected by a number of reaction conditions, including temperature.



The reactions of 1,3-butadiene are reasonably typical of conjugated dienes. The compound undergoes the usual reactions of alkenes, such as catalytic hydrogenation or radical and polar additions, but it does so *more readily* than most alkenes or dienes that have isolated double bonds. Furthermore, the products frequently are those of 1,2 *and* **1,4 addition:**



Formation of both 1,2- and 1,4-addition products occurs not only with halogens, but also with other electrophiles such as the hydrogen halides. The mechanistic course of the reaction of 1,3-butadiene with hydrogen chloride is shown in Equation 13-1. The first step, as with alkenes, is formation of a carbocation. However, with 1,3-butadiene, if the proton is added to C_1 (but not C_2), the resulting cation has a substantial delocalization energy, with the charge distributed over two carbons (review Sections 6-5 and 6-5C if this is not clear to you). Attack of $Cl^{\ominus}$ as a nucleophile at one or the other of the positive carbons yields the 1,2- or the 1,4- addition product:



An important feature of reactions in which 1,2 and 1,4 additions occur in competition with one another is that the ratio of the products can depend on the temperature, the solvent, and also on the *total time of reaction*.

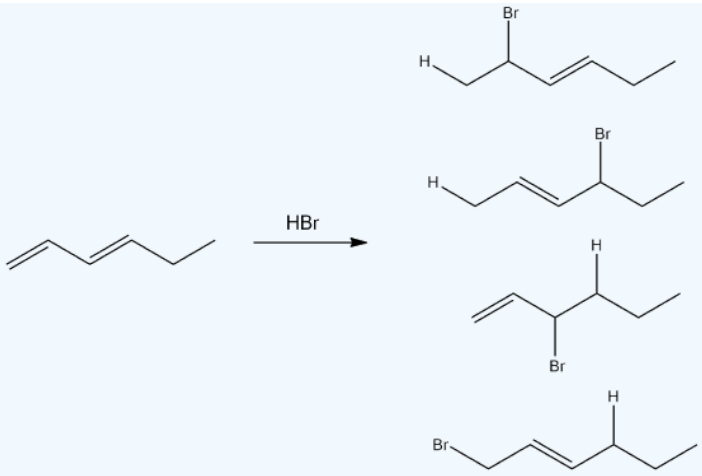
EXERCISE

? EXERCISE 14.2.1

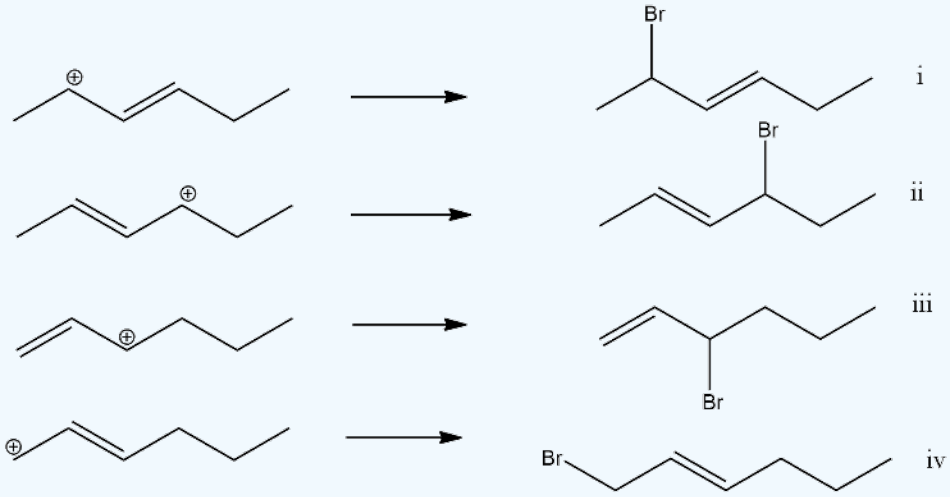
1. Give the 1,2 and the 1,4 products of the addition of one equivalent of HBr to 1,3-hexa-diene.
2. Look at the previous addition reaction of HBr with a diene. Consider the transition states, predict which of them would be the major products and which will be the minor.
3. Write out the products of 1,2 addition and 1,4- addition of HBr to 1,3-cyclohexadiene.
4. What is unusual about the products of 1,2- and 1,4- addition of HX to an unsubstituted cyclic 1,3-diene?
5. Write out the products of 1,2 addition and 1,4- addition of Br2 to 1,3-cyclohexadiene.

Answer

1)



2) The products i-iii all show a secondary cation intermediate which is more stable than primary. Therefore those would be major products and the iv product would be the minor product.

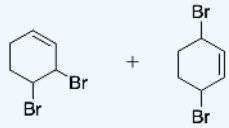


3) The same product will result from 1,2 and 1,4 addition.



4) Addition of the HX to unsubstituted cycloalka-1,3-dienes in either 1,2- or 1,4- manner gives the same product because of symmetry.

5) Both 1,2 and 1,4 products will form.



QUESTIONS

Q14.2.1

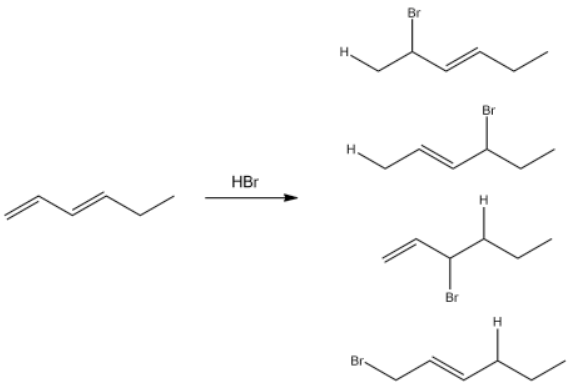
Give the 1,2 and the 1,4 products of the addition of one equivalent of HBr to 1,3-hexa-diene.

Q14.2.2

Look at the previous addition reaction of HBr with a diene. Consider the transition states, predict which of them would be the major products and which will be the minor.

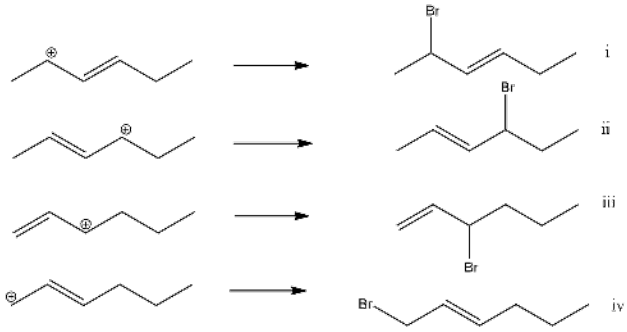
SOLUTIONS

S14.2.1



S14.2.2

The products i-iii all show a secondary cation intermediate which is more stable than primary. Therefore those would be major products and the iv product would be the minor product.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

14.2: Electrophilic Additions to Conjugated Dienes- Allylic Carbocations is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

14.3: KINETIC VS. THERMODYNAMIC CONTROL OF REACTIONS

Objectives

After completing this section, you should be able to

1. explain the difference between thermodynamic and kinetic control of a chemical reaction; for example, the reaction of a conjugated diene with one equivalent of hydrogen halide.
2. draw a reaction energy diagram for a reaction which can result in both a thermodynamically controlled product and a kinetically controlled product.
3. explain how reaction conditions can determine the product ratio in a reaction in which there is competition between thermodynamic and kinetic control.

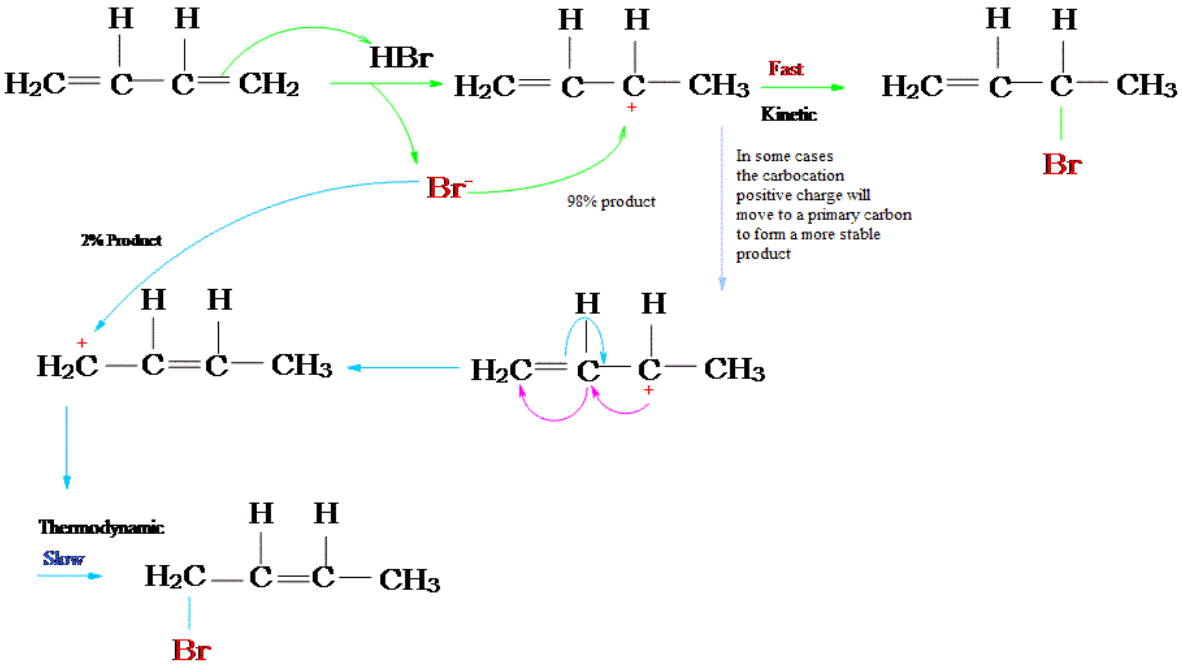
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- kinetic control
- thermodynamic control

Like nonconjugated dienes, conjugated dienes are subject to attack by electrophiles. In fact, conjugated electrophiles experience relatively greater kinetic reactivity when reacted with electrophiles than nonconjugated dienes do. Upon electrophilic addition, the conjugated diene forms a mixture of two products—the kinetic product and the thermodynamic product—whose ratio is determined by the conditions of reaction. A reaction yielding more thermodynamic product is under thermodynamic control, and likewise, a reaction that yields more kinetic product is under kinetic control.

The reaction of one equivalent of hydrogen bromide with 1,3-butadiene gives different products at under different conditions and is a classic example of the concept of *thermodynamic* versus *kinetic* control of a reaction



Take a look at this energy profile diagram in Figure **14.3.1**. In this scenario, the starting material **A** can react to form either **B** (to the left) or **C** (to the right). The formation of the product **B** involves overcoming barriers with *lower* *activation energies*, which means that it will form faster (ignoring the pre-exponential constant effects).

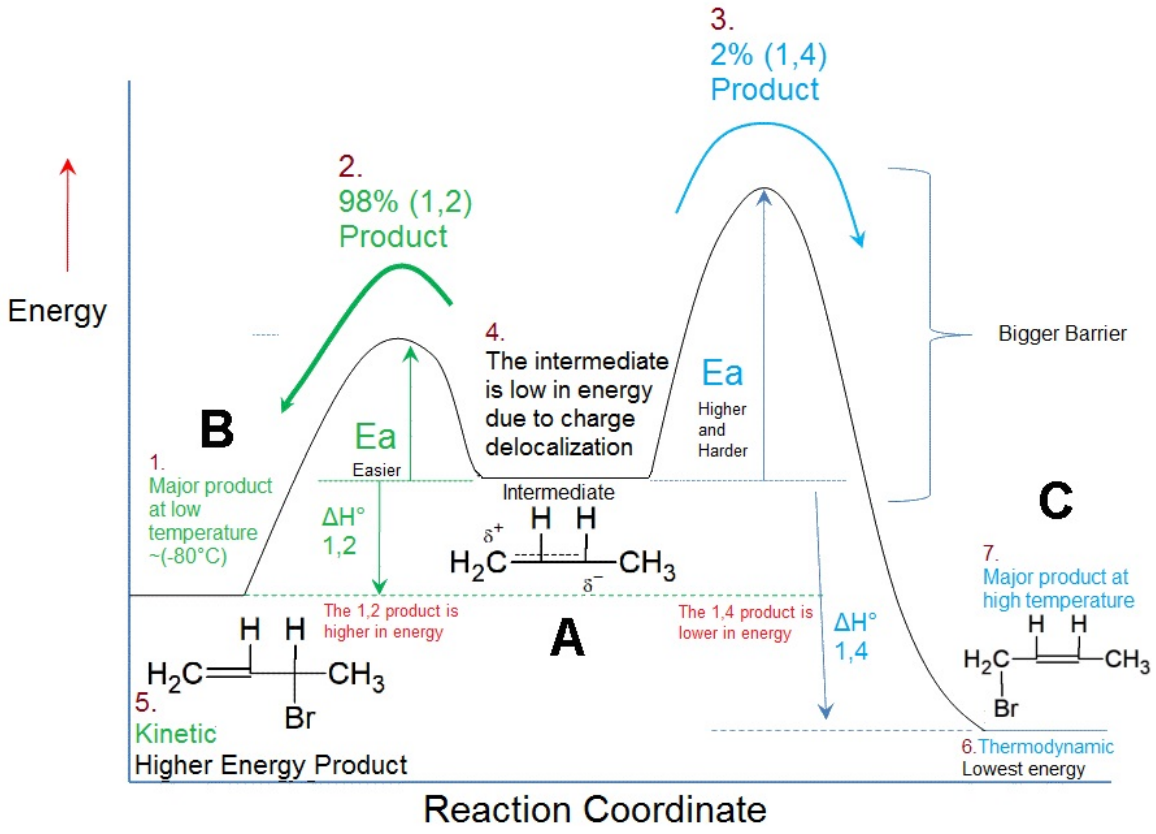


Figure* 14.3.1*: *Energy profile diagram for A → B (left) and A → C (right). The horizontal axis is a reaction coordinate, and the vertical axis represents Gibbs energy. The delocalized carbocation intermediate (A) is the protonated form of 1,3-butadiene (first step of the reaction of 1,3-butadiene with HBr).*

If we keep the temperature sufficiently *low*, the molecules of **B**, which are inevitably formed faster, will probably not have enough energy to overcome the reverse activation barrier (i.e., **B** → **A**) to regenerate **A** (Table **14.3.1**). The forward reactions **A** ⟶ **B** and **A** ⟶ **C** are, under such conditions, effectively irreversible. Since the formation of **B** is faster, it will predominate, and the major product formed will be **B**. This is known as *kinetic control* and **B** is the *kinetic product*.

At elevated temperatures, **B** is still going to be the product that is formed *faster*. However, it also means that all the reactions will be reversible. This means that molecules of **B** can revert back to **A**. Since the system is no longer limited by temperature, the system will minimize its Gibbs free energy, which is the thermodynamic criterion for chemical equilibrium. This means that, as the most thermodynamically stable molecule, **C** will be predominantly formed.[2] The reaction is said to be under *thermodynamic control* and **C** is the *thermodynamic product*.

Table **14.3.1**: Conjugated Dienese: Kinetic vs. Thermodynamic Conditions

Temperature	Kinetic or Thermodynamically Controlled	Speed of Reaction	1,2-adduct (B) : 1,4-adduct (C) Ratio
-15 °C	Kinetic	Fast	70:30
0 °C	Kinetic	Fast	60:40
40 °C	Thermodynamic	Slow	15:85
60 °C	Thermodynamic	Slow	10:90

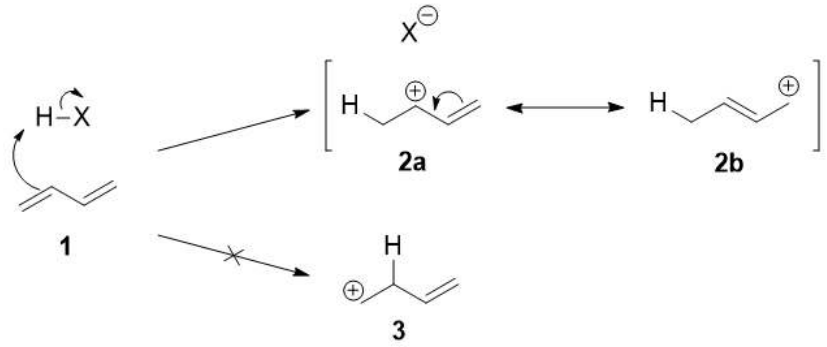
> *A simple definition is that the kinetic product is the product that is formed faster, and the thermodynamic product is the product that is more stable. This is precisely what is happening here. The kinetic product is 3-bromobut-1-ene, and the thermodynamic product is 1-bromobut-2-ene (specifically, the trans isomer).*

A WARNING: NOT EVERY REACTION HAS DIFFERENT THERMODYNAMIC AND KINETIC PRODUCTS!

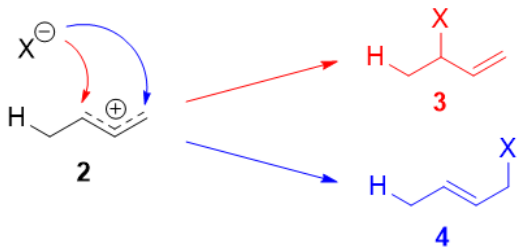
Note that not every reaction has an energy profile diagram like Figure **14.3.1**, and not every reaction has different thermodynamic and kinetic products! If the transition states leading to the formation of **B** were to be higher in energy than that leading to **C**, then **C** would simultaneously be both the thermodynamic and kinetic product. There are plenty of reactions in which the more stable product (*thermodynamic*) is also formed faster (*kinetic*).

THE REACTION MECHANISM

The first step is the protonation of one of the **C=C** double bonds. In butadiene (**1**), both double bonds are the same, so it does not matter which one is protonated. The protonation occurs regioselectively to give the more stable carbocation (i.e., I_B=I_C in Figure **14.3.1**1):



The more stable cation is not only secondary, but also *allylic*, and therefore enjoys stabilization via resonance (or conjugation). This is depicted in the resonance forms **2a** and **2b** above. This allylic carbocation, more properly denoted as the resonance hybrid **2**, has two carbons which have significant positive charge, and the bromide ion (here denoted as **X⁻**) can attack either carbon. Attacking the central carbon, adjacent to the site of protonation, leads to the kinetic product **3** (called the 1,2-adduct); attacking the terminal carbon, distant from the site of protonation, leads to the thermodynamic product **4** (called the 1,4-adduct).



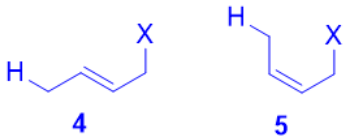
A COMMON MISTAKE: RESONANCE STRUCTURES DO NOT INDEPENDENTLY EXIST

There are some people who write that **3** results from attack of **X⁻** on resonance form **2a**, and **4** from attack of **X⁻** on resonance form **2b**. ***This is not correct!*** Resonance forms do not separately exist, and they are not distinct species that rapidly interconvert. As such, one cannot speak of *one single resonance form* undergoing a reaction.

Now, why **4** is the thermodynamic product, and why **3** is the kinetic product for this reaction?

THE THERMODYNAMIC PRODUCT: *TRANS*-1-BROMOBUT-2-ENE

It is perhaps simple enough to see why **4** is more stable than **3**. It has an internal, disubstituted double bond, and we know that as a general rule of thumb, the thermodynamic stability of an alkene increases with increasing substitution. So, compared to the terminal, monosubstituted alkene **3**, **4** is more stable.



Both the *trans* isomer **4** as well as the *cis* isomer **5** can be formed via attack of the nucleophile at the terminal carbon, and both are disubstituted alkenes. However, the *trans* isomer **4** is more stable than the *cis* isomer **5**, because there is less steric repulsion between the two substituents on the double bond. As such, **4** is the thermodynamic product.

THE KINETIC PRODUCT: 3-BROMOBUT-1-ENE

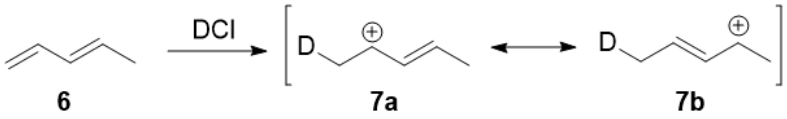
Several explanations may be proposed to explain the nature of the kinetic product.

The worst possible argument argues that the resonance form **2a**, being an allylic *secondary* carbocation, is more stable than resonance form **2b**, which is an allylic *primary* carbocation. Therefore, resonance form **2a** exists in greater relative proportion (i.e., more molecules will look like **2a** than **2b**), and the nucleophile preferentially reacts with this specific carbocation, leading to the formation of **3**. However, this is incorrect, since individual resonance forms do not exist. Moreover, such an argument suggests that we are looking for the more stable *intermediate* (I_B or I_C in Figure **14.3.1**). In fact, we should be looking for the more stable *transition states* (T_{B1}, T_{B2}, T_{C1}, *and* T_{C2} in Figure **14.3.1**). The carbocation is an *intermediate*, and not a *transition state*.

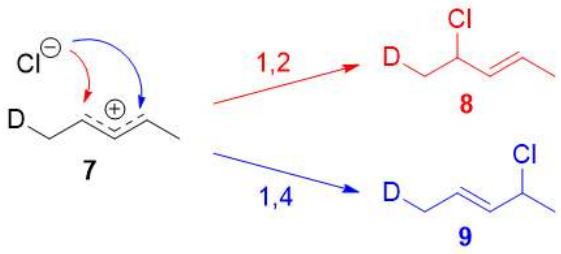
The most common argument is since resonance form **2a** is more stable than **2b**, is that it contributes more towards the *resonance hybrid* **2**. As such, the positive charge on the internal carbon is greater than the positive charge on the terminal carbon. The nucleophile, being negatively charged, is more strongly attracted to the more positively charged or more electrophilic carbon, and therefore attack there occurs faster (the transition state being stabilized by greater electrostatic interactions). That's actually a very sensible explanation; with only the data that has been presented so far, we would not be able to disprove it, and it was indeed the accepted answer for quite a while.

EXPERIMENTAL RESULTS

In 1979, Nordlander *et al.* carried out a similar investigation on the addition of \(\ce{DCl}\) to a different substrate, 1,3-pentadiene.[7] This experiment was ingenious, because it was designed to proceed via an almost symmetrical intermediate:



Resonance forms **7a** and **7b** are both allylic and secondary. There is a very minor difference in their stabilities arising from the different hyperconjugative ability of **C–D** *vs* **C–H** bonds, but in any case, it is not very large. Therefore, if we adopt the explanation in the previous section, one would expect there not to be any major *kinetic* pathway, and both 1,2- and 1,4-addition products (**8** and **9**) would theoretically be formed roughly equally.



Instead, it was found that the 1,2-addition product was favored over the 1,4-addition product. For example, at **–78 °C** in the absence of solvent, there was a roughly **75 : 25** ratio of 1,2- to 1,4-addition products. Clearly, there is a factor that favors 1,2-addition that does not depend on the electrophilicity of the carbon being attacked! The authors attributed this effect to an *ion pair* mechanism. This means that, after the double bond is protonated (deuterated in this case), the chloride counterion remains in close proximity to the carbocation generated. Immediately following dissociation of **DCl**, the chloride ion is going to be much closer to **C-2** than it is to **C-4**, and therefore attack at **C-2** is much faster. In fact, normal electrophilic addition of **HX** to conjugated alkenes in polar solvents can also proceed via similar ion pair mechanisms. This is reflected by the greater proportion of *syn* addition products to such substrates.[11]

> *The mechanism that favors 1,2-addition clearly does not depend on the electrophilicity of the carbon being attacked.*

This ion pair mechanism is a pre-exponential constant effects that is attributed to the proximity and frequency of collision rather than a activation barrier effect.

CONCLUSION

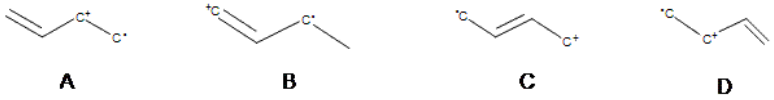
The reactivity of conjugated dienes (hydrocarbons that contain two double bonds) varies depending on the location of double bonds and temperature of the reaction.These reactions can produce both thermodynamic and kinetic products. Isolated double bonds provide dienes with less stability thermodynamically than conjugated dienes. However, they are more reactive kinetically in the presence of electrophiles and other reagents. This is a result of Markovnikov addition to one of the double bonds. A carbocation is formed after a double bond is opened. This carbocation has two resonance structures and addition can occur at either of the positive carbons.

REFERENCES

1. Smith, M. B. *March's Advanced Organic Chemistry*, 7th ed., p 272
2. This does not mean that *all* of **A** will be converted to **B**; the reaction is still an *equilibrium*, and equilibria always go forward and backward. In general, the minimum system Gibbs free energy (G_{syst}) will occur at a certain proportion of **A**, **B**, and **C**. However, since **B** has the lowest Gibbs free energy, it will be formed in a greater proportion than **C**.
3. http://www.ochempal.org/index.php/alphabetical/a-b/14-addition/
4. *J. Am. Chem. Soc.* **1979,** *101* (5), 1288–1289
5. Because of the larger reduced mass and lower zero-point energy, a $\ce{C-D}$ bond is stronger and therefore less willing to donate electron density into an adjacent empty p orbital. This is the origin of some secondary kinetic isotope effects; in our case, it means that **7a** is marginally less stable than **7b**.
6. *J. Am. Chem. Soc.* **1969,** *91* (14), 3865–3869
7. Addition of **HX** to butadiene in the gas phase gives approximately a **1 : 1** ratio of 1,2- to 1,4-addition product, suggesting that an ion pair mechanism (which would favor the 1,2-addition product) does not operate: *J. Org. Chem.*, **1991,** *56* (2), 595–601

PRACTICE PROBLEMS

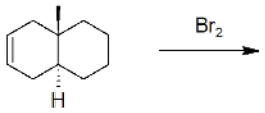
1. Write out the products of 1,2 addition and 1,4- addition of a) HBr and b) DBr to 1,3-cyclo-hexadiene. What is unusual about the products of 1,2- and 1,4- addition of HX to unsubstituted cyclic 1,3-dienes?
2. Is the 1,2-addition product formed more rapidly at higher temperatures, even though it is the 1,4-addition product that predominates under these conditions?
3. Why is the 1,4-addition product the thermodynamically more stable product?
4. Out of the following radical cations which one is not a reasonable resonance structure?

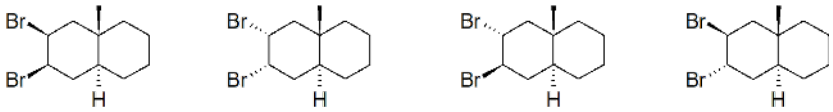


5. Addition of 1 equivalent of Bromine to 2,4-hexadiene at 0 degrees C gives 4,5-dibromo-2-hexene plus an isomer. Which of the following is that isomer:

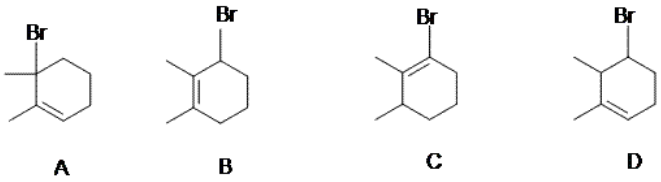
a. 5,5-dibromo-2-hexene
b. 2,5-dibromo-3-hexene
c. 2,2-dibromo-3-hexene
d. 2,3-dibromo-4-hexene

6. Which of the following will be the kinetically favored product from the depicted reaction?

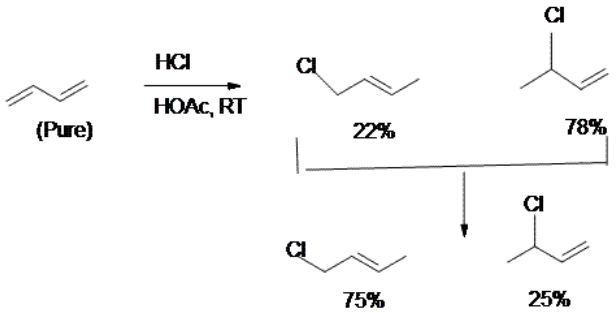




7. Addition of HBr to 2,3-dimethyl-1,3-cyclohexadiene may occur in the absence or presence of peroxides. In each case two isomeric $C_8H_{13}Br$ products are obtained. Which of the following is a common product from both reactions?



8. and 9.



8. The kinetically controlled product in the above reaction is:

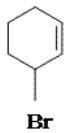
a. 3-Chloro-1-Butene
b. 1-Chloro-2-Butene

9. For the reaction in question 8, which one is the result of 1,4-addition?

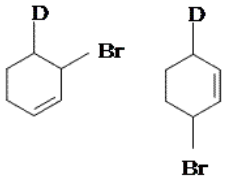
a. 3-Chloro-1-Butene
b. 1-Chloro-2-Butene

ANSWERS TO PROBLEMS

1. A) Same product for both modes of addition.



B) Both cis and trans isomers will form.



Addition of the HX to unsubstituted cycloalka-1,3-dienes in either 1,2- or 1,4- manner gives the same product becasuse of symmetry.

2. Yes. the Kinetic Product will still form faster but in this case there will be enough energy to form the thermodynamic product because the thermodynamic product is still more stable.

3. The 1,4- product is more thermodynamically stable because there are two alkyl groups on each side of the double bond. This form offers stability to the overall structure.

4. All of these isomers are viable.

5. B

6. C

7. D

8. A

9. B

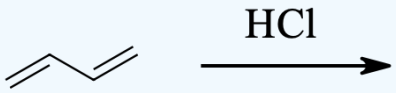
EXERCISE

? EXERCISE 14.3.1

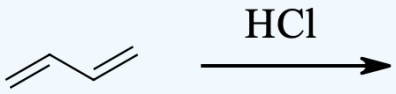
1) Why is the 1,4-addition product the thermodynamically more stable product?

2) Addition of 1 equivalent of bromine to 2,4-hexadiene at 0 degrees C gives 4,5-dibromo-2-hexene plus an isomer. What is the structure of that isomer?

3) The kinetically controlled product in the below reaction is:



4) For the reaction above, which product is the result of 1,4-addition?



5) What would be the major product of the addition of HBr to 2,3-dimethyl-1,3-cyclohexadiene under thermodynamic conditions?

6) Consider the reaction with 1,3-buta-diene reacting with HCl. Propose a mechanism for the reaction. Also, Predict why the 1,4 adduct is the major product in this reaction compared to the 1,2.

Answer

1) The 1,4- product is more thermodynamically stable because there are two alkyl groups on each side of the double bond and more substituted alkenes are more stable.

2) 2,5-Dibromo-3-hexene

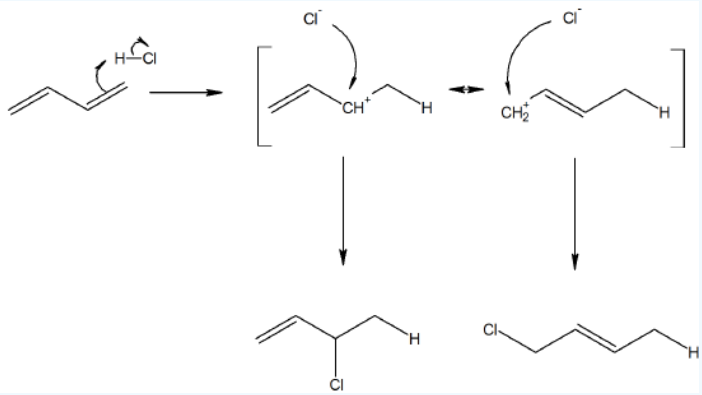
3) 3-Chloro-1-butene

4) 1-Chloro-2-butene

5)



6)



Even though the cation would prefer to be in a secondary position in the transition state, the final product is less stable with a terminal alkene. Therefore the major product will be the 1,4 adduct.

QUESTIONS

Q14.3.1

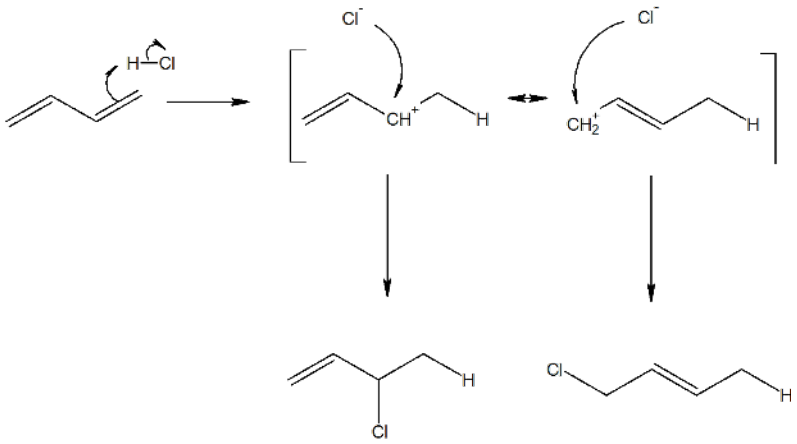
Consider the reaction with 1,3-buta-diene reacting with HCl. Propose a mechanism for the reaction.

Q14.3.2

Predict why the 1,4 adduct is the major product in this reaction compared to the 1,2.

SOLUTIONS

S14.3.1



S14.3.2

Even though the cation would prefer to be in a secondary position in the transition state, the final product is less stable with a terminal alkene. Therefore the major product will be the 1,4 adduct.

CONTRIBUTORS AND ATTRIBUTIONS

- Orthocresol (@chemistry StackExchange)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Natasha Singh

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14.4: THE DIELS-ALDER CYCLOADDITION REACTION

Objectives

After completing this section, you should be able to

1. write an equation to represent a typical Diels-Alder reaction.
2. draw the structure of the product formed when a given conjugated diene reacts with a given dienophile in a Diels-Alder reaction.
3. identify the diene and dienophile that must be used to prepare a given compound by a Diels-Alder reaction.
4. explain the general mechanism of the Diels-Alder reaction, without necessarily being able to describe it in detail.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

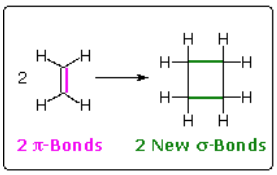
- Diels-Alder cycloaddition
- pericyclic reaction

STUDY NOTES

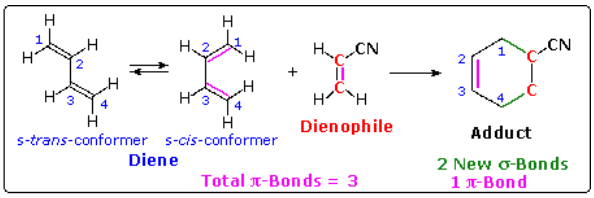
The Diels-Alder reaction is an example of an organic chemical reaction which does not proceed by either a polar or a free radical pathway, but rather a pericyclic reaction.

Although we do not expect you to be able to provide a detailed account of the mechanism of this reaction, you should learn enough about the Diels-Alder reaction to fulfil the objectives stated above. You will find it useful to contrast the mechanism of the Diels-Alder reaction with the polar and radical mechanisms studied earlier.

The unique character of conjugated dienes manifests itself dramatically in the **Diels-Alder Cycloaddition Reaction**. A cycloaddition reaction is the concerted bonding together of two independent pi-electron systems to form a new ring of atoms. When this occurs, two pi-bonds are converted to two sigma-bonds, the simplest example being the hypothetical combination of two ethene molecules to give cyclobutane. This does not occur under normal conditions, but the cycloaddition of 1,3-butadiene to cyanoethene (acrylonitrile) does, and this is an example of the Diels-Alder reaction. The following diagram illustrates two cycloadditions, and introduces several terms that are useful in discussing reactions of this kind.



A [2+2] Cycloaddition



A [4+2] Cycloaddition

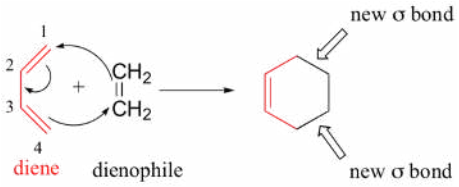
In the hypothetical ethylene dimerization on the left, each reactant molecule has a pi-bond (colored orange) occupied by two electrons. The cycloaddition converts these pi-bonds into new sigma-bonds (colored green), and this transformation is then designated a [2+2] cycloaddition, to enumerate the reactant pi-electrons that change their bonding location.

The Diels-Alder reaction is an important and widely used method for making six-membered rings, as shown on the right. The reactants used in such reactions are a conjugated diene, simply referred to as the **diene**, and a double or triple bond coreactant called the **dienophile**, because it combines with (has an affinity for) the diene. The Diels-Alder cycloaddition is classified as a [4+2] process because the diene has four pi-electrons that shift position in the reaction and the dienophile has two.

The Diels-Alder reaction is a single step process, so the diene component must adopt an s-cisconformation in order for the end carbon atoms (#1 & #4) to bond simultaneously to the dienophile. For many acyclic dienes the s-trans conformer is more stable than the s-cis conformer (due to steric crowding of the end groups), but the two are generally in rapid equilibrium, permitting the use of all but the most hindered dienes as reactants in Diels-Alder reactions. In its usual form, the diene component is electron rich, and the best dienophiles are electron poor due to electron withdrawing substituents such as CN, C=O & NO_2. The initial bonding interaction reflects this electron imbalance, with the two new sigma-bonds being formed simultaneously, but not necessarily at equal rates.

MECHANISM

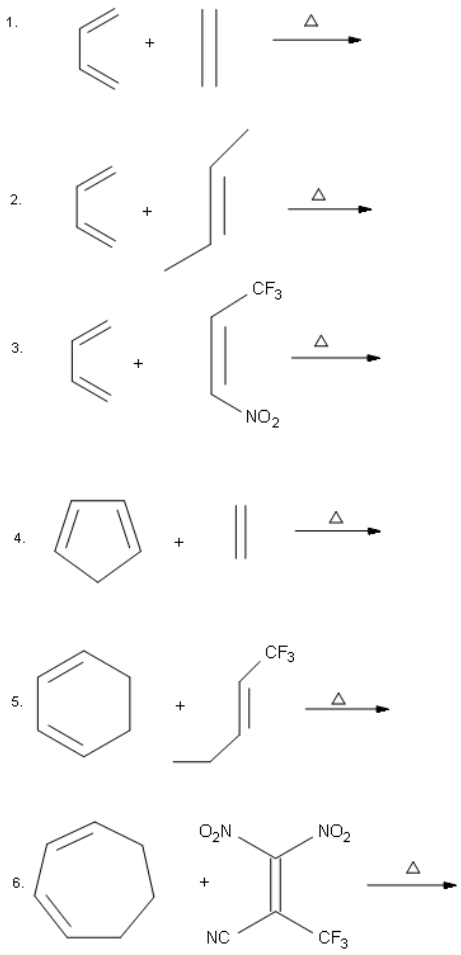
We end this chapter with a discussion of a type of reaction that is different from anything we have seen before. In the Diels-Alder cycloaddition reaction, a conjugated diene reacts with an alkene to form a ring structure.



In a Diels-Alder reaction, the alkene reacting partner is referred to as the **dienophile**. Essentially, this process involves overlap of the 2p orbitals on carbons 1 and 4 of the diene with 2p orbitals on the two sp^2-hybridized carbons of the dienophile. Both of these new overlaps end up forming new sigma bonds, and a new pi bond is formed between carbon 2 and 3 of the diene.

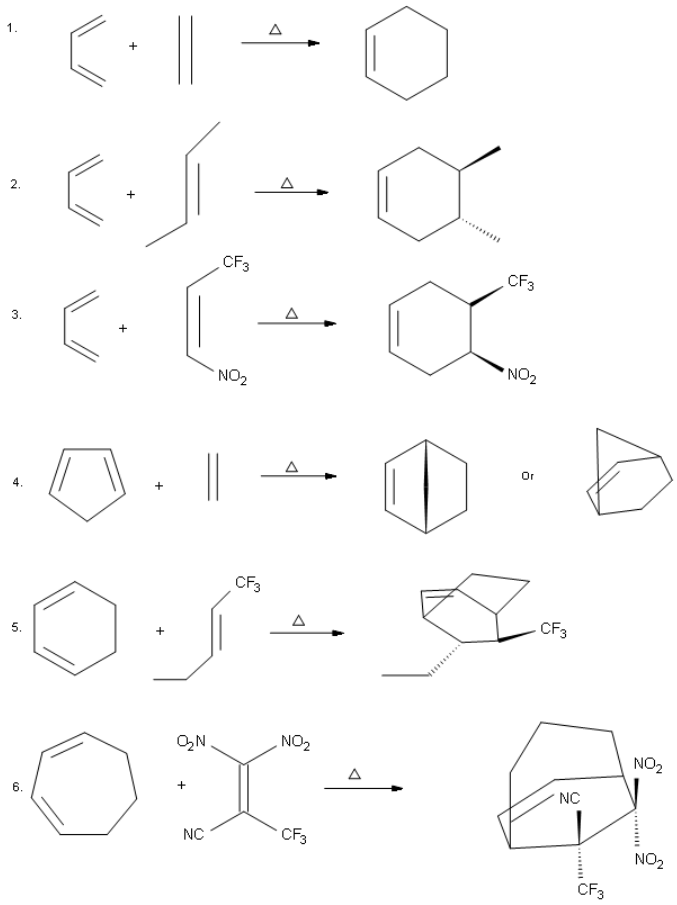
One of the most important things to understand about this process is that it is *concerted* – all of the electron rearrangement takes place at once, with no carbocation intermediates.

PROBLEMS



https://chem.libretexts.org/@go/page/67306

ANSWERS



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Amar Patel (UCD)

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14.5: CHARACTERISTICS OF THE DIELS-ALDER REACTION

Objectives

After completing this section, you should be able to

1. determine whether or not a given compound would behave as a reactive dienophile in a Diels-Alder reaction.
2. predict the stereochemistry of the product obtained from the reaction of a given diene with a given dienophile.
3. recognize that in order to undergo a Diels-Alder reaction, a diene must be able to assume ans-cis geometry, and determine whether or not a given diene can assume this geometry.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- dienophile
- dimerization

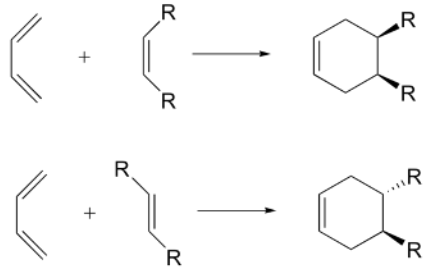
STUDY NOTES

Make sure that you understand that the *s*-cis and *s*-trans forms of a diene such as 1,3-butadiene are conformers, not isomers. Note that some textbooks can confuse the issue further by referring to a compound such as (2Z, 4Z)-hexadiene as cis, cis-2,4-hexadiene, and saying that the most stable form of this compound is its *s*-trans conformer!

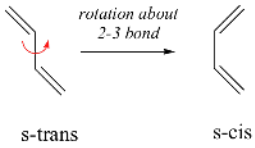
In fulfilling Objective 2, above, you must recognize that the Diels-Alder reaction is stereospecific.

Finally, note reaction **B** in the reading shows 1,3-cyclopentadiene reacting with another molecule of 1,3-cyclopentadiene. When the same compound acts as both diene and dienophile in a Diels-Alder reaction to couple it is a dimerization.

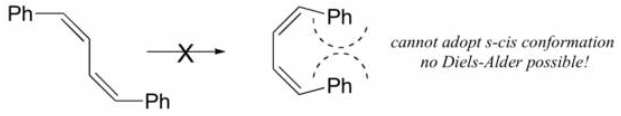
The Diels-Alder reaction is enormously useful for synthetic organic chemists, not only because ring-forming reactions are useful in general but also because in many cases two new stereocenters are formed, and the reaction is inherently stereospecific. A *cis* dienophile will generate a ring with *cis* substitution, while a *trans* dienophile will generate a ring with *trans* substitution:



In order for a Diels-Alder reaction to occur, the diene molecule must adopt what is called the **s-cis conformation**:



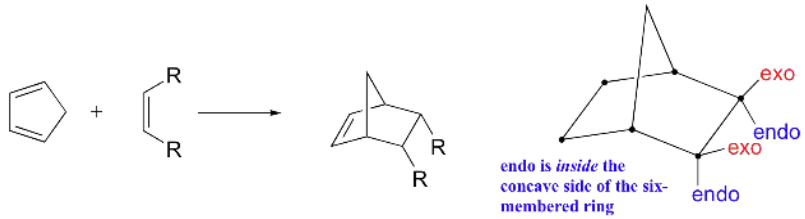
The s-cis conformation is higher in energy than the s-trans conformation, due to steric hindrance. For some dienes, extreme steric hindrance causes the s-cis conformation to be highly strained, and for this reason such dienes do not readily undergo Diels-Alder reactions.



Cyclic dienes, on the other hand, are 'locked' in the s-cis conformation, and are especially reactive. The result of a Diels-Alder reaction involving a cyclic diene is a **bicyclic** structure:

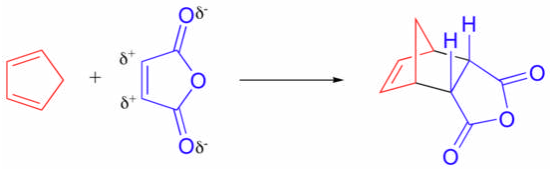


Here, we see another element of stereopecificity: Diels-Alder reactions with cyclic dienes favor the formation of bicyclic structures in which substituents are in the **endo position**.



The endo position on a bicyclic structure refers to the position that is *inside* the concave shape of the larger (six-membered) ring. As you might predict, the **exo position** refers to the *outside* position.

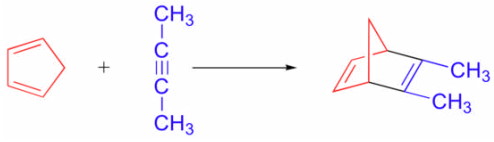
The rate at which a Diels-Alder reaction takes place depends on electronic as well as steric factors. A particularly rapid Diels-Alder reaction takes place between cyclopentadiene and maleic anhydride.



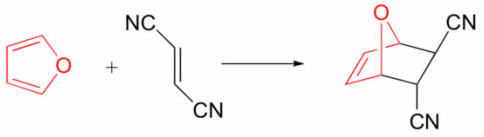
We already know that cyclopentadiene is a good diene because of its inherent s-cis conformation. Maleic anhydride is also a very good dienophile, because the electron-withdrawing effect of the carbonyl groups causes the two alkene carbons to be electron-poor, and thus a good target for attack by the pi electrons in the diene.

In general, Diels-Alder reactions proceed fastest with electron-donating groups on the diene (eg. alkyl groups) and electron-withdrawing groups on the dienophile.

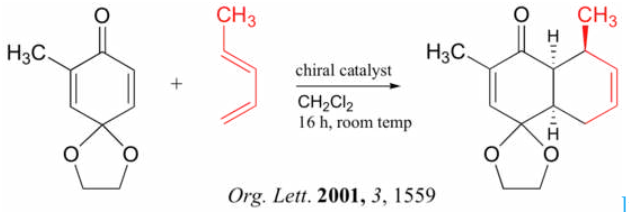
Alkynes can also serve as dienophiles in Diels-Alder reactions:



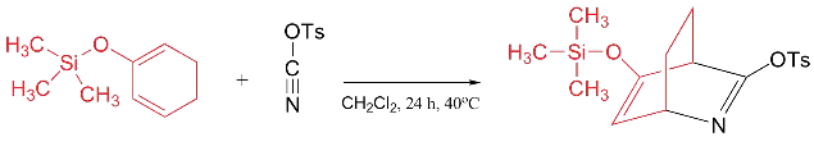
Below are just three examples of Diels-Alder reactions that have been reported in recent years:



J. Med. Chem. **2008,** *51*, 424 link



Org. Lett. **2001,** *3*, 1559 link



J. Org. Chem. **2003,** *68,* 8256 link

The Diels-Alder reaction is just one example of a **pericyclic** reaction: this is a general term that refers to concerted rearrangements that proceed though cyclic transition states. Two well-studied intramolecular pericyclic reactions are known as the Cope rearrangement . . .

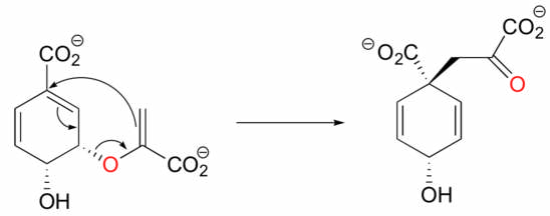


. . .and the Claisen rearrangement (when an oxygen is involved):



Notice that the both of these reactions require compounds in which two double bonds are separated by three single bonds.

Pericyclic reactions are rare in biological chemistry, but here is one example: the Claisen rearrangement catalyzed by chorismate mutase in the aromatic amino acid biosynthetic pathway.

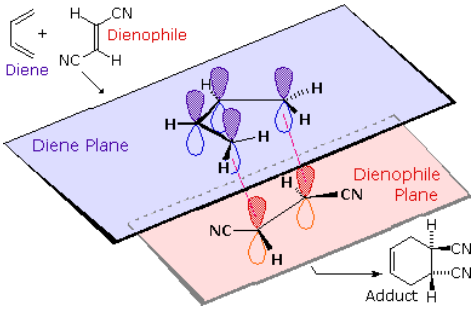


chorismate prephenate

The study of pericyclic reactions is an area of physical organic chemistry that blossomed in the mid-1960s, due mainly to the work of R.B. Woodward, Roald Hoffman, and Kenichi Fukui. The **Woodward-Hoffman rules** for pericyclic reactions (and a simplified version introduced by Fukui) use molecular orbital theory to explain why some pericyclic processes take place and others do not. A full discussion is beyond the scope of this text, but if you go on to study organic chemistry at the advanced undergraduate or graduate level you are sure to be introduced to this fascinating area of inquiry.

STEREOCHEMISTRY OF THE DIELS-ALDER REACTION

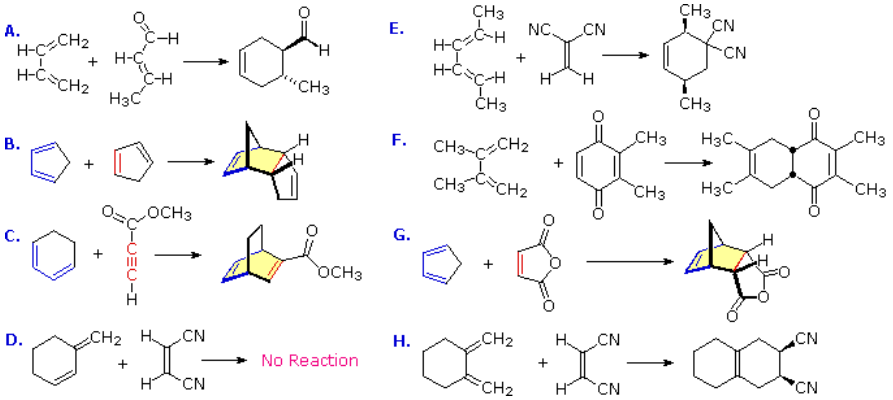
We noted earlier that addition reactions of alkenes often exhibited stereoselectivity, in that the reagent elements in some cases added syn and in other cases anti to the the plane of the double bond. Both reactants in the Diels-Alder reaction may demonstrate stereoisomerism, and when they do it is found that the relative configurations of the reactants are preserved in the product (the adduct). The following drawing illustrates this fact for the reaction of 1,3-butadiene with (E)-dicyanoethene. The trans relationship of the cyano groups in the dienophile is preserved in the six-membered ring of the adduct. Likewise, if the terminal carbons of the diene bear substituents, their relative configuration will be retained in the adduct. Using the earlier terminology, we could say that bonding to both the diene and the dienophile is syn. An alternative description, however, refers to the planar nature of both reactants and terms the bonding in each case to be **suprafacial** (i.e. to or from the same face of each plane). This stereospecificity also confirms the synchronous nature of the 1,4-bonding that takes place.



The essential characteristics of the Diels-Alder cycloaddition reaction may be summarized as follows:

i. The reaction always creates a new six-membered ring. When intramolecular, another ring may also be formed.
ii. The diene component must be able to assume a s-cis conformation.
iii. Electron withdrawing groups on the dienophile facilitate reaction.
iv. Electron donating groups on the diene facilitate reaction.
v. Steric hindrance at the bonding sites may inhibit or prevent reaction.
vi. The reaction is stereospecific with respect to substituent configuration in both the dienophile and the diene.

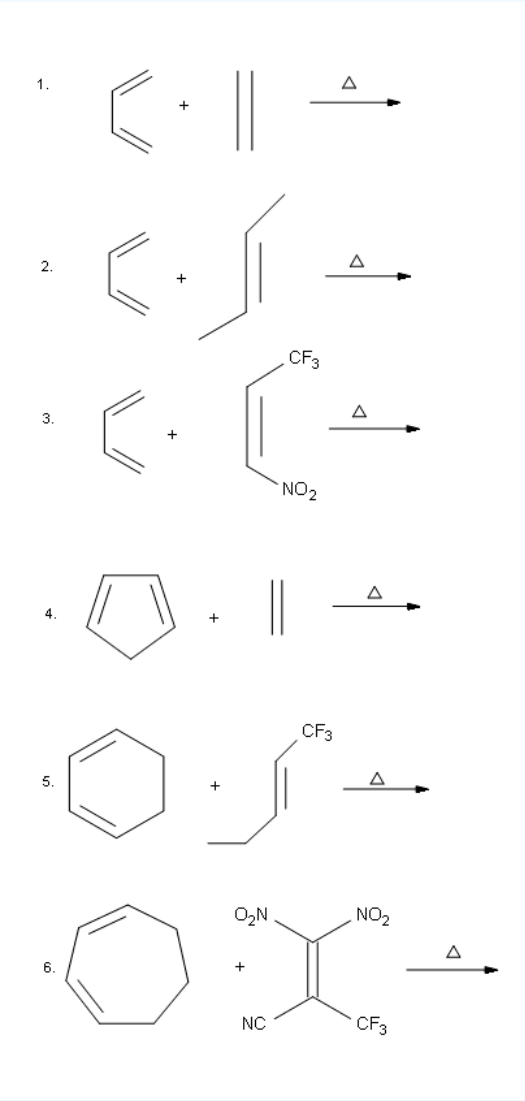
These features are illustrated by the following eight examples, one of which does not give a Diels-Alder cycloaddition.



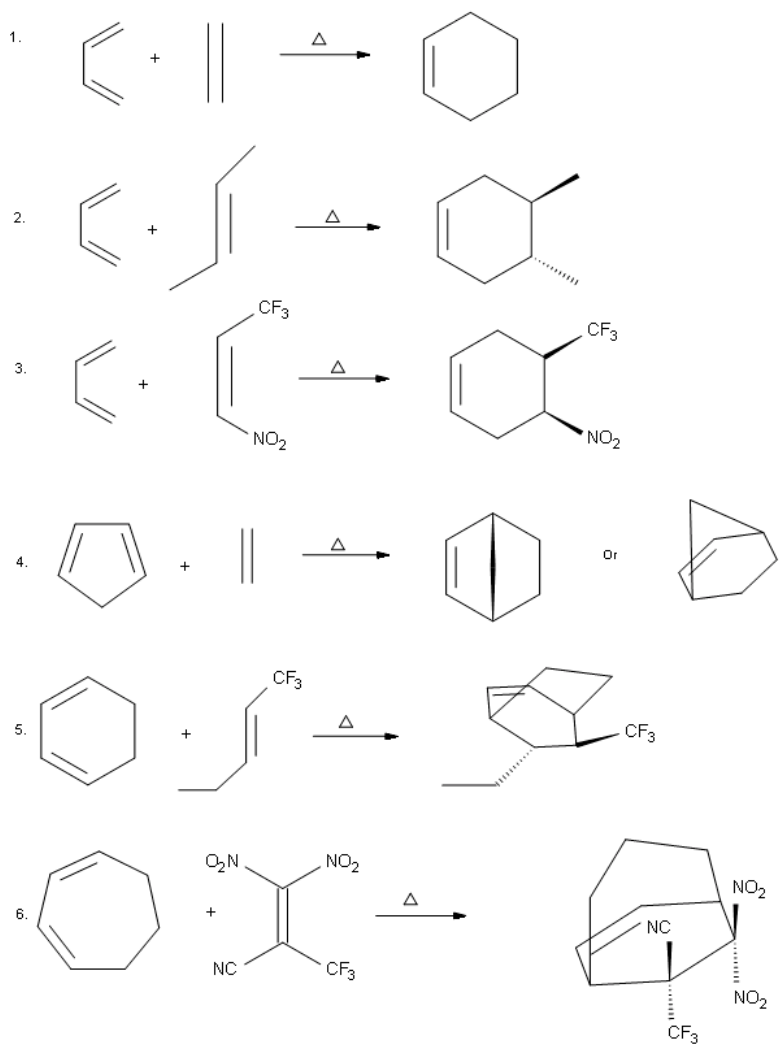
There is no reaction in example **D** because this diene cannot adopt an s-cis orientation. In examples **B, C, F, G & H** at least one of the reactants is cyclic so that the product has more than one ring, but the newly formed ring is always six-membered. In example **B** the the same cyclic compound acts as both the diene colored blue) and the dienophile (colored red). The adduct has three rings, two of which are the five-membered rings present in the reactant, and the third is the new six-membered ring (shaded light yellow). Example **C** has an alkyne as a dienophile (colored red), so the adduct retains a double bond at that location. This double bond could still serve as a dienophile, but in the present case the diene is sufficiently hindered to retard a second cycloaddition. The quinone dienophile in reaction **F** has two dienophilic double bonds. However, the double bond with two methyl substituents is less reactive than the unsubstituted dienophile due in part to the electron donating properties of the methyl groups and in part to steric hindrance. The stereospecificity of the Diels-Alder reaction is demonstrated by examples **A, E & H**. In **A & H** the stereogenic centers lie on the dienophile, whereas in **E** these centers are on the diene. In all cases the configuration of the reactant is preserved in the adduct.

EXERCISES

EXERCISE 14.5.1

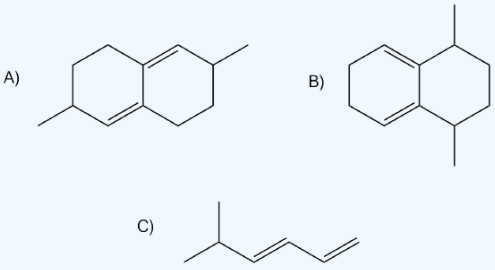


Answer



EXERCISE 14.5.2

Of the following dienes, which are *s*-trans and which are *s*-cis? Of those that are *s*-trans, are they able to rotate to become *s*-cis?



Answer

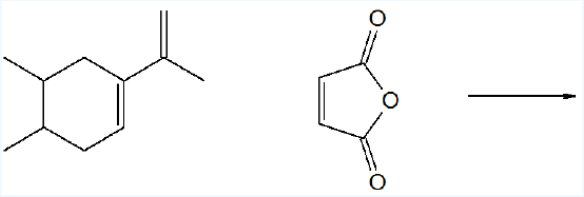
A) s-trans, unable to rotate to become s-cis

B) s-cis

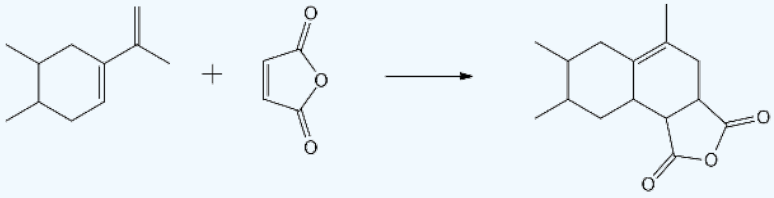
C) s-trans, can rotate to become s-cis.

EXERCISE 14.5.3

Predict the product of the following reaction.



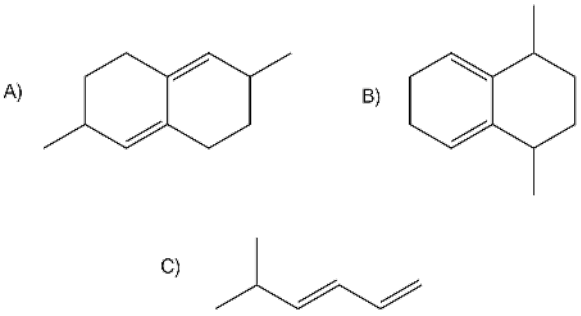
Answer



QUESTIONS

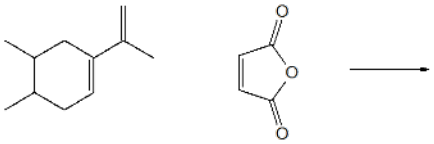
Q14.5.1

Of the following dienes, which are S-trans and which are s-cis? Of those that are s-trans, are they able to rotate to become s-cis?



Q14.5.2

Predict the product of the following reaction.



SOLUTIONS

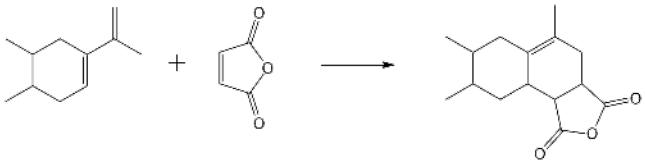
S14.5.1

A) s-trans, unable to rotate to become s-cis

B) s-cis

C) s-trans, can rotate to become s-cis.

S14.5.2



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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14.6: DIENE POLYMERS- NATURAL AND SYNTHETIC RUBBERS

Objectives

After completing this section, you should be able to

1. show that the polymerization of a diene, such as 1,3-butadiene or isoprene (2-methyl-1,3-butadiene), can result in the formation of either a cis or trans polymer.
2. draw the structure of natural rubber.
3. explain, briefly, the process of vulcanization.

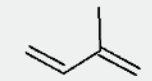
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

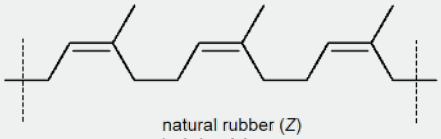
- cross-link
- vulcanization

STUDY NOTES

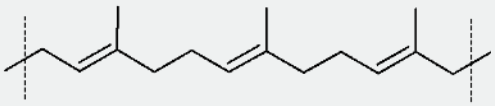
Natural rubber is formed from the isoprene monomer and has *Z* stereochemistry. The *E* polymer gutta-percha also occurs naturally, but is more brittle than rubber. Uses of this thermoplastic include dentistry, electrical insulators and the covering on golf balls.



isoprene
2-methyl-1,3-butadiene



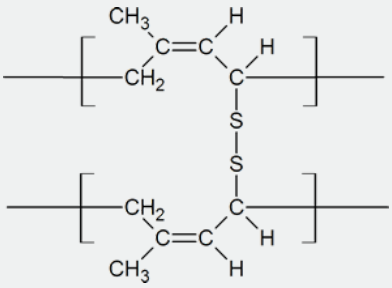
natural rubber (*Z*)
cis-1,4-polyisoprene



gutta-percha (*E*)
trans-1,4-polyisoprene

Before 1839, the uses of natural rubber were somewhat limited. It became sticky in summer, hardened and cracked in winter, and was susceptible to attack by a variety of solvents. Charles Goodyear became interested in rubber in 1831, and bought the Eagle India Rubber Company of Woburn, Massachusetts, in 1838. In January of 1839, Goodyear accidentally placed a sample of rubber that had been mixed with sulfur and lead(II) oxide on a hot stove; the result was a product similar to charred leather, which did not melt below 138°C. Goodyear was granted a U.S. patent for his process (called vulcanization) in June of 1844. The story of vulcanization is an example of how major scientific and technological advances are often brought about as a result of an accidental discovery.

Notice that in the vulcanization process, the sulfur bridges are attached to allylic carbon atoms which connect the long *Z* polymer chains of rubber.



Vulcanized rubber

The amount of sulfur used in the vulcanization process will depend on the rigidity required in the product. For example, about 5% sulfur is used when producing rubber for rubber bands; about 30% sulfur is used when making rubber for use in battery casings. There

are several characteristics of dienes and rubbers that you should recognize. First, be aware of the similarity between the polymerization of a diene and the 1,4-addition reactions of dienes. Second, recognize the similarity between a vulcanized rubber and a peptide containing cysteine cross-links. Third, be aware that as natural rubber contains double bonds, it will display some of the properties of simple alkenes.

The 1,4 polymerization of 1,3-butadiene shown in the reading produces the *trans* form of polybutadiene. However, it should be noted that the *cis* form shown here can also be formed.

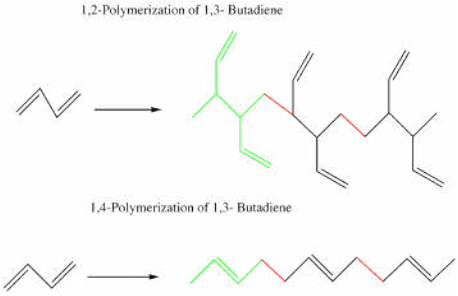


cis- polbutadiene

Conjugated dienes (alkenes with two double bonds and a single bond in between) can be polymerized to form important compounds like rubber. This takes place, in different forms, both in nature and in the laboratory. Interactions between double bonds on multiple chains leads to cross-linkage which creates elasticity within the compound.

POLYMERIZATION OF 1,3-BUTADIENE

For rubber compounds to be synthesized, 1,3-butadiene must be polymerized. Below is a simple illustration of how this compound is formed into a chain. The 1,4 polymerization is much more useful to polymerization reactions.



Above, the green structures represent the base units of the polymers that are synthesized and the red represents the bonds between these units which form these polymers. Whether the 1,3 product or the 1,4 product is formed depends on whether the reaction is thermally or kinetically controlled.

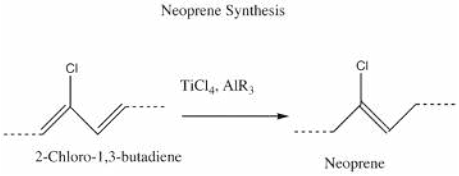
NATURAL RUBBER

Natural rubber is an addition polymer that is obtained as a milky white fluid known as latex from a tropical rubber tree. Natural rubber is from the monomer isoprene (2-methyl-1,3-butadiene), which is a conjugated diene hydrocarbon as mentioned above. In natural rubber, most of the double fonds formed in the polymer chain have the Z configuration, resulting in natural rubber's elastomer qualities.

Charles Goodyear accidentally discovered that by mixing sulfur and rubber, the properties of the rubber improved in being tougher, resistant to heat and cold, and increased in elasticity. This process was later called vulcanization after the Roman god of fire. Vulcanization causes shorter chains to cross link through the sulfur to longer chains. The development of vulcanized rubber for automobile tires greatly aided this industry.

SYNTHETIC RUBBER

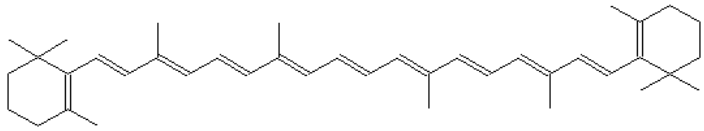
The most important synthetic rubber is Neoprene which is produced by the polymerization of 2-chloro-1,3-butadiene.



In this illustration, the dashed lines represent repetition of the same base units, so both the products and reactants are polymers. The reaction proceeds with a mechanism similar to the Friedel-Crafts mechanism. Cross-linkage between the chlorine atom of one chain and the double bond of another contributes to the overall elasticity of neoprene. This cross-linkage occurs as the chains lie next to each other at random angles, and the attractions between double bonds prevent them from sliding back and forth.

COLORED MOLECULES

The counjugated double bonds in beta-carotene produce the orange color in carrots. The conjugated double bons in lycopene produce the red color in tomatoes.



ß carotene



lycopene

OUTSIDE LINKS

- "Dienes," http://en.Wikipedia.org/wiki/Diene
- "Rubber," http://en.Wikipedia.org/wiki/Rubber
- "Neoprene," http://en.Wikipedia.org/wiki/Neoprene

REFERENCES

1. Vollhardt, Peter, and Neil E. Schore. Organic Chemistry: Structure and Function. New York: W. H. Freeman & Company, 2007.
2. Buehr, Walter. Rubber: Natural and Synthetic. Morrow, 1964.

EXERCISE

? EXERCISE 14.6.1

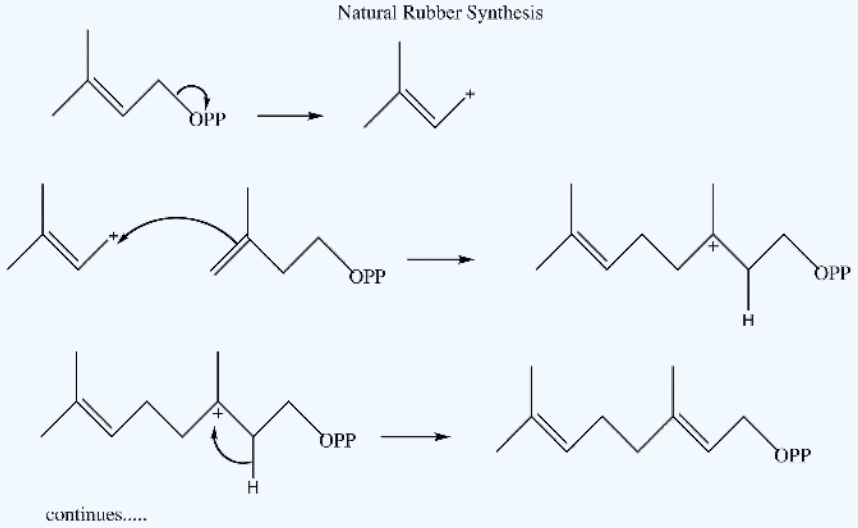
a. Draw out the mechanism for the natural synthesis of rubber from 3-methyl-3-butenyl pyrophosphate and 2-methyl-1,3-butadiene. Show the movement of electrons with arrows

b. Draw a segment for the polymer that may be made from 2-*tert*-butyl-1,3-butadiene.

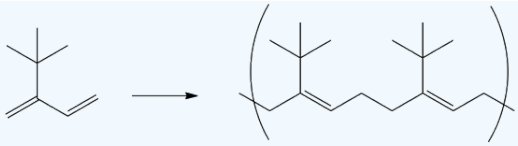
c. Propose the mechanism for the acid catalyzed polymerization of 2-methyl-1,3-butadiene.

Answer

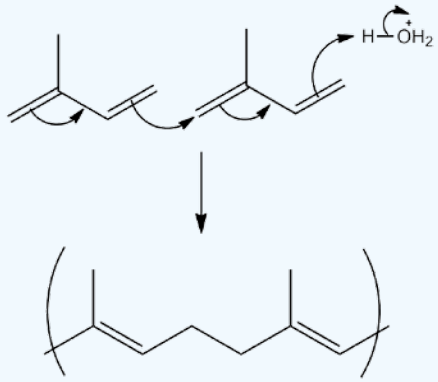
a.



b.



c.



QUESTIONS

Q14.6.1

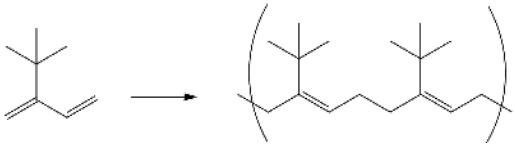
Draw a segment for the polymer that may be made from 2-*tert*-butyl-1,3-butadiene.

Q14.6.2

Propose the mechanism for the acid catalyzed polymerization of 2-methyl-1,3-butadiene.

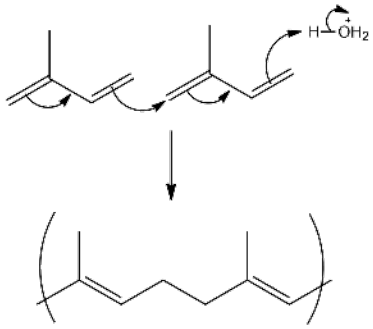
SOLUTIONS

S14.6.1



S14.6.2

The initial step is an addition of a hydrogen from the acid, followed by the polymerization.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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14.7: STRUCTURE DETERMINATION IN CONJUGATED SYSTEMS-ULTRAVIOLET SPECTROSCOPY

Objectives

After completing this section, you should be able to

1. identify the ultraviolet region of the electromagnetic spectrum which is of most use to organic chemists.
2. interpret the ultraviolet spectrum of 1,3-butadiene in terms of the molecular orbitals involved.
3. describe in general terms how the ultraviolet spectrum of a compound differs from its infrared and NMR spectra.

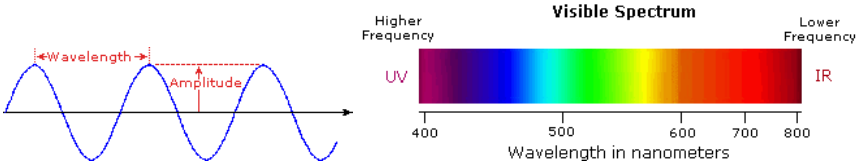
KEY TERMS

Make certain that you can define, and use in context, the key term below.

- ultraviolet (UV) spectroscopy

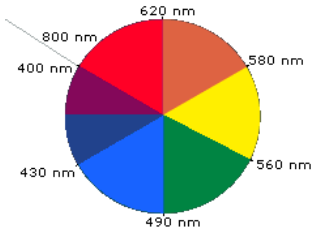
STUDY NOTES

Ultraviolet spectroscopy provides much less information about the structure of molecules than do the spectroscopic techniques studied earlier (infrared spectroscopy, mass spectroscopy, and NMR spectroscopy). Thus, your study of this technique will be restricted to a brief overview. You should, however, note that for an organic chemist, the most useful ultraviolet region of the electromagnetic spectrum is that in which the radiation has a wavelength of between 200 and 400 nm.



- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

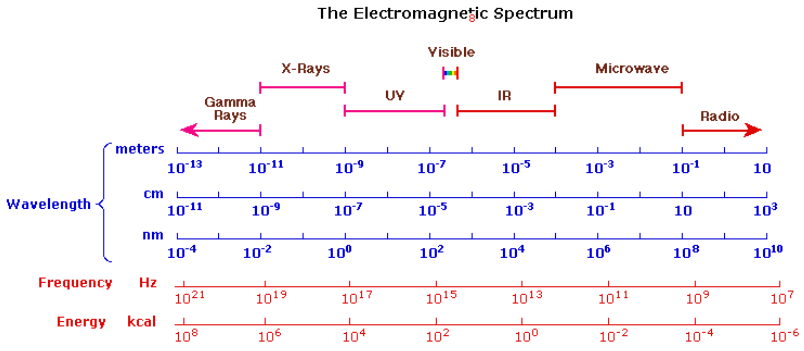
When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other. Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absoption close to 400 nm as well as absorption near 800 nm.



Early humans valued colored pigments, and used them for decorative purposes. Many of these were inorganic minerals, but several important organic dyes were also known. These included the crimson pigment, kermesic acid, the blue dye, indigo, and the yellow saffron pigment, crocetin. A rare dibromo-indigo derivative, punicin, was used to color the robes of the royal and wealthy. The deep orange hydrocarbon carotene is widely distributed in plants, but is not sufficiently stable to be used as permanent pigment, other than for food coloring. A common feature of all these colored compounds, displayed below, is a system of **extensively conjugated π-electrons**.

THE ELECTROMAGNETIC SPECTRUM

The visible spectrum constitutes but a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments. This **electromagnetic spectrum** ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency (shown in the top equation below the chart).



The energy associated with a given segment of the spectrum is proportional to its frequency. The bottom equation describes this relationship, which provides the energy carried by a photon of a given wavelength of radiation.

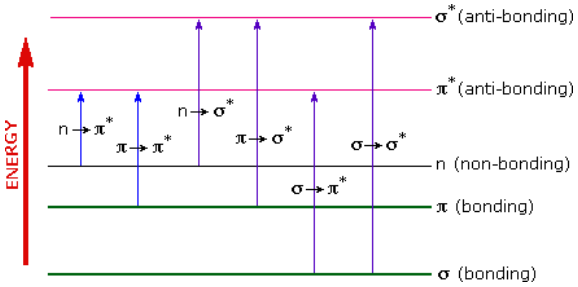
$\upsilon = c/\lambda$ υ=frequency, λ=wavelength, c=velocity of light ($c = 3 \cdot 10^{10}$ cm/sec)
$\Delta E = h\upsilon$ E=energy, υ=frequency, h=Planck's constant ($h = 6.6 \cdot 10^{-27}$ erg sec)

To obtain specific frequency, wavelength and energy values use this calculator.

UV-VISIBLE ABSORPTION SPECTRA

To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum. Commercial optical spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum.

The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole. Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.



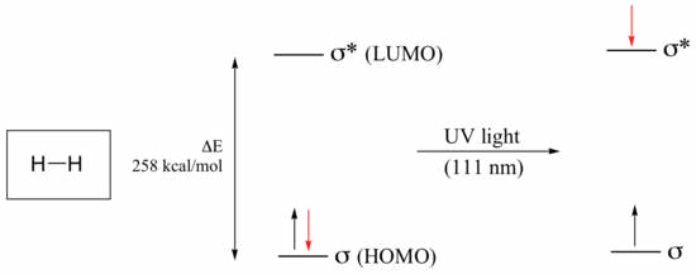
The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy". A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown on the left. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an **excited state**.

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colorless, it does not absorb in the visible

part of the spectrum and this region is not displayed on the graph. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.

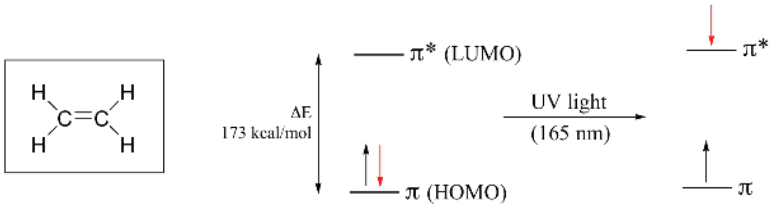
ELECTRONIC TRANSITIONS

Let's take as our first example the simple case of molecular hydrogen, H_2. As you may recall from section 2.1A, the molecular orbital picture for the hydrogen molecule consists of one bonding σ MO, and a higher energy antibonding σ* MO. When the molecule is in the ground state, both electrons are paired in the lower-energy bonding orbital – this is the Highest Occupied Molecular Orbital (HOMO). The antibonding σ* orbital, in turn, is the Lowest Unoccupied Molecular Orbital (LUMO).



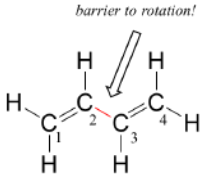
If the molecule is exposed to light of a wavelength with energy equal to **Δ**E, the HOMO-LUMO energy gap, this wavelength will be absorbed and the energy used to bump one of the electrons from the HOMO to the LUMO – in other words, from the σ to the σ* orbital. This is referred to as a **σ - σ* transition**. **Δ**E for this electronic transition is 258 kcal/mol, corresponding to light with a wavelength of 111 nm.

When a double-bonded molecule such as ethene (common name ethylene) absorbs light, it undergoes a **π - π* transition.** Because π- π* energy gaps are narrower than σ - σ* gaps, ethene absorbs light at 165 nm - a longer wavelength than molecular hydrogen.



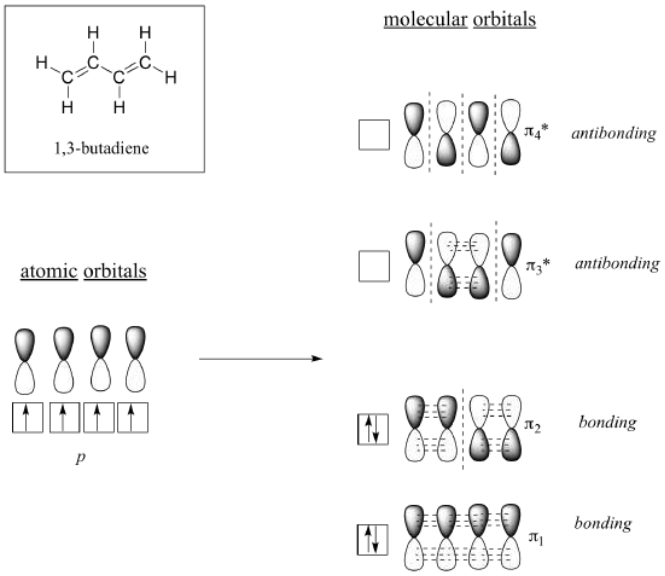
The electronic transitions of both molecular hydrogen and ethene are too energetic to be accurately recorded by standard UV spectrophotometers, which generally have a range of 220 – 700 nm. Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated pi systems. In these groups, the energy gap for π -π* transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer. Molecules or parts of molecules that absorb light strongly in the UV-vis region are called **chromophores**.

Next, we'll consider the 1,3-butadiene molecule. From valence orbital theory alone we might expect that the C_2-C_3 bond in this molecule, because it is a sigma bond, would be able to rotate freely.



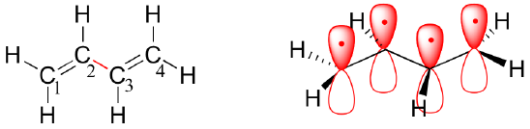
Experimentally, however, it is observed that there is a significant barrier to rotation about the C_2-C_3 bond, and that the entire molecule is planar. In addition, the C_2-C_3 bond is 148 pm long, shorter than a typical carbon-carbon single bond (about 154 pm), though longer than a typical double bond (about 134 pm).

Molecular orbital theory accounts for these observations with the concept of **delocalized π bonds**. In this picture, the four *p* atomic orbitals combine mathematically to form four pi molecular orbitals of increasing energy. Two of these - the bonding pi orbitals - are lower in energy than the *p* atomic orbitals from which they are formed, while two - the antibonding pi orbitals - are higher in energy.



The lowest energy molecular orbital, pi_1, has only constructive interaction and zero nodes. Higher in energy, but still lower than the isolated *p* orbitals, the pi_2 orbital has one node but two constructive interactions - thus it is still a bonding orbital overall. Looking at the two antibonding orbitals, pi_3* has two nodes and one constructive interaction, while pi_4* has three nodes and zero constructive interactions.

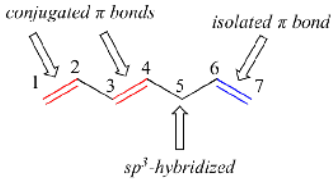
By the *aufbau* principle, the four electrons from the isolated $2p_z$ atomic orbitals are placed in the bonding pi_1 and pi_2 MO's. Because pi_1 includes constructive interaction between C_2 and C_3, there is a degree, in the 1,3-butadiene molecule, of pi-bonding interaction between these two carbons, which accounts for its shorter length and the barrier to rotation. The valence bond picture of 1,3-butadiene shows the two pi bonds as being isolated from one another, with each pair of pi electrons 'stuck' in its own pi bond. However, molecular orbital theory predicts (accurately) that the four pi electrons are to some extent delocalized, or 'spread out', over the whole pi system.



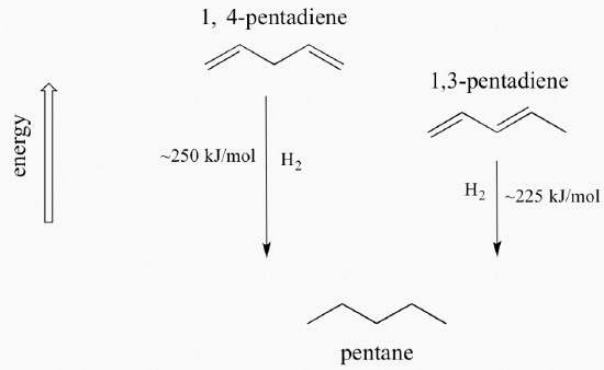
1,3-butadiene

space-filling view

1,3-butadiene is the simplest example of a system of **conjugated pi bonds**. To be considered conjugated, two or more pi bonds must be separated by only one single bond – in other words, there cannot be an intervening sp^3-hybridized carbon, because this would break up the overlapping system of parallel *p* orbitals. In the compound below, for example, the C_1-C_2 and C_3-C_4 double bonds are conjugated, while the C_6-C_7 double bond is **isolated** from the other two pi bonds by sp^3-hybridized C_5.

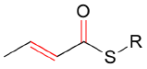


A very important concept to keep in mind is that *there is an inherent thermodynamic stability associated with conjugation.* This stability can be measured experimentally by comparing the **heat of hydrogenation** of two different dienes. (Hydrogenation is a reaction type that we will learn much more about in chapter 15: essentially, it is the process of adding a hydrogen molecule - two protons and two electrons - to a p bond). When the two *conjugated* double bonds of 1,3-pentadiene are 'hydrogenated' to produce pentane, about 225 kJ is released per mole of pentane formed. Compare that to the approximately 250 kJ/mol released when the two *isolated* double bonds in 1,4-pentadiene are hydrogenated, also forming pentane.

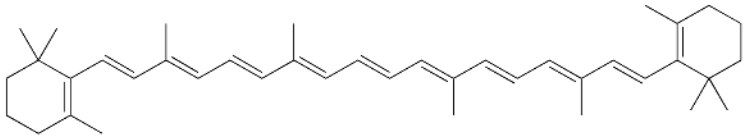


The conjugated diene is lower in energy: in other words, it is more stable. In general, conjugated pi bonds are more stable than isolated pi bonds.

Conjugated pi systems can involve oxygen and nitrogen atoms as well as carbon. In the metabolism of fat molecules, some of the key reactions involve alkenes that are conjugated to carbonyl groups.



In molecules with extended pi systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather then the UV region of the electromagnetic spectrum. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region - to be transmitted. This is why carrots are orange.

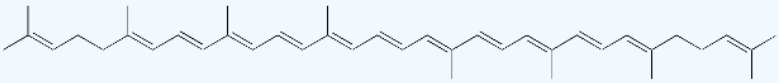


β-carotene

EXERCISE

? EXERCISE 14.7.1

1. 50 microliters of an aqueous sample of double stranded DNA is dissolved in 950 microliters of water. This diluted solution has a maximal absorbance of 0.326 at 260 nm. What is the concentration of the original (more concentrated) DNA sample, expressed in micrograms per microliter?
2. What is the energy range for 300 nm to 500 nm in the ultraviolet spectrum? How does this compare to energy values from NMR and IR spectroscopy?
3. Identify all isolated and conjugated pi bonds in lycopene, the red-colored compound in tomatoes. How many pi electrons are contained in the conjugated pi system?



lycopene

Answer

1) Using ε = A/c, we plug in our values for ε and A and find that c = 3.27 x 10^{-5}M, or 32.7 mM.

2)

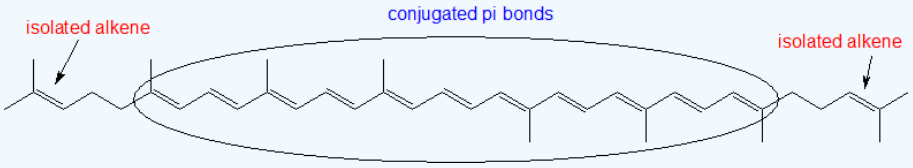
$E = hc/\lambda$

$E = (6.62 \times 10^{-34}\ \text{Js})(3.00 \times 10^{8}\ \text{m/s})/(3.00 \times 10^{-7}\ \text{m})$

$E = 6.62 \times 10^{-19}\ \text{J}$

The range of 3.972×10^{-19} to 6.62×10^{-19} joules. This energy range is greater in energy than the in NMR and IR.

3)



QUESTIONS

Q14.7.1

What is the energy range for 300 nm to 500 nm in the ultraviolet spectrum? How does this compare to energy values from NMR and IR spectroscopy?

SOLUTIONS

S14.7.1

$E = hc/\lambda$

$E = (6.62 \times 10^{-34}\ \text{Js})(3.00 \times 10^{8}\ \text{m/s})/(3.00 \times 10^{-7}\ \text{m})$

$E = 6.62 \times 10^{-19}\ \text{J}$

The range of 3.972×10^{-19} to 6.62×10^{-19} joules. This energy range is greater in energy than the in NMR and IR.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

14.7: Structure Determination in Conjugated Systems- Ultraviolet Spectroscopy is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

14.8: INTERPRETING ULTRAVIOLET SPECTRA- THE EFFECT OF CONJUGATION

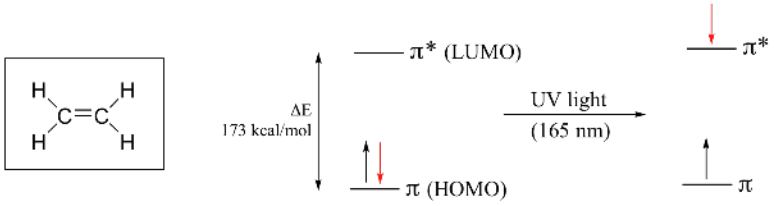
Objective

After completing this section, you should be able to use data from ultraviolet spectra to assist in the elucidation of unknown molecular structures.

STUDY NOTES

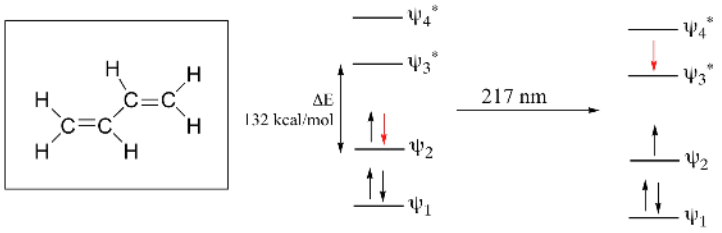
It is important that you recognize that the ultraviolet absorption maximum of a conjugated molecule is dependent upon the extent of conjugation in the molecule.

When a double-bonded molecule such as ethene (common name ethylene) absorbs light, it undergoes a **π - π* transition.** Because π- π* energy gaps are narrower than σ - σ***** gaps, ethene absorbs light at 165 nm - a longer wavelength than molecular hydrogen.



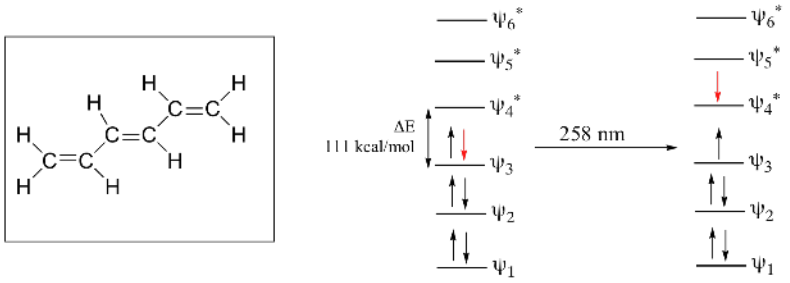
The electronic transitions of both molecular hydrogen and ethene are too energetic to be accurately recorded by standard UV spectrophotometers, which generally have a range of 220 – 700 nm. Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated pi systems. In these groups, the energy gap for π -π* transitions is smaller than for isolated double bonds, and thus the wavelength absorbed is longer. Molecules or parts of molecules that absorb light strongly in the UV-vis region are called **chromophores**.

Let's revisit the MO picture for 1,3-butadiene, the simplest conjugated system (see section 2.1B). Recall that we can draw a diagram showing the four pi MO's that result from combining the four $2p_z$ atomic orbitals. The lower two orbitals are bonding, while the upper two are antibonding.



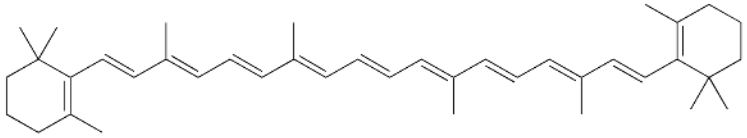
Comparing this MO picture to that of ethene, our isolated pi-bond example, we see that the HOMO-LUMO energy gap is indeed smaller for the conjugated system. 1,3-butadiene absorbs UV light with a wavelength of 217 nm.

As conjugated pi systems become larger, the energy gap for a π - π* transition becomes increasingly narrow, and the wavelength of light absorbed correspondingly becomes longer. The absorbance due to the π - π* transition in 1,3,5-hexatriene, for example, occurs at 258 nm, corresponding to a **Δ**E of 111 kcal/mol.



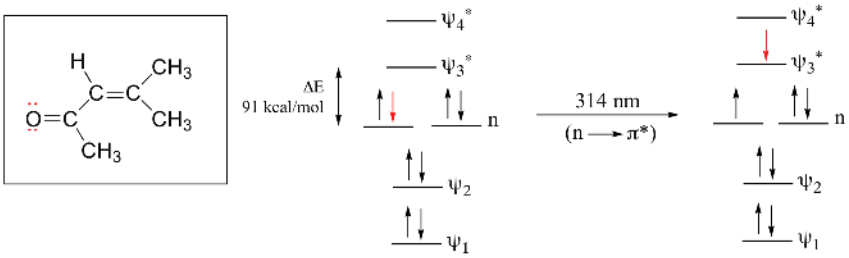
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In molecules with extended pi systems, the HOMO-LUMO energy gap becomes so small that absorption occurs in the visible rather then the UV region of the electromagnetic spectrum. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths – mainly those in the red-yellow region - to be transmitted. This is why carrots are orange.



β-carotene

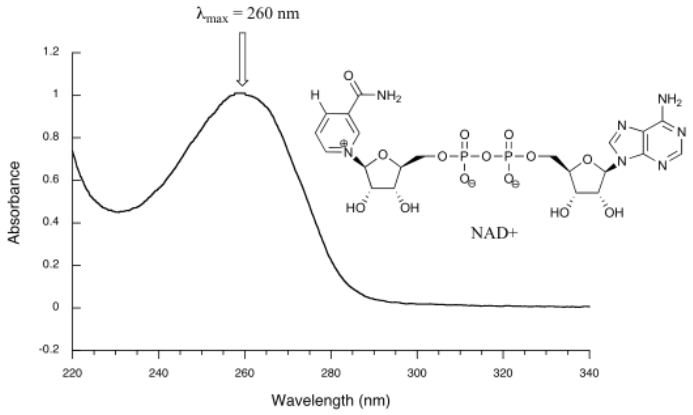
The conjugated pi system in 4-methyl-3-penten-2-one gives rise to a strong UV absorbance at 236 nm due to a π - π* transition. However, this molecule also absorbs at 314 nm. This second absorbance is due to the transition of a non-bonding (lone pair) electron on the oxygen up to a π* antibonding MO:



This is referred to as an **n - π* transition**. The nonbonding (n) MO's are higher in energy than the highest bonding p orbitals, so the energy gap for an n - π* transition is smaller that that of a π - π* transition – and thus the n - π* peak is at a longer wavelength. In general, n - π* transitions are weaker (less light absorbed) than those due to π - π* transitions.

LOOKING AT UV-VIS SPECTRA EDIT SECTION

We have been talking in general terms about how molecules absorb UV and visible light – now let's look at some actual examples of data from a UV-vis absorbance spectrophotometer. The basic setup is the same as for IR spectroscopy: radiation with a range of wavelengths is directed through a sample of interest, and a detector records which wavelengths were absorbed and to what extent the absorption occurred. Below is the absorbance spectrum of an important biological molecule called nicotinamide adenine dinucleotide, abbreviated NAD^+ (we'll learn what it does in section 16.4) This compound absorbs light in the UV range due to the presence of conjugated pi-bonding systems.



You'll notice that this UV spectrum is much simpler than the IR spectra we saw earlier: this one has only one peak, although many molecules have more than one. Notice also that the convention in UV-vis spectroscopy is to show the baseline at the bottom of the graph with the peaks pointing up. Wavelength values on the x-axis are generally measured in nanometers (nm) rather than in cm^{-1} as is the convention in IR spectroscopy.

Peaks in UV spectra tend to be quite broad, often spanning well over 20 nm at half-maximal height. Typically, there are two things that we look for and record from a UV-Vis spectrum.. The first is $\lambda_{max,}$ which is the wavelength at maximal light absorbance. As you can see, NAD^+ has $\lambda_{max,}$ = 260 nm. We also want to record how much light is absorbed at $\lambda_{max.}$ Here we use a unitless number called **absorbance**,

abbreviated 'A'. This contains the same information as the 'percent transmittance' number used in IR spectroscopy, just expressed in slightly different terms. To calculate absorbance at a given wavelength, the computer in the spectrophotometer simply takes the intensity of light at that wavelength *before* it passes through the sample (I_0), divides this value by the intensity of the same wavelength *after* it passes through the sample (I), then takes the $\log_{10}$ of that number:

$A = \log I_0/I$

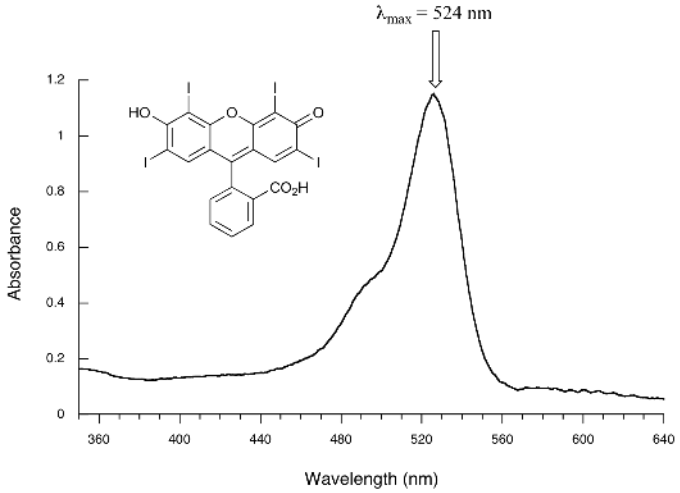
You can see that the absorbance value at 260 nm (A_{260}) is about 1.0 in this spectrum.

EXAMPLE 14.8.1

Express A = 1.0 in terms of percent transmittance (%T, the unit usually used in IR spectroscopy (and sometimes in UV-vis as well).

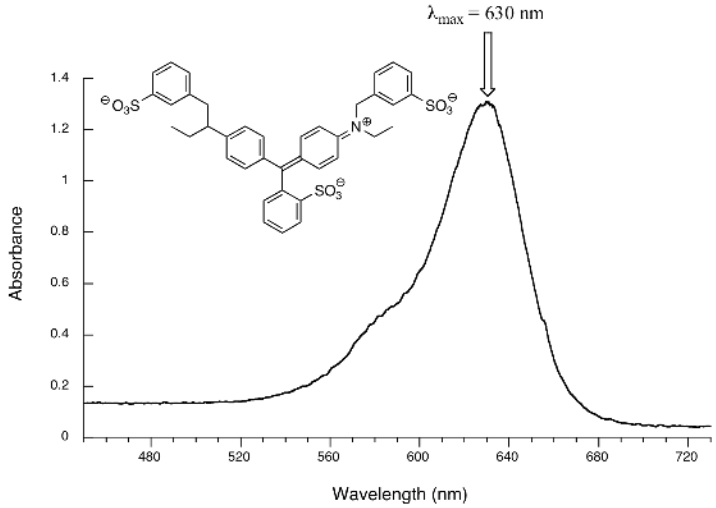
Solution

Here is the absorbance spectrum of the common food coloring Red #3:



Here, we see that the extended system of conjugated pi bonds causes the molecule to absorb light in the visible range. Because the λ_{max} of 524 nm falls within the green region of the spectrum, the compound appears red to our eyes.

Now, take a look at the spectrum of another food coloring, Blue #1:

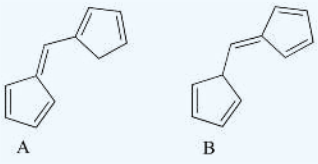


Here, maximum absorbance is at 630 nm, in the orange range of the visible spectrum, and the compound appears blue.

EXERCISES

EXERCISE 14.8.1

Which of the following molecules would you expect absorb at a longer wavelength in the UV region of the electromagnetic spectrum? Explain your answer.

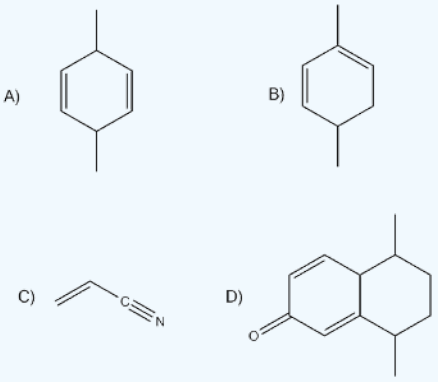


Answer

Compound A would have the longer wavelength as all 5 allylic fragments are conjugated, whereas Compound B has a group of 3 and a group of 2 allyic fragments congugated.

EXERCISE 14.8.2

Which of the following would show UV absorptions in the 200-300 nm range?



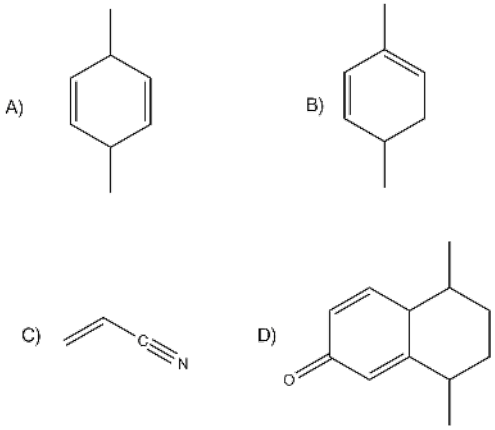
Answer

B and D would be in that range.

QUESTIONS

Q14.8.1

Which of the following would show UV absorptions in the 200-300 nm range?



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SOLUTIONS

S14.8.1

B and D would be in that range.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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14.9: CONJUGATION, COLOR, AND THE CHEMISTRY OF VISION

Objectives

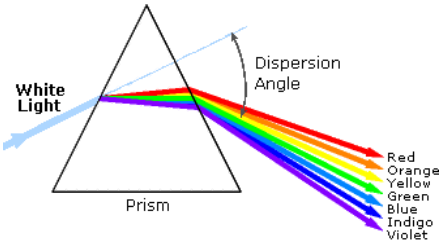
After completing this section, you should be able to

1. explain why some organic compounds have different colours based on compound structure and our perception of light.
2. state the relationship between frequency of light absorbed and the extent of conjugation in an extended pi electron system.

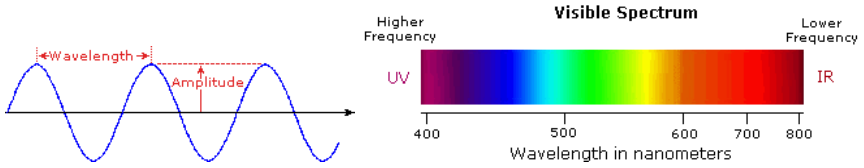
Eyes receive light energy then transfer and passing the energy into neural impulses to brain. This page will show the role of light plays in vision.

INTRODUCTION

An obvious difference between certain compounds is their color. Thus, quinone is yellow; chlorophyll is green; and aspirin is colorless. In this respect the human eye is functioning as a spectrometer analyzing the light reflected from the surface of a solid or passing through a liquid. Although we see sunlight (or white light) as uniform or homogeneous in color, it is actually composed of a broad range of radiation wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum. As shown on the image below, the component colors of the visible portion can be separated by passing sunlight through a prism, which acts to bend the light in differing degrees according to wavelength.

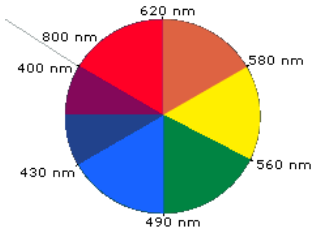


Visible wavelengths cover a range from approximately 400 to 800 nm. The longest visible wavelength is red and the shortest is violet. The wavelengths of what we perceive as particular colors in the visible portion of the spectrum are displayed and listed below.



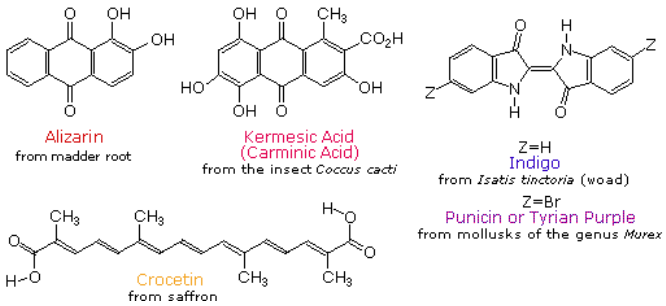
- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other. Thus, absorption of violet (400-440 nm) light renders a substance yellow, and absorption of 490-560 nm (green) light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

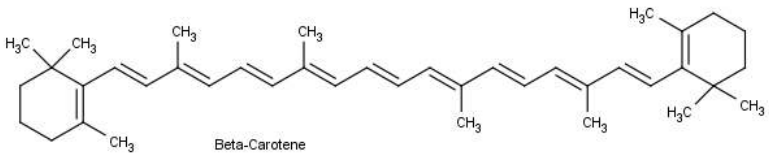


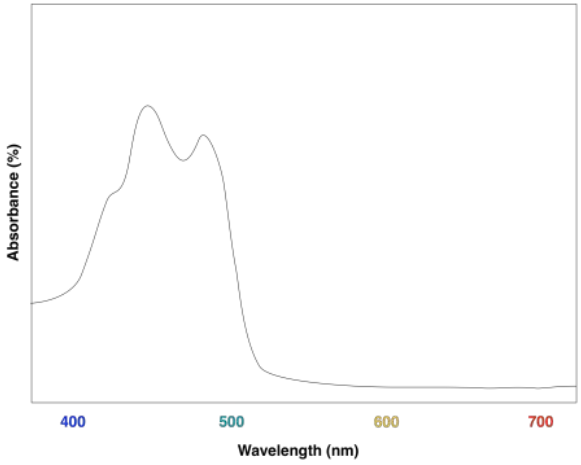
Early humans valued colored pigments, and used them for decorative purposes. Many of these were inorganic minerals, but several important organic dyes were also known. These included the crimson pigment, kermesic acid, the blue dye, indigo, and the yellow saffron pigment, crocetin. A rare dibromo-indigo derivative, punicin, was used to color the robes of the royal and wealthy. A common feature of all these colored compounds, displayed below, is a system of **extensively conjugated π-electrons**.

Some Natural Organic Pigments

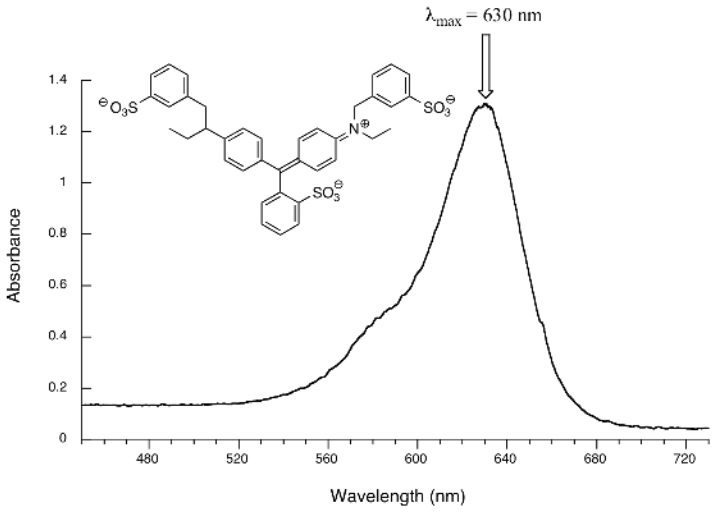


By understanding visible light, complementary colors, and adsorption the color of organic compounds can be understood. Beta-carotene, a compound found in carrots, is a deep orange color. Beta-carotene has 11 conjugated double bonds which places its λ_{max} at 455 nm which is within the blue region of the visible spectrum. The Beta-carotene compound absorbs blue from white light so it appears orange which is the the complementary color of blue.





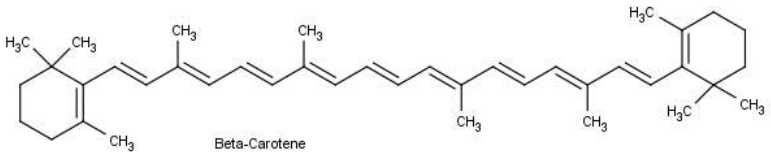
Another example is seen in the absorption spectrum of another food coloring, Blue #1:

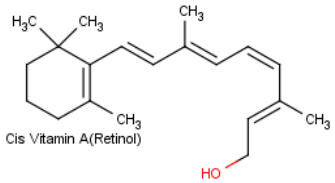


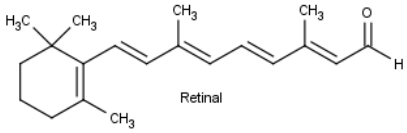
Blue #1 absorbs at a λ_{max} at 630 nm which is the color red in the visible spectrum. Blue is the complementary color of red.

MECHANISM OF VISION

Conjugation is also important in light sensitive compounds used for vision. Beta carotene, found in carrots and other natural products is cleaved into the liver and converted into Vitamin A, also known as retinol. Vitamin A is critical for vision because it is needed by the retina of eye. Retinol can be oxidized to an aldehyde called retinal which is also important for vision.



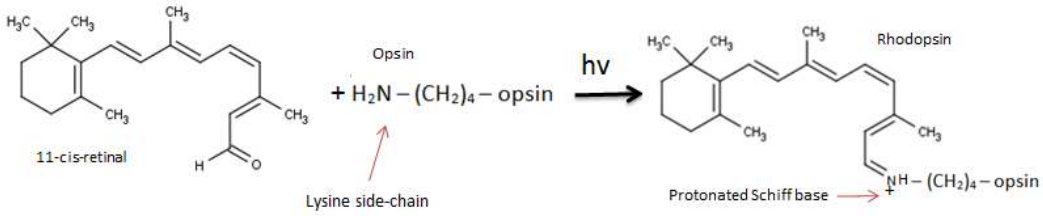




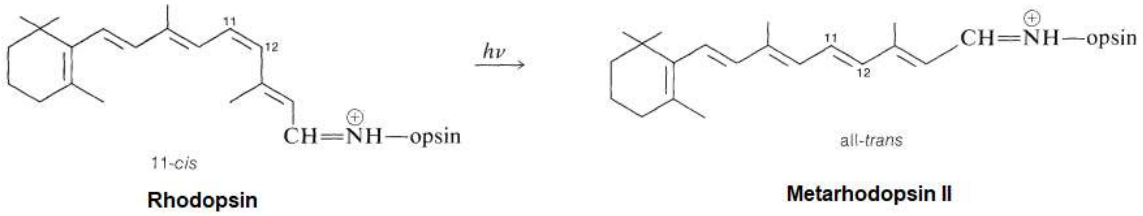
The eye is an extraordinarily sensitive instrument. Although its wavelength response is restricted to 400-800 nm, but its degree of sensitivity is such that a fully dark-adapted eye can clearly detect objects in light so dim as to correspond to a light input over the retina of only about 10,000 quanta per second - one light quantum per three minutes per receptor cell in the retina!

The retina is made up of two kinds of light-sensitive (photoreceptor) cells, known as rods and cones. The rods are the more sensitive and are responsible for vision in dim light. The cones are much fewer in number than the rods and provide detail and color vision in good light. The part of the retina that corresponds to the center of the visual field contains only cones. A red pigment called **rhodopsin** is the photosensitive substance in the rod cells of the retina. It absorbs most strongly in the blue-green region of the visible spectrum (λ_{max} = 500nm) and is essentially unaffected by the far-red end of the spectrum. Cone vision appears to involve a different pigment called **iodopsin**, which absorbs farther toward the red than does rhodopsin.

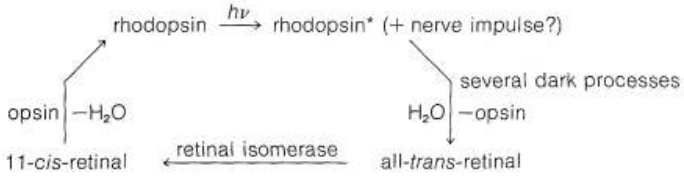
Rhodopsin, is made up of a protein (opsin) and retinal. Opsin does not absorb visible light, but when it is bonded with 11-cis-retinal to from rhodopsin, the new molecule has a very broad absorption band in the visible region of the spectrum. Rhodopsin is formed by an an imine (Schiff base) functional group formed between the aldehyde group of the retinal and the side-chain amino function of a lysine unit of opsin.



Opsin itself is colorless, whereas 11-cis-retinal absorbs strongly at 370 nm. The combination of opsin with 11-cis-retinal produces a remarkable shift of λ_{max} to longer wavelengths (430 nm to 620 nm, depending on the species). Light striking the retina changes the color of rhodopsin from red to yellow. The primary photochemical event in this process was established by G. Wald (Nobel Laureate in Physiology and Medicine, 1967), who showed that light absorption led to a change of configuration about the C_{11}-C_{12} double bond of the retinal moiety fo rhodopsin from *cis* to *trans* to form a compound called metarhodopsin II. The new form of trans-retinal does not fit as well into the opsin protein, and so a series of geometry changes in the protein begins. As the protein changes its geometry, it initiates a cascade of biochemical reactions that result in changes in charge so that a large potential difference builds up across the neuron membranes. This potential difference is passed along to an adjoining nerve cell as an electrical impulse. The nerve cell carries this impulse to the brain, where the visual information is interpreted.



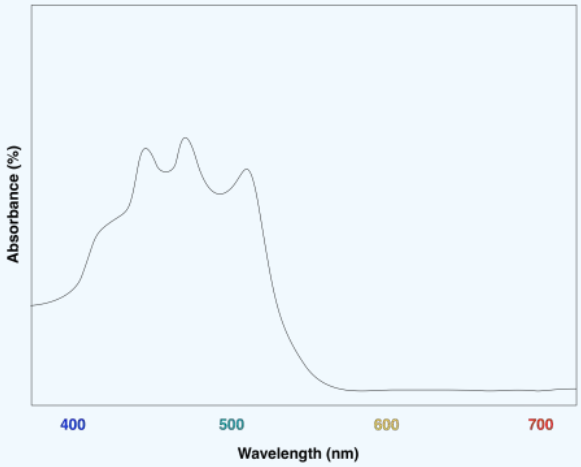
Metarhodopsin II can then be recycled back to rhodopsin by first cleaving to form all-*trans*-retinal and the isomerization back to 11-*cis*-retinal by the enzyme retinal isomerase. Finally, 11-*cis*-retinal is once again coupled with opsin to form rhodopsin.



EXERCISES

? EXERCISE 14.9.1

Lycopene is conjugated compound found in tomatoes. What colors correspond to the UV-Vis absorption maxima of lycopene? What color do we see when we look at lycopene?



Answer

The absorption maxima of lycopene are regions of blue and green in the visible spectrum. Lycopene would be expected to appears orange and red.

? EXERCISE 14.9.2

Asprin has a λ_{max} of 220 nm. Briefly explain why Asprin appears white.

Answer

Asprin absorbs in the ultraviolet portion of the electromagnetic spectrum. Asprin cannot remove any colors from white light by absorption so the compound itself appears white. Many compounds with a relatively small amount of conjugation appear white because they only absorb in the ultraviolet and not the visible region.

REFERENCES

1. Biochemistry, L. Stryer (W.H. Freeman and Co, San Francisco, 1975).
2. *The Cambridge Guide to the Material World*, Rodney Cotterill (Cambridge University Press, Cambridge, 1985)

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14.S: CONJUGATED COMPOUNDS AND ULTRAVIOLET SPECTROSCOPY (SUMMARY)

CONCEPTS & VOCABULARY

14.0 Introduction

- Dienes that consist of two double bonds separated by a single bond are conjugated.
- Dienes that have the double bonds separated by more than one single bond are isolated (non-conjugated)

14.1 Stability of Conjugated Dienes - Molecular Orbital Theory

- Conjugated dienes are more stable than non-conjugated dienes.
- Electrons in conjugated dienes are delocalized due to overlap of all 4 p-orbitals.
- Molecular orbitals show stability of dienes and allylic carbocations.

14.2 Electrophilic Additions to Conjugated Dienes - Allylic Carbocations

- Addition to conjugated dienes occur at multiple positions due to resonance of the allyl carbocation intermediate called 1,2 and 1,4 addition.

14.3 Kinetic vs. Thermodynamic Control of Reactions

- Lower transition states lead to kinetic products.
- More stable products lead to thermodynamic products.
- Kinetic reaction conditions favor 1,2 addition to conjugated dienes.
- Thermodynamic reaction conditions favor 1,4 addition to conjugated dienes.
- For some reactions, the kinetic and thermodynamic products are the same molecule.

14.4 The Diels-Alder Cycloaddition Reaction

- Cycloaddition reactions involve concerted bonding of two independent pi-electron systems for form a new ring.
- The Diels-Alder reaction is a widely used [4+2] cycloaddition that froms two new sigma bonds.

14.5 Characteristics of the Diels-Alder Reaction

- The Diels-Alder reaction is stereospecific with cis dienophiles yielding *cis* substitution and *trans* dienophiles generate trans substitution.
- The diene in a Diels-Alder reaction must be able to adopt an s-cis conformation.
- Diels-Alder reactions with cyclic dienes favor endo substituents.

14.6 Diene Polymers - Natural and Synthetic Rubbers

- Dienes can form polymers including natural examples such as rubber which is formed from isoprene monomers.

14.7 Ultraviolet Spectroscopy

- When UV and visible light is absorbed, electrons are excited from a bonding or non-bonding orbital to a nearby anti-bonding orbital.
- Colored organic molecules all include extensive conjugated pi electron systems.
- UV absorbance is higher energy than visible light, allowing for excitation of electrons without the low energy pi-bonding to pi anti-bonding transitions available in highly conjugated molecules.
- Chromophores are molecules or structural features that absorb light in the UV-Visible range.

14.8 Interpreting Ultraviolet Spectra: The Effect of Conjugation

- Conjugated pi systems lowers the energy gap for π -π^* transitions causing the molecule to absorb light of a longer wavelength.
- Many molecules absorb in the UV spectrum. As the energy gap becomes smaller, these absorbances move into the visible spectrum, starting with violet light which makes the resulting molecules appear yellow.

14.9 Conjugation, Color, and the Chemistry of Vision

- Absorption of light causes chemical changes in the rods and cones in eyes leading to visual sensations.

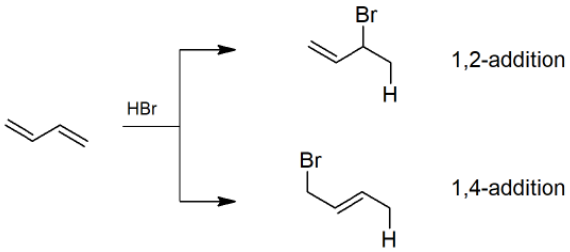
SKILLS TO MASTER

- Skill 14.1 Differentiate between conjugated and isolated dienes.
- Skill 14.2 Explain stability of conjugated dienes using Molecular Orbital Theory.
- Skill 14.3 Draw mechanisms for 1,2 and 1,4 addition to conjugated dienes.

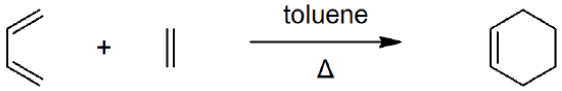
- Skill 14.4 Predict kinetic and thermodynamic products of addition reactions to conjugated dienes.
- Skill 14.5 Explain kinetic and thermodynamic control of reactions.
- Skill 14.6 Identify dienes and dienophiles for Diels-Alder Cycloaddition reactions.
- Skill 14.7 Determine products of Diels-Alder Cycloaddition, including stereochemistry and endo/exo.
- Skill 14.8 Draw mechanisms for Diels-Alder Cycloaddition.
- Skill 14.9 Apply reactions of conjugated dienes to polymerization and natural rubber formation.
- Skill 14.10 Explain the electronic transitions that occur with absorption of UV-Visible light.
- Skill 14.11 Explain the effects of conjugation on wavelength of light absorbed in π -π* transitions.

SUMMARY OF REACTIONS

Electrophilic Addition



Diels−Alder Cycloaddition



CONTRIBUTORS

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- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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CHAPTER OVERVIEW

15: BENZENE AND AROMATICITY

LEARNING OBJECTIVES

After you have completed Chapter 15, you should be able to

1. fulfill all of the detailed objectives listed under each individual section.
2. use the information presented in this chapter, along with material from earlier chapters, to solve problems, particularly road-map problems and those requiring an understanding of spectroscopy.
3. explain the concept of aromaticity and the stability of aromatic compounds.
4. define, and use in context, the key terms introduced.

In Chapter 3, we identified an aromatic compound as being a compound which contains a benzene ring (or phenyl group). It is now time to define aromaticity in a more sophisticated manner. In this chapter, we discuss the stability of benzene and other aromatic compounds, explaining it in terms of resonance and molecular orbital theory. You will study the nomenclature of aromatic compounds and the Hückel ($4n + 2$) rule for predicting aromaticity. The chapter concludes with a brief summary of the spectroscopic properties of arenes.

Topic hierarchy

15.0: Introduction
15.1: Sources and Names of Aromatic Compounds
15.2: Structure and Stability of Benzene
15.3: Aromaticity and the Huckel 4n + 2 Rule
15.4: Aromatic Ions
15.5: Aromatic Heterocycles- Pyridine and Pyrrole
15.6: Polycyclic Aromatic Compounds
15.7: Spectroscopy of Aromatic Compounds
15.S: Benzene and Aromaticity (Summary)

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15.0: INTRODUCTION

Objectives

After completing this section, you should be able to

1. explain what is meant by the term “aromatic compound.”
2. identify the aromatic portions present in naturally occurring compounds, given the necessary structures.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- aromatic

STUDY NOTES

At this point in the course, we shall use the term *aromatic* to describe those compounds which contain a benzene ring. A broader definition of aromaticity will be given in Section 15.3.

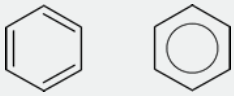


Figure 15.1: Two common ways of representing a benzene ring

CONTRIBUTORS AND ATTRIBUTIONS

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Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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15.1: SOURCES AND NAMES OF AROMATIC COMPOUNDS

Objectives

After completing this section, you should be able to

1. draw the structure of each of the common aromatic compounds in Figure 16 (Common benzene derived compounds with various substituents), given their IUPAC-accepted trivial names.
2. write the IUPAC-accepted trivial name for each of the compounds in Figure 16, given the appropriate Kekulé, condensed or shorthand structure.
3. identify the ortho, meta and para positions in a monosubstituted benzene ring.
4. use the ortho/meta/para system to name simple disubstituted aromatic compounds.
5. draw the structure of a simple disubstituted aromatic compound, given its name according to the ortho/meta/para system.
6. provide the IUPAC name of a given aromatic compound containing any number of the following substituents: alkyl, alkenyl or alkynyl groups; halogens; nitro groups; carboxyl groups; amino groups; hydroxyl groups.
7. draw the structure of an aromatic compound containing any number of the substituents listed in Objective 6, above, given the IUPAC name.
8. provide the IUPAC name of a given aromatic compound in which the phenyl group is regarded as a substituent.
9. draw the Kekulé, condensed or shorthand structure of an aromatic compound in which the phenyl group is regarded as a substituent, given its IUPAC name.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- arene
- benzyl group
- phenyl group

STUDY NOTES

You should already know the names and structures of several of the hydrocarbons shown in Figure 15.1. A compound containing a benzene ring which has one or more alkyl substituents is called an arene. You will meet these compounds frequently throughout the remainder of this course.

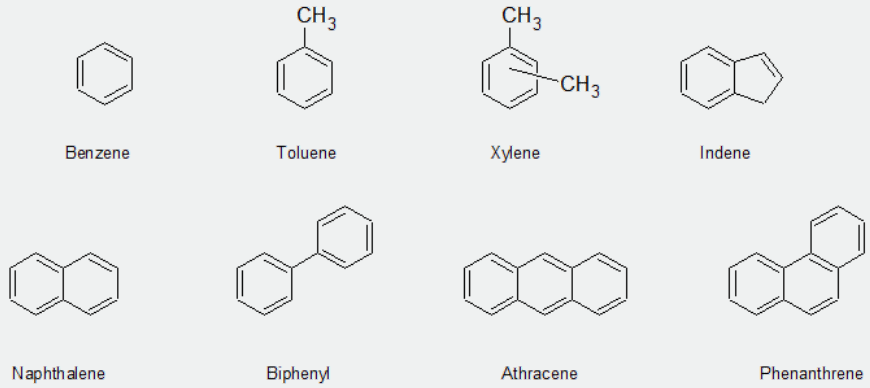


Figure 15.1: Some aromatic hydrocarbons found in coal tar.

A phenyl group consists of a benzene ring with one of its hydrogens removed.

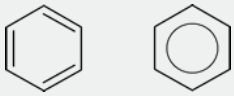


Figure 15.2: Two ways of representing a phenyl group

> Note that the ortho/meta/para system cannot be used when more than two substituents are present in the benzene ring. The "numbering system" can be used instead of the ortho/meta/para system in most cases when only two substituents are present.

Unlike aliphatic organics, nomenclature of benzene-derived compounds can be confusing because a single aromatic compound can have multiple possible names (such as common and systematic names) be associated with its structure. In these sections, we will analyze some of the ways these compounds can be named.

SIMPLE BENZENE NAMING

Some common substituents, like NO_2, Br, and Cl, can be named this way when it is attached to a phenyl group. Long chain carbons attached can also be named this way. The general format for this kind of naming is:

(positions of substituents (if >1)- + # (di, tri, ...) + substituent)$_n$ + benzene.

For example, chlorine (Cl) attached to a phenyl group would be named **chlorobenzene (chloro + benzene)**. Since there is only one substituent on the benzene ring, we do not have to indicate its position on the benzene ring (as it can freely rotate around and you would end up getting the same compound.)

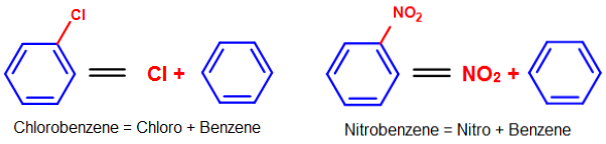


Figure 8. Example of simple benzene naming with chlorine and NO_2 as substituents.

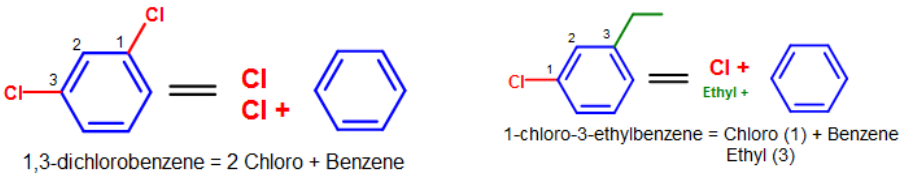


Figure 9. More complicated simple benzene naming examples - Note that standard nomenclature priority rules are applied here, causing the numbering of carbons to switch. See Nomenclature of Organic Compounds for a review on naming and priority rules.

ORTHO-, META-, PARA- (OMP) NOMENCLATURE FOR DISUBSTITUTED BENZENES

EDIT SECTION

Instead of using numbers to indicate substituents on a benzene ring, ***ortho- (o-), meta- (m-), or para (p-)*** can be used in place of positional markers when there are **two** substituents on the benzene ring (disubstituted benzenes). They are defined as the following:

- ***ortho- (o-):*** 1,2- (next to each other in a benzene ring)
- ***meta- (m):*** 1,3- (separated by one carbon in a benzene ring)
- ***para- (p):*** 1,4- (across from each other in a benzene ring)

Using the same example above in figure 9a (1,3-dichlorobenzene), we can use the ortho-, meta-, para- nomenclature to transform the chemical name into m-dichlorobenzene, as shown in the figure below.

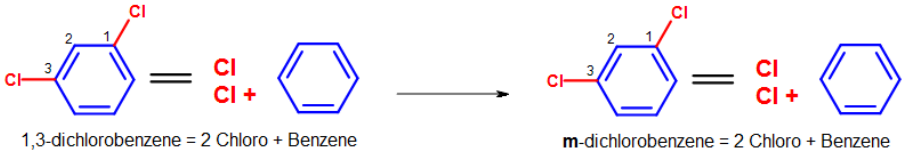


Figure 10. Transformation of 1,3-dichlorobenzene into m-dichlorobenzene.

Here are some other examples of ortho-, meta-, para- nomenclature used in context:

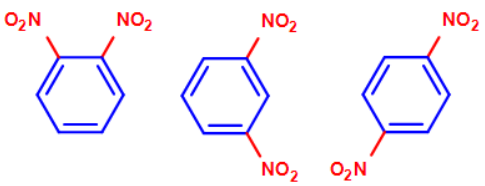


Figure 11. Example of o-, m-, p- nomenclature.
Listed in order:
1) o-dinitrobenzene
2) m-dinitrobenzene
3) p-dinitrobenzene

However, the substituents used in ortho-, meta-, para- nomenclature do not have to be the same. For example, we can use chlorine and a nitro group as substituents in the benzene ring.

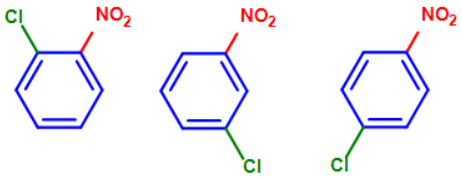
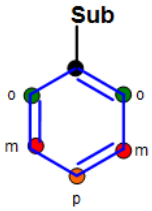


Figure 12. Example of o-, m-, p- nomenclature.
Listed in order:
1) o-nitrochlorobenzene
2) m-nitrochlorobenzene
3) p-nitrochlorobenzene
Note that the two substituents do not have to be the same.

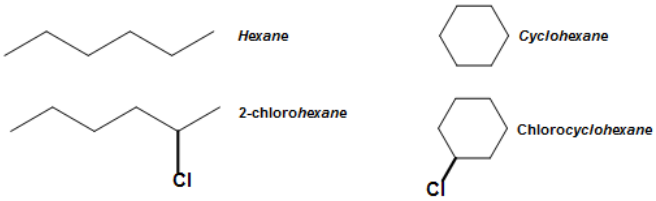
In conclusion, these can be pieced together into a summary diagram, as shown below:

Figure 13. A benzene ring with a primary substituent and the possible locations for the secondary substituent.
As shown:
1,2- (green) = ortho, o-
1,3- (red) = meta, m-
1,4- (orange) = para, p-
For clarity, the benzene ring has been rotated 30° relatively to the other benzenes in this article.

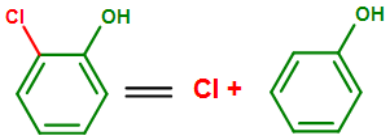


BASE NAME NOMENCLATURE EDIT SECTION

In addition to simple benzene naming and OMP nomenclature, benzene derived compounds are also sometimes used as **bases**. The concept of a base is similar to the nomenclature of aliphatic and cyclic compounds, where the parent for the organic compound is used as a base (a name for its chemical name. For example, the following compounds have the base names ***hexane*** and ***cyclohexane***, respectively. See Nomenclature of Organic Compounds for a review on naming organic compounds.



Benzene, similar to these compounds shown above, also has base names from its derived compounds. **Phenol (C_6H_5OH)**, as introduced previously in this article, for example, serves as a base when other substituents are attached to it. This is best illustrated in the diagram below.



o-chlorophenol = Chloro (o-) + Phenol

Figure 14. An example showing phenol as a base in its chemical name. Note how benzene no longer serves as a base when an OH group is added to the benzene ring.

Alternatively, we can use the numbering system to indicate this compound. When the numbering system is used, the carbon where the substituent is attached on the base will be given the first priority and named as carbon #1 (C_1). The normal priority rules then apply in the nomenclature process (give the rest of the substituents the lowest numbering as you could).

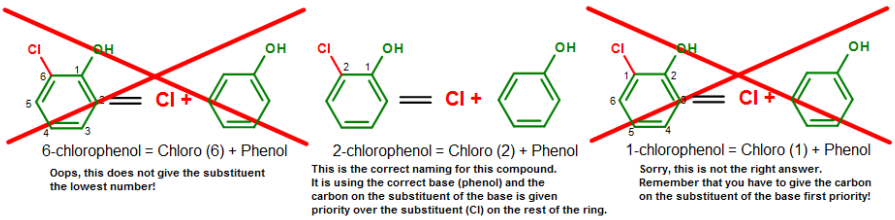


Figure 15. The naming process for 2-chlorophenol (o-chlorophenol). Note that 2-chlorophenol = o-chlorophenol.

Below is a list of commonly seen benzene-derived compounds. Some of these mono-substituted compounds (labeled in red and green), such as phenol or toluene, can be used in place of benzene for the chemical's base name.

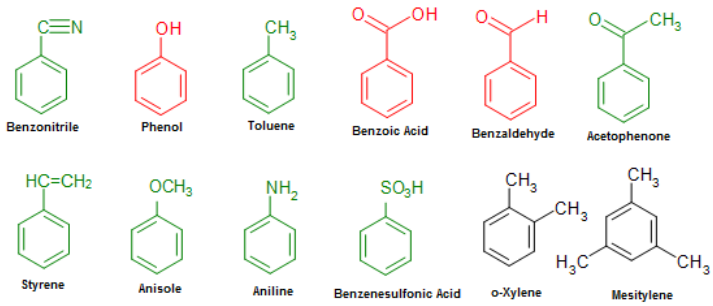


Figure 16. Common benzene derived compounds with various substituents.

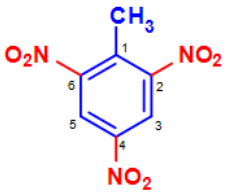


Figure 17. 2,4,6-Trinitrotoluene, or **TNT**, a common explosive used for both industrial and military purposes, is consisted of a **toluene** base (labeled in blue), along with three **nitro** groups attached as substituents (labeled in red).
The explosive is characteristic for its resistance to external shock and friction, making it useful in many applications where other highly sensitive explosives would simultaneously detonate.

COMMON VS. SYSTEMATIC (IUPAC) NOMENCLATURE EDIT SECTION

According to the indexing preferences of the *Chemical Abstracts*, **phenol, benzaldehyde, and benzoic acid (labeled in red in Figure 16)** are some of the common names that are retained in the IUPAC (systematic) nomenclature. Other names such as toluene, styrene, naphthalene, or phenanthrene can also be seen in the IUPAC system in the same way. While the use of other common names are usually acceptable in IUPAC, their use are discouraged in the nomenclature of compounds.

Nomenclature for compounds which has such discouraged names will be named by the simple benzene naming system. An example of this would include **toluene derivatives like TNT.** (Note that toluene by itself is retained by the IUPAC nomenclature, but its derivatives, which contains additional substituents on the benzene ring, might be excluded from the convention). For this reason, the **common chemical name** 2,4,6-trinitrotoluene, or TNT, as shown in figure 17, would not be advisable under the IUPAC (**systematic**) nomenclature.

To correctly name TNT under the IUPAC system, the simple benzene naming system should be used:

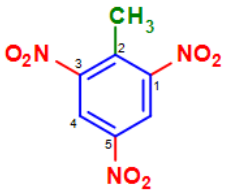


Figure 18. TNT, as named under the IUPAC nomenclature.
Note that since the IUPAC nomenclature does not recognize toluene as the primary base of this compound, substituent priorities are reverted to normal defaults.
As a result, TNT in IUPAC is named (systematic name):
2-methyl-1,3,5-trinitrobenzene

Figure 18. Systematic (IUPAC) name of 2,4,6-trinitrotoluene (common name), or TNT.
Note that the methyl group is individually named due to the exclusion of toluene from the IUPAC nomenclature.

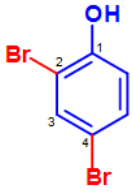


Figure 19. 2,4-dibromophenol, as shown in this diagram, is valid in both the common nomenclature as well as the IUPAC nomenclature. As mentioned previously, **phenol, benzoic acid, and benzaldehyde** substituents are allowed to be used in the IUPAC naming conventions and the base naming priority rules are applied in the nomenclature process.

Figure 19. The common name 2,4-dibromophenol, is shared by the IUPAC systematic nomenclature. Only substituents **phenol, benzoic acid, and benzaldehyde** share this commonality.

Since the IUPAC nomenclature primarily rely on the simple benzene naming system for the nomenclature of different benzene derived compounds, the OMP (ortho-, meta-, para-) system is not accepted in the IUPAC nomenclature. For this reason, the OMP system will yield common names that can be converted to systematic names by using the same method as above. For example, o-Xylene from the OMP system can be named 1,2-dimethylbenzene by using simple benzene naming (IUPAC standard).

THE PHENYL AND BENZYL GROUPS EDIT SECTION

THE PHENYL GROUP EDIT SECTION

As mentioned previously, the phenyl group (Ph-R, C_6H_5-R) can be formed by removing a hydrogen from benzene and attaching a substituent to where the hydrogen was removed. To this phenomenon, we can name compounds formed this way by applying this rule: **(phenyl + substituent)**. For example, a chlorine attached in this manner would be named **phenyl chloride**, and a bromine attached in this manner would be named **phenyl bromide**. (See below diagram)

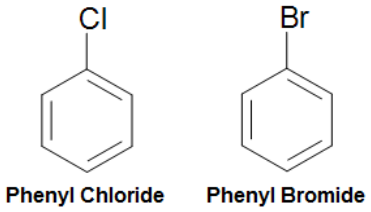


Figure 20. Naming of Phenyl Chloride and Phenyl Bromide

While compounds like these are usually named by simple benzene type naming (chlorobenzene and bromobenzene), the phenyl group naming is usually applied to benzene rings where a substituent with six or more carbons is attached, such as in the diagram below.

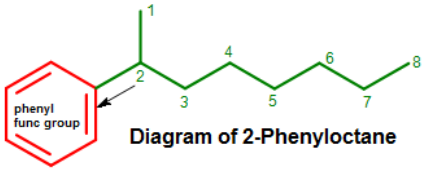


Figure 21. Diagram of 2-phenyloctane.

Although the diagram above might be a little daunting to understand at first, it is not as difficult as it seems after careful analysis of the structure is made. By looking for the longest chain in the compound, it should be clear that the longest chain is eight (8) carbons long (octane, as shown in green) and that a benzene ring is attached to the second position of this longest chain (labeled in red). As this rule suggests that the benzene ring will act as a function group (a substituent) whenever a substituent of more than six (6) carbons is attached to it, the name "benzene" is changed to **phenyl** and is used the same way as any other substituents, such as **methyl, ethyl, or bromo.** Putting it all together, the name can be derived as: **2-phenyloctane** (phenyl is attached at the second position of the longest carbon chain, octane).

THE BENZYL GROUP EDIT SECTION

The benzyl group (abbv. Bn), similar to the phenyl group, is formed by manipulating the benzene ring. In the case of the benzyl group, it is formed by taking the phenyl group and adding a CH_2 group to where the hydrogen was removed. Its molecular fragment can be written as $C_6H_5CH_2$-R, $PhCH_2$-R, or Bn-R. Nomenclature of benzyl group based compounds are very similar to the phenyl group compounds. For example, a chlorine attached to a benzyl group would simply be called benzyl chloride, whereas an OH group attached to a benzyl group would simply be called benzyl alcohol.

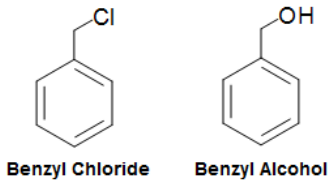


Figure 22. Benzyl Group Nomenclature

Additionally, other substituents can attach on the benzene ring in the presence of the benzyl group. An example of this can be seen in the figure below:

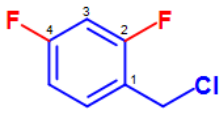
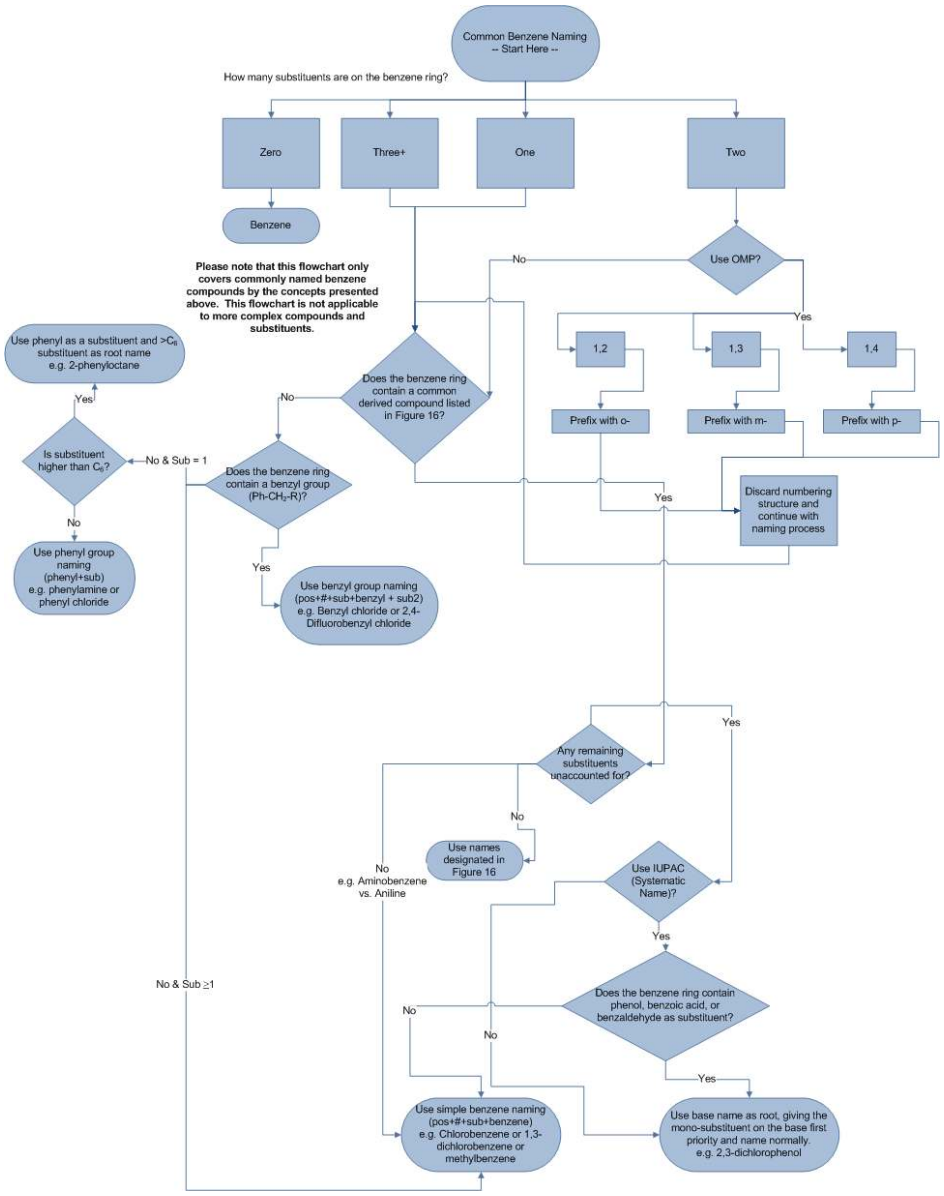


Figure 23. Nomenclature of 2,4-difluorobenzyl chloride. Similar to the base name nomenclatures system, the carbon in which th base substitutent is attached on the benzene ring is given the first priority and the rest of the substituents are given the lowest number order possible.

Similar to the base name nomenclature system, the carbon in which the base substituent is attached on the benzene ring is given the first priority and the rest of the substituents are given the lowest number order possible. Under this consideration, the above compound can be named: **2,4-difluorobenzyl chloride.**

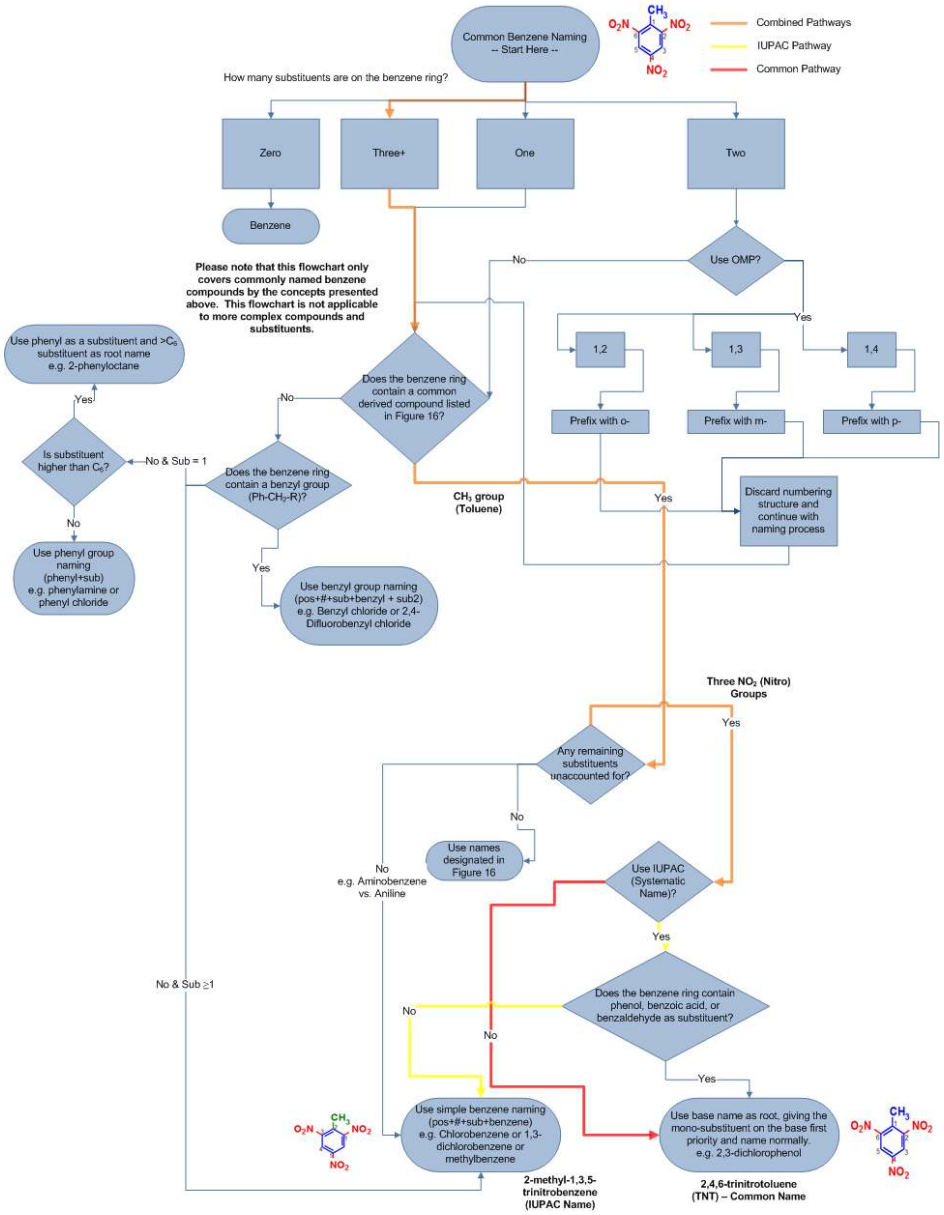
COMMONLY NAMED BENZENE COMPOUNDS NOMENCLATURE SUMMARY FLOWCHART EDIT SECTION



Summary Flowchart (Figure 24). Summary of nomenclature rules used in commonly benzene derived compounds. As benzene derived compounds can be extremely complex, only compounds covered in this article and other commonly named compounds can be named using this flowchart.

DETERMINATION OF COMMON AND SYSTEMATIC NAMES USING FLOWCHART EDIT SECTION

To demonstrate how this flowchart can be used to name TNT in its common and systematic (IUPAC) name, a replica of the flowchart with the appropriate flow paths are shown below:

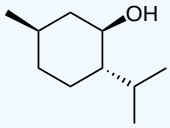


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EXERCISES

EXERCISE 15.1.1



(True/False) The compound above contains a benzene ring and thus is aromatic.

Answer

False, this compound does not contain a benzene ring in its structure.

EXERCISE 15.1.2

Benzene unusual stability is caused by how many conjugated pi bonds in its cyclic ring? ____

Answer

3

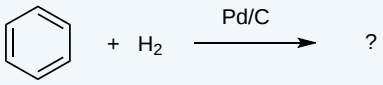
EXERCISE 15.1.3

Menthol, a topical analgesic used in many ointments for the relief of pain, releases a peppermint aroma upon exposure to the air. Based on this conclusion, can you imply that a benzene ring is present in its chemical structure? Why or why not?

Answer

No, a substance that is fragrant does not imply a benzene ring is in its structure. See camphor example (figure 1)

EXERCISE 15.1.4



Answer

No reaction, benzene requires a special catalyst to be hydrogenated due to its unusual stability given by its three conjugated pi bonds.

EXERCISE 15.1.5

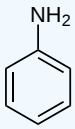
At normal conditions, benzene has ___ resonance structures.

Answer

2

EXERCISE 15.1.6

Which of the following name(s) is/are correct for the following compound?



a. nitrohydride benzene
b. phenylamine
c. phenylamide
d. aniline
e. nitrogenhydrogen benzene
f. All of the above is correct

Answer

b, d

EXERCISE 15.1.7

Convert 1,4-dimethylbenzene into its common name.

Answer

p-Xylene

EXERCISE 15.1.8

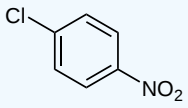
TNT's common name is: _____

Answer

2,4,6-trinitrotoluene

EXERCISE 15.1.9

Name the following compound using OMP nomenclature:



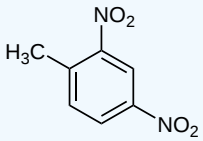
Answer

p-chloronitrobenzene

EXERCISE 15.1.10

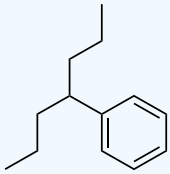
Draw the structure of 2,4-dinitrotoluene.

Answer



EXERCISE 15.1.11

Name the following compound:

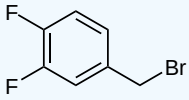


Answer

4-phenylheptane

EXAMPLE 15.1.12

Which of the following is the correct name for the following compound?



a. 3,4-difluorobenzyl bromide
b. 1,2-difluorobenzyl bromide
c. 4,5-difluorobenzyl bromide
d. 1,2-difluoroethyl bromide
e. 5,6-difluoroethyl bromide
f. 4,5-difluoroethyl bromide

Solution

a

EXERCISE 15.1.13

(True/False) Benzyl chloride can be abbreviated Bz-Cl.

Answer

False, the correct abbreviation for the benzyl group is Bn, not Bz. The correct abbreviation for Benzyl chloride is Bn-Cl.

EXERCISE 15.1.14

Benzoic Acid has what R group attached to its phenyl functional group?

Answer

COOH

EXERCISE 15.1.15

(True/False) A single aromatic compound can have multiple names indicating its structure.

Answer

True. TNT, for example, has the common name 2,4,6-trinitrotoluene and its systematic name is 2-methyl-1,3,5-trinitrobenzene.

EXERCISE 15.1.16

List the corresponding positions for the OMP system (o-, m-, p-).

Answer

Ortho - 1,2 ; Meta - 1,3 ; Para - 1,4

EXERCISE 15.1.17

A scientist has conducted an experiment on an unknown compound. He was able to determine that the unknown compound contains a cyclic ring in its structure as well as an alcohol (-OH) group attached to the ring. What is the unknown compound?

a. Cyclohexanol
b. Cyclicheptanol
c. Phenol
d. Methanol
e. Bleach
f. Cannot determine from the above information

Answer

The correct answer is f). We cannot determine what structure this is since the question does not tell us what kind of cyclic ring the -OH group is attached on. Just as cyclohexane can be cyclic, benzene and cycloheptane can also be cyclic.

EXERCISE 15.1.18

Which of the following statements is **false** for the compound, phenol?

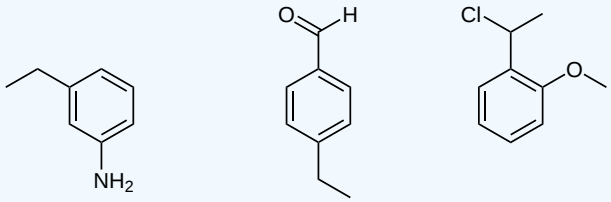
a. Phenol is a benzene derived compound.
b. Phenol can be made by attaching an -OH group to a phenyl group.
c. Phenol is highly toxic to the body even in small doses.
d. Phenol can be used as a catalyst in the hydrogenation of benzene into cyclohexane.
e. Phenol is used as an antiseptic in minute doses.
f. Phenol is amongst one of the three common names retained in the IUPAC nomenclature.

Answer

d

EXERCISE 15.1.19

State wither the following is para, meta, or ortho substituted.



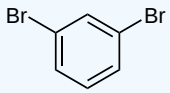
A B C

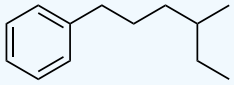
Answer

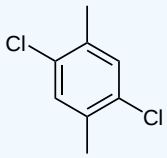
A – meta; B – para; C – ortho

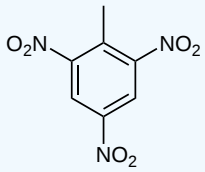
EXERCISE 15.1.20

Name the following compounds.

A) 

B) 

C) 

D) 

Answer

a. 1,3-Dibromobenzene

b. 1-phenyl-4-methylhexane

c. 1,4-Dichloro-2,5-dimethylbenzene

d. 2-methyl-1,3,5-trinitrobenzene. (Also known as trinitrotoluene, or TNT)

EXERCISE 15.1.21

Draw the following structures

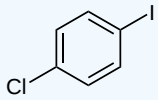
a. p-chloroiodobenzene

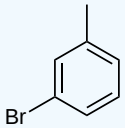
b. m-bromotoluene

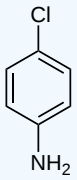
c. p-chloroaniline

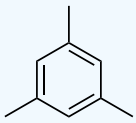
d. 1,3,5-trimethylbenzene

Answer

A) 

C) 

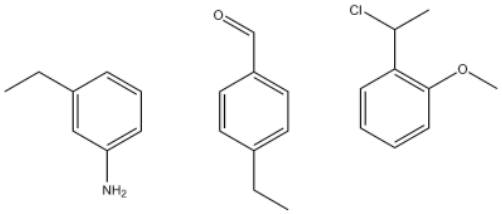
B) 

D) 

QUESTIONS

Q15.1.1

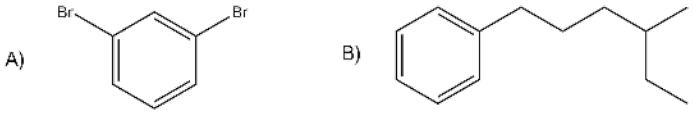
State wither the following is para, meta, or ortho substituted.

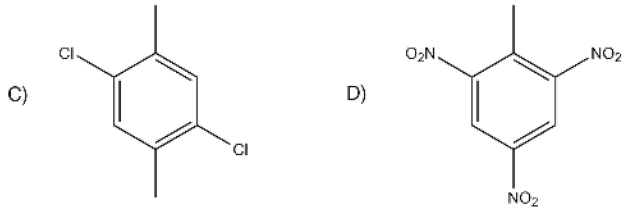


A B C

Q15.1.2

Name the following compounds.





Q15.1.3

Draw the following structures

a. p-chloroiodobenzene
b. m-bromotoluene
c. p-chloroaniline
d. 1,3,5-trimethylbenzene

SOLUTIONS

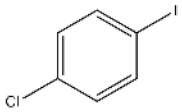
S15.1.1

A – meta; B – para; C – ortho

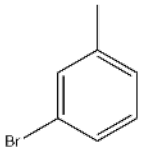
S15.1.2

a. 1,3-Dibromobenzene
b. 1-phenyl-4-methylhexane
c. 1,4-Dichloro-2,5-dimethylbenzene
d. 2-methyl-1,3,5-trinitrobenzene. (Also known as trinitrotoluene, or TNT)

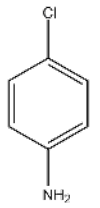
S15.1.3



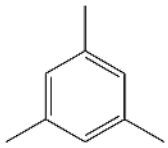
(A)



(B)



(C)



(D)

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- David Lam

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15.2: STRUCTURE AND STABILITY OF BENZENE

Objectives

After completing this section, you should be able to

1. compare the reactivity of a typical alkene with that of benzene.
2. Use the heat of hydrogenation data to show that benzene is more stable than might be expected for “cyclohexatriene.”
3. state the length of the carbon-carbon bonds in benzene, and compare this length with those of bonds found in other hydrocarbons.
4. describe the geometry of the benzene molecule.
5. describe the structure of benzene in terms of resonance.
6. describe the structure of benzene in terms of molecular orbital theory.
7. draw a molecular orbital diagram for benzene.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- degenerate

STUDY NOTES

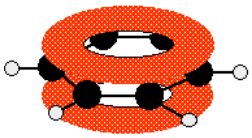
You may wish to review Sections 1.5 and 14.1 before you begin to study this section.

Note that the figure showing the molecular orbitals of benzene has two bonding (π_2 and π_3) and two anti-bonding (π^* and π_5^*) orbital pairs at the same energy levels. Orbitals with the same energy are described as degenerate orbitals.

Among the many distinctive features of benzene, its aromaticity is the major contributor to why it is so unreactive. This section will try to clarify the theory of aromaticity and why aromaticity gives unique qualities that make these conjugated alkenes inert to compounds such as Br_2 and even hydrochloric acid. It will also go into detail about the unusually large resonance energy due to the six conjugated carbons of benzene.



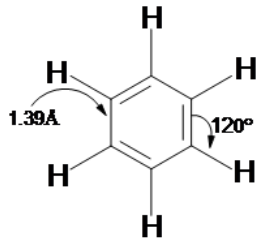
The delocalization of the p-orbital carbons on the sp^2 hybridized carbons is what gives the aromatic qualities of benzene.



This diagram shows one of the molecular orbitals containing two of the delocalized electrons, which may be found anywhere within the two "doughnuts". The other molecular orbitals are almost never drawn.

- Benzene (C_6H_6) is a planar molecule containing a ring of six carbon atoms, each with a hydrogen atom attached.
- The six carbon atoms form a perfectly regular hexagon. All of the carbon-carbon bonds have exactly the same lengths - somewhere between single and double bonds.
- There are delocalized electrons above and below the plane of the ring, which makes benzene particularly stable.
- Benzene resists addition reactions because those reactions would involve breaking the delocalization and losing that stability.

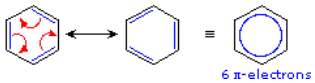
Because of the aromaticity of benzene, the resulting molecule is planar in shape with each C-C bond being 1.39 Å in length and each bond angle being 120°. You might ask yourselves how it's possible to have all of the bonds to be the same length if the ring is conjugated with both single (1.47 Å) and double (1.34 Å), but it is important to note that there are no distinct single or double bonds within the benzene. Rather, the delocalization of the ring makes each count as one and a half bonds between the carbons which makes sense because experimentally we find that the actual bond length is somewhere in between a single and double bond. Finally, there are a total of six p-orbital electrons that form the stabilizing electron clouds above and below the aromatic ring.



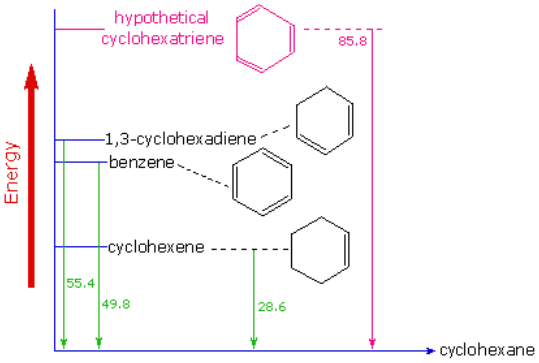
If benzene is forced to react by increasing the temperature and/or by addition of a catalyst, It undergoes **substitution reactions** rather than the addition reactions that are typical of alkenes. This further confirms the previous indication that the six-carbon benzene core is unusually stable to chemical modification. The conceptual contradiction presented by a high degree of unsaturation (low H:C ratio) and high chemical stability for benzene and related compounds remained an unsolved puzzle for many years. Eventually, the presently accepted structure of a regular-hexagonal, planar ring of carbons was adopted, and the exceptional thermodynamic and chemical stability of this system was attributed to resonance stabilization of a conjugated cyclic triene.

THE HIGH STABILITY OF BENZENE

Here, two structurally and energetically equivalent electronic structures for a stable compound are written, but no single structure provides an accurate or even an adequate representation of the true molecule. The six-membered ring in benzene is a perfect hexagon (all carbon-carbon bonds have an identical length of 1.40 Å). The cyclohexatriene contributors would be expected to show alternating bond lengths, the double bonds being shorter (1.34 Å) than the single bonds (1.54 Å). An alternative representation for benzene (circle within a hexagon) emphasizes the pi-electron delocalization in this molecule, and has the advantage of being a single diagram. In cases such as these, the electron delocalization described by resonance enhances the stability of the molecules, and compounds composed of such molecules often show exceptional stability and related properties.



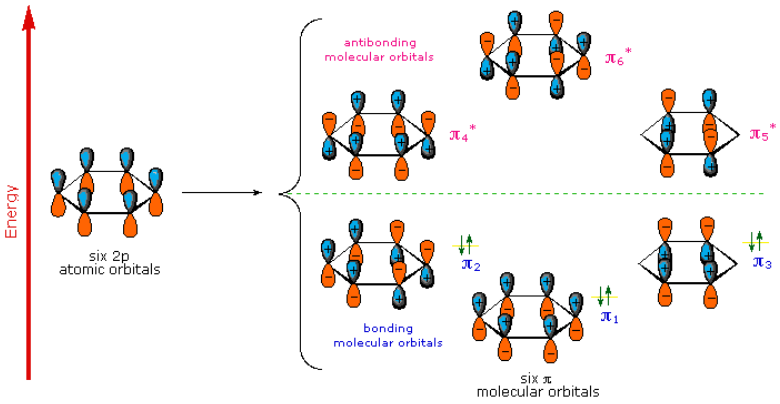
Evidence for the enhanced thermodynamic stability of benzene was obtained from measurements of the heat released when double bonds in a six-carbon ring are hydrogenated (hydrogen is added catalytically) to give cyclohexane as a common product. In the following diagram cyclohexane represents a low-energy reference point. Addition of hydrogen to cyclohexene produces cyclohexane and releases heat amounting to 28.6 kcal per mole. If we take this value to represent the energy cost of introducing one double bond into a six-carbon ring, we would expect a cyclohexadiene to release 57.2 kcal per mole on complete hydrogenation, and 1,3,5-cyclohexatriene to release 85.8 kcal per mole. These **heats of hydrogenation** would reflect the relative thermodynamic stability of the compounds. In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about 2 kcal, presumably due to conjugation of the double bonds. **Benzene, however, is an extraordinary 36 kcal/mole more stable than expected**. This sort of stability enhancement is now accepted as a characteristic of all aromatic compounds.



A molecular orbital description of benzene provides a more satisfying and more general treatment of "aromaticity". We know that benzene has a planar hexagonal structure in which all the carbon atoms are sp^2 hybridized, and all the carbon-carbon bonds are equal in length. As shown below, the remaining cyclic array of six p-orbitals (one on each carbon) overlap to generate six molecular orbitals, three bonding and three antibonding. The plus and minus signs shown in the diagram do not represent electrostatic charge, but refer to phase signs in the equations that describe these orbitals (in the diagram the phases are also color coded). When the phases correspond, the orbitals overlap to generate a common region of like phase, with those orbitals having the greatest overlap (e.g. π_1) being lowest in energy. The remaining

carbon valence electrons then occupy these molecular orbitals in pairs, resulting in a fully occupied (6 electrons) set of bonding molecular orbitals. It is this completely filled set of bonding orbitals, or **closed shell**, that gives the benzene ring its thermodynamic and chemical stability, just as a filled valence shell octet confers stability on the inert gases.

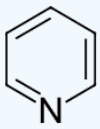
THE MOLECULAR ORBITALS OF BENZENE



EXERCISES

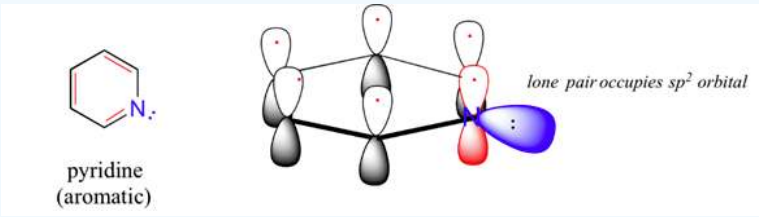
? EXERCISE 15.2.1

The molecule, pyridine, is planar with bond angles of 120º. Pyridine has many other characteristics similar to benzene. Draw a diagram showing the p orbitals in pyridine and use it to explain its similarity to benzene.



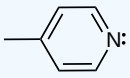
Answer

The nitrogen and each carbon in the pyridine ring is sp^2 hybridized. In the bonding picture for pyridine, the nitrogen is sp^2-hybridized, with two of the three sp^2 orbitals forming sigma overlaps with the sp^2 orbitals of neighboring carbon atoms, and the third nitrogen sp^2 orbital containing the lone pair electrons. The unhybridized p orbital contains a single electron, which is part of the 6 pi-electron system delocalized around the ring. Pyridine is most likely aromatic which gives it its planar shape and 120º bond angles.

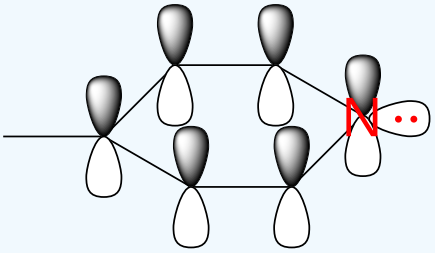


? EXERCISE 15.2.2

The molecule shown, *p*-methylpyridine, has similar properties to benzene (flat, 120° bond angles). Draw the pi-orbitals for this compound.



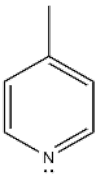
Answer



QUESTIONS

Q15.2.1

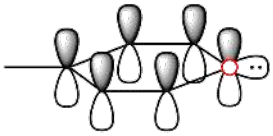
The molecule shown, *p*-methylpyridine, has similar properties to benzene (flat, 120° bond angles). Draw the pi-orbitals for this compound.



SOLUTIONS

S15.2.1

The nitrogen has a lone pair of electrons perpendicular to the ring.



○ =N

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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15.3: AROMATICITY AND THE HUCKEL 4N + 2 RULE

Objectives

After completing this section, you should be able to

1. define aromaticity in terms of the Hückel 4*n* + 2 rule.
2. use the Hückel 4*n* + 2 rule to determine whether or not a given polyunsaturated cyclic hydrocarbon should exhibit aromatic properties.
3. describe the difference in properties between an aromatic hydrocarbon, such as benzene, and a non-aromatic polyunsaturated cyclic hydrocarbon, such as cyclobutadiene or cyclooctatetraene.
4. draw molecular orbital diagrams for aromatic species, such as benzene, the cyclopentadienyl anion and pyridine, and compare these diagrams with those obtained for non-aromatic species, such as cyclobutadiene and the cyclopentadienyl cation.

STUDY NOTES

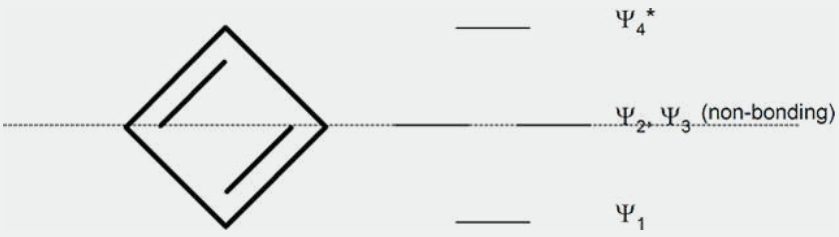
The following mnemonic device will help you establish the approximate energy levels for the molecular orbitals of various organic ring systems.

Whatever the size of the ring, place one point of the ring down to the bottom. The corners of the ring, where the carbons are located, will roughly approximate the location and pattern of the molecular orbital energy levels. Cut the ring exactly in half. The energy levels in the top half will be anti-bonding (Ψ^*) orbitals and those in the bottom will be bonding (Ψ) orbitals. If the carbons fall directly in the centre of the ring (e.g., four-membered rings) the energy levels there are non-bonding.

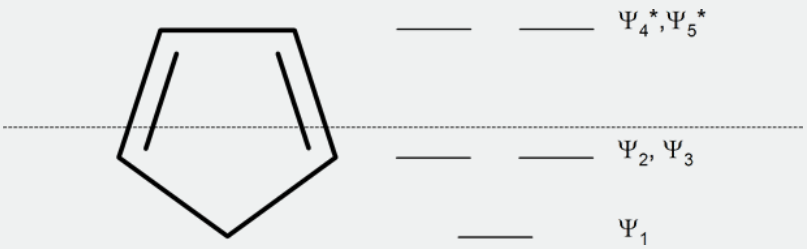
cyclopropenyl ring (three-membered ring)



cyclobutadienyl ring (four-membered ring)



cyclopentadienyl ring (five-membered ring)



In 1931, German chemist and physicist Erich Hückel proposed a theory to help determine if a planar ring molecule would have aromatic properties. His rule states that if a cyclic, planar molecule has 4n+2 π electrons, it is considered aromatic. This rule would come to be known as Hückel's Rule.

FOUR CRITERIA FOR AROMATICITY

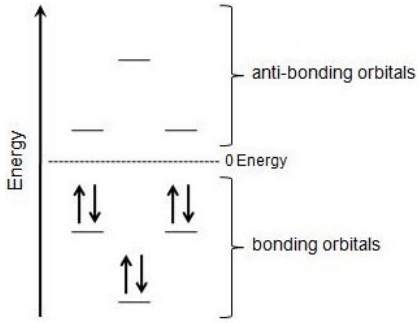
When deciding if a compound is aromatic, go through the following checklist. If the compound does not meet all the following criteria, it is likely not aromatic.

1. The molecule is cyclic (a ring of atoms)

2. The molecule is planar (all atoms in the molecule lie in the same plane)
3. The molecule is fully conjugated (p orbitals at every atom in the ring)
4. The molecule has 4n+2 π electrons (n=0 or any positive integer)

WHY 4N+2 Π ELECTRONS?

According to Hückel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons. This is true of aromatic compounds, meaning they are quite stable. With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by n), leaving all bonding orbitals filled and no anti-bonding orbitals occupied. This gives a total of 4n+2 π electrons. You can see how this works with the molecular orbital diagram for the aromatic compound, benzene, below. Benzene has 6 π electrons. Its first 2 π electrons fill the lowest energy orbital, and it has 4 π electrons remaining. These 4 fill in the orbitals of the succeeding energy level. Notice how all of its bonding orbitals are filled, but none of the anti-bonding orbitals have any electrons.



molecular orbital diagram for benzene

To apply the 4n+2 rule, first count the number of π electrons in the molecule. Then, set this number equal to 4n+2 and solve for n. If is 0 or any positive integer (1, 2, 3,...), the rule has been met. For example, benzene has six π electrons:

$$4n + 2 = 6 \tag{15.3.1}$$

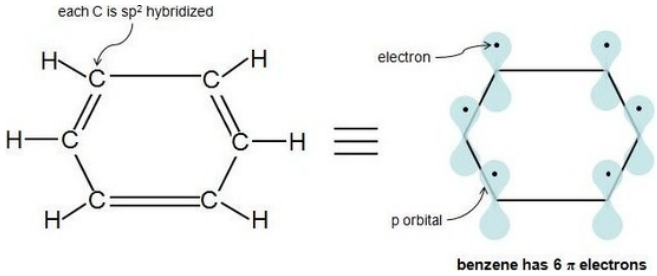
$$4n = 4 \tag{15.3.2}$$

$$n = 1 \tag{15.3.3}$$

For benzene, we find that $n = 1$, which is a positive integer, so the rule is met.

HOW CAN YOU TELL WHICH ELECTRONS ARE Π ELECTRONS?

Perhaps the toughest part of Hückel's Rule is figuring out which electrons in the compound are actually π electrons. Once this is figured out, the rule is quite straightforward. π electrons lie in p orbitals and sp^2 hybridized atoms have 1 p orbital each. So if every molecule in the cyclic compound is sp2 hybridized, this means the molecule is fully conjugated (has 1 p orbital at each atom), and the electrons in these p orbitals are the π electrons. A simple way to know if an atom is sp2 hybridized is to see if it has 3 attached atoms and no lone pairs of electrons. This video provides a very nice tutorial on how to determine an atom's hybridization. In a cyclic hydrocarbon compound with alternating single and double bonds, each carbon is attached to 1 hydrogen and 2 other carbons. Therefore, each carbon is sp2 hybridized and has a p orbital. Let's look at our previous example, benzene:

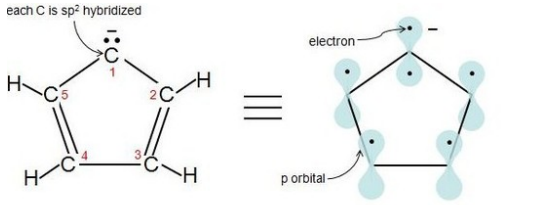


benzene has 6 π electrons

Each double bond (π bond) always contributes 2 π electrons. Benzene has 3 double bonds, so it has 6 π electrons.

AROMATIC IONS

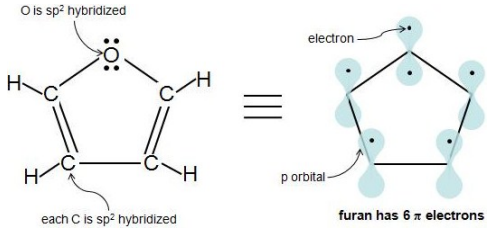
Hückel's Rule also applies to ions. As long as a compound has 4n+2 π electrons, it does not matter if the molecule is neutral or has a charge. For example, cyclopentadienyl anion is an aromatic ion. How do we know that it is fully conjugated? That is, how do we know that each atom in this molecule has 1 p orbital? Let's look at the following figure. Carbons 2-5 are sp^2 hybridized because they have 3 attached atoms and have no lone electron pairs. What about carbon 1? Another simple rule to determine if an atom is sp^2 hybridized is if an atom has 1 or more lone pairs and is attached to an sp^2 hybridized atom, then that atom is sp^2 hybridized also. This video explains the rule very clearly. Therefore, carbon 1 has a p orbital. Cyclopentadienyl anion has 6 π electrons and fulfills the 4n+2 rule.



cyclopentadienyl anion has 6 π electrons

HETEROCYCLIC AROMATIC COMPOUNDS

So far, you have encountered many carbon homocyclic rings, but compounds with elements other than carbon in the ring can also be aromatic, as long as they fulfill the criteria for aromaticity. These molecules are called heterocyclic compounds because they contain 1 or more different atoms other than carbon in the ring. A common example is furan, which contains an oxygen atom. We know that all carbons in furan are sp^2 hybridized. But is the oxygen atom sp^2 hybridized? The oxygen has at least 1 lone electron pair and is attached to an sp^2 hybridized atom, so it is sp^2 hybridized as well. Notice how oxygen has 2 lone pairs of electrons. How many of those electrons are π electrons? An sp^2 hybridized atom only has 1 p orbital, which can only hold 2 electrons, so we know that 1 electron pair is in the p orbital, while the other pair is in an sp^2 orbital. So, only 1 of oxygen's 2 lone electron pairs are π electrons. Furan has 6 π electrons and fulfills the 4n+2 rule.



furan has 6 π electrons

ANSWERS

1. Aromatic - only 1 of S's lone pairs counts as π electrons, so there are 6 π electrons, n=1
2. Not aromatic - not fully conjugated, top C is sp^3 hybridized
3. Not aromatic - top C is sp^2 hybridized, but there are 4 π electrons, n=1/2
4. Aromatic - N is using its 1 p orbital for the electrons in the double bond, so its lone pair of electrons are not π electrons, there are 6 π electrons, n=1
5. Aromatic - there are 6 π electrons, n=1
6. Not aromatic - all atoms are sp^2 hybridized, but only 1 of S's lone pairs counts as π electrons, so there 8 π electrons, n=1.5
7. Not aromatic - there are 4 π electrons, n=1/2
8. Aromatic - only 1 of N's lone pairs counts as π electrons, so there are 6 π electrons, n=1
9. Not aromatic - not fully conjugated, top C is sp^3 hybridized
10. Aromatic - O is using its 1 p orbital for the elections in the double bond, so its lone pair of electrons are not π electrons, there are 6 π electrons, n=1

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2. Berson, Jerome. Chemical Creativity: Ideas from the Work of Woodward, Hückel, Meerwein, and Others. New York: Wiley-VCH, 1999.
3. Badger, G.M. Aromatic Character and Aromaticity. London, England: Cambridge University Press, 1969.
4. Lewis, David and David Peters. Facts and Theories of Aromaticity. London, England: Macmillan Press, 1975.

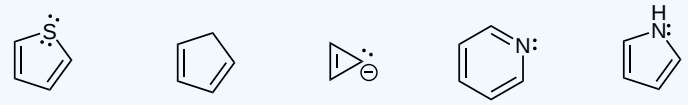
INTERNAL LINKS

- Aromaticity

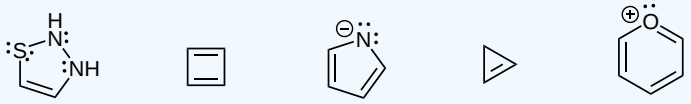
EXERCISES

EXERCISE 15.3.1

Using the criteria for aromaticity, determine if the following molecules are aromatic:



a) b) c) d) e)



f) g) h) i) j)

Answer

a) Aromatic - only 1 of S's lone pairs counts as π electrons, so there are 6 π electrons, n=1

b) Not aromatic - not fully conjugated, top C is sp^3 hybridized

c) Not aromatic - top C is sp^2 hybridized, but there are 4 π electrons, n=1/2

d) Aromatic - N is using its 1 p orbital for the electrons in the double bond, so its lone pair of electrons are not π electrons, there are 6 π electrons, n=1

e) Aromatic - there are 6 π electrons, n=1

f) Not aromatic - all atoms are sp^2 hybridized, but only 1 of S's lone pairs counts as π electrons, so there 8 π electrons, n=1.5

g) Not aromatic - there are 4 π electrons, n=1/2

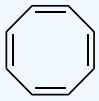
h) Aromatic - only 1 of N's lone pairs counts as π electrons, so there are 6 π electrons, n=1

i) Not aromatic - not fully conjugated, top C is sp^3 hybridized

j) Aromatic - O is using its 1 p orbital for the elections in the double bond, so its lone pair of electrons are not π electrons, there are 6 π electrons, n=1

EXERCISE 15.3.2

To be aromatic, a molecule must be planar conjugated, and obey the 4n+2 rule. The following is the following molecule aromatic?



Answer

No, it is not. It does not obey the 4n+2 rule. Also it is not planar.

QUESTIONS

Q15.3.1

To be aromatic, a molecule must be planar conjugated, and obey the 4n+2 rule. The following is the following molecule aromatic?



SOLUTIONS

S15.3.1

No, it is not. It does not obey the 4n+2 rule. Also it is not planar.

CONTRIBUTORS AND ATTRIBUTIONS

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- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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15.4: AROMATIC IONS

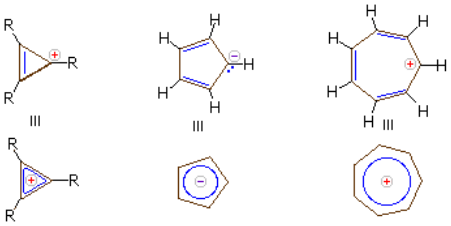
Objectives

After completing this section, you should be able to

1. use the Hückel 4*n* + 2 rule to explain the stability of the cyclopentadienyl anion, the cycloheptatrienyl cation and similar species.
2. use the Hückel 4*n* + 2 rule to determine whether or not a given unsaturated cyclic hydrocarbon anion or cation is aromatic.
3. draw the resonance contributors for the cyclopentadienyl anion, cation and radical, and similar species.

CHARGED AROMATIC COMPOUNDS

Carbanions and carbocations may also show aromatic stabilization. Some examples are:



The three-membered ring cation has 2 π-electrons and is surprisingly stable, considering its ring strain. Cyclopentadiene is as acidic as ethanol, reflecting the stability of its 6 π-electron conjugate base. Salts of cycloheptatrienyl cation (tropylium ion) are stable in water solution, again reflecting the stability of this 6 π-electron cation.

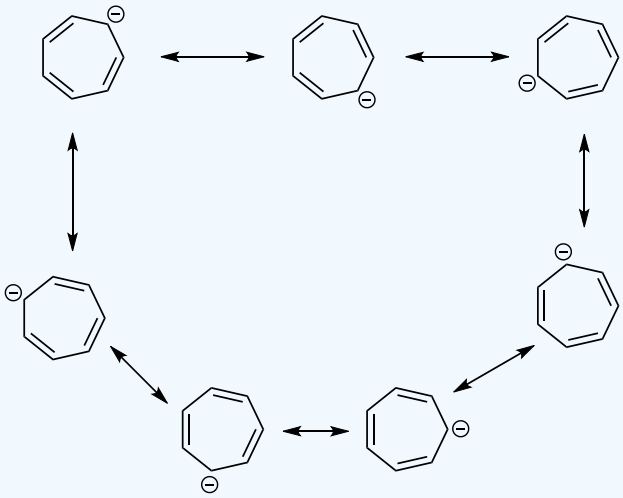
EXERCISES

? EXERCISE 15.4.1

Draw the resonance structures for cycloheptatriene anion. Are all bonds equivalent? How many lines (signals) would you see in a H^1 NMR?

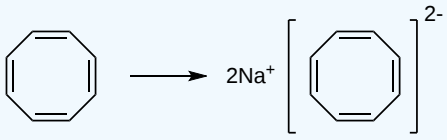
Answer

All protons and carbons are the same, so therefore each spectrum will only have one signal in the proton NMR.



EXERCISE 15.4.2

The following reaction occurs readily. Propose a reason why this occurs?



Answer

The ring becomes aromatic with the addition of two electrons. Thereby obeying the 4n+2 rule.

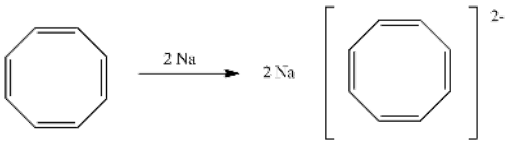
QUESTIONS

Q15.4.1

Draw the resonance structures for cycloheptatriene anion. Are all bonds equivalent? How many lines (signals) would you see in a H^1 C^{13} NMR?

Q15.4.2

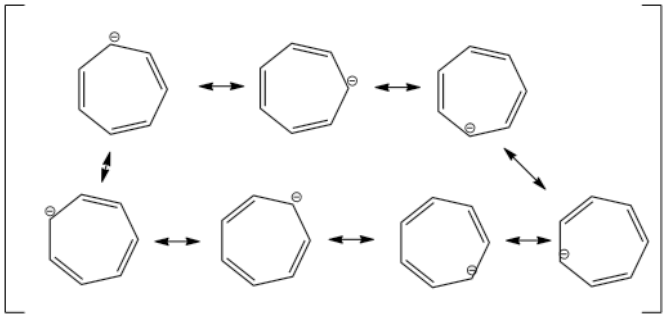
The following reaction occurs readily. Propose a reason why this occurs?



SOLUTIONS

S15.4.1

All protons and carbons are the same, so therefore each spectrum will only have one signal each.



S15.4.2

The ring becomes aromatic with the addition of two electrons. Thereby obeying the 4n+2 rule.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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15.5: AROMATIC HETEROCYCLES- PYRIDINE AND PYRROLE

Objectives

After completing this section, you should be able to

1. draw the structure of the common aromatic heterocycles pyridine and pyrrole.
2. use the Hückel $4n + 2$ rule to explain the aromaticity of each of pyridine and pyrrole.
3. draw a diagram to show the orbitals involved in forming the conjugated six-pi-electron systems present in aromatic heterocycles such as pyridine, pyrrole, etc.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

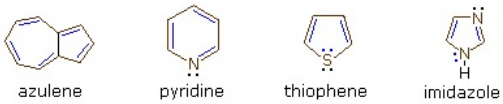
- carbocycles
- heterocycles

AROMATIC HETEROCYCLES

Many unsaturated cyclic compounds have exceptional properties that we now consider characteristic of "aromatic" systems. The following cases are illustrative:

Compound	Structural Formula	Reaction with Br_2	Thermodynamic Stabilization
1,3-Cyclopentadiene		Addition (0 ºC)	Slight
1,3,5-Cycloheptatriene		Addition (0 ºC)	Slight
1,3,5,7-Cyclooctatetraene		Addition (0 ºC)	Slight
Benzene		Substitution	Large
Pyridine		Substitution	Large
Furan		Substitution (0 ºC)	Moderate
Pyrrole		Substitution	Moderate

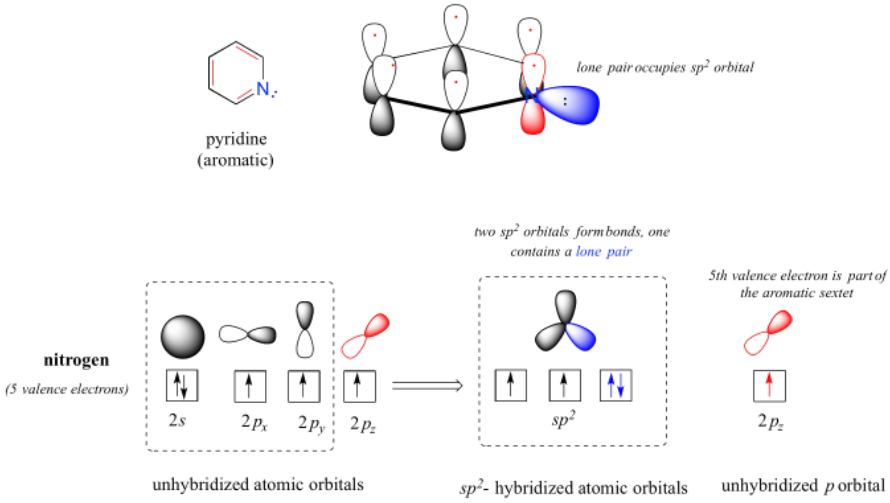
Benzene is the archetypical aromatic compound. It is planar, bond angles=120º, all carbon atoms in the ring are sp^2 hybridized, and the pi-orbitals are occupied by 6 electrons. The aromatic heterocycle pyridine is similar to benzene, and is often used as a weak base for scavenging protons. Furan and pyrrole have heterocyclic five-membered rings, in which the heteroatom has at least one pair of non-bonding valence shell electrons. By hybridizing this heteroatom to a sp2 state, a p-orbital occupied by a pair of electrons and oriented parallel to the carbon p-orbitals is created. The resulting planar ring meets the first requirement for aromaticity, and the π-system is occupied by 6 electrons, 4 from the two double bonds and 2 from the heteroatom, thus satisfying the Hückel Rule.



Four illustrative examples of aromatic compounds are shown above. The sp2 hybridized ring atoms are connected by brown bonds, the π-electron pairs and bonds that constitute the aromatic ring are colored blue. Electron pairs that are not part of the aromatic π-electron system

are black. The first example is azulene, a blue-colored 10 π-electron aromatic hydrocarbon isomeric with naphthalene. The second and third compounds are heterocycles having aromatic properties. Pyridine has a benzene-like six-membered ring incorporating one nitrogen atom. The non-bonding electron pair on the nitrogen is not part of the aromatic π-electron sextet, and may bond to a proton or other electrophile without disrupting the aromatic system. In the case of thiophene, a sulfur analog of furan, one of the sulfur electron pairs (colored blue) participates in the aromatic ring π-electron conjugation. The last compound is imidazole, a heterocycle having two nitrogen atoms. Note that only one of the nitrogen non-bonding electron pairs is used for the aromatic π-electron sextet. The other electron pair (colored black) behaves similarly to the electron pair in pyridine.

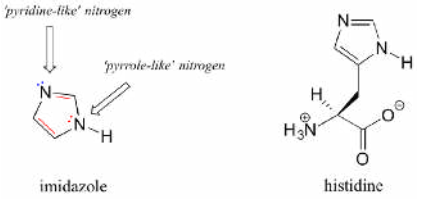
Heterocycles - cyclic structures in which the ring atoms may include oxygen or nitrogen - can also be aromatic. Pyridine, for example, is an aromatic heterocycle. In the bonding picture for pyridine, the nitrogen is sp^2-hybridized, with two of the three sp^2 orbitals forming sigma overlaps with the sp^2 orbitals of neighboring carbon atoms, and the third nitrogen sp^2 orbital containing the lone pair. The unhybridized p orbital contains a single electron, which is part of the 6 pi-electron system delocalized around the ring.



another image of orbitals in pyridine

Why do we not assume that the nitrogen in pyrrole is sp^3-hybridized, like a normal secondary amine? The answer is simple: if it were, then pyrrole could not be aromatic, and thus it would not have the stability associated with aromaticity. In general, *if a molecule or group can be aromatic, it will be,* just as water will always flow downhill if there is a downhill pathway available.

Imidazole is another important example of an aromatic heterocycle found in biomolecules - the side chain of the amino acid histidine contains an imidazole ring.



In imidazole, one nitrogen is 'pyrrole-like' (the lone pair contributes to the aromatic sextet) and one is 'pyridine-like' (the lone pair is located in an sp^2 orbital, and is *not* part of the aromatic sextet).

EXERCISES

? EXERCISE 15.5.1

Draw the orbitals of thiophene to show that is aromatic.



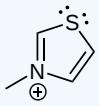
Answer

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This drawing shows it has 6 electrons in the pi-orbital.

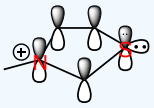
EXERCISE 15.5.2

The following ring is called a thiazolium ring. Describe how it is aromatic.



Answer

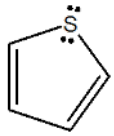
Similar to the last question, the drawing shows that there is only 6 electrons in the pi-system.



QUESTIONS

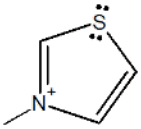
Q15.5.1

Draw the orbitals of thiophene to show that is aromatic.



Q15.5.2

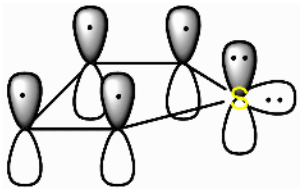
The following ring is called a thiazolium ring. Describe how it is aromatic.



SOLUTIONS

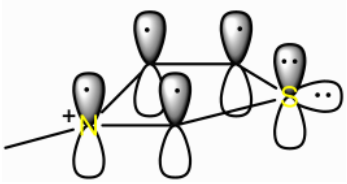
S15.5.1

This drawing shows it has 6 electrons in the pi-orbital.



S15.5.2

Similar to the last question, the drawing shows that there is only 6 electrons in the pi-system.



CONTRIBUTORS AND ATTRIBUTIONS

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- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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15.6: POLYCYCLIC AROMATIC COMPOUNDS

Objectives

After completing this section, you should be able to draw the resonance contributors for polycyclic aromatic compounds, such as naphthalene, anthracene, etc.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- polycyclic aromatic compounds

STUDY NOTES

As their name indicates, *polycyclic aromatic hydrocarbons* are aromatic hydrocarbons which contain more than one benzenoid (i.e., benzene-like) ring. This section deals only with those compounds in which the benzenoid rings are fused together; in other words, compounds in which at least one carbon-carbon bond is common to two aromatic rings. Another type of polycyclic aromatic hydrocarbon contains two or more benzenoid rings joined by a carbon-carbon single bond. The simplest compound of this type is biphenyl, the compound from which PCBs (polychlorinated biphenyls) are derived.

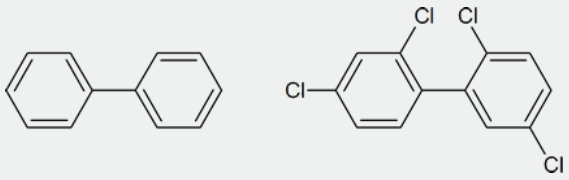
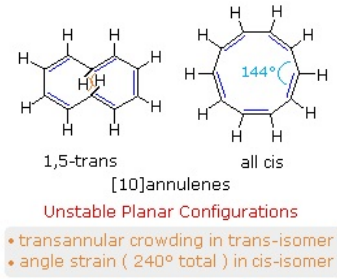
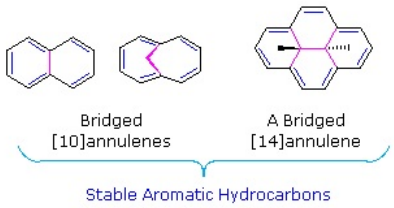


Figure 15.3: Structures of biphenyl and a typical PCB

AROMATIC COMPOUND WITH A SINGLE RING





AROMATIC COMPOUNDS WITH MORE THAN ONE RING

Benzene rings may be joined together (fused) to give larger polycyclic aromatic compounds. A few examples are drawn below, together with the approved numbering scheme for substituted derivatives. The peripheral carbon atoms (numbered in all but the last three examples) are all bonded to hydrogen atoms. Unlike benzene, all the C-C bond lengths in these fused ring aromatics are not the same, and there is some localization of the pi-electrons.

The six benzene rings in coronene are fused in a planar ring; whereas the six rings in hexahelicene are not joined in a larger ring, but assume a helical turn, due to the crowding together of the terminal ring atoms. This helical configuration renders the hexahelicene molecule chiral, and it has been resolved into stable enantiomers.

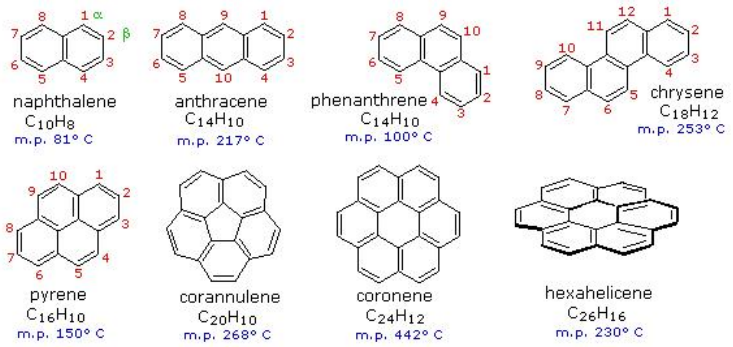
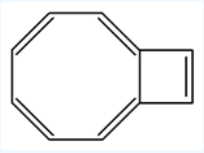


***Figure 2**: Examples of Polycyclic Aromatic Hydrocarbons (PAHs).*

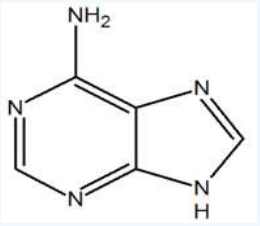
EXERCISES

? EXERCISE 15.6.1

1) The following molecule is an isomer of naphthalene. Is it aromatic? Draw a resonance structure for it.

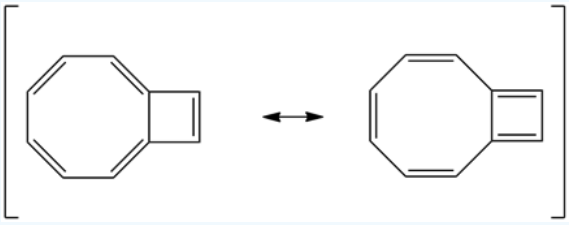


2) The following molecule is adenine. It has a purine core. Of the nitrogen in the core, how many electrons are donated into the pi system?

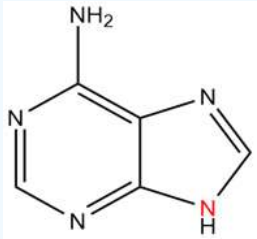


Answer

1) It has 10 pi electrons which follows the 4n+2 rule making it aromatic.



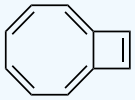
2) There is only one nitrogen of the core that contributes a set of lone pair electrons as 2 pi electrons (in red). All of the other nitrogens are sp2 hybrized and contribute 1 pi electron each. In total, the core is aromatic with 10 electrons in the pi-system.



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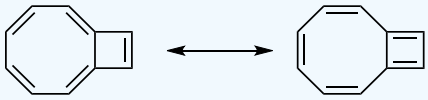
EXERCISE 15.6.2

This is an isomer of naphthalene. Is it aromatic? Draw a resonance structure for it.



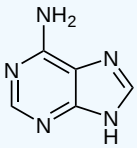
Answer

Yes, it is aromatic. 4n+2 pi-electrons.



EXERCISE 15.6.3

The following molecule is adenine. It has a purine core. Of the nitrogen in the core, how many electrons are donated into the pi system?



Answer

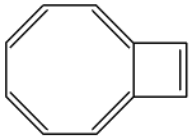
There is only one nitrogen of the core that contributes to the pi-system (in red). With this one lone pair the core is aromatic with 10 electrons in the pi-system.



QUESTIONS

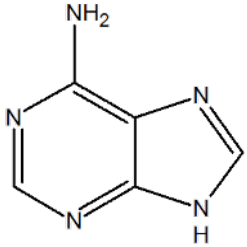
Q15.6.1

This is an isomer of naphthalene. Is it aromatic? Draw a resonance structure for it.



Q15.6.2

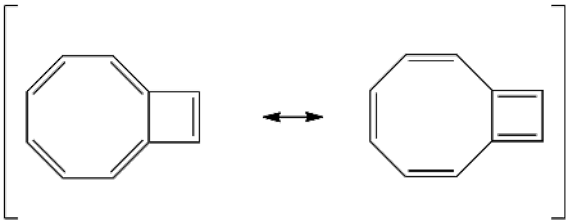
The following molecule is adenine. It has a purine core. Of the nitrogen in the core, how many electrons are donated into the pi system?



SOLUTIONS

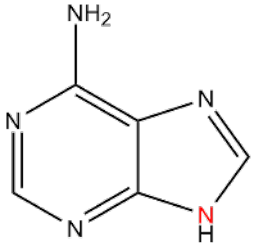
S15.6.1

Yes, it is aromatic. 4n+2 pi-electrons.



S15.6.2

There is only one nitrogen of the core that contributes to the pi-system (in red). With this one lone pair the core is aromatic with 10 electrons in the pi-system.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
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15.7: SPECTROSCOPY OF AROMATIC COMPOUNDS

Objectives

After completing this section, you should be able to

1. determine whether an unknown compound contains an aromatic ring by inspection of its infrared spectrum, given a table of characteristic infrared absorptions.
2. state the approximate chemical shift of aryl protons in a proton NMR spectrum.
3. explain why signals resulting from the presence of aryl protons are found downfield from those caused by vinylic protons in a proton NMR spectrum.
4. propose possible structures for an unknown aromatic compound, given its proton NMR spectrum, other spectroscopic data (such as a ^{13}C NMR or infrared spectrum), or both.

KEY TERMS

Make certain that you can define, and use in context, the key term below.

- ring current

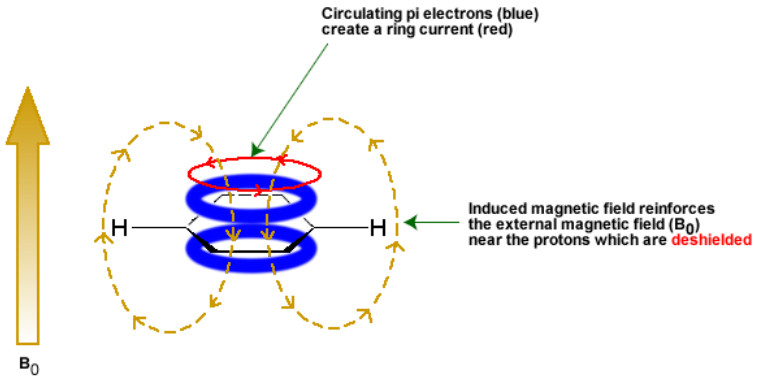
STUDY NOTES

It is not necessary that you memorize detailed spectroscopic data. In the laboratory, on assignments and when writing examinations, you will be provided with a table of characteristic infrared absorptions to assist you in interpreting infrared spectra.

The important points to note about the proton NMR of aromatic compounds are the approximate chemical shifts of such protons and the complex splitting pattern that is sometimes observed. You are advised not to spend too long trying to understand why the signal for an aryl proton is found downfield from the signal for a vinylic proton. In general, we want you to be able to interpret NMR spectra, and leave the underlying theory for subsequent chemistry courses.

THE CHEMICAL SHIFTS OF AROMATIC PROTONS

Some protons resonate much further downfield than can be accounted for simply by the deshielding effect of nearby electronegative atoms. Vinylic protons (those directly bonded to an alkene carbon) and aromatic (benzylic) protons are dramatic examples.



We'll consider the aromatic proton first. Recall that in benzene and many other aromatic structures, a sextet of pelectrons is delocalized around the ring. When the molecule is exposed to B_0, these pelectrons begin to circulate in a **ring current**, generating their own induced magnetic field that opposes B_0. In this case, however, the induced field of the pelectrons does not shield the benzylic protons from B_0 as you might expect– rather, it causes the protons to experience a *stronger* magnetic field in the direction of B_0 – in other words, it *adds* to B_0 rather than subtracting from it.

To understand how this happens, we need to understand the concept of **diamagnetic anisotropy** (anisotropy means `non-uniformity`). So far, we have been picturing magnetic fields as being oriented in a uniform direction. This is only true over a small area. If we step back and take a wider view, however, we see that the lines of force in a magnetic field are actually anisotropic. They start in the 'north' direction, then loop around like a snake biting its own tail.

If we are outside the ring in the figure above, we feel a magnetic field pointing in a northerly direction. If we are inside the ring, however, we feel a field pointing to the south.

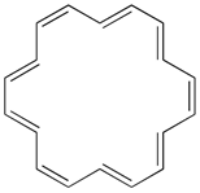
In the induced field generated by the aromatic ring current, the benzylic protons are outside the ring – this means that the induced current in this region of space is oriented in the *same* direction as B_0.

In total, the benzylic protons are subjected to three magnetic fields: the applied field (B_0) and the induced field from the electrons pointing in one direction, and the induced field of the non-aromatic electrons pointing in the opposite (shielding) direction. The end result is that benzylic protons, due to the anisotropy of the induced field generated by the ring current, appear to be highly deshielded. Their chemical shift is far downfield, in the 6.5-8 ppm region.

The presence of anisotropy effects is often used to indicate aromaticity in a molecule. An example is the nonaromatic 8 pi electron cyclooctatetraene. In order to avoid anti-aromatic destabilization, the molecule takes a non-planar conformation which prevents conjugation and ring currents. Consequently, the molecule's protons absorbed at 5.8 ppm which is within the alkene region of ^{1}H NMR.

? EXERCISE 15.7.1

The ^{1}H-NMR spectrum of [18] annulene has two peaks, at 8.9 ppm and -1.8 ppm (upfield of TMS!) with an integration ratio of 2:1. Explain the unusual chemical shift of the latter peak.



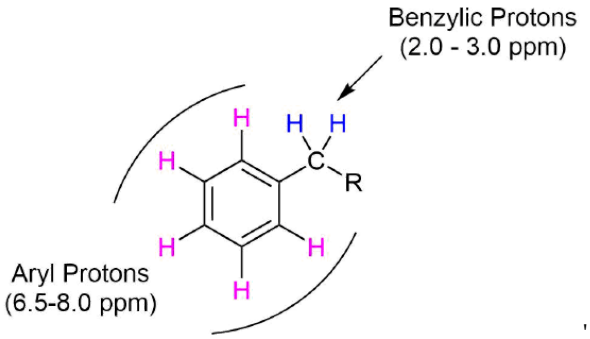
[18] annulene

Answer

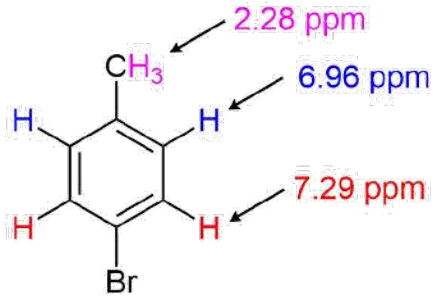
The molecule contains two groups of equivalent protons: the twelve pointing to the outside of the ring, and the six pointing into the center of the ring. The molecule is aromatic, as evidenced by the chemical shift of the 'outside' protons' (and the fact that there are 18 pelectrons, a Hückel number). The inside protons are *shielded* by the induced field of the aromatic ring current, because *inside the ring this field points in the opposite direction of B_0*. This is the source of the unusually low (negative relative to TMS) chemical shift for these protons.

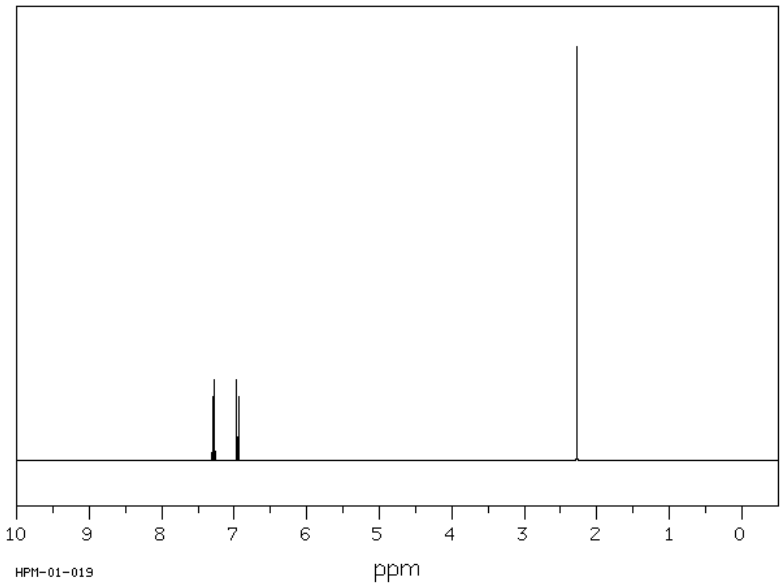
CHARACTERISTIC ^{1}H NMR ABSORPTIONS OF AROMATIC COMPOUNDS

Protons directly attached to an aromatic ring, commonly called aryl protons, show up about 6.5-8.0 PPM. This range is typically called the aromatic region of an ^{1}H NMR spectrum. Protons on carbons directly bonded to an aromatic ring, called benzylic protons, show up about 2.0-3.0 PPM.



For the ^{1}H NMR spectrum of p-bromotoluene, the absorption for the benzylic protons appears as a strong singlet at 2.28 ppm. Due to the molecule's symmetry, the aryl protons appear as two doublets at 6.96 & 7.29 ppm.





CHARATERISTIC IR ABSORPTION OF BENZENE DERIVATIVES

Arenes have absorption bands in the 650-900 cm^{-1} region due to bending of the C–H bond out of the plane of the ring. The exact placement of these absorptions can indicate the pattern of substitution on a benzene ring. However, this is beyond the scope of introductory organic chemistry. Arenes also possess a characteristic absorption at about 3030-3100 cm^{-1} as a result of the aromatic C–H stretch. It is somewhat higher than the alkyl C–H stretch (2850–2960 cm^{-1}), but falls in the same region as olefinic compounds. Two bands (1500 and 1660 cm^{-1}) caused by C=C in plane vibrations are the most useful for characterization as they are intense and are likely observed.

In aromatic compounds, each band in the spectrum can be assigned:

- C–H stretch from 3100-3000 cm^{-1}
- overtones, weak, from 2000-1665 cm^{-1}
- C–C stretch (in-ring) from 1600-1585 cm^{-1}
- C–C stretch (in-ring) from 1500-1400 cm^{-1}
- C–H "oop" from 900-675 cm^{-1}

Note that this is at slightly higher frequency than is the –C–H stretch in alkanes. This is a very useful tool for interpreting IR spectra. Only alkenes and aromatics show a C–H stretch slightly higher than 3000 cm^{-1}.

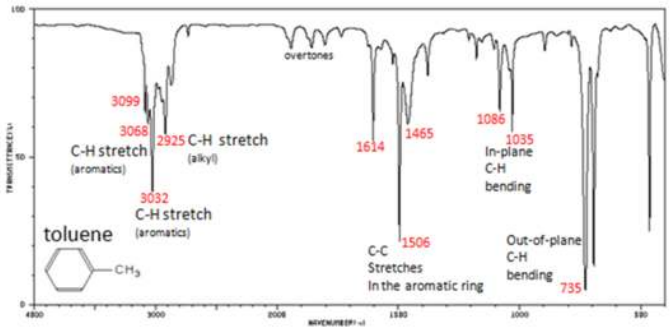


Figure 6. Infrared Spectrum of Toluene

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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15.S: BENZENE AND AROMATICITY (SUMMARY)

CONCEPTS & VOCABULARY

15.0 Introduction

- Aromatic compounds contain ring structures with a special type of resonance delocalization.
- Aromatic compounds can be drawn with alternating single and double bonds, each atom in the ring must have a p-orbital available.

15.1 Naming Aromatic Compounds

- Disubstituted benzene derivatives are often named using ortho (1,2), meta (1,3) and para (1,4).
- There are common benzene derivative names that are used by IUPAC such as toluene, phenol, benzoic acid and benzaldehyde.
- A benzene group that is named as a substituent is called phenyl.
- A benzene with a CH_2 as a substituent group is called benzyl.

15.2 Structure and Stability of Benzene

- Benzene does not undergo the same reactions that alkenes do, due to its aromatic stability.
- Aromatic molecules must have all ring atoms in the same plane to allow delocalization of the pi electrons.
- Heats of hydrogenation can be used to show the special stability of benzene compared to what would be expected for a theoretical cyclohexatriene molecule.

15.3 Aromaticity and the Hückel 4n + 2 Rule

- The four criteria for aromaticity are that the molecule must:
  - be cyclic
  - be planar
  - be fully conjugated
  - have 4n+2 π Electrons
- Ionic molecules and heterocyclic molecules can also be aromatic if they meet the four criteria.

15.4 Aromatic Ions

- Carbanions and carbocations that meet the rules for aromaticity are also aromatic.

15.5 Aromatic Heterocycles: Pyridine and Pyrrole

- Heterocycles that meet the rules for aromaticty are also aromatic.
- If a lone pair of electrons on a ring atom can result in 4n+2 π Electrons, they will be in a p-orbital. If not, they will remain in hybrid orbitals.

15.6 Polycyclic Aromatic Compounds

- Benzene rings can be fused together to give larger aromatic compounds with mutliple rings called polycyclic aromatic compounds (or polycyclic aromatic hydrocarbons).

15.7 Spectroscopy of Aromatic Compounds

- Aromatic compounds can be identified by common infrared absorptions in the 3000-3100 cm^{-1} and 1500-1600 cm^{-1}.
- In ^1H NMR, aromatic hydrogens appear in the 6.5-8 ppm region.

SKILLS TO MASTER

- Skill 15.1 Using IUPAC rules to name substituted benzene molecules.
- Skill 15.2 Use heats of hydrogenation to explain aromatic stabilization.
- Skill 15.3 Draw molecular orbital diagram for benzene (all 6 MO's).
- Skill 15.4 Use the criteria for aromaticity to determine if a molecule is aromatic or not.
- Skill 15.5 Determine whether lone pairs of electrons for ions and heterocycles will be in p orbitals or hybrid orbitals.
- Skill 15.6 Identify aromatic absorbances in infrared spectroscopy.
- Skill 15.7 Identify aromatic resonances in ^1H NMR spectroscopy.

CONTRIBUTORS

- Layne Morsch (University of Illinois Springfield)

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CHAPTER OVERVIEW

16: CHEMISTRY OF BENZENE- ELECTROPHILIC AROMATIC SUBSTITUTION

LEARNING OBJECTIVES

When you have completed Chapter 16, you should be able to

1. fulfil all of the detailed objectives listed under each individual section.
2. solve road-map problems that require an understanding of the chemistry discussed in this chapter and those that preceded it.
3. design multistep syntheses using the reactions discussed in this and the preceding chapters. In particular you should be prepared to show how an aromatic compound containing two or more substituents could be synthesized, taking care to introduce the substituents into the ring in the correct order.
4. define, and use in context, the key terms introduced.

In the preceding chapter, you studied the concept of aromaticity and spent considerable time on the theoretical aspects of the chemistry of aromatic compounds. In this chapter, you will begin to study the chemical reactions of aromatic compounds, focusing in particular on electrophilic aromatic substitution, and to a lesser extent on nucleophilic aromatic substitution. We will discuss, in detail, the mechanism of electrophilic substitution, paying particular attention to the factors that determine both the rate and position of substitution in those aromatic compounds which already have one or more substituents present in the aromatic ring. When we discuss nucleophilic aromatic substitution, you will see that it can be achieved by two different mechanisms, one of which involves the formation of an unusual looking intermediate, benzyne.

You will also see how alkyl and acyl groups can be introduced on to an aromatic ring; how, once introduced, alkyl groups can be converted to carboxyl groups; and how bromine can be introduced to the alkyl side chain of alkylbenzene. The latter reaction is particularly useful because the benzylic bromide so produced undergoes the reactions of a typical alkyl bromide, thus providing us with a synthetic route to a large variety of compounds.

16.0: Introduction
16.1: Electrophilic Aromatic Substitution Reactions- Bromination
16.2: Other Aromatic Substitutions
16.3: Alkylation and Acylation of Aromatic Rings- The Friedel-Crafts Reaction
16.4: Substituent Effects in Substituted Aromatic Rings
16.5: An Explanation of Substituent Effects
16.6: Trisubstituted Benzenes- Additivity of Effects
16.7: Nucleophilic Aromatic Substitution
16.8: Benzyne
16.9: Oxidation of Aromatic Compounds
16.10: Reduction of Aromatic Compounds
16.11: Synthesis of Polysubstituted Benzenes
16.S: Chemistry of Benzene - Electrophilic Aromatic Substitution (Summary)

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16.0: INTRODUCTION

Objective

After completing this section, you should be able to

1. identify electrophilic substitution as the single most important reaction of aromatic compounds.
2. explain why aromatic compounds, such as benzene, are susceptible to attack by electrophiles.

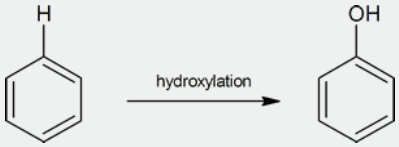
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- acylation
- alkylation
- electrophilic substitution
- halogenation
- hydroxylation
- nitration
- sulfonation

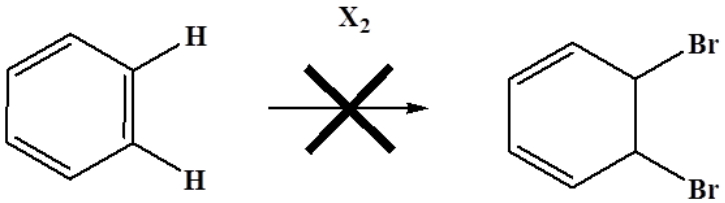
STUDY NOTES

In this chapter, you will study all of the reactions shown in the Reaction Type table. In addition to these five reaction types, we also add a sixth common electrophilic substitution known as hydroxylation.



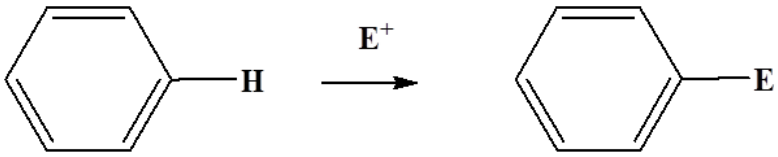
It is important that you recognize the similarities between these reactions to minimize the amount you must memorize.

The six pi electrons obey Huckel's rule so benzene is especially stable. This means that the aromatic ring want to be retained during reactions. Because of this benzene does not undergo addition like other unsaturated hydrocarbons.



Non-Aromatic

Benzene can undergo electrophilic aromatic substitution because aromaticity is maintained.



Product is Aromatic

OTHER EXAMPLES OF ELECTOPHILIC AROMATIC SUBSTITUTION

Many other substitution reactions of benzene have been observed, the five most useful are listed below (chlorination and bromination are the most common halogenation reactions). Since the reagents and conditions employed in these reactions are electrophilic, these reactions are commonly referred to as **Electrophilic Aromatic Substitution**. The catalysts and co-reagents serve to generate the strong electrophilic species needed to effect the initial step of the substitution. The specific electrophile believed to function in each type of reaction is listed in the right hand column.

Reaction Type	Typical Equation				Electrophile $E^{(+)}$
Halogenation:	C_6H_6	+ Cl_2 & heat $FeCl_3$ catalyst	⟶	C_6H_5Cl + HCl Chlorobenzene	$Cl^{(+)}$ or $Br^{(+)}$
Nitration:	C_6H_6	+ HNO_3 & heat H_2SO_4 catalyst	⟶	$C_6H_5NO_2$ + H_2O Nitrobenzene	$NO_2^{(+)}$
Sulfonation:	C_6H_6	+ H_2SO_4 + SO_3 & heat	⟶	$C_6H_5SO_3H$ + H_2O Benzenesulfonic acid	$SO_3H^{(+)}$
Alkylation: Friedel-Crafts	C_6H_6	+ R-Cl & heat $AlCl_3$ catalyst	⟶	C_6H_5-R + HCl An Arene	$R^{(+)}$
Acylation: Friedel-Crafts	C_6H_6	+ RCOCl & heat $AlCl_3$ catalyst	⟶	C_6H_5COR + HCl An Aryl Ketone	$RCO^{(+)}$

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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16.1: ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS- BROMINATION

Objectives

After completing this section, you should be able to

1. write the detailed mechanism for the reaction of bromine with benzene in the presence of a suitable catalyst.
2. draw the resonance contributors for the carbocation which is formed during the reaction of bromine with benzene.
3. compare the reaction which takes place between bromine and benzene and the reaction which takes place between bromine and an alkene.
4. draw an energy diagram for the reaction of bromine with benzene.
5. identify the reagents required to bring about aromatic bromination.
6. write an equation to represent aromatic bromination.

STUDY NOTES

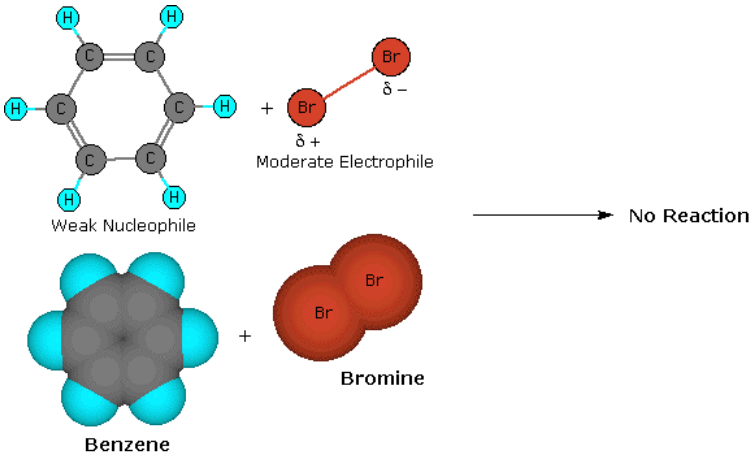
The Mechanism for Electrophilic Substitution Reactions of Benzene is the key to understanding electrophilic aromatic substitution. You will see similar equations written for nitration, sulphonation, acylation, etc., with the major difference being the identity of the electrophile in each case.

Note that the carbocation intermediate formed has a number of resonance forms. Also, you may wish to review Section 8.2 to meet Objective 3.

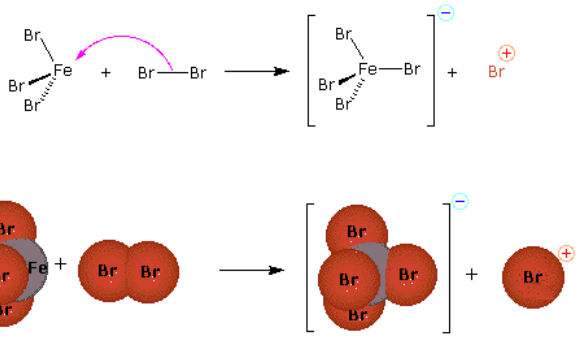
Halogenation is an example of electrophillic aromatic substitution. In electrophilic aromatic substitutions, a benzene is attacked by an electrophile which results in substition of hydrogens. However, halogens are not electrophillic enough to break the aromaticity of benzenes, which require a catalyst to activate.

A MECHANISM FOR ELECTROPHILIC SUBSTITUTION REACTIONS OF BENZENE

A two-step mechanism has been proposed for these electrophilic substitution reactions. In the first, slow or rate-determining, step the electrophile forms a sigma-bond to the benzene ring, generating a positively charged **benzenonium intermediate**. In the second, fast step, a proton is removed from this intermediate, yielding a substituted benzene ring. The following four-part illustration shows this mechanism for the bromination reaction. Also, an animated diagram may be viewed.

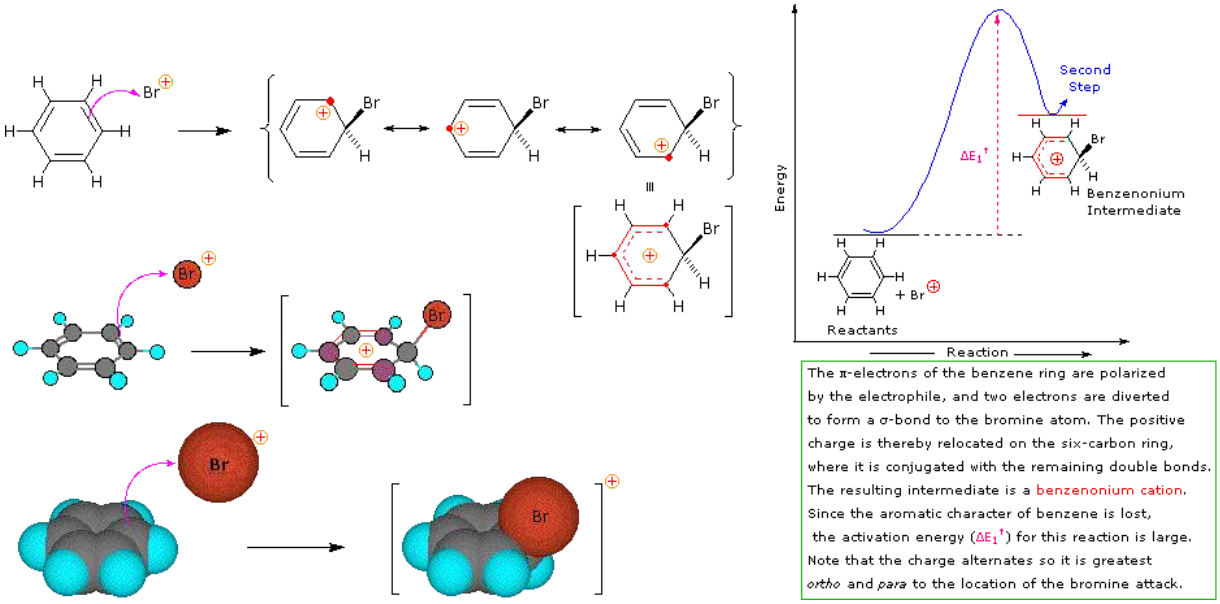


The bromine molecule is polarized so that one end is electrophilic and the other nucleophilic. Although the electrophilic end reacts easily with simple alkenes and dienes, it fails to react with the more stable and weaker nucleophilic π-electron system of benzene.



Ferric bromide and other Lewis acids enhance the electrophilic strength of bromine by forming a complex anion, in this case $FeBr_4^{\ominus}$. At the same time, this complexation creates the strongly electrophilic bromine cation, which reacts with nucleophiles.

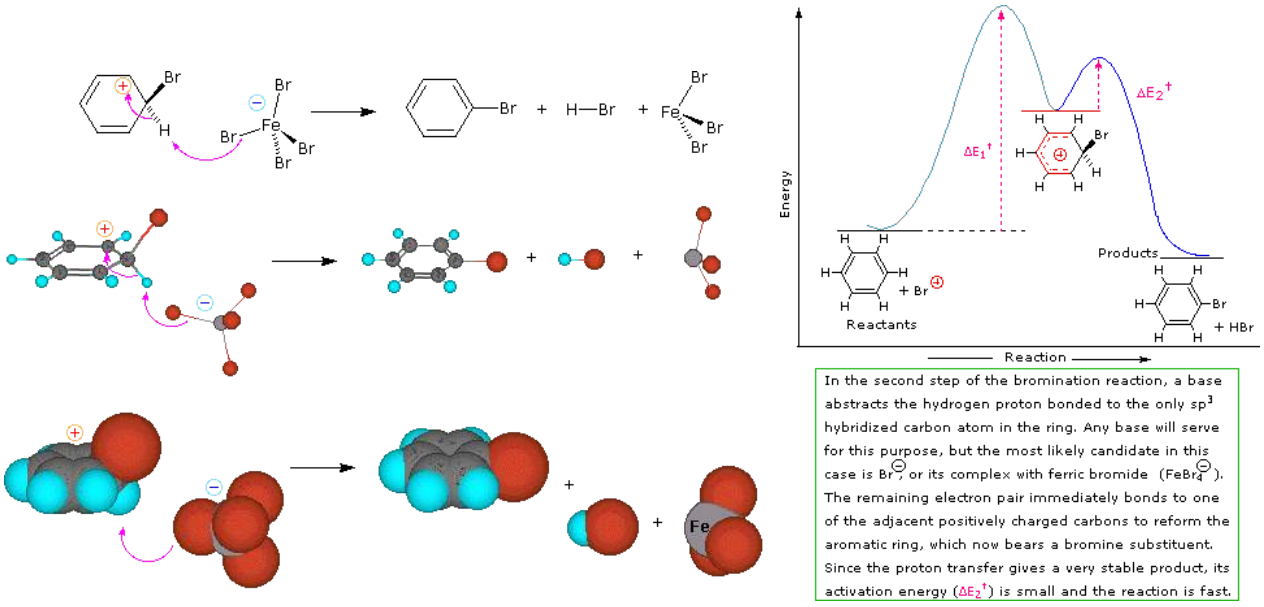
Preliminary step: Formation of the strongly electrophilic bromine cation



The π-electrons of the benzene ring are polarized by the electrophile, and two electrons are diverted to form a σ-bond to the bromine atom. The positive charge is thereby relocated on the six-carbon ring, where it is conjugated with the remaining double bonds. The resulting intermediate is a benzenonium cation. Since the aromatic character of benzene is lost, the activation energy ($\Delta E_1^{\ddagger}$) for this reaction is large. Note that the charge alternates so it is greatest *ortho* and *para* to the location of the bromine attack.

Step 1: The electrophile forms a sigma-bond to the benzene ring, generating a positively charged benzenonium intermediate

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Step 2: A proton is removed from this intermediate, yielding a substituted benzene ring

This mechanism for electrophilic aromatic substitution should be considered in context with other mechanisms involving carbocation intermediates. These include S_N1 and E1 reactions of alkyl halides, and Brønsted acid addition reactions of alkenes.

To summarize, when carbocation intermediates are formed one can expect them to react further by one or more of the following modes:

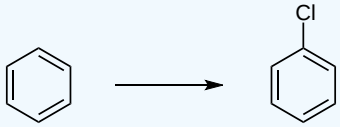
1. The cation may bond to a nucleophile to give a substitution or addition product.
2. The cation may transfer a proton to a base, giving a double bond product.
3. The cation may rearrange to a more stable carbocation, and then react by mode #1 or #2.

S_N1 and E1 reactions are respective examples of the first two modes of reaction. The second step of alkene addition reactions proceeds by the first mode, and any of these three reactions may exhibit molecular rearrangement if an initial unstable carbocation is formed. The carbocation intermediate in electrophilic aromatic substitution (the benzenonium ion) is stabilized by charge delocalization (resonance) so it is not subject to rearrangement. In principle it could react by either mode 1 or 2, but the energetic advantage of reforming an aromatic ring leads to exclusive reaction by mode 2 (*ie.* proton loss).

EXERCISES

? EXERCISE 16.1.1

What reagents would you need to get the given product?

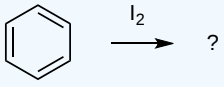


Answer

Cl_2 and $AlCl_3$ or Cl_2 and $FeCl_3$

? EXERCISE 16.1.2

What product would result from the given reagents?

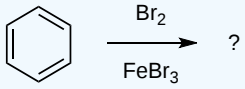


Answer

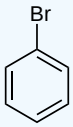
No Reaction

EXERCISE 16.1.3

What is the major product given the reagents below?



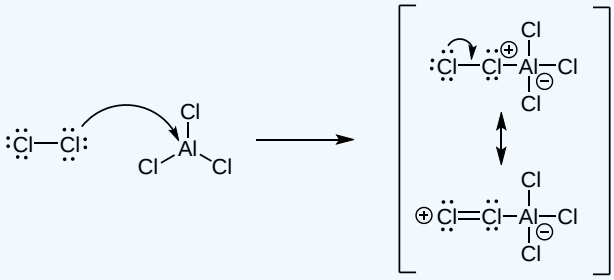
Answer



EXERCISE 16.1.4

Draw the formation of Cl^+ from $AlCl_3$ and Cl_2.

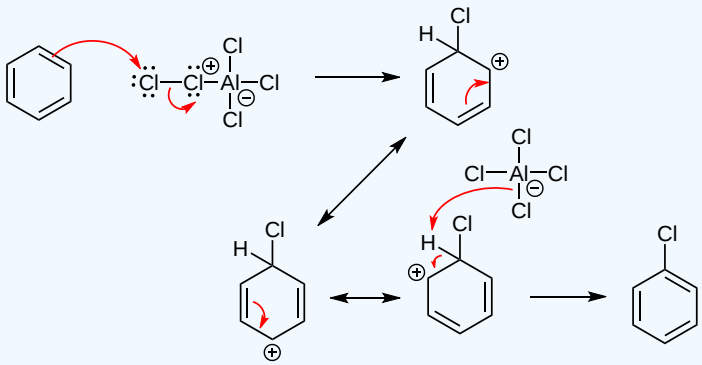
Answer



EXERCISE 16.1.5

Draw the mechanism of the reaction between Cl^+ and a benzene.

Answer



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Catherine Nguyen
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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16.2: OTHER AROMATIC SUBSTITUTIONS

Objectives

After completing this section, you should be able to

1. write a balanced equation for the halogenation (F, Cl, Br, I) of benzene in the presence of a suitable catalyst or promoter.
2. draw the resonance contributors for the carbocation which is formed during the reaction of chlorine or bromine with benzene.
3. write the equation for the nitration and sulfonation of benzene.
4. write the detailed mechanism for the nitration and sulfonation of benzene.
5. write the equation for the reduction of an aromatic nitro compound to an amine.
6. identify aromatic sulfonation as being a reversible process, and describe the conditions under which the forward and reverse reactions are favoured.
7. write the equation for the desulfonation of an aromatic sulfonic acid.
8. identify aromatic sulfonic acids as being key intermediates in the manufacture of sulfa drugs.

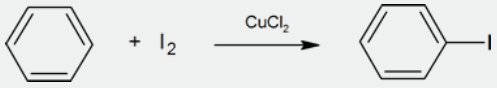
KEY TERMS

Make certain that you can define, and use in context, the key term below.

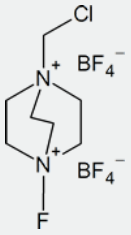
- nitronium ion, (NO^{+2})

STUDY NOTES

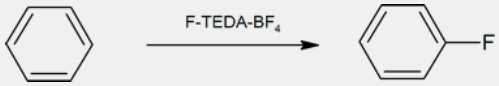
You should be careful to remember that iodine and fluorine cannot be introduced into an aromatic ring by the method used for bromine and chlorine. On its own, iodine is unreactive with aromatic rings, but one method for aromatic iodination is treatment in the presence of a copper salt such as copper(II)chloride where I2 is oxidized to the more electrophilic species I^+.



In contrast, fluorine is too reactive, so it cannot be used directly for aromatic flourination. However, fluorinating agents like 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane ditetrafluoroborate (also known as F-TEDA-BF_4) sold commercially as Sectfluor® offer convenient sources of "F^+" for this type of reaction.



F-TEDA-BF_4

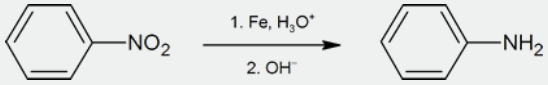


The overall equation for the formation of nitronium ions by the action of sulfuric acid on nitric acid is

$$HNO_3 + 2\,H_2SO_4 \rightleftharpoons H_3O^+ + NO_2^+ + HSO_4^-$$

The ability of compounds such as nitronium tetrafluoroborate to bring about the nitration of aromatic compounds is good evidence in support of the proposed mechanism.

The nitration of an aromatic ring is an important synthetic pathway to generating arylamines. The reaction below shows one common method of reducing the nitro group. (Amines are examined in more detail in Chapter 24.)



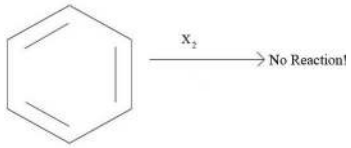
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HALOGENATION OF BENZENE

Halogenation is an example of electrophillic aromatic substitution. In electrophilic aromatic substitutions, a benzene is attacked by an electrophile which results in substition of hydrogens. However, halogens are not electrophillic enough to break the aromaticity of benzenes, which require a catalyst to activate.

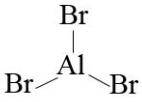
ACTIVATION OF HALOGEN

(where X= Br or Cl, we will discuss further in detail later why other members of the halogen family Flourine and Iodine are not used in halogenation of benzenes)

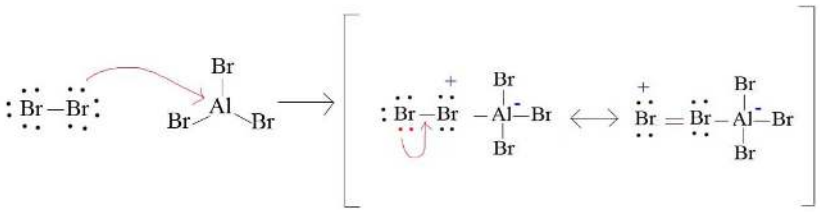


Hence, Halogen needs the help and aid of Lewis Acidic Catalysts to activate it to become a very strong electrophile. Examples of these activated halogens are Ferric Hallides (FeX_3) Aluminum Halides (AlX_3) where X= Br or Cl. In the following examples, the halogen we will look at is Bromine.

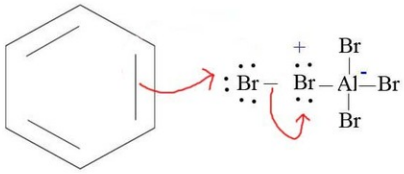
In the example of bromine, in order to make bromine electrophillic enough to react with benzene, we use the aid of an aluminum halide such as aluminum bromide.



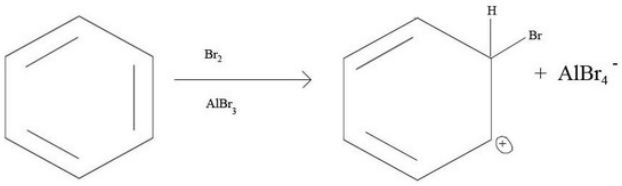
With aluminum bromide as a Lewis acid, we can mix Br_2 with $AlBr_3$ to give us Br^+. The presence of Br^+ is a much better electrophile than Br_2 alone. Bromination is acheived with the help of $AlBr_3$ (Lewis acid catalysts) as it polarizes the Br-Br bond. The polarization causes polarization causes the bromine atoms within the Br-Br bond to become more electrophillic. The presence of Br^+ compared to Br_2 alone is a much better electrophille that can then react with benzene.



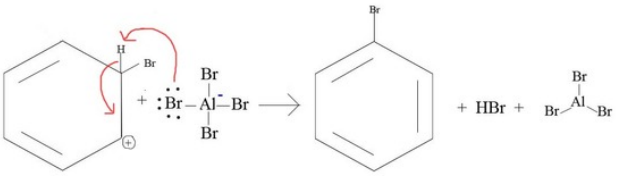
As the bromine has now become more electrophillic after activation of a catalyst, an electrophillic attack by the benzene occurs at the terminal bromine of Br-Br-$AlBr_3$. This allows the other bromine atom to leave with the $AlBr_3$ as a good leaving group, $AlBr_4$-.



https://chem.libretexts.org/@go/page/67326



After the electrophilic attack of bromide to the benzene, the hydrogen on the same carbon as bromine substitutes the carbocation in which resulted from the attack. Hence it being an electrophilic aromatic SUBSTITUTION. Since the by-product aluminum tetrabromide is a strong nucleophile, it pulls of a proton from the Hydrogen on the same carbon as bromine.



In the end, $AlBr_3$was not consumed by the reaction and is regenerated. It serves as our catalyst in the halogenation of benzenes.

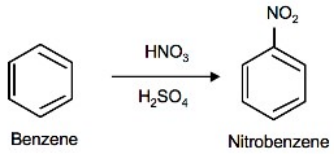
DISSOCIATION ENERGIES OF HALOGENS AND ITS EFFECT ON HALOGENATION OF BENZENES

The electrophillic bromination of benzenes is an exothermic reaction. Considering the exothermic rates of aromatic halogenation decreasing down the periodic table in the Halogen family, Flourination is the most exothermic and Iodination would be the least. Being so exothermic, a reaction of flourine with benzene is explosive! For iodine, electrophillic iodination is generally endothermic, hence a reaction is often not possible. Similar to bromide, chlorination would require the aid of an activating presence such as Alumnium Chloride or Ferric Chloride. The mechanism of this reaction is the same as with Bromination of benzene.

Nitration and sulfonation of benzene are two examples of electrophilic aromatic substitution. The nitronium ion (NO_2^+) and sulfur trioxide (SO_3) are the electrophiles and individually react with benzene to give nitrobenzene and benzenesulfonic acid respectively.

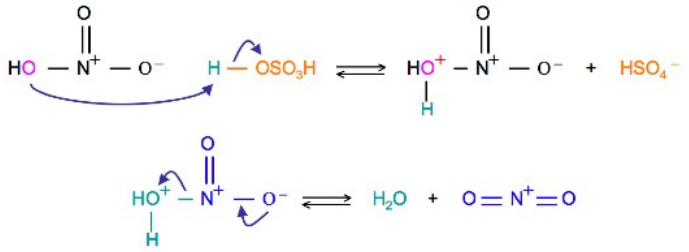
NITRATION OF BENZENE

The source of the nitronium ion is through the protonation of nitric acid by sulfuric acid, which causes the loss of a water molecule and formation of a nitronium ion.



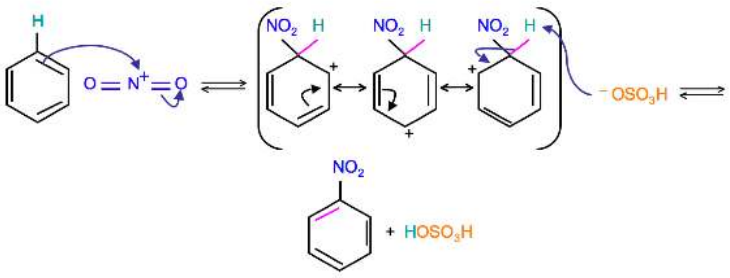
SULFURIC ACID ACTIVATION OF NITRIC ACID

The first step in the nitration of benzene is to activate $HNO_3$with sulfuric acid to produce a stronger electrophile, the nitronium ion.



Because the nitronium ion is a good electrophile, it is attacked by benzene to produce Nitrobenzene.

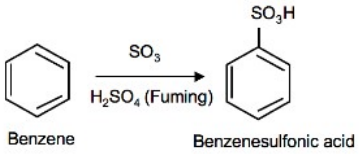
MECHANISM



(Resonance forms of the intermediate can be seen in the generalized electrophilic aromatic substitution)

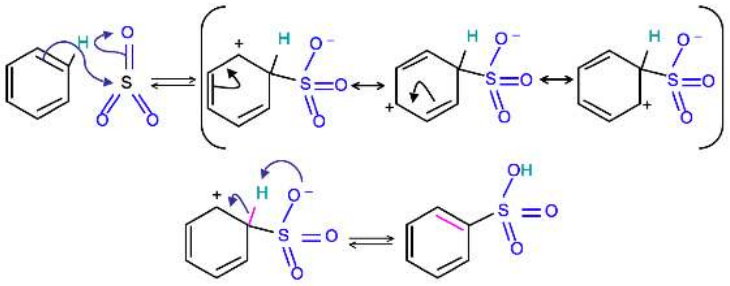
SULFONATION OF BENZENE

Sulfonation is a reversible reaction that produces benzenesulfonic acid by adding sulfur trioxide and fuming sulfuric acid. The reaction is reversed by adding hot aqueous acid to benzenesulfonic acid to produce benzene.



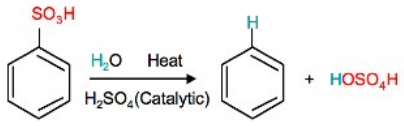
MECHANISM

To produce benzenesulfonic acid from benzene, fuming sulfuric acid and sulfur trioxide are added. Fuming sulfuric acid, also refered to as *oleum*, is a concentrated solution of dissolved sulfur trioxide in sulfuric acid. The sulfur in sulfur trioxide is electrophilic because the oxygens pull electrons away from it because oxygen is very electronegative. The benzene attacks the sulfur (and subsequent proton transfers occur) to produce benzenesulfonic acid.



REVERSE SULFONATION

Sulfonation of benzene is a reversible reaction. Sulfur trioxide readily reacts with water to produce sulfuric acid and heat. Therefore, by adding heat to benzenesulfonic acid in diluted aqueous sulfuric acid the reaction is reversed.



FURTHER APPLICATIONS OF NITRATION AND SULFONATION

Nitration is used to add nitrogen to a benzene ring, which can be used further in substitution reactions. The nitro group acts as a ring deactivator. Having nitrogen present in a ring is very useful because it can be used as a directing group as well as a masked amino group. The products of aromatic nitrations are very important intermediates in industrial chemistry.

Because sulfonation is a reversible reaction, it can also be used in further substitution reactions in the form of a directing blocking group because it can be easily removed. The sulfonic group blocks the carbon from being attacked by other substituents and after the reaction is completed it can be removed by reverse sulfonation. Benzenesulfonic acids are also used in the synthesis of detergents, dyes, and sulfa drugs. Bezenesulfonyl Chloride is a precursor to sulfonamides, which are used in chemotherapy.

OUTSIDE LINKS

Aromatic Halogenation

- http://www.chemguide.co.uk/mechanism...ogenation.html
- http://en.Wikipedia.org/wiki/Electro...c_halogenation

Aromatic Sulfonation

- Wikipedia: http://en.Wikipedia.org/wiki/Aromatic_sulfonation
- Video: http://www.youtube.com/watch?v=s1qJ1...eature=related
- Interactive 3D Reaction: http://www.chemtube3d.com/Electrophi...20benzene.html

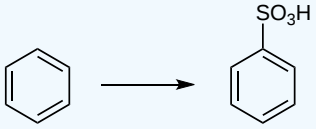
Aromatic Nitration

- Wikipedia: http://en.Wikipedia.org/wiki/Nitration
- Video: http://www.youtube.com/watch?v=i7ucl...eature=related
- Interactive 3D Reaction: http://www.chemtube3d.com/Electrophi...20benzene.html

EXERCISES

? EXERCISE \PageIndex1

1. What is/are the required reagent(s)for the following reaction:

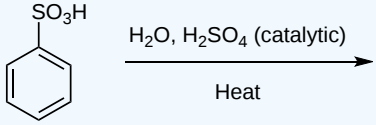


Answer

SO_3 and H_2SO_4 (fuming)

? EXERCISE \PageIndex2

What is the product of the following reaction:



Answer



EXERCISE \PageIndex3

Why is it important that the nitration of benzene by nitric acid occurs in sulfuric acid?

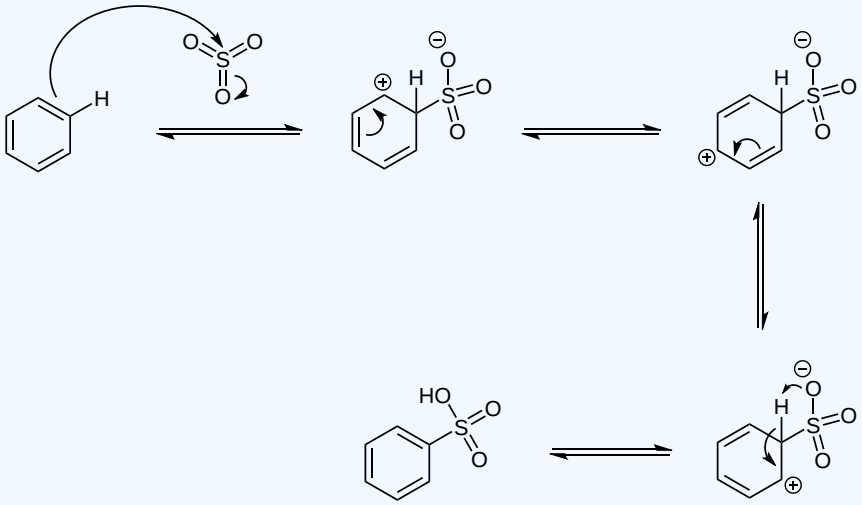
Answer

Sulfuric acid is needed in order for a good electrophile to form. Sulfuric acid protonates nitric acid to form the nitronium ion (water molecule is lost). The nitronium ion is a very good electrophile and is open to attack by benzene. Without sulfuric acid the reaction would not occur.

EXERCISE \PageIndex4

Write a detailed mechanism for the sulfonation of benzene, including all resonance forms.

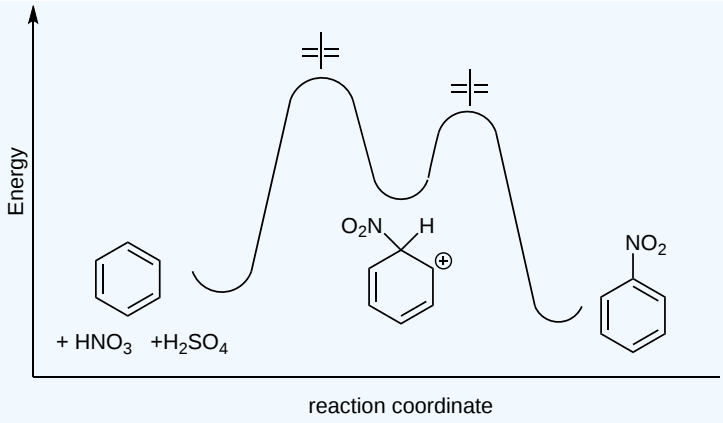
Answer



EXERCISE \PageIndex5

Draw an energy diagram for the nitration of benzene. Draw the intermediates, starting materials, and products. Label the transition states.

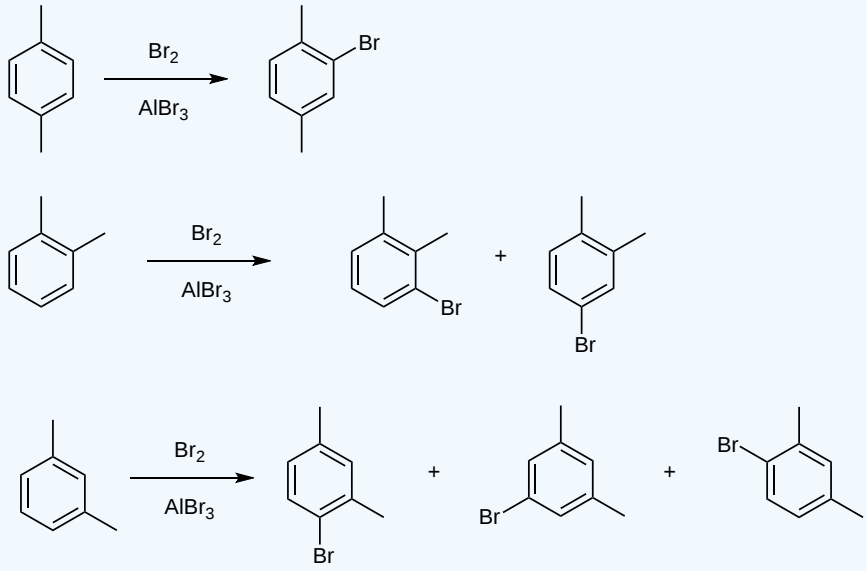
Answer



EXERCISE \PageIndex6

In each case, how many products would be possible for the bromination of *p*-xylene, *o*-xylene, and *m*-xylene?

Answer

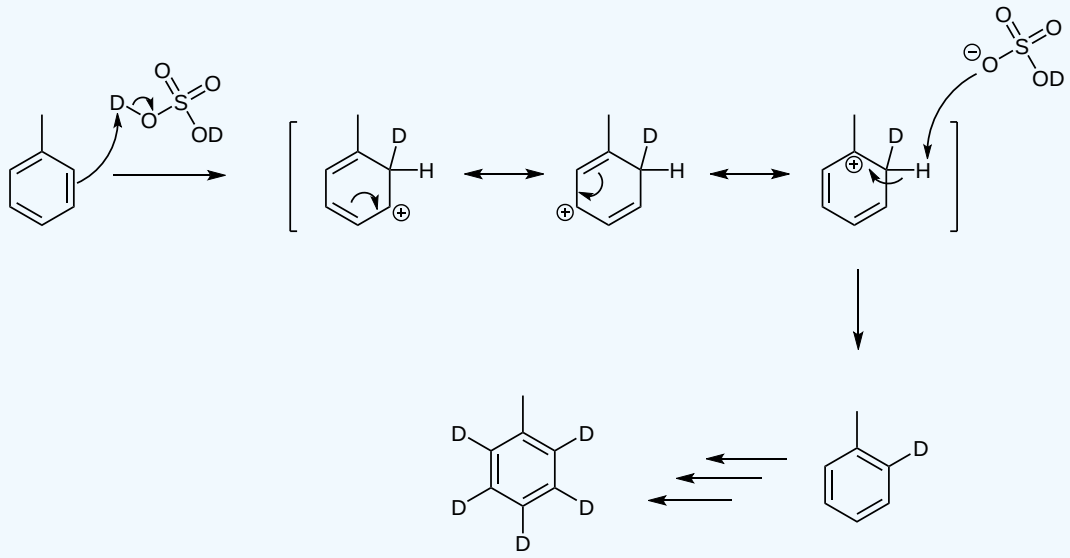


EXERCISE \PageIndex7

If toluene is treated with D_2SO_4 all the hydrogen's are replaced with deuterium. Explain.

Answer

The deuterium is added to the ring. When the ring "re-aromatizes" the base scavenges the hydrogen before the deuterium and therefore is left on the ring. Continues for the rest of the hydrogen on the ring.



REFERENCES

1. Laali, Kenneth K., and Volkar J. Gettwert. “Electrophilic Nitration of Aromatics in Ionic Liquid Solvents.” The Journal of Organic Chemistry 66 (Dec. 2000): 35-40. American Chemical Society.
2. Malhotra, Ripudaman, Subhash C. Narang, and George A. Olah. Nitration: Methods and Mechanisms. New York: VCH Publishers, Inc., 1989.
3. Sauls, Thomas W., Walter H. Rueggeberg, and Samuel L. Norwood. “On the Mechanism of Sulfonation of the Aromatic Nucleus and Sulfone Formation.” The Journal of Organic Chemistry 66 (1955): 455-465. American Chemical Society.
4. Vollhardt, Peter. Organic Chemistry : Structure and Function. 5th ed. Boston: W. H. Freeman & Company, 2007.

QUESTIONS

Q16.2.1

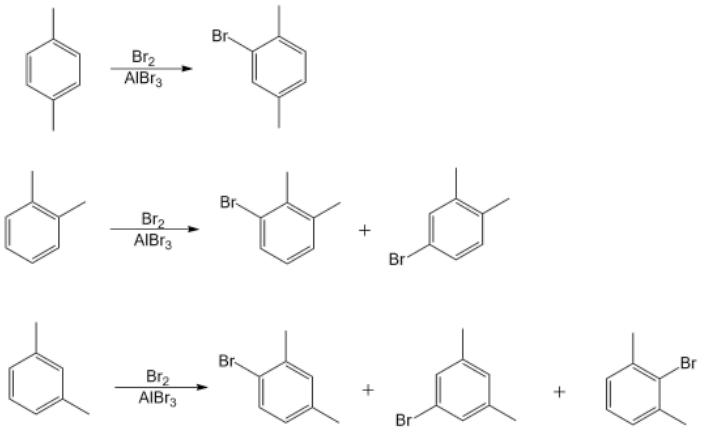
In each case, how many products would be expected for the bromination of *p*-xylene, *o*-xylene, and *m*-xylene?

Q16.2.2

If toluene is treated with D_2SO_4 all the hydrogen’s are replaced with deuterium. Explain. (might need to draw mechanism)

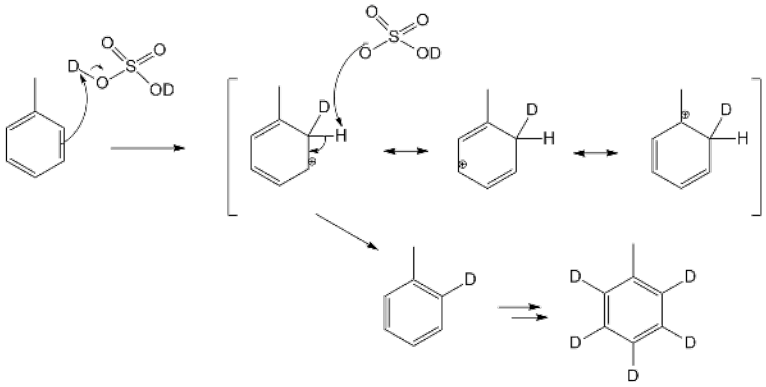
SOLUTIONS

S16.2.1



S16.2.2

The deuterium is added to the ring. When the ring “re-aromatizes” the base scavenges the hydrogen before the deuterium and therefore is left on the ring. Continues for the rest of the hydrogen on the ring.



CONTRIBUTORS AND ATTRIBUTIONS

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- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Catherine Nguyen

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16.3: ALKYLATION AND ACYLATION OF AROMATIC RINGS- THE FRIEDEL-CRAFTS REACTION

Objectives

After completing this section, you should be able to

1. write the equation for the preparation of an alkylbenzene by a Friedel-Crafts alkylation reaction.
2. identify the product formed from the Friedel-Crafts alkylation of a given aromatic compound.
3. identify the aromatic compound needed to prepare a given arene by a Friedel-Crafts alkylation.
4. identify the alkyl halide and catalyst needed to form a specified arene from a given aromatic compound.
5. write the detailed mechanism for the Friedel-Crafts alkylation reaction, and identify the similarities between this reaction and those electrophilic aromatic substitution reactions you studied in Sections 16.1 and 16.2.
6. show how alkyl halides and acylhalides can be used as alkylating agents in Friedel-Crafts alkylation reactions.
7. discuss the limitations of the Friedel-Crafts alkylation reaction, paying particular attention to the structure of the alkyl halide, the structure of the aromatic substrate and the problem of polyalkylation.
8. write an equation for a typical Friedel-Crafts acylation.
9. write the detailed mechanism of the Friedel-Crafts acylation reaction.
10. identify the product formed by the Friedel-Crafts acylation of a given aromatic compound.
11. identify the aromatic compound, and the reagent and catalyst needed to prepare a given ketone through a Friedel-Crafts acylation reaction.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- acyl group
- Friedel-Crafts acylation reaction
- Friedel-Crafts alkylation reaction
- polyalkylation

STUDY NOTES

A Friedel-Crafts alkylation reaction is an electrophilic aromatic substitution reaction in which a carbocation attacks an aromatic ring with the net result that one of the aromatic protons is replaced by an alkyl group. If you prefer, you may regard these reactions as involving an attack by an aromatic ring on a carbocation. The latter approach is the one used in the textbook, but the former approach is probably more common.

When more than one alkyl group is introduced into an aromatic ring during the course of a Friedel-Crafts alkylation reaction, polyalkylation is said to have occurred.

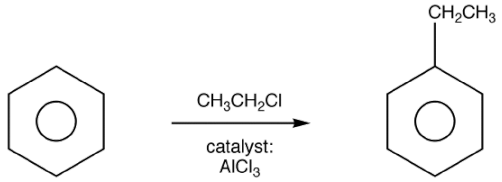
The four limitations on the use of Friedel-Crafts alkylations are as follows:

1. vinyl and aryl halides cannot be used to form carbocations.
2. the aromatic substrate must not contain a strongly deactivating group, or groups, such as NH_2, NHR or NR_2, which form complexes with the Lewis acid catalyst and in so doing become strongly deactivating.
3. polyalkylation, which can be overcome by using a large excess of the aromatic substrate.
4. carbocation rearrangements may occur in any reaction that involves a carbocation.

The reaction of an aromatic substrate with an acid chloride (or acid anhydride) in the presence of an aluminum chloride catalyst is used to introduce an acyl group $(R—C(=O)—)$ into the aromatic ring through an electrophilic aromatic substitution mechanism. Such reactions are Friedel-Crafts acylation reactions.

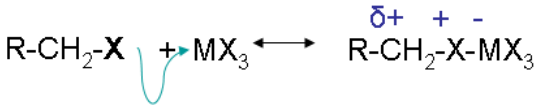
FRIEDEL-CRAFTS ALKYLATION

Friedel-Crafts Alkylation was first discovered by French scientist Charles Friedel and his partner, American scientist James Crafts, in 1877. This reaction allowed for the formation of alkyl benzenes from alkyl halides, but was plagued with unwanted supplemental activity that reduced its effectivity.



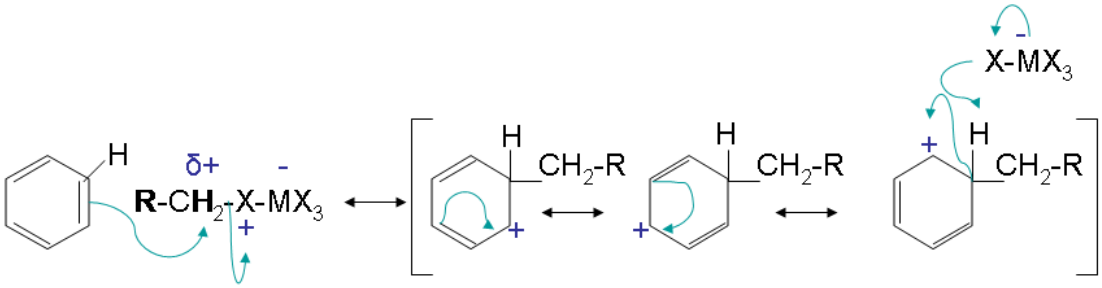
The mechanism takes place as follows:

Step 1:



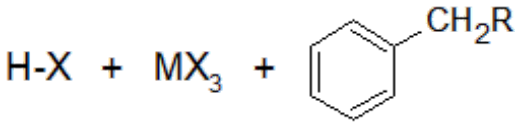
Step one creates a carbocation that acts as the electrophile in the reaction. This steps activates the haloalkane. Secondary and tertiary halides only form the free carbocation in this step.

Steps 2 and 3:



Step 2 has an electrophilic attack on the benzene resulting in multiple resonance forms. The halogen reacts with the intermediate and picks up the hydrogen to eliminate the positively charge

Final Products



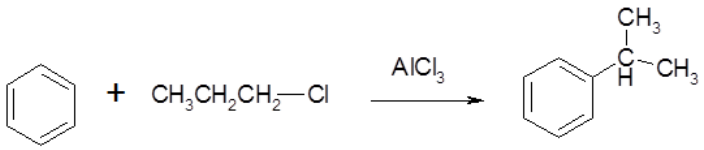
The reactivity of haloalkanes increases as you move up the periodic table and increase polarity. This means that an RF haloalkane is most reactive followed by RCl then RBr and finally RI. This means that the Lewis acids used as catalysts in Friedel-Crafts Alkylation reactions tend have similar halogen combinations such as BF_3, $SbCl_5$, $AlCl_3$, $SbCl_5$, and $AlBr_3$, all of which are commonly used in these reactions.

SOME LIMITATIONS OF FRIEDEL-CRAFTS ALKYLATION

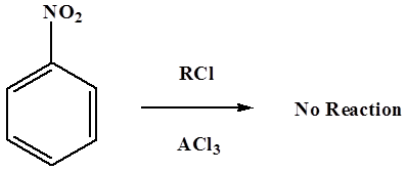
There are possibilities of carbocation rearrangements when you are trying to add a carbon chain greater than two carbons. The rearrangements occur due to hydride shifts and methyl shifts. For example, the product of a Friedel-Crafts Alkylation will show an iso rearrangement when adding a three carbon chain as a substituent. Also, the reaction will only work if the ring you are adding a substituent to is not deactivated. For a look at substituents that activate or deactivate a benzene ring, check out the wiki page: Activating and Deactivating Benzene Rings One way to resolve these problems is through Friedel-Crafts Acylation.

SOME LIMITATIONS OF FRIEDEL-CRAFTS ALKYLATION

There are possibilities of carbocation rearrangements when you are trying to add a carbon chain greater than two carbons. The rearrangements occur due to hydride shifts and methyl shifts. For example, the product of a Friedel-Crafts Alkylation will show an iso rearrangement when adding a three carbon chain as a substituent. One way to resolve these problems is through Friedel-Crafts Acylation.



Also, the reaction will only work if the ring you are adding a substituent to is not deactivated. Friedel-Crafts fails when used with compounds such as nitrobenzene and other strong deactivating systems.

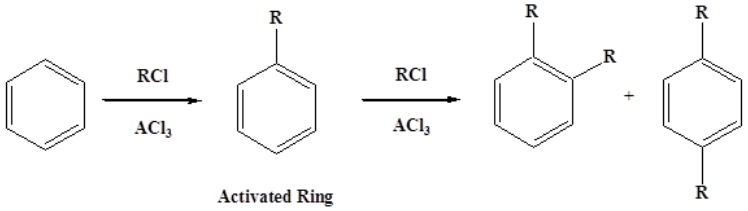


Friedel-Crafts reactions cannot be preformed then the aromatic ring contains a NH_2, NHR, or NR_2 substituent. The lone pair electrons on the amines react with the Lewis acid $AlCl_3$. This places a positive charge next to the benzene ring, which is so strongly activating that the Friedel-Crafts reaction cannot occur.



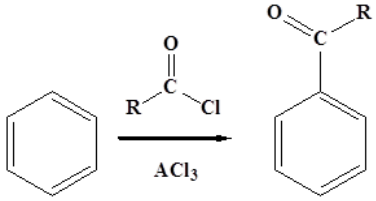
The positive charge strongly deactivates the benzene ring

Lastly, Friedel-Crafts alkylation can undergo polyalkylation. The reaction adds an electron donating alkyl group, which activates the benzene ring to further alkylation.



Activated Ring

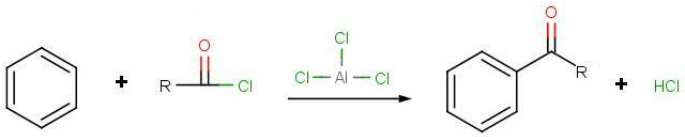
This problem does not occure during Friedel-Crafts Acylation because an acyl group is deactivating. The prevents further actylations.



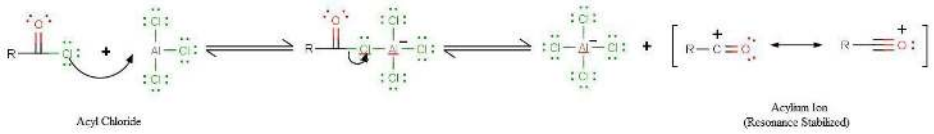
Dectivated Ring

FRIEDEL-CRAFTS ACYLATION

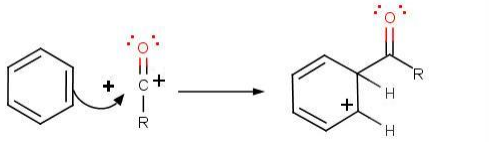
The goal of the reaction is the following:



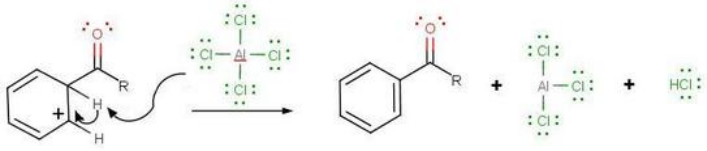
The very first step involves the formation of the acylium ion which will later react with benzene:



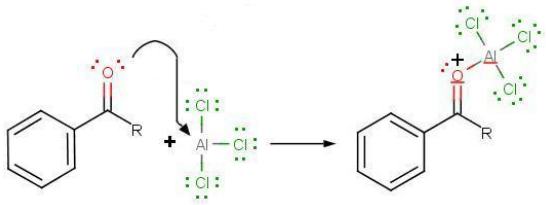
The second step involves the attack of the acylium ion on benzene as a new electrophile to form one complex:



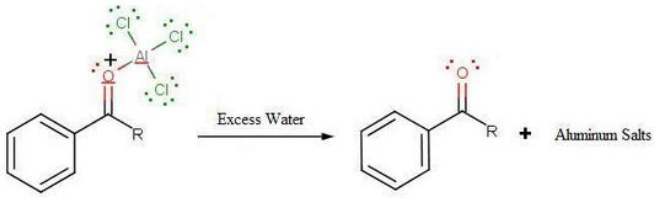
The third step involves the departure of the proton in order for aromaticity to return to benzene:



During the third step, $AlCl_4$ returns to remove a proton from the benzene ring, which enables the ring to return to aromaticity. In doing so, the original $AlCl_3$ is regenerated for use again, along with HCl. Most importantly, we have the first part of the final product of the reaction, which is a ketone. Thie first part of the product is the complex with aluminum chloride as shown:



The final step involves the addition of water to liberate the final product as the acylbenzene:

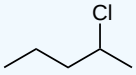
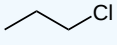


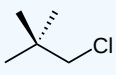
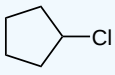
Because the acylium ion (as was shown in step one) is stabilized by resonance, no rearrangement occurs (Limitation 1). Also, because of of the deactivation of the product, it is no longer susceptible to electrophilic attack and hence, is no longer susceptible to electrophilic attack and hence, no longer goes into further reactions (Limitation 3). However, as not all is perfect, Limitation 2 still prevails where Friedel-Crafts Acylation fails with strong deactivating rings.

EXERCISES

? EXERCISE \PageIndex1

Which of the following will NOT undergo a rearrangement in a Friedel-Crafts reaction?

A) CH_3Cl B)  C) 

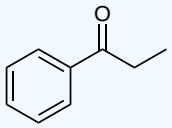
D)  E) 

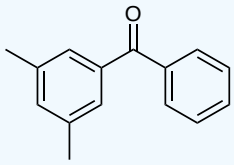
Answer

A and E will not undergo a rearrangement.

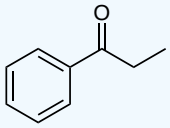
EXERCISE \PageIndex2

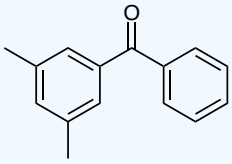
Suggest an acyl chloride that was used to make the following compounds:

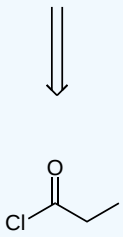
A) 

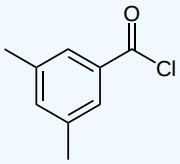
B) 

Answer

A) 

B) 



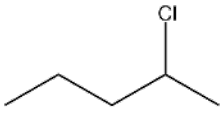


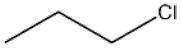
QUESTIONS

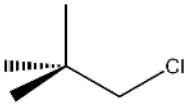
Q16.3.1

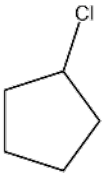
Which of the following will NOT undergo a rearrangement in a Friedel-Crafts reaction?

A) CH_3Cl

B) 

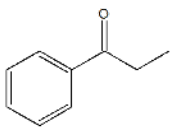
C) 

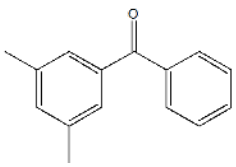
D) 

E) 

Q16.3.2

Suggest an acyl chloride that was used to make the following compounds:



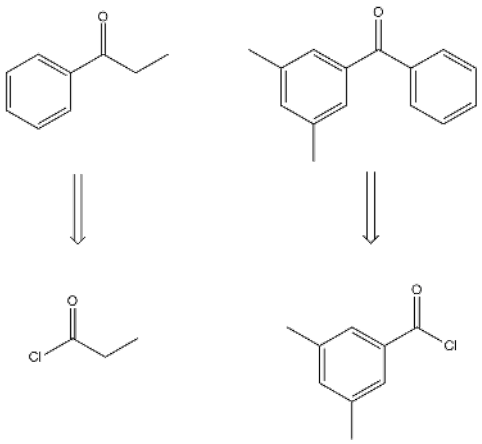


SOLUTIONS

S16.3.1

A and E will not undergo a rearrangement.

S16.3.2



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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16.4: SUBSTITUENT EFFECTS IN SUBSTITUTED AROMATIC RINGS

Objectives

After completing this section, you should be able to

1. describe the two ways in which a substituent influences the electrophilic substitution of a monosubstituted aromatic compound.
2. classify each of the following substituents as being either activating or deactivating with respect to electrophilic aromatic substitution: $-NH_2$, $-OH$, $-NHR$, $-NR_2$, $-OR$, $-NHCOR$, alkyl (R), phenyl, R_3N^+, $-NO_2$, $-CN$, $-COR$, $-CO_2H$, $-CO_2R$, $-CHO$, halogens.
3. list a given series of substituents (selected from those given in Objective 2) in order of increasing or decreasing ability to activate or deactivate an aromatic ring with respect to electrophilic substitution.
4. explain, in general terms, the factors that determine whether a given substituent will activate or deactivate an aromatic ring with respect to electrophilic substitution.
5. list a given series of aromatic compounds in order of increasing or decreasing reactivity with respect to electrophilic substitution.
6. explain the inductive effects displayed by substituents such as nitro, carboxyl, alkyl and the halogens during electrophilic aromatic substitution reactions.
7. explain the resonance effects displayed by substituents such as nitro, carbonyl-containing, hydroxy, alkoxy and amino groups during electrophilic aromatic substitution reactions.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- inductive effect
- resonance effect

STUDY NOTES

On reading Objective 2 students may exclaim “How am I ever going to memorize all of this!”—or words to that effect. The answer is that if you are trying to memorize such things, you are taking the wrong approach to organic chemistry. What you should be doing is trying to understand the factors that determine whether a given substituent will activate or deactivate a benzene ring with respect to electrophilic substitution.

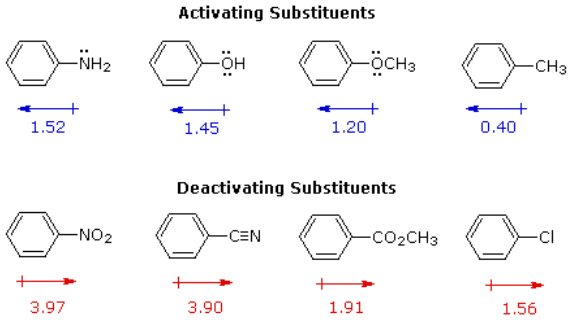
You may wish to review earlier material on to the inductive effect. If so, refer to Sections 2.1, 7.9 (paying particular attention to the “Study Notes”) and 14.5.

Note that one argument sometimes used to explain the ability of alkyl groups to donate electrons inductively to an aromatic ring is that sp^2-hybridized carbon atoms are more electronegative than sp^3-hybridized carbon atoms. Thus, a sigma bond between sp^2- and sp^3-carbon is slightly polarized, as follows:



When substituted benzene compounds undergo electrophilic substitution reactions of the kind discussed above, **two related features must be considered:**

I. The first is the relative reactivity of the compound compared with benzene itself. Experiments have shown that substituents on a benzene ring can influence reactivity in a profound manner. For example, a hydroxy or methoxy substituent increases the rate of electrophilic substitution about ten thousand fold, as illustrated by the case of anisole in the virtual demonstration (above). In contrast, a nitro substituent decreases the ring's reactivity by roughly a million. This **activation** or **deactivation** of the benzene ring toward electrophilic substitution may be correlated with the electron donating or electron withdrawing influence of the substituents, as measured by molecular dipole moments. In the following diagram we see that electron donating substituents (blue dipoles) activate the benzene ring toward electrophilic attack, and electron withdrawing substituents (red dipoles) deactivate the ring (make it less reactive to electrophilic attack).

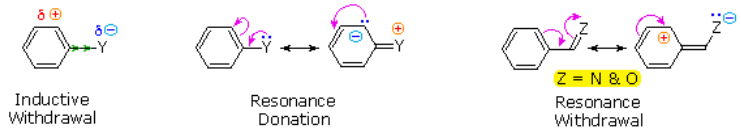


The influence a substituent exerts on the reactivity of a benzene ring may be explained by the interaction of two effects:

The first is the **inductive effect** of the substituent. Most elements other than metals and carbon have a significantly greater electronegativity than hydrogen. Consequently, substituents in which nitrogen, oxygen and halogen atoms form sigma-bonds to the aromatic ring exert an inductive electron withdrawal, which deactivates the ring (left-hand diagram below).

The second effect is the result of **conjugation** of a substituent function with the aromatic ring. This conjugative interaction facilitates electron pair donation or withdrawal, to or from the benzene ring, in a manner different from the inductive shift. If the atom bonded to the ring has one or more non-bonding valence shell electron pairs, as do nitrogen, oxygen and the halogens, electrons may flow into the aromatic ring by p-π conjugation (resonance), as in the middle diagram. Finally, polar double and triple bonds conjugated with the benzene ring may withdraw electrons, as in the right-hand diagram. Note that in the resonance examples all the contributors are not shown. In both cases the charge distribution in the benzene ring is greatest at sites ortho and para to the substituent.

In the case of the nitrogen and oxygen activating groups displayed in the top row of the previous diagram, electron donation by resonance dominates the inductive effect and these compounds show exceptional reactivity in electrophilic substitution reactions. Although halogen atoms have non-bonding valence electron pairs that participate in p-π conjugation, their strong inductive effect predominates, and compounds such as chlorobenzene are less reactive than benzene. The three examples on the left of the bottom row (in the same diagram) are examples of electron withdrawal by conjugation to polar double or triple bonds, and in these cases the inductive effect further enhances the deactivation of the benzene ring. Alkyl substituents such as methyl increase the nucleophilicity of aromatic rings in the same fashion as they act on double bonds.

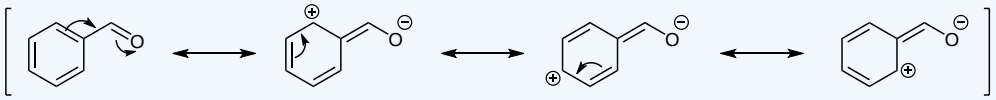


EXERCISES

? EXERCISE \PageIndex1

Draw the resonance structures for benzaldehyde to show the electron-withdrawing group.

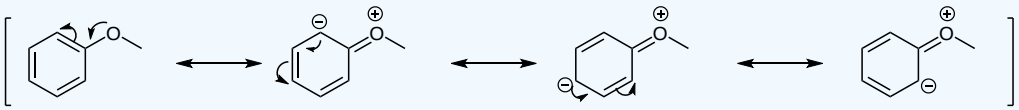
Answer



? EXERCISE \PageIndex2

Draw the resonance structures for methoxybenzene to show the electron-donating group.

Answer



QUESTIONS

Q16.4.1

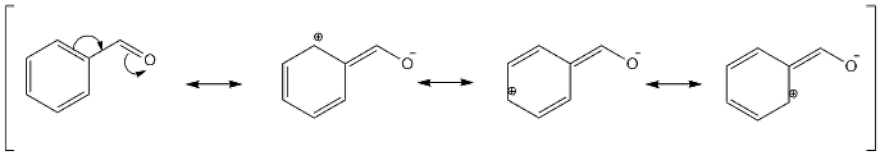
Draw the resonance structures for benzaldehyde to show the electron-withdrawing group.

Q16.4.2

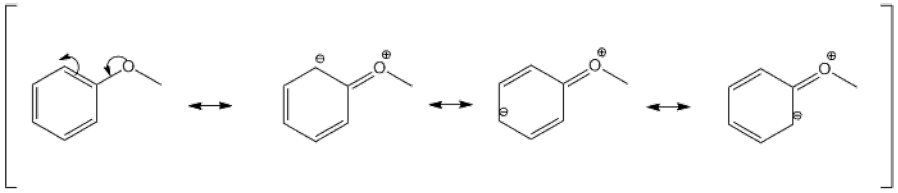
Draw the resonance structures for methoxybenzene to show the electron-donating group.

SOLUTIONS

S16.4.1



S16.4.2



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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16.5: AN EXPLANATION OF SUBSTITUENT EFFECTS

Objectives

After completing this section, you should be able to

1. draw the resonance contributors for the carbocation intermediate formed during the reaction of a given monosubstituted benzene derivative with any of the electrophiles discussed in this chapter.
2. classify each of the substituents listed in Objective 2 of Section 16.4 as being either meta or ortho/para directing.
3. classify each of the substituents listed in Objective 2 of Section 16.4 as being ortho/para directing activators, ortho/para directing deactivators, or meta directing deactivators.
4. predict the product or products formed from the reaction of a given monosubstituted benzene derivative with each of the electrophiles discussed in this chapter.
5. explain, by drawing the resonance contributors for the intermediate carbocation, why the electrophilic substitution of an alkyl benzene results in a mixture of mainly ortho- and para- substituted products.
6. explain why the electrophilic substitution of phenols, amines and their derivatives proceeds more rapidly than the electrophilic substitution of benzene itself.
7. explain, by drawing the resonance contributors for the intermediate carbocation, why meta substitution predominates in electrophilic aromatic substitution reactions carried out on benzene derivatives containing one of the substituents R_3N^+, NO_2, CO_2H, CN, CO_2R, COR or CHO.
8. explain why electrophilic aromatic substitution of benzene derivatives containing one of the substituents listed in Objective 7, above, proceeds more slowly than the electrophilic substitution of benzene itself.
9. explain, by drawing the resonance contributors for the intermediate carbocation, why the electrophilic aromatic substitution of halobenzenes produces a mixture of mainly ortho- and para-substituted products.
10. explain why the electrophilic aromatic substitution of halobenzenes proceeds more slowly than does the electrophilic substitution of benzene itself.
11. use the principles developed in this chapter to predict in which of the three categories listed in Objective 3, above, a previously unencountered substituent should be placed.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- steric effect
- steric hindrance

STUDY NOTES

As you saw in Section 16.4, a substituent on a benzene ring can be an activator or a deactivator. At the same time, a substituent can also be a meta director or an ortho/para director. Of the four possible combinations, only three are known—there are no meta directing activators.

If you look at the data for the nitration of toluene, you will see that the yield of *o*-nitrotoluene is 63% and that of *p*-nitrotoluene is 34%. Statistically, we should expect to obtain twice as much ortho product as para product, because the former is produced by attack at either of two carbon atoms whereas the latter is produced by attack at only one carbon atom (see Figure 16.1, below).

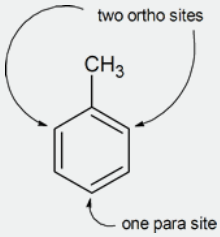


Figure 16.1: Proportions of *o*-nitrotoluene and *p*-nitrotoluene produced by the nitration of toluene

In this instance, the observed ortho/para ratio is almost 2:1, as we might expect. However, if we study the ortho/para ratio found in the nitration of a number of other arenes, we see that this is not always the case. Note that the data for the nitration of toluene given in the

table below differ from those presented elsewhere. The variation may result from a difference in temperature, reaction conditions or reagent, and emphasizes the point that it is the trends which are important, not the numbers themselves.

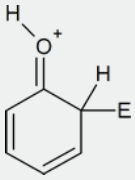
Substrate	% ortho	% para	ortho/para ratio
toluene	58	37	1.57:1
ethylbenzene	45	49	0.92:1
isopropylbenzene	30	62	0.48:1
tert-butylbenzene	16	73	0.22:1

[**Source:** These data were taken from the audiocassette *Some Organic Reaction Pathways*, by Peter Sykes. London: Educational Techniques Subject Group, The Chemical Society, 1975.]

Table 16.1: Nitration of arenes

The table above shows us that as the size of the alkyl substituent already present in the ring increases, attack at the ortho position becomes more difficult, and the percentage of ortho isomers in the mixture of products decreases. This is an example of a *steric effect*—an effect caused by the size of the substituent—and we would say that as the size of the alkyl group increases, attack at the ortho position becomes less favourable as a result of *steric hindrance*. Note that the size of the electrophile can also be a factor in determining the ortho/para ratio: the larger the electrophile, the less able it is to attack at the ortho position, particularly if the substituent already present in the ring is itself quite bulky.

When drawing the resonance contributors to the carbocation formed during an electrophilic aromatic substitution, bear in mind that those of the type



are particularly important, because in such structures each atom possesses a complete octet of electrons.

Note that, as do the hydroxyl and amino groups, the halogens have an inductive electron-withdrawing effect and a resonance electron-releasing effect on a benzene ring. The difference in behaviour during electrophilic substitutions arises because, with the hydroxyl and amino groups, the resonance effect completely swamps the inductive effect, whereas with the halogens, there is a much finer balance. In the case of the latter, the inductive effect reduces the overall reactivity, but the resonance effect means that this reduction is felt less at the ortho and para positions than at the meta position.

Substituted rings are divided into two groups based on the type of the substituent that the ring carries:

- **Activated rings**: the substituents on the ring are groups that donate electrons.
- **Deactivated rings**: the substituents on the ring are groups that withdraw electrons.

INTRODUCTION

Examples of activating groups in the relative order from the most activating group to the least activating:

$$-NH_2, -NR_2 > -OH, -OR > -NHCOR > -CH_3 \text{ and other alkyl groups}$$

with R as alkyl groups (C_nH_{2n+1})

Examples of deactivating groups in the relative order from the most deactivating to the least deactivating:

$$-NO_2, -CF_3 > -COR, -CN, -CO_2R, -SO_3H > \text{Halogens}$$

with R as alkyl groups (C_nH_{2n+1})

The order of reactivity among Halogens from the more reactive (least deactivating substituent) to the least reactive (most deactivating substituent) halogen is:

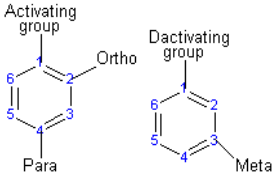
$$F > Cl > Br > I$$

The order of reactivity of the benzene rings toward the electrophilic substitution when it is substituted with a halogen groups, follows the order of electronegativity. The ring that is substituted with the most electronegative halogen is the most reactive ring (less deactivating substituent) and the ring that is substituted with the least electronegatvie halogen is the least reactive ring (more deactivating substituent),

when we compare rings with halogen substituents. Also the size of the halogen effects the reactivity of the benzene ring that the halogen is attached to. As the size of the halogen increase, the reactivity of the ring decreases.

THE DIRECTION OF THE REACTION

The activating group directs the reaction to the ortho or para position, which means the electrophile substitute the hydrogen that is on carbon 2 or carbon 4. The deactivating group directs the reaction to the meta position, which means the electrophile substitute the hydrogen that is on carbon 3 with the exception of the halogens that is a deactivating group but directs the ortho or para substitution.

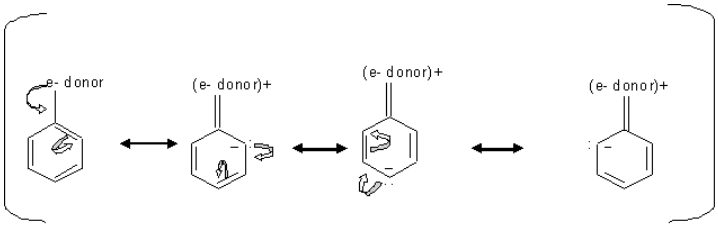


SUBSTITUENTS DETERMINE THE REACTION DIRECTION BY RESONANCE OR INDUCTIVE EFFECT

Resonance effect is the conjugation between the ring and the substituent, which means the delocalizing of the π electrons between the ring and the substituent. Inductive effect is the withdraw of the sigma (the single bond) electrons away from the ring toward the substituent, due to the higher electronegativity of the substituent compared to the carbon of the ring.

ACTIVATING GROUPS (ORTHO OR PARA DIRECTORS)

When the substituents like -OH have an unshared pair of electrons, the resonance effect is stronger than the inductive effect which make these substituents stronger activators, since this resonance effect direct the electron toward the ring. In cases where the subtituents is esters or amides, they are less activating because they form resonance structure that pull the electron density away from the ring.

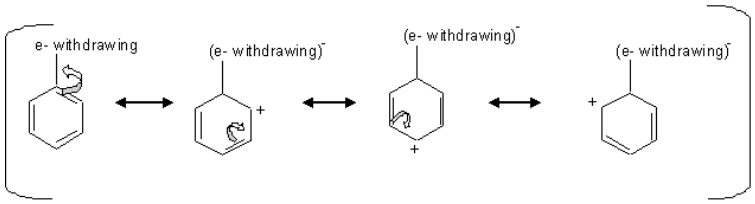


By looking at the mechanism above, we can see how groups donating electron direct the ortho, para electrophilic substition. Since the electrons locatinn transfer between the ortho and para carbons, then the electrophile prefer attacking the carbon that has the free electron.

Inductive effect of alkyl groups activates the direction of the ortho or para substitution, which is when s electrons gets pushed toward the ring.

DEACTIVATING GROUP (META DIRECTORS)

The deactivating groups deactivate the ring by the inductive effect in the presence of an electronegative atom that withdraws the electrons away from the ring.



we can see from the mechanism above that when there is an electron withdraw from the ring, that leaves the carbons at the ortho, para positions with a positive charge which is unfavorable for the electrophile, so the electrophile attacks the carbon at the meta positions.

Halogens are an exception of the deactivating group that directs the ortho or para substitution. The halogens deactivate the ring by inductive effect not by the resonance even though they have an unpaired pair of electrons. The unpaired pair of electrons gets donated to the ring, but

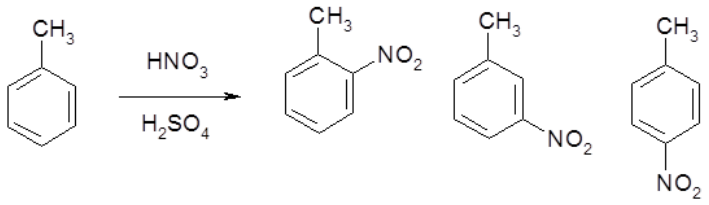
the inductive effect pulls away the s electrons from the ring by the electronegativity of the halogens.

SUBSTITUENTS DETERMINE THE REACTIVITY OF RINGS

The reaction of a substituted ring with an activating group is faster than benzene. On the other hand, a substituted ring with a deactivated group is slower than benzene.

Activating groups speed up the reaction because of the resonance effect. The presence of the unpaired electrons that can be donated to the ring, stabilize the carbocation in the transition state. Thus; stabilizing the intermediate step, speeds up the reaction; and this is due to the decrease of the activating energy. On the other hand, the deactivating groups, withdraw the electrons away from the carbocation formed in the intermediate step, thus; the activation energy is increased which slows down the reaction.

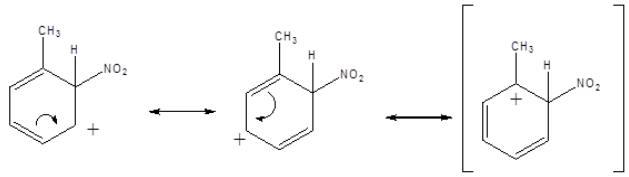
THE CH_3GROUP IS AND ORTHO, PARA DIRECTOR



Alkyl groups are Inductive activators

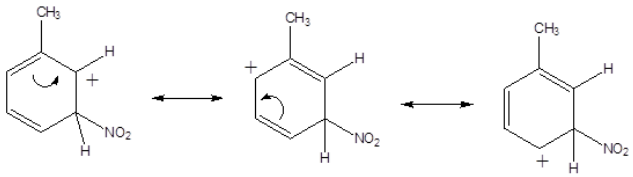
With o/p attack the form a tertiary arenium carbocation which speeds up the reaction

Ortho Attack

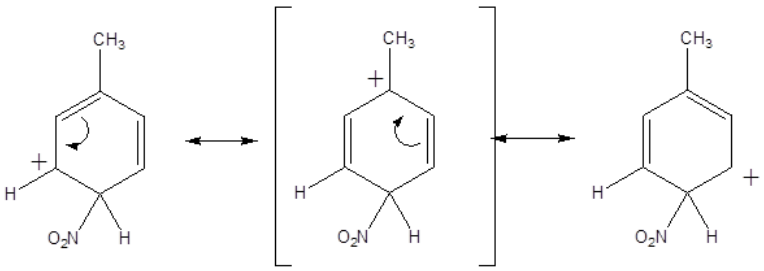


Tertiary Carbocation

Meta Attack

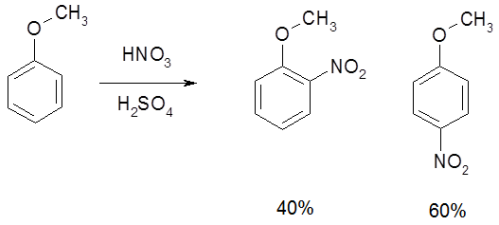


Para Attack



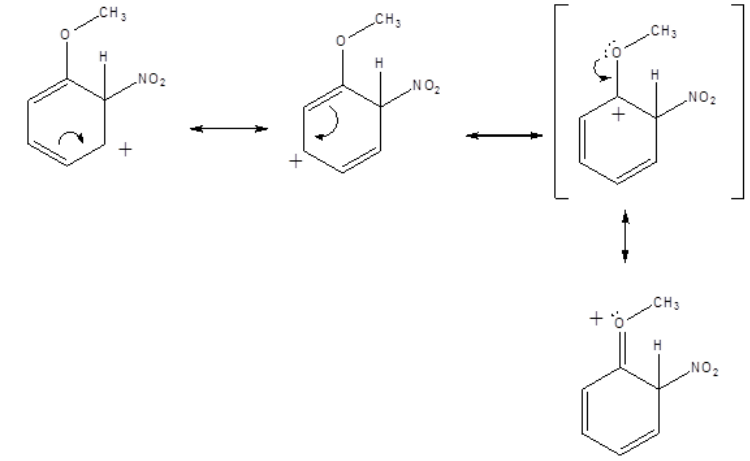
Tertiary Carbocation

THE O-CH_3 GROUP IS AN ORTHO, PARA DIRECTOR

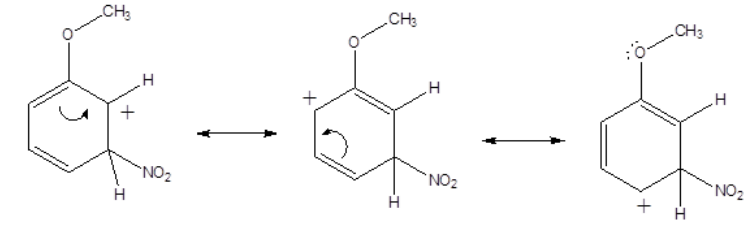


Ortho and Para producst produces a resonance structure which stabilizes the arenium ion. This causes the ortho and para products for form faster than meta. Generally, the para product is preferred because of steric effects.

Ortho Attack

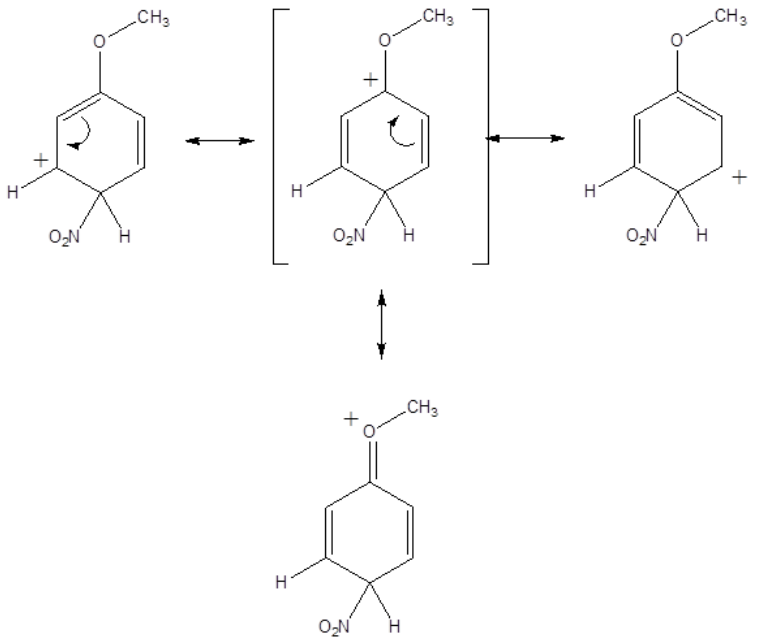


Meta Attack

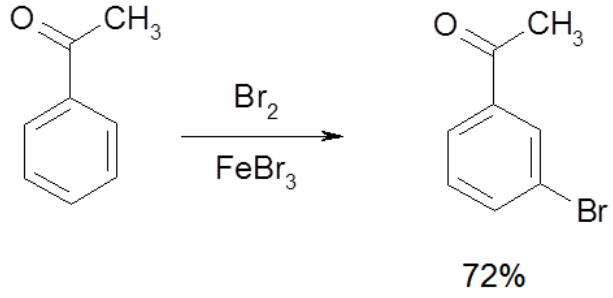


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Para Attack



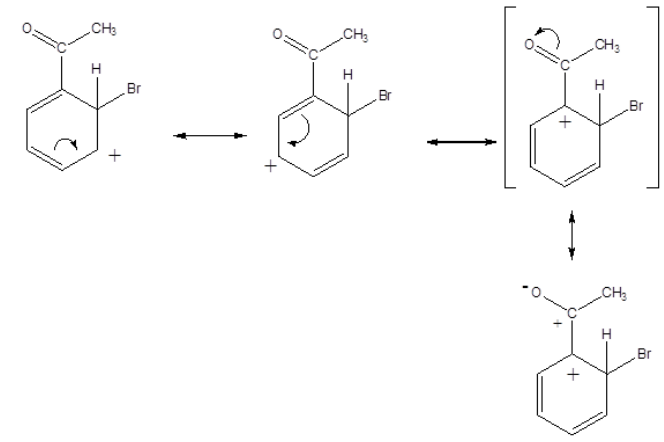
ACYL GROUPS ARE META DIRECTORS



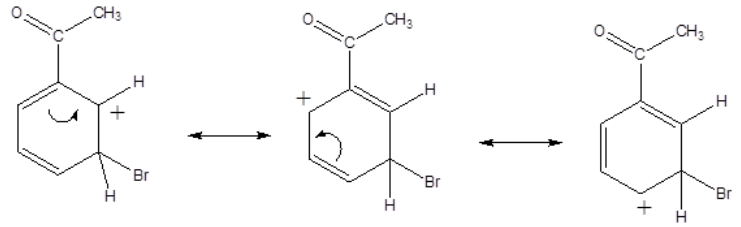
72%

Acyl groups are resonance deactivators. Ortho and para attack produces a resonance structure which places the arenium cation next to and additional cation. This destabilizes the arenium cation and slows down ortho and para reaction. By default the meta product forms faster because it lacks this destablizing resonance structure.

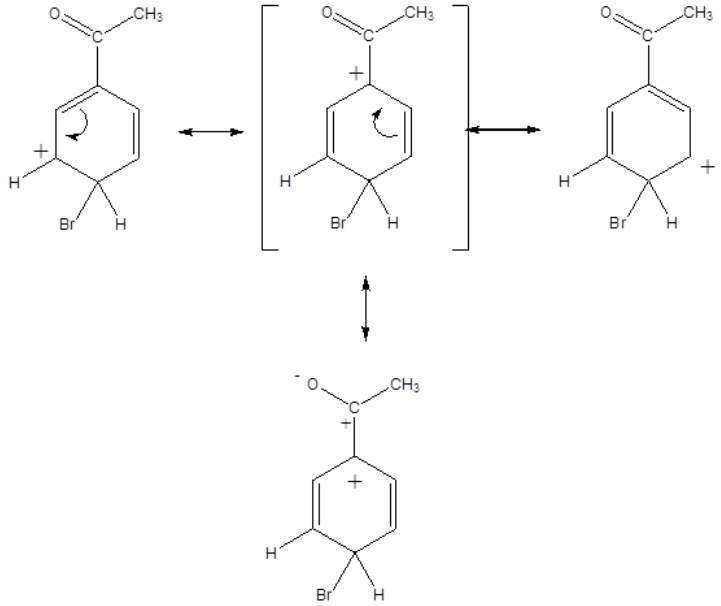
Ortho Attack



Meta Attack



Para Attack



REFERENCES

1. Schore, N.E. and P.C. Vollhardt. 2007. *Organic Chemistry, structure and function*, 5th ed. New York,NY: W.H. Freeman and Company.
2. Fryhle, C.B. and G. Solomons. 2008. *Organic Chemistry*, 9th ed.Danvers,MA: Wiley.

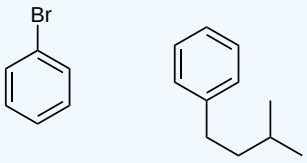
OUTSIDE LINKS

- http://en.Wikipedia.org/wiki/Activating_group
- http://en.Wikipedia.org/wiki/Deactivating_group
- http://www.columbia.edu/itc/chemistry/c3045/client_edit/ppt/PDF/12_12_14.pdf

EXERCISES

? EXERCISE 16.5.1

Predict the pattern of the electrophilic substitution on these rings:



Answer

The first substitution is going to be ortho and/or para substitution since we have a halogen subtituent. The second substitution is going to be ortho and/or para substitution also since we have an alkyl substituent.

EXERCISE 16.5.2

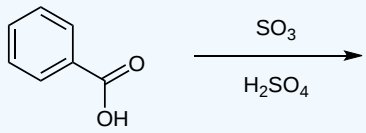
Which nitration product is going to form faster: nitration of aniline or nitration of nitrobenzene?

Answer

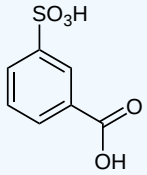
The nitration of aniline is going to be faster than the nitration of nitrobenzene, since the aniline is a ring with NH_2 substituent and nitrobenzene is a ring with NO_2 substituent. As described above NH_2 is an activating group which speeds up the reaction and NO_2 is a deactivating group that slows down the reaction.

EXERCISE 16.5.3

Predict the product of the following sulfonation reaction:



Answer



EXERCISE 16.5.4

Classify these two groups as activating or deactivating groups:

A. alcohol

B. ester

Answer

A. alcohol is an activating group.

B. Esters can be either. If the oxygen atom is next to the ring, esters are activating. However if the carbonyl is next to the ring, the ester is a deactivating group.

EXERCISE 16.5.5

Does a chloride substituent activate or deactivate an aromatic ring?

Answer

Chloride deactivate an aromatic ring due to the inductive effect.

EXERCISE 16.5.6

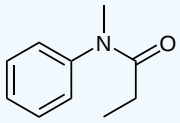
(Trichloromethyl)benzene has a strong concentration of electrons at the methyl substituent. Comparing this toluene, which is more reactive toward electrophilic substitution?

Answer

The trichloromethyl group is an electron donor into the benzene ring, therefore making it more stable and therefore more reactive compared to electrophilic substitution.

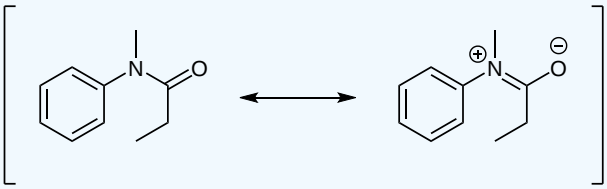
EXERCISE 16.5.7

The following compound is less reactive towards electrophilic substitution than aniline? Explain.



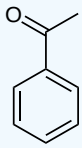
Answer

As seen in resonance the electron density is also localized off of the ring, thereby deactivating it compared to aniline.

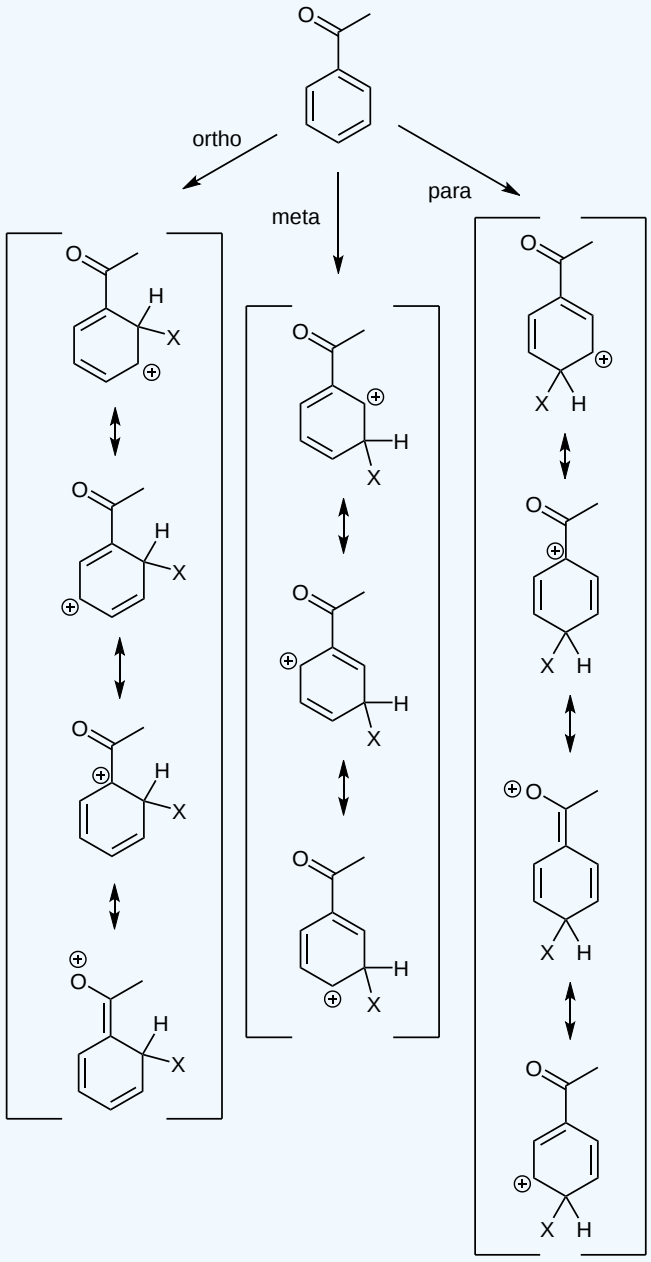


EXERCISE 16.5.8

Consider the intermediates of the following molecule during an electrophilic substitution. Draw resonance structures for ortho, meta, and para attacks.



Answer



QUESTIONS

Q16.5.1

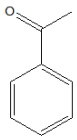
(Trichlorometyl)benzene has a strong concentration of electrons at the methyl substituent. Comparing this toluene, which is more reactive toward electrophilic substitution?

Q16.5.2

The following compound is less reactive towards electrophilic substitution than aniline? Explain.

Q16.5.3

Consider the intermediates of the following molecule during an electrophilic substitution. Draw resonance structures for ortho, meta, and para attacks.



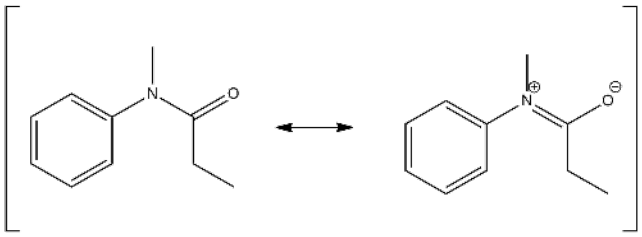
SOLUTIONS

S16.5.1

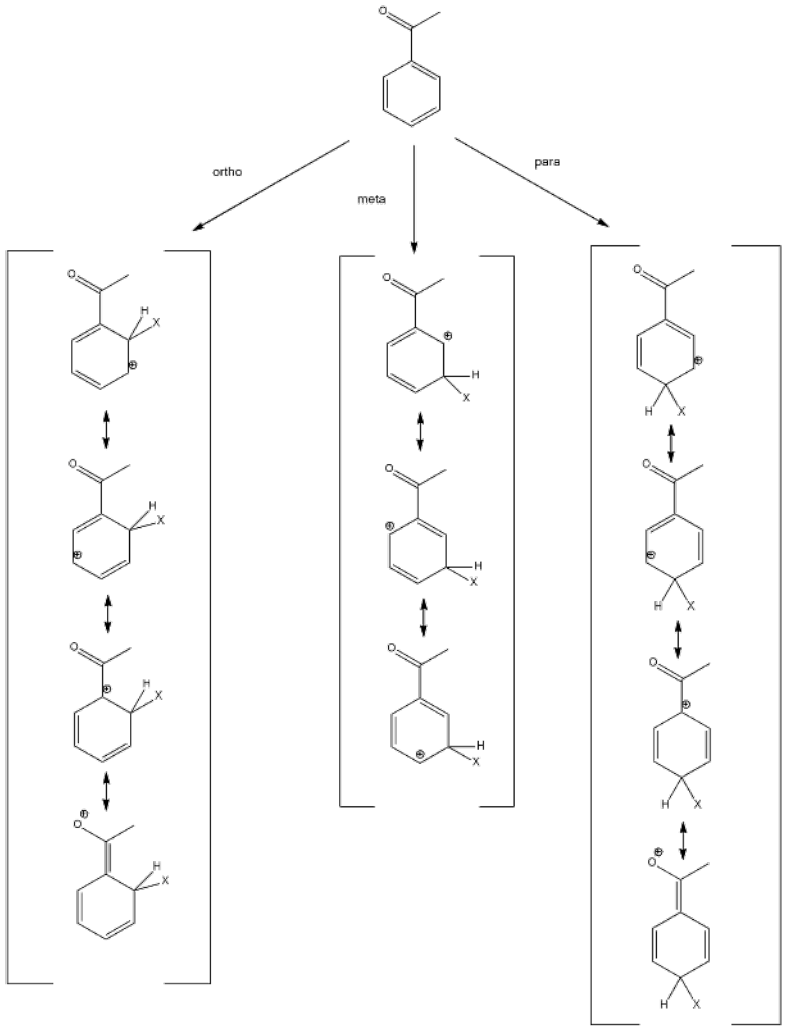
The trichloromethyl group is an electron donor into the benzene ring, therefore making it more stable and therefore more reactive compared to electrophilic substitution.

S16.5.2

As seen in resonance the electron density is also localized off of the ring, thereby deactivating it compared to aniline.



S16.5.3



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Lana Alawwad (UCD)
-

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16.6: TRISUBSTITUTED BENZENES- ADDITIVITY OF EFFECTS

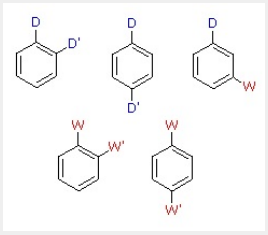
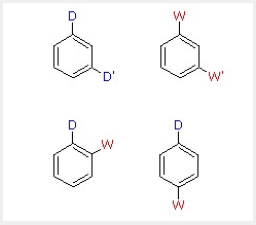
Objectives

After completing this section, you should be able to

1. predict the position or positions at which electrophilic substitution will occur when a third substituent is introduced into a disubstituted benzene ring.
2. explain the observed substitution pattern when a third substituent is introduced into a disubstituted benzene ring.

ORIENTATIONAL INTERACTION OF SUBSTITUENTS EDIT SECTION

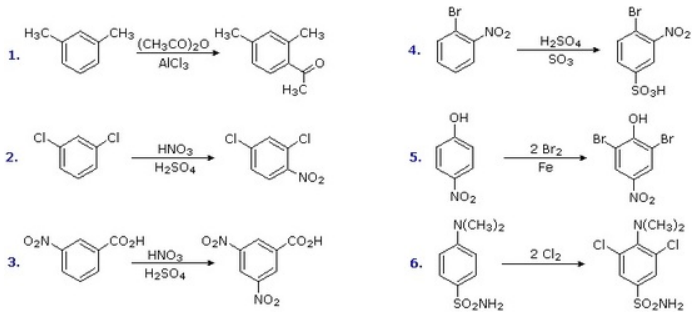
When a benzene ring has two substituent groups, each exerts an influence on subsequent substitution reactions. The activation or deactivation of the ring can be predicted more or less by the sum of the individual effects of these substituents. The site at which a new substituent is introduced depends on the orientation of the existing groups and their individual directing effects. We can identify two general behavior categories, as shown in the following table. Thus, the groups may be oriented in such a manner that their directing influences act in concert, reinforcing the outcome; or are opposed (antagonistic) to each other. Note that the orientations in each category change depending on whether the groups have similar or opposite individual directing effects.

Antagonistic or Non-Cooperative	Reinforcing or Cooperative
	

D = Electron Donating Group (ortho/para-directing)
W = Electron Withdrawing Group (meta-directing)

REINFORCING OR COOPERATIVE SUBSTITUTIONS EDIT SECTION

The products from substitution reactions of compounds having a reinforcing orientation of substituents are easier to predict than those having antagonistic substituents. For example, the six equations shown below are all examples of reinforcing or cooperative directing effects operating in the expected manner. Symmetry, as in the first two cases, makes it easy to predict the site at which substitution is likely to occur. Note that if two different sites are favored, substitution will usually occur at the one that is least hindered by ortho groups.

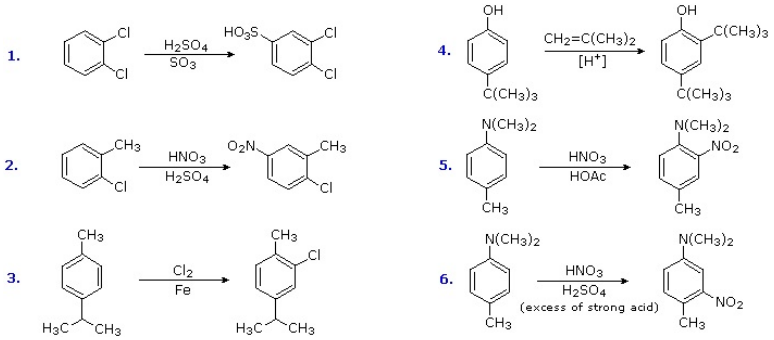


The first three examples have two similar directing groups in a meta-relationship to each other. In examples 4 through 6, oppositely directing groups have an ortho or para-relationship. The major products of electrophilic substitution, as shown, are the sum of the individual group effects. The strongly activating hydroxyl (–OH) and amino ($–NH_2$) substituents favor dihalogenation in examples 5 and six.

ANTAGONISTIC OR NON-COOPERATIVE SUBSTITUTIONS EDIT SECTION

Substitution reactions of compounds having an antagonistic orientation of substituents require a more careful analysis. If the substituents are identical, as in example 1 below, the symmetry of the molecule will again simplify the decision. When one substituent has a pair of non-bonding electrons available for adjacent charge stabilization, it will normally exert the product determining influence, examples 2, 4 & 5, even though it may be overall deactivating (case 2). Case 3 reflects a combination of steric hindrance and the superior innate stabilizing

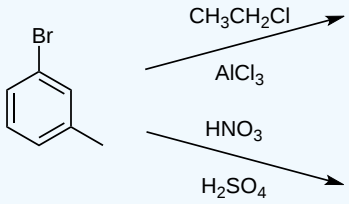
ability of methyl groups relative to other alkyl substituents. Example 6 is interesting in that it demonstrates the conversion of an activating ortho/para-directing group into a deactivating meta-directing "onium" cation [$-NH(CH_3)_2^{(+)}$] in a strong acid environment.

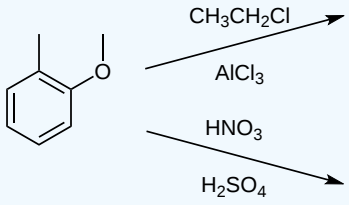


EXERCISE

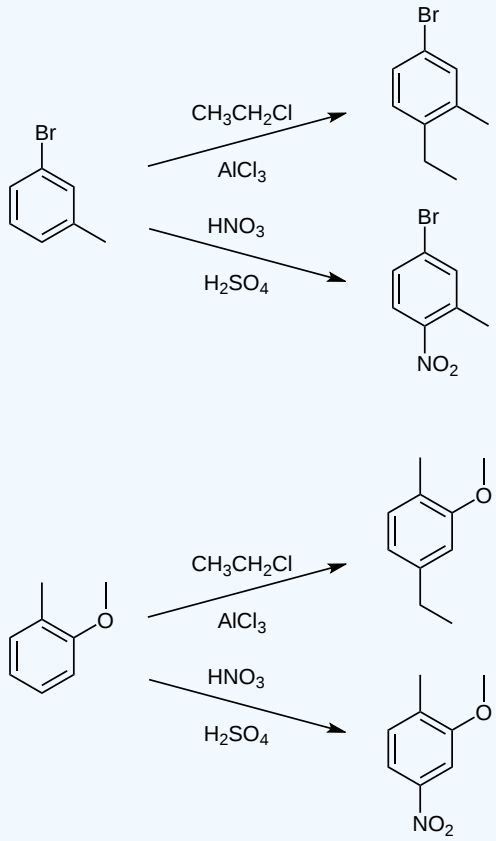
? EXERCISE 16.6.1

Predict the products of the following reactions:





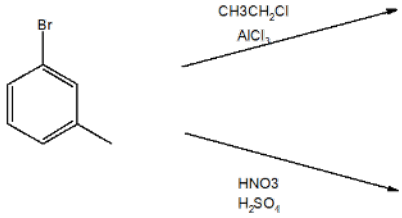
Answer

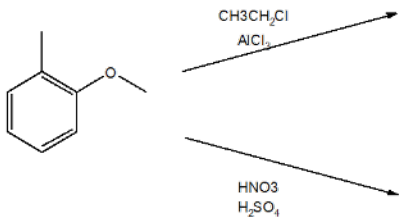


QUESTIONS

Q16.6.1

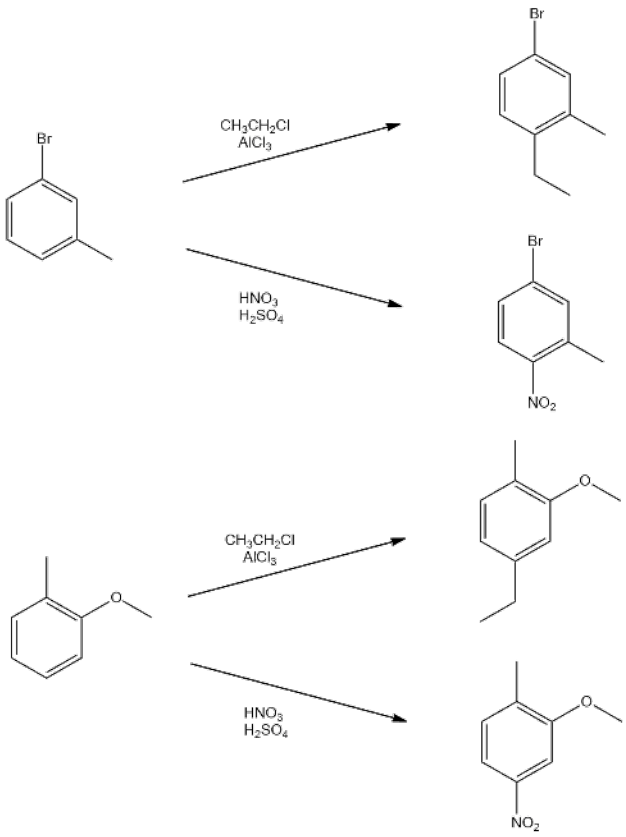
Predict the products of the following reactions:





SOLUTIONS

S16.6.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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16.7: NUCLEOPHILIC AROMATIC SUBSTITUTION

Objectives

After completing this section, you should be able to

1. identify the conditions necessary for an aryl halide to undergo nucleophilic aromatic substitution, and give an example of such a reaction.
2. write the detailed mechanism for a nucleophilic aromatic substitution reaction.
3. compare the mechanism of a nucleophilic aromatic substitution reaction and the S_N1 and S_N2 mechanisms discussed earlier.
4. identify the product formed when a given nucleophile reacts with a given aryl halide in a nucleophilic aromatic substitution reaction.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- Meisenheimer complex
- nucleophilic aromatic substitution

STUDY NOTES

A *nucleophilic aromatic substitution reaction* is a reaction in which one of the substituents in an aromatic ring is replaced by a nucleophile.

A *Meisenheimer complex* is a negatively charged intermediate formed by the attack of a nucleophile upon one of the aromatic-ring carbons during the course of a nucleophilic aromatic substitution reaction. A typical Meisenheimer complex is shown in the reaction scheme below. Notice how this particular complex can be formed from two different starting materials by using a different nucleophile in each case.

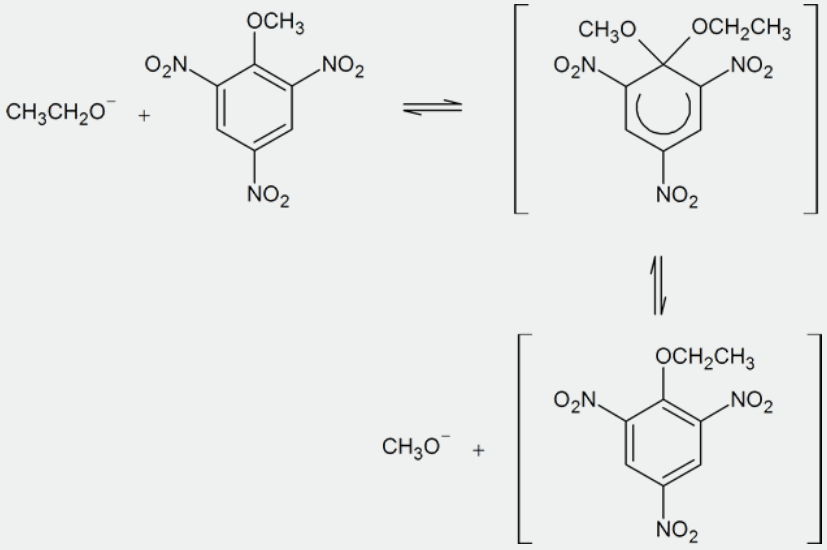


Figure 16.2: The formation of a typical Meisenheimer complex

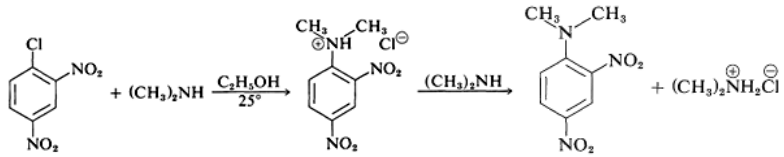
A NUCLEOPHILIC AROMATIC DISPLACEMENT REACTIONS OF ARYL HALIDES

The carbon-halogen bonds of aryl halides are like those of alkenyl halides in being much stronger than those of alkyl halides (see Table 4-6). The simple aryl halides generally are resistant to attack by nucleophiles in either S_N1 or S_N2 reactions (Table 14-6). However, this low reactivity can be changed dramatically by changes in the reaction conditions and the structure of the aryl halide. In fact, nucleophilic displacement becomes quite rapid

a. when the aryl halide is activated by substitution with strongly electron-attracting groups such as NO_2, and
b. when very strongly basic nucleophilic reagents are used.

ADDITION-ELIMINATION MECHANISM OF NUCLEOPHILIC SUBSTITUTION OF ARYL HALIDES

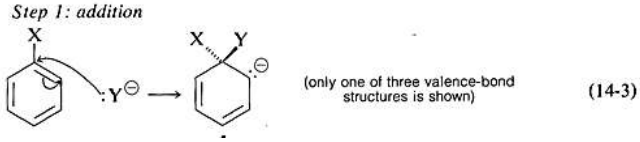
Although the simple aryl halides are inert to the usual nucleophilic reagents, considerable activation is produced by strongly electron-attracting substituents provided these are located in either the ortho or para positions, or both. For example, the displacement of chloride ion from 1-chloro-2,4-dinitrobenzene by dimethylamine occurs readily in ethanol solution at room temperature. Under the same conditions chlorobenzene completely fails to react; thus the activating influence of the two nitro groups amounts to a factor of at least 108:



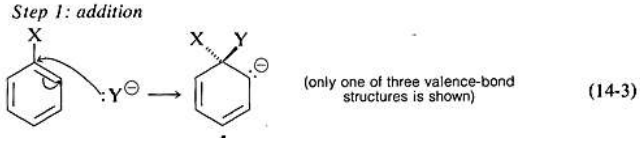
A related reaction is that of 2,4-dinitrofluorobenzene with the amino groups of peptides and proteins, and this reaction provides a means for analysis of the N-terminal amino acids in polypeptide chains. (See Section 25-7B.)

In general, the reactions of activated aryl halides closely resemble the SN2-displacement reactions of aliphatic halides. The same nucleophilic reagents are effective (e.g., CH_3O^-, HO^-, and RNH_2); the reactions are second order overall (first order in halide and first order in nucleophile); and for a given halide the more nucleophilic the attacking reagent, the faster the reaction. However, there must be more than a subtle difference in mechanism because an aryl halide is unable, to pass through the same type of transition state as an alkyl halide in SN2 displacements.

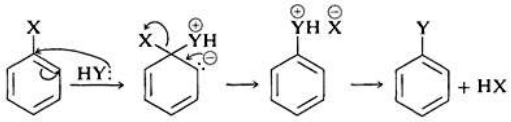
The generally accepted mechanism of nucleophilic aromatic substitution of aryl halides carrying activating groups involves two steps that are closely analogous to those briefly described in Section 14-4 for alkenyl and alkynyl halides. The first step involves attack of the nucleophile $Y:^-$ at the carbon bearing the halogen substituent to form an intermediate carbanion 4 (Equation 14-3). The aromatic system is destroyed on forming the anion, and the carbon at the reaction site changes from planar (sp2 bonds) to tetrahedral (sp3 bonds).



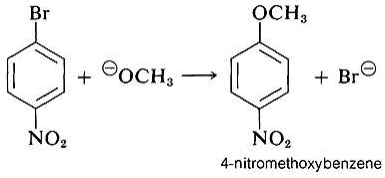
In the second step, loss of an anion, X^- or Y^-, regenerates an aromatic system, and, if X^- is lost, the overall reaction is nucleophilic displacement of X by Y (Equation 14-4).



In the case of a neutral nucleophilic reagent, Y or HY, the reaction sequence would be the same except for the necessary adjustments in the charge of the intermediate:

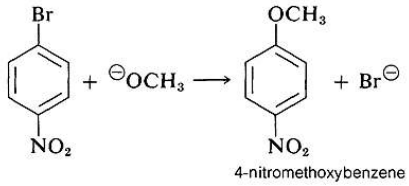


Why is this reaction pathway generally unfavorable for the simple aryl halides? The answer is that the intermediate 4, which we can express as a hybrid of the valence-bond structures 4a-4c, is too high in energy to be formed at any practical rate. Not only has 4 lost the aromatic stabilization of the benzene ring, but its formation results in transfer of negative charge to the ring carbons, which themselves are not very electronegative:



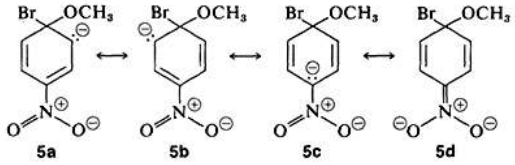
However, when strongly electron-attracting groups are located on the ring at the ortho-para positions, the intermediate anion is stabilized by delocalization of electrons from the ring carbons to more favorable locations on the substituent groups. As an example, consider the

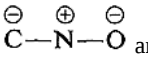
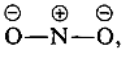
displacement of bromine by OCH3 in the reaction of 4-bromonitrobenzene and methoxide ion:



4-nitromethoxybenzene

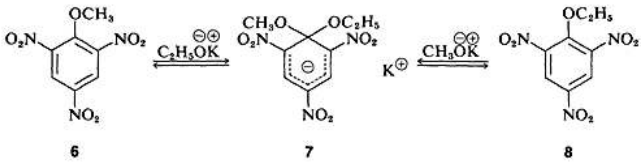
The anionic intermediate formed by addition of methoxide ion to the aryl halide can be described by the valence-bond structures 5a-5d. Of these structures 5d is especially important because in it the charge is transferred from the ring carbons to the oxygen of the nitro substituent:



Substituents in the meta positions have much less effect on the reactivity of an aryl halide because delocalization of electrons to the substituent is not possible. No formulas can be written analogous to 5c and 5d in which the negative charges are both on atoms next to positive nitrogen,  and  ,



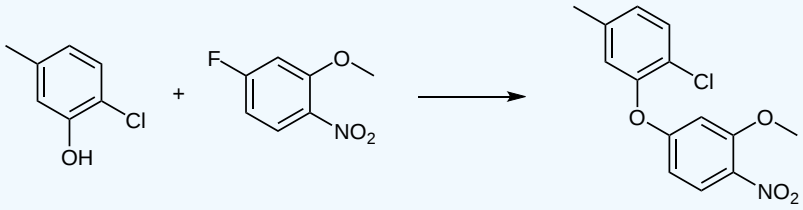
In a few instances, stable compounds resembling the postulated reaction intermediate have been isolated. One classic example is the complex 7 (isolated by J. Meisenheimer), which is the product of the reaction of either the methyl aryl ether 6 with potassium ethoxide, or the ethyl aryl ether 8 and potassium methoxide:



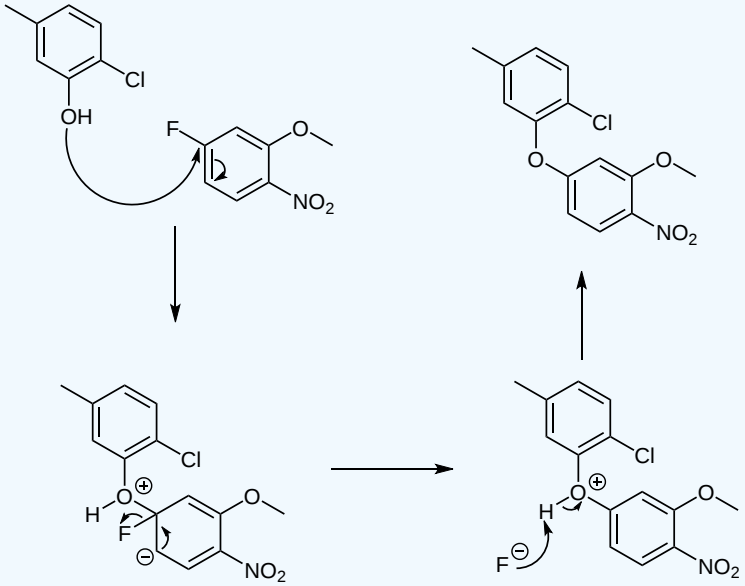
EXERCISE

? EXERCISE 16.7.1

Propose a mechanism for the following reaction:



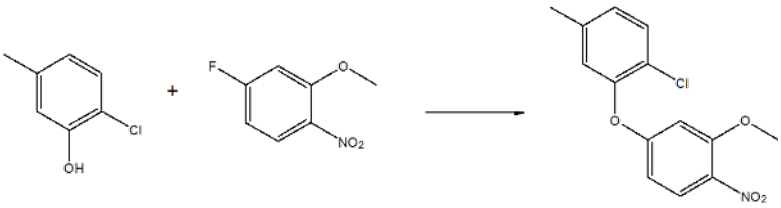
Answer



QUESTIONS

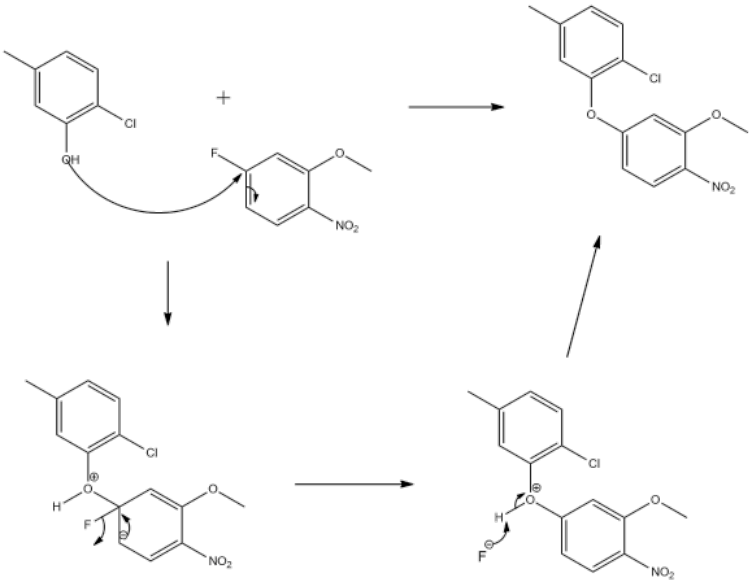
Q16.7.1

Propose a mechanism for the following reaction:



SOLUTIONS

S16.7.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

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16.8: BENZYNE

Objectives

After completing this section, you should be able to

1. identify the reagents and conditions required to produce phenol from chlorobenzene on an industrial scale.
2. write the mechanism for the conversion of an alkyl halide to a phenol through a benzyne intermediate.
3. discuss the experimental evidence which supports the existence of benzyne intermediates.
4. discuss the bonding in benzyne, and hence account for its high reactivity.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- benzyne
- elimination-addition mechanism

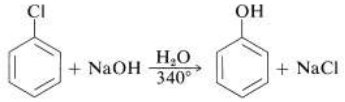
STUDY NOTES

An elimination-addition mechanism involves the elimination of the elements of a small molecule from a substrate to produce a highly reactive intermediate, which then undergoes an addition reaction.

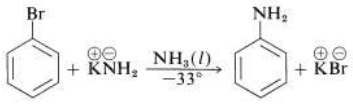
The elimination-addition mechanism of nucleophilic aromatic substitution involves the remarkable intermediate called benzyne or arynes.

14-6C ELIMINATION-ADDITION MECHANISM OF NUCLEOPHILIC AROMATIC SUBSTITUTION. ARYNES

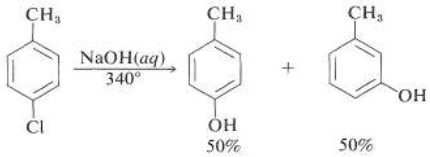
The reactivities of aryl halides, such as the halobenzenes, are exceedingly low toward nucleophilic reagents that normally effect displacements with alkyl halides and activated aryl halides. Substitutions do occur under forcing conditions of either high temperatures or very strong bases. For example, chlorobenzene reacts with sodium hydroxide solution at temperatures around **340°** and this reaction was once an important commercial process for the production of benzenol (phenol):



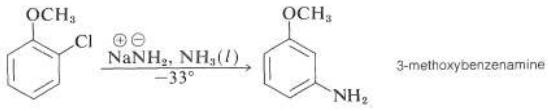
In addition, aryl chlorides, bromides, and iodides can be converted to areneamines **$ArNH_2$** by the conjugate bases of amines. In fact, the reaction of potassium amide with bromobenzene is extremely rapid, even at temperatures as low as **−33°** with liquid ammonia as solvent:



However, displacement reactions of this type differ from the previously discussed displacements of activated aryl halides in that rearrangement often occurs. That is, *the entering group does not always occupy the same position on the ring as that vacated by the halogen substituent*. For example, the hydrolysis of 4-chloromethylbenzene at **340°** gives an equimolar mixture of 3- and 4-methylbenzenols:

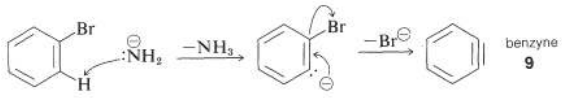


Even more striking is the exclusive formation of 3-methoxybenzenamine in the amination of 2-chloromethoxybenzene. Notice that this result is a violation of the principle of least structural change (Section 1-1H):



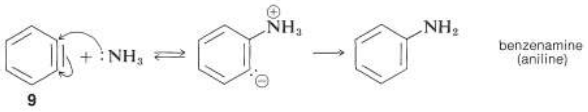
The mechanism of this type of reaction has been studied extensively, and much evidence has accumulated in support of a stepwise process, which proceeds first by base-catalyzed *elimination* of hydrogen halide (**HX**) from the aryl halide - as illustrated below for the amination of bromobenzene:

Elimination

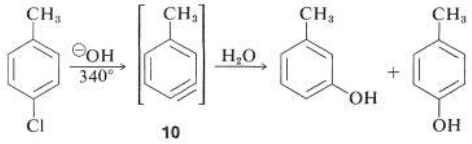


The product of the elimination reaction is a highly reactive intermediate **9** called **benzyne**, or **dehydrobenzene**, which differs from benzene in having two less hydrogen and an extra bond between two ortho carbons. Benzyne reacts rapidly with any available nucleophile, in this case the solvent, ammonia, to give an addition product:

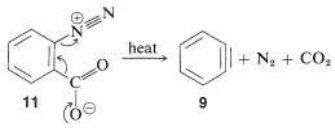
Addition



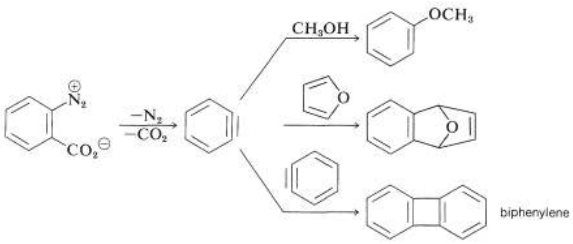
The rearrangements in these reactions result from the attack of the nucleophile at one or the other of the carbons of the extra bond in the intermediate. With benzyne the symmetry is such that no rearrangement would be detected. With substituted benzynes isomeric products may result. Thus 4-methylbenzyne, **10**, from the reaction of hydroxide ion with 4-chloro-1-methylbenzene gives both 3- and 4-methylbenzenols:



In the foregoing benzyne reactions the base that produces the benzyne in the elimination step is derived from the nucleophile that adds in the addition step. This need not always be so, depending on the reaction conditions. In fact, the synthetic utility of aryne reactions depends in large part of the success with which the aryne can be generated by one reagent but captured by another. One such method will be discussed in Section 14-10C and involves organometallic compounds derived from aryl halides. Another method is to generate the aryne by thermal decomposition of a 1,2-disubstituted arene compound such as **11**, in which both substituents are leaving groups - one leaving with an electron pair, the other leaving without:



When **11** decomposes in the presence of an added nucleophile, the benzyne intermediate is trapped by the nucleophile as it is formed. Or, if a conjugated diene is present, benzyne will react with it by a [4 + 2] cycloaddition. In the absence of other compounds with which it can react, benzyne will undergo [2 + 2] cycloaddition to itself:



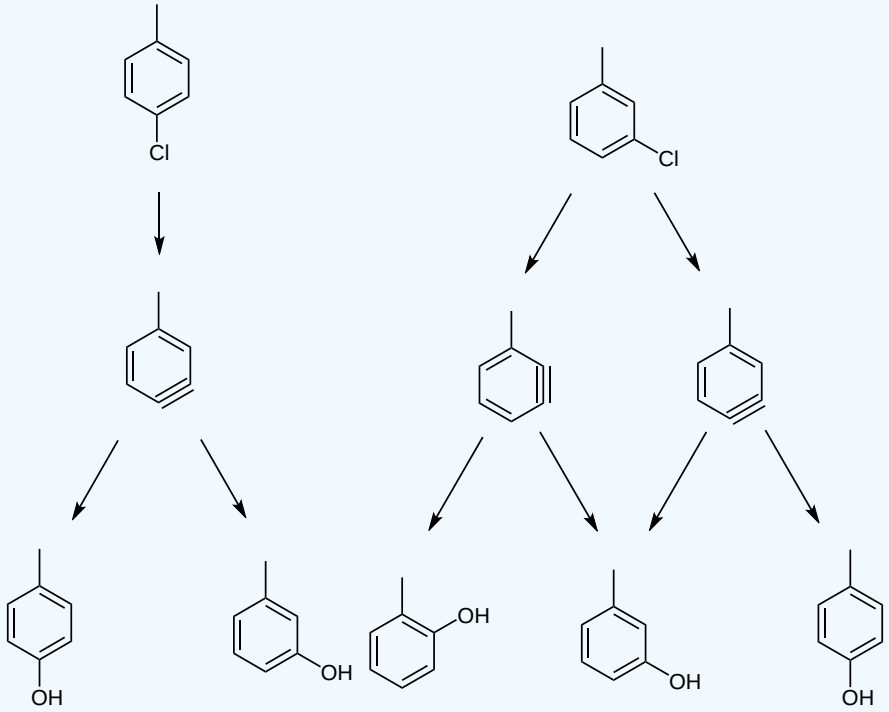
EXERCISE

EXERCISE 16.8.1

When *p*-chlorotoluene is reacted with NaOH, two products are seen. While when *m*-chlorotoluene is reacted with NaOH, three products are seen. Explain this.

Answer

You need to look at the benzyne intermediates. The para substituted only allows for two products, while the para produces two different alkynes which give three different products.



QUESTIONS

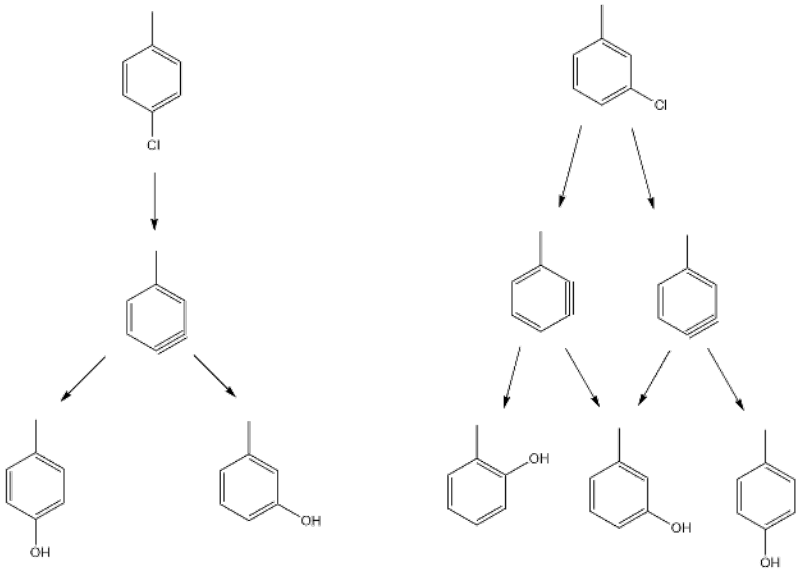
Q16.8.1

When *p*-chlorotoluene is reacted with NaOH, two products are seen. While when *m*-chlorotoluene is reacted with NaOH, three products are seen. Explain this.

SOLUTIONS

S16.8.1

You need to look at the benzyne intermediates. The para substituted only allows for two products, while the para produces two different alkynes which give three different products.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)

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16.9: OXIDATION OF AROMATIC COMPOUNDS

Objectives

After completing this section, you should be able to

1. write an equation to describe the oxidation of an alkylbenzene to a carboxylic acid.
2. identify the reagents required to oxidize a given alkylbenzene to a carboxylic acid.
3. identify the product formed from the side-chain oxidation of a given alkylbenzene.
4. identify the aromatic compound needed to produce a given carboxylic acid through side-chain oxidation.
5. write the equation for the bromination of an alkylbenzene side chain.
6. identify the reagents and conditions necessary to bring about bromination in the side chain of an alkylbenzene.
7. identify the product formed when a given alkylbenzene undergoes side-chain bromination.
8. identify the alkylbenzene needed to prepare a given benzylic bromide by radical substitution.
9. write the mechanism for the radical substitution at the benzylic position of an alkylbenzene.
10. explain the stability of benzylic radicals in terms of resonance, and draw the resonance contributors of a given benzyl radical.
11. explain, and illustrate with appropriate examples, the importance of benzylic bromides as intermediates in organic syntheses.
12. arrange a given series of radicals (including benzylic type radicals) in order of increasing or decreasing stability. (Review Section 10.3 if necessary.)

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- benzylic oxidation
- benzylic position
- side-chain oxidation

STUDY NOTES

As you can see from the examples, no matter what the length of the alkyl group in the arene substrate, the product is always a one-carbon carboxyl group. Thus, the benzylic carbon atom has been oxidized and the term *benzylic oxidation* is appropriate. The term *side-chain oxidation* is also commonly used.

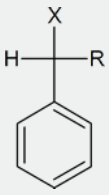
In alkylbenzenes, the carbon atom which is attached to the aromatic ring is particularly reactive. Reactions taking place at this carbon atom are said to occur at the *benzylic position*.

You may wish to review Section 10.3 to remind yourself about allylic bromination using N-bromosuccinimide.

Benzylic halides undergo the typical reactions of alkyl halides; thus, you can expect to see such compounds used frequently in multistep syntheses.

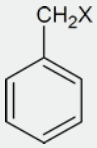
Note that we have adopted the terminology given below.

Any compound of the type



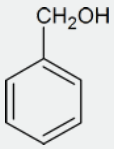
(where X = halogen) will be referred to as a “benzylic halide.”

Compounds of the type



are actually called benzyl chloride, benzyl bromide, etc.

The compound

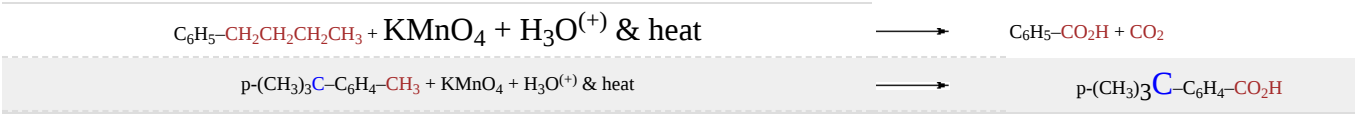


is called benzyl alcohol.

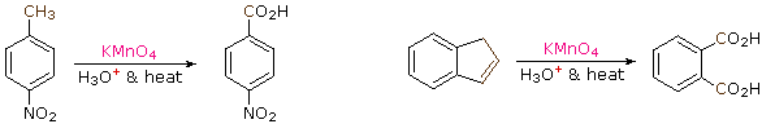
OXIDATION OF ALKYL SIDE-CHAINS

EDIT SECTION

The benzylic hydrogens of alkyl substituents on a benzene ring are activated toward free radical attack, as noted earlier. Furthermore, S_N1, S_N2 and E1 reactions ofbenzylic halides, show enhanced reactivity, due to the adjacent aromatic ring. The possibility that these observations reflect a general benzylic activation is supported by the susceptibility of alkyl side-chains to oxidative degradation, as shown in the following examples (the oxidized side chain is colored). Such oxidations are normally effected by hot acidic pemanganate solutions, but for large scale industrial operations catalyzed air-oxidations are preferred. Interestingly, if the benzylic position is completely substituted this oxidative degradation does not occur (second equation, the substituted benzylic carbon is colored blue).

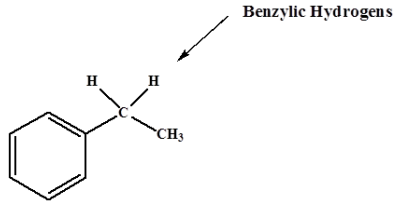


These equations are not balanced. The permanganate oxidant is reduced, usually to Mn(IV) or Mn(II). Two other examples of this reaction are given below, and illustrate its usefulness in preparing substituted benzoic acids.

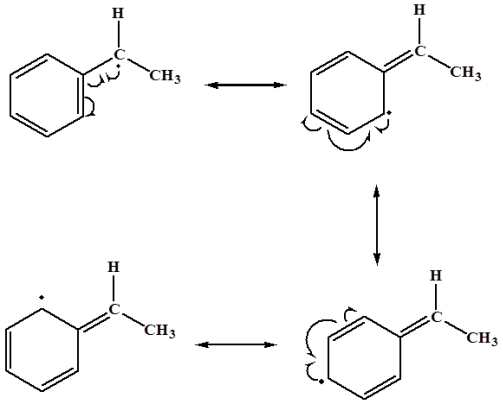


BROMINATION OF THE BENZYLIC CARBON

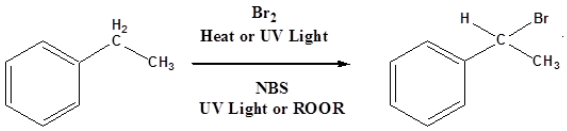
The benzylic C-H bonds weaker than most sp^3 hybridized C-H. This is because the radical formed from homolysis is resonance stabilized.



Resonance stabilization of the benzylic radical

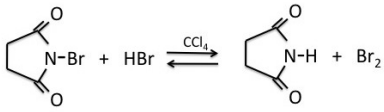


Because of the weak C-H bonds, benzylic hydrogens can form benzylic halides under radical conditions.



NBS AS A BROMINE SOURCE

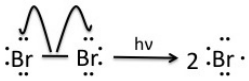
NBS (N-bromosuccinimide) is the most commonly used reagent to produce low concentrations of bromine. When suspended in tetrachloride (CCl_4), NBS reacts with trace amounts of HBr to produce a low enough concentration of bromine to facilitate the allylic bromination reaction.



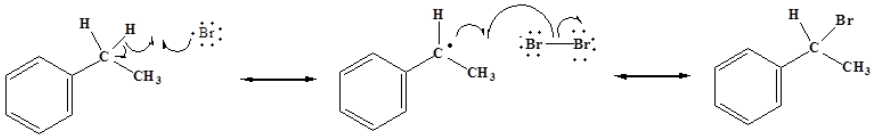
ALLYLIC BROMINATION MECHANISM

Step 1: Initiation

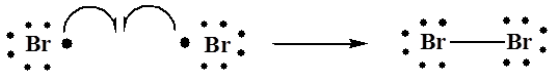
Once the pre-initiation step involving NBS produces small quantities of Br_2, the bromine molecules are homolytically cleaved by light to produce bromine radicals.



Step 2 and 3: Propagation



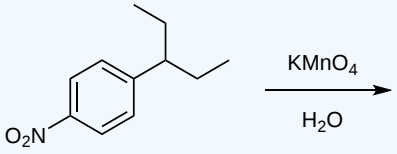
Step 4: Termination

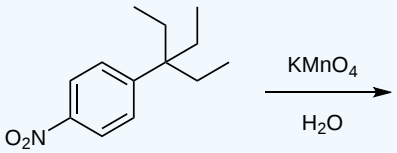


EXERCISES

? EXERCISE 16.9.1

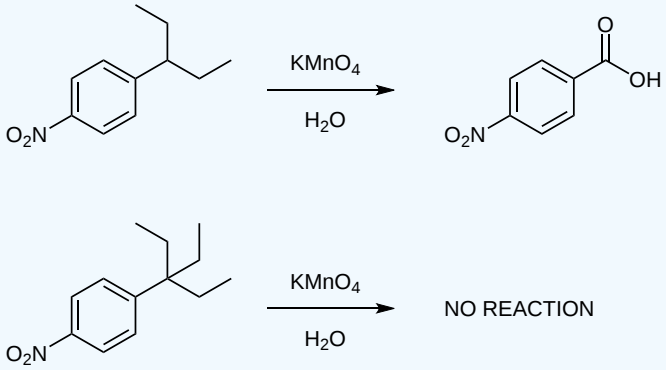
Predict the products of the following two reactions.





Answer

The second one leads to no reaction because it requires a hydrogen just off the phenyl ring.



EXERCISE 16.9.2

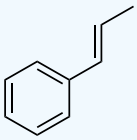
Consider a benzyl radical. Would it be more stable than an alkyl radical? Explain.

Answer

Yes it would be more stable than an alkyl radical. The benzyl radical is stabilized through several resonance structures where the radical is moved through the ring via the pi system there.

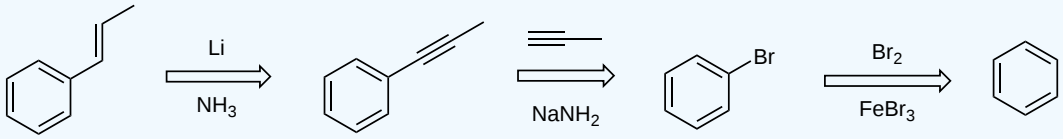
EXERCISE 16.9.3

How would you make the following molecule?



Answer

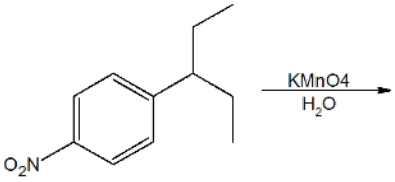
The following is just one possibility.

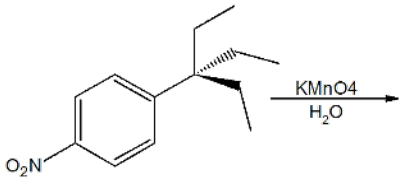


QUESTIONS

Q16.9.1

Predict the products.



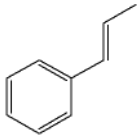


Q16.9.2

Consider a benzyl radical. Would it be more stable than an alkyl radical? Explain.

Q16.9.3

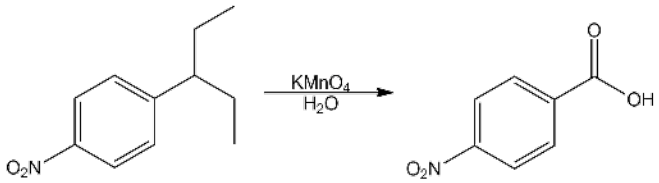
How would you make the following molecule?

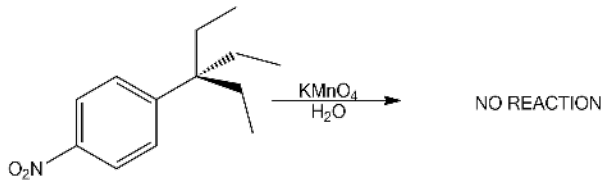


SOLUTIONS

S16.9.1

The second one leads to no reaction because it requires a hydrogen just off the phenyl ring.



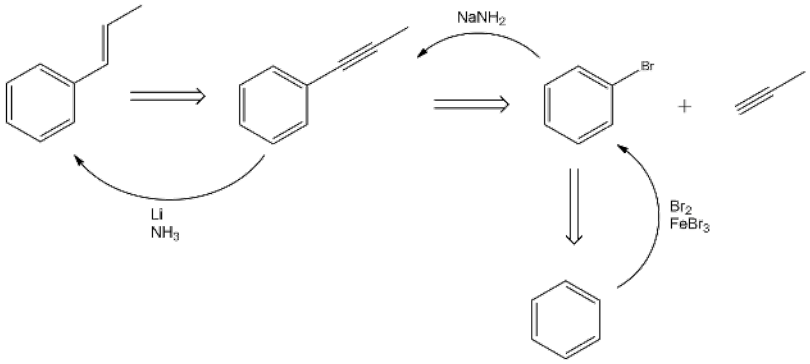


S16.9.2

Yes it would be more stable than an alkyl radical, consider the pi system able to stabilize through resonance.

S16.9.3

The following is just one possibility.



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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16.10: REDUCTION OF AROMATIC COMPOUNDS

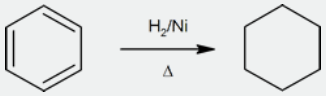
Objectives

After completing this section, you should be able to

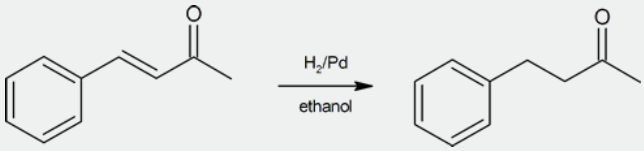
1. write an equation to represent the reduction of a substituted benzene to a substituted cyclohexane.
2. identify the catalyst and reagents used to reduce aromatic rings.
3. compare the ease of reduction of alkenes with the difficulty in reducing benzene rings, and show how this difference in reactivity can be used in organic synthesis.
4. write an equation to illustrate the reduction of an aromatic ketone to an arene.
5. explain why Friedel-Crafts acylation, followed by reduction, provides a better route to primary alkylbenzenes than does direct alkylation.
6. show how a specified alkylbenzene may be prepared by a Friedel-Crafts acylation, followed by reduction. Specify all reagents, the structure of the intermediate ketone, and the necessary starting material.

STUDY NOTES

Catalytic hydrogenation of aromatic rings requires forcing conditions (high heat and hydrogen pressure).

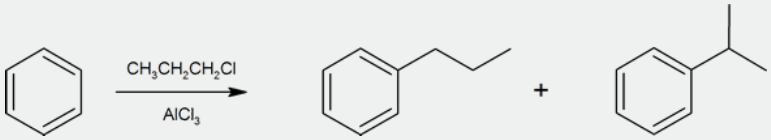


Under milder conditions it is possible to reduce the double-bond of an alkene without reducing the aromatic ring.

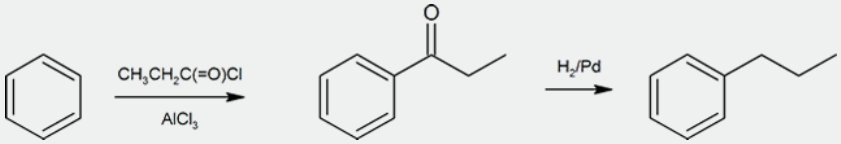


Notice in the above equation that H_2/Pd does not reduce the keto-carbonyl group. Remember, however, that H_2/Pd will reduce a keto-carbonyl group when it is directly attached to an aromatic ring (see equations 4 and 5 under Carbonyl Reductions).

This reduction of the C=O group next to an aromatic ring is an important synthetic tool. Recall the Friedel-Crafts alkylation from Section 16.3. When attaching larger alkyl groups to arenes there is a possibility of rearrangement of the alkyl group structure.

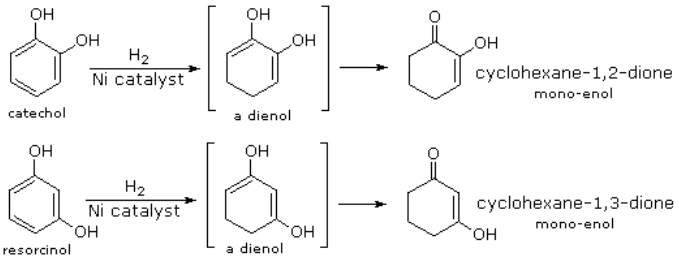


To generate the target compound (in this case *n*-propylbenzene) in a more controlled fashion, one can simply use the equivalent Friedel-Crafts acylation and then reduce the keto-carbonyl group next to the ring as a final step.

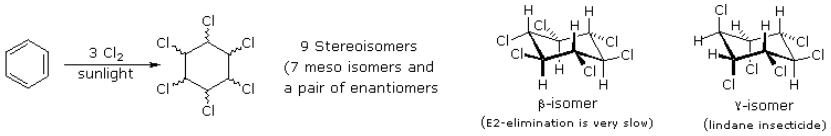


NUCLEOPHILIC ADDITION REACTIONS EDIT SECTION

Although it does so less readily than simple alkenes or dienes, benzene adds hydrogen at high pressure in the presence of Pt, Pd or Ni catalysts. The product is cyclohexane and the heat of reaction provides evidence of benzene's thermodynamic stability. Substituted benzene rings may also be reduced in this fashion, and hydroxy-substituted compounds, such as phenol, catechol and resorcinol, give carbonyl products resulting from the fast ketonization of intermediate enols. Nickel catalysts are often used for this purpose, as noted in the following equations.

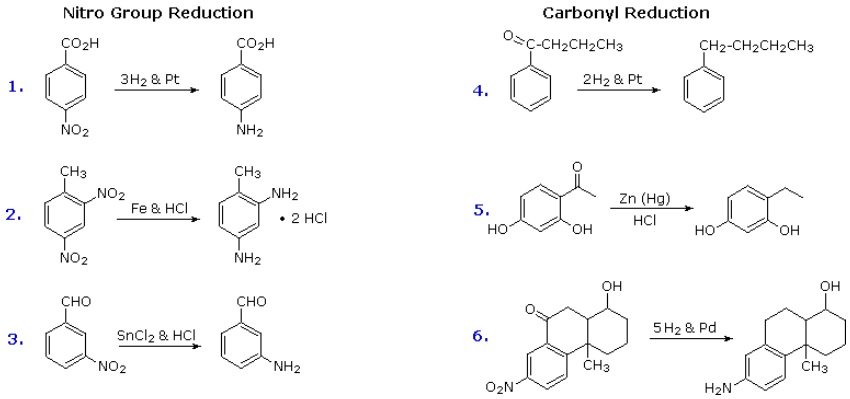


Benzene is more susceptible to radical addition reactions than to electrophilic addition. We have already noted that benzene does not react with chlorine or bromine in the absence of a catalyst and heat. In strong sunlight or with radical initiators benzene adds these halogens to give hexahalocyclohexanes. It is worth noting that these same conditions effect radical substitution of cyclohexane, the key factors in this change of behavior are the pi-bonds array in benzene, which permit addition, and the weaker C-H bonds in cyclohexane. The addition of chlorine is shown below on the left; two of the seven meso-stereoisomers are displayed to the right.



REDUCTION OF NITRO GROUPS AND ARYL KETONES

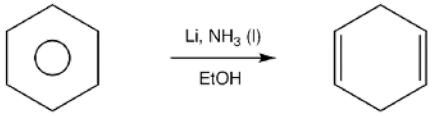
Electrophilic nitration and Friedel-Crafts acylation reactions introduce deactivating, meta-directing substituents on an aromatic ring. The attached atoms are in a high oxidation state, and their reduction converts these electron withdrawing functions into electron donating amino and alkyl groups. Reduction is easily achieved either by catalytic hydrogenation (H2 + catalyst), or with reducing metals in acid. Examples of these reductions are shown here, equation 6 demonstrating the simultaneous reduction of both functions. Note that the butylbenzene product in equation 4 cannot be generated by direct Friedel-Crafts alkylation due to carbocation rearrangement. The zinc used in ketone reductions, such as 5, is usually activated by alloying with mercury (a process known as amalgamation).



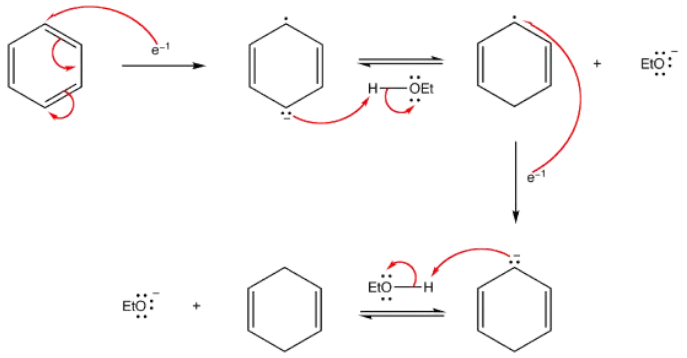
Several alternative methods for reducing nitro groups to amines are known. These include zinc or tin in dilute mineral acid, and sodium sulfide in ammonium hydroxide solution. The procedures described above are sufficient for most cases.

THE BIRCH REDUCTION

Another way of adding hydrogen to the benzene ring is by treatment with the electron rich solution of alkali metals, usually lithium or sodium, in liquid ammonia. See examples of this reaction, which is called the **Birch Reduction.** The Birch reduction is the dissolving-metal reduction of aromatic rings in the presence of an alcohol.



MECHANISM:

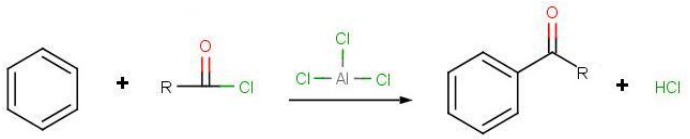


LIMITATIONS OF FRIEDEL-CRAFTS ALKYLATION

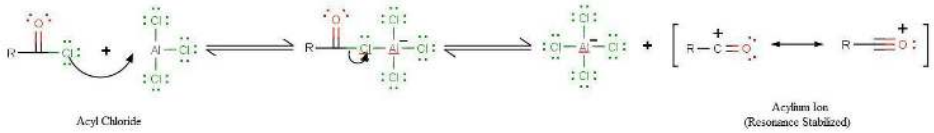
1. Carbocation Rearrangement - Only certain alkylbenzenes can be made due to the tendency of cations to rearrange.
2. **Compound Limitations** - Friedel-Crafts fails when used with compounds such as nitrobenzene and other strong deactivating systems.
3. **Polyalkylation** - Products of Friedel-Crafts are even more reactive than starting material. Alkyl groups produced in Friedel-Crafts Alkylation are electron-donating substituents meaning that the products are more susceptible to electrophilic attack than what we began with. For synthetic purposes, this is a big dissapointment.

To remedy these limitations, a new and improved reaction was devised: The Friedel-Crafts Acylation, also known as Friedel-Crafts Alkanoylation.

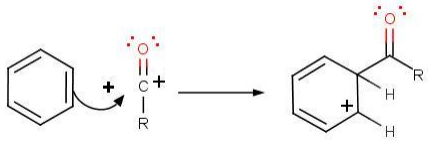
The goal of the reaction is the following:



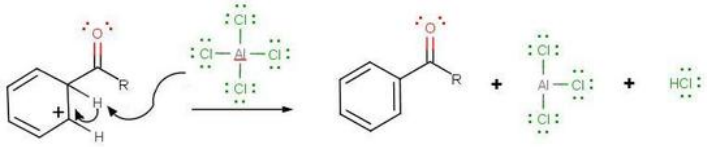
The very first step involves the formation of the acylium ion which will later react with benzene:



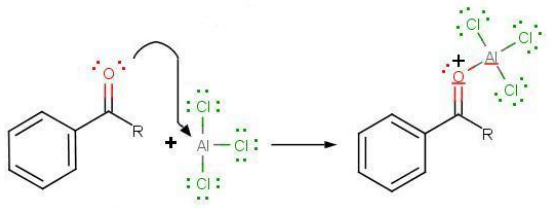
The second step involves the attack of the acylium ion on benzene as a new electrophile to form one complex:



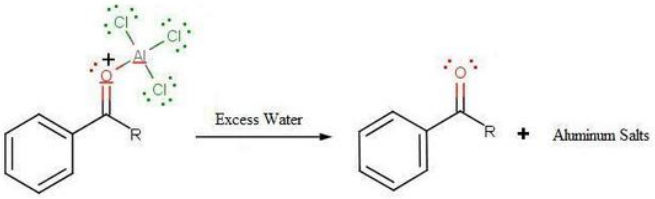
The third step involves the departure of the proton in order for aromaticity to return to benzene:



During the third step, $AlCl_4$ returns to remove a proton from the benzene ring, which enables the ring to return to aromaticity. In doing so, the original $AlCl_3$ is regenerated for use again, along with HCl. Most importantly, we have the first part of the final product of the reaction, which is a ketone. Thie first part of the product is the complex with aluminum chloride as shown:



The final step involves the addition of water to liberate the final product as the acylbenzene:

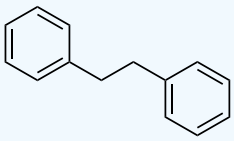


Because the acylium ion (as was shown in step one) is stabilized by resonance, no rearrangement occurs (Limitation 1). Also, because of of the deactivation of the product, it is no longer susceptible to electrophilic attack and hence, is no longer susceptible to electrophilic attack and hence, no longer goes into further reactions (Limitation 3). However, as not all is perfect, Limitation 2 still prevails where Friedel-Crafts Acylation fails with strong deactivating rings.

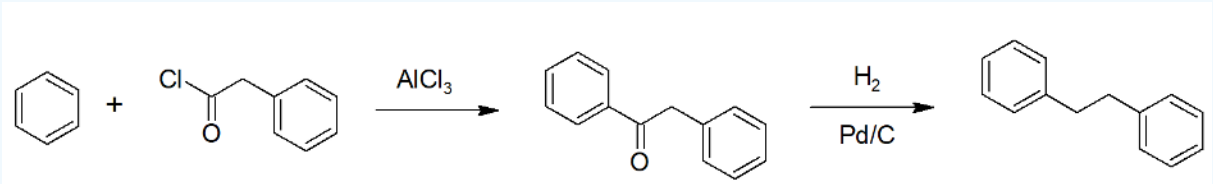
EXERCISE

? EXERCISE \PageIndex1

How would you make the following from benzene and an acid chloride?



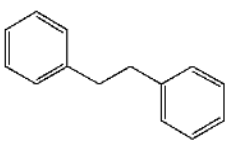
Answer



QUESTIONS

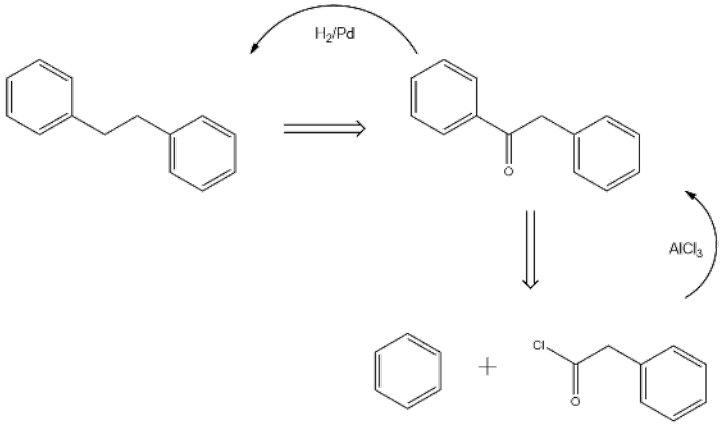
Q16.10.1

How would you make the following from benzene and an acid chloride?



SOLUTIONS

S16.10.1



CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Mario Morataya (UCD)
- Gamini Gunawardena from the OChemPal site (Utah Valley University)

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16.11: SYNTHESIS OF POLYSUBSTITUTED BENZENES

Objectives

After completing this section, you should be able to

1. design a multistep synthesis which may involve reactions in the alkyl side chain of an alkylbenzene and the electrophilic substitution reactions discussed in this chapter. You should pay particular attention to
   a. carrying out the reactions in the correct order.
   b. using the most appropriate reagents and conditions.
   c. the limitations of certain types of reactions.
2. analyze a proposed multistep synthesis involving aromatic substitution to determine its feasibility, point out any errors in the proposal and identify possible problem areas.

STUDY NOTES

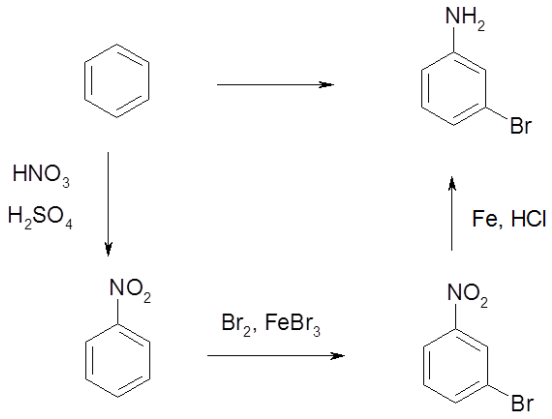
As you can see, designing a multistep synthesis requires an analytical mind and an ability to think logically, as well as a knowledge of organic reactions. The best way to become an expert in designing such syntheses is to get lots of practice by doing plenty of problems.

FROM BENZENE MAKE *M*-BROMOANILINE

In this reaction three reactions are required.

1. A nitration
2. A conversion from the nitro group to an amine
3. A bromination

Because the end product is meta a meta directing group must be utilized. Of the nitro, bromine, and amine group, only the nitro group is meta direction. This means that the first step need to be the nitration and not the bromination. Also, the conversion of the nitro group to an amine must occur last because the amine group is ortho/para direction.

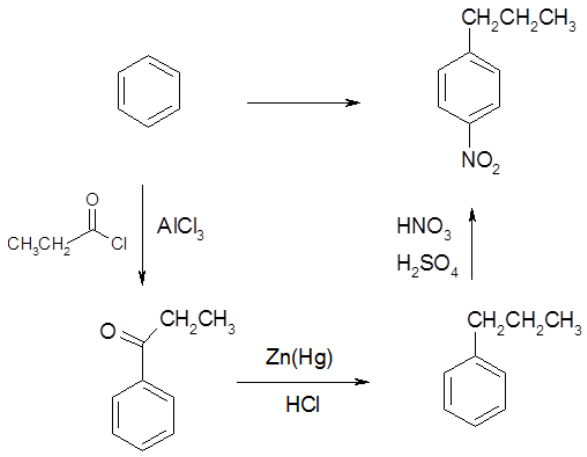


FROM BENZENE MAKE *P*-NITROPROPYLBENZENE :

In this reaction three reactions are required.

1. A Friedel Crafts acylation
2. A conversion from the acyl group to an alkane
3. A nitration

Because the propyl group has more than two carbons, it must be added in two steps. A Friedel Crafts acylation followed by a Clemmensen Reduction. Remeber that Friedel Crafts reactions are hindered if the benzene ring is strongly deactivated. This means that the acyl group must go on first. Because the end product is para a para directing group must be utilized. Of the nitro, acyl, and alkane group, only the alkane group is meta direction. This means that the acyl group must be converted to an alkane prior to the nitration step.



EXERCISES

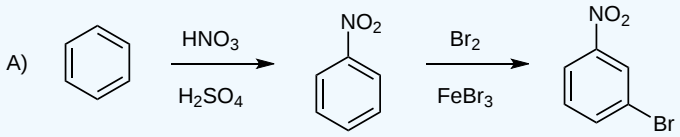
EXERCISE 16.11.1

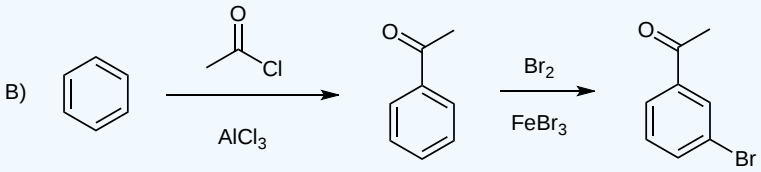
How would make the following compounds from benzene?

a. *m*-bromonitrobenzene
b. *m*-bromoethylbenzene

Answer

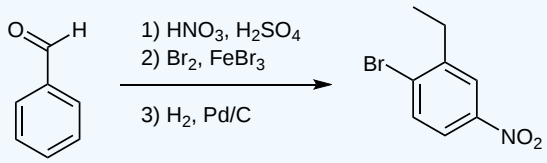
Only one possible synthesis is shown for each compound. There are multiple possibilities.





EXERCISE 16.11.2

There is something wrong with the following reaction, what is it?



Answer

The bromine should be in the meta position. Right now it is in the ortho position, from perhaps having the ethyl group present first and then the having it substituted there. BUT the ethyl group is last to form, and the aldehyde and nitro groups would both encourage a meta substitution.

QUESTIONS

Q16.11.1

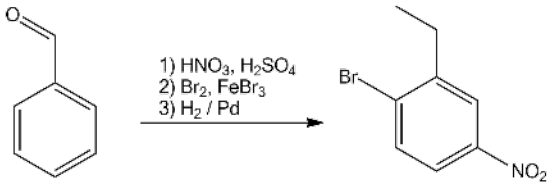
How would make the following compounds from benzene?

A) *m*-bromonitrobenzene

B) *m*-bromoethylbenzene

Q16.11.2

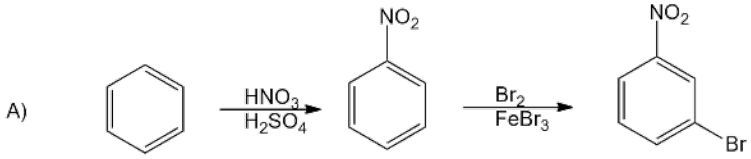
There is something wrong with the following reaction, what is it?

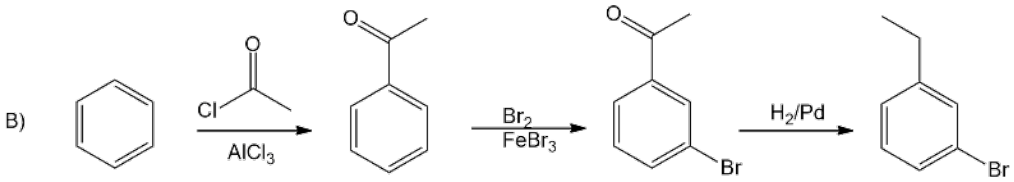


SOLUTIONS

S16.11.1

This is just one possible way to synthesize it.





S16.11.2

The bromine should be in the meta position. Right now it is in the ortho position, from perhaps having the ethyl group present first and then the having it substituted there. BUT the ethyl group is last to form, and the aldehyde and nitro groups would both encourage a meta substitution.

CONTRIBUTORS AND ATTRIBUTIONS

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
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- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

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16.S: CHEMISTRY OF BENZENE - ELECTROPHILIC AROMATIC SUBSTITUTION (SUMMARY)

CONCEPTS & VOCABULARY

16.0 Introduction

- Aromatic compounds don't typically undergo addition reactions.
- Aromatic compounds typically undergo substitution reactions.

16.1 Electrophilic Aromatic Substitution Reactions: Bromination

- Aromatic molecules only react with strong electrophiles.
- The first step in many electrophilic aromatic substitution mechanisms is activation or formation of the electrophile.
- The electrophilic aromatic substitution mechanism occurs in two steps. The first is addition of the electrophile to the ring and the second is elimination of a hydrogen from the ring to re-form the pi bond and restore aromaticity.
- In bromination of an aromatic ring, molecular bromine (Br_2) is reacted with iron tribromide ($FeBr_3$) to form the strongly electrophilic bromine cation and $FeBr_4$. Following this, the aromatic ring is reacted with the bromine cation and adds to the ring to form a benzenonium cation. This molecule then reacts with one of the bromine atoms from $FeBr_4$ to lose a hydrogen forming the product and HBr as well as reforming the iron tribromide.

16.2 Other Aromatic Substitutions

- Aluminum bromide ($AlBr_3$) can be used in place of $FeBr_3$ to create the bromine cation. Also the chlorides of alumnium and iron can also be used to create a chlorine cation which will also undergo electrophilic aromatic substitution.
- Reacting nitric acid and sulfuric acid forms nitronium (NO_2^+), which will react with aromatics for form nitro compounds.
- Sulfonation of aromatics can be accomplished by reacting with sulfur trioxide and sulfuric acid to yield sulfonic acids.

16.3 Alkylation and Acylation of Aromatic Rings - The Friedel-Crafts Reaction

- Friedel-Crafts reactions incorporate activation of alkyl and acyl halides by reacting them with a Lewis Acid catalyst, $AlCl_3$.
- Friedel-Crafts alkylations allow for adding alkyl chains to aromatic rings.
- After activation with aluminum chloride, alkyl carbocations can undergo rearrangement if it leads to a more stable intermediate.
- Friedel-Crafts acylations add alkyl ketones to aromatic rings.

16.4 Substituent Effects in Substituted Aromatic Rings

- Aromatic inductive effects are caused by differences in electronegativity between atoms bonded to the ring and the ring carbons.
- Most common heteroatoms (N, O, halogens) donate electron density toward the ring inductively.
- Aromatic resonance effects are caused by conjugation of substituents with the pi bonds of the ring.
- Substituents that increase the electron density of the ring activate the ring (make more reactive) toward electrophilic substitution.
- Substituents that decrease the electron density of the ring deactivate the ring (make less reactive) toward electrophilic substitution.

16.4b An Explanation of Substituent Effects

- Steric effects can increase para substitution as ortho/para directors become larger.
- Activating groups are ortho/para (o, p) directors.
- Deactivating groups are meta directors.
- Alkyl groups inductively donate electron density to the ring making them o, p directors.
- Groups with an O or N attached to the aromatic ring are activators and o, p directors due to resonance.
- Groups with a pi bond attached to the aromatic ring are deactivators and m directors due to resonance.
- Halogens are o, p directors, but are deactivators.

16.5 Trisubstituted Benzenes: Additivity of Effects

- When there is more than one group attached to an aromatic ring, these groups may reinforce directing effects (cooperative) or have opposing directing effects (non-cooperative).

16.6 Nucleophilic Aromatic Substitution

- Highly activated aromatic rings can react with strong nucleophiles through a substitution mechanism.
- The mechanism typically begins with addition of a nucleophile followed by elimination of a leaving group.

16.7 Benzyne

- Under highly reactive conditions, a mechanism that begins with elimination for form a benzyne molecule intermediate followed by addition of a nucleophile resulting in nucleophilic aromatic substitution.

16.8 Oxidation of Aromatic Compounds

- Alkyl side-chains can be oxidized to benzoic acid (or a benzoic acid derivative if there are other groups present on the ring) by potassium permanganate ($KMnO_4$) as long as the benzylic carbon has at least one hydrogen attached.
- Radical halogenation will occur at the benzylic carbon, due to stabilization of radical intermediates.

16.9 Reduction of Aromatic Compounds

- Catalytic hydrogenation (H_2 and a catalyst) can be used to reduce many aromatic side-chains.
- Nitro groups can be selectively reduced to amines with $SnCl_2$ and HCl or with Fe and HCl.
- Carbonyls adjacent to the ring can be reduced by either Clemmensen reduction (Zn(Hg) and HCl.
- Birch reductions can reduce aromatic rings.

16.10 Synthesis of Polysubstituted Benzenes

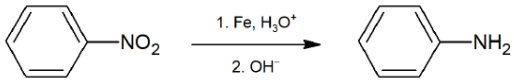
- Multistep synthesis requires a combination of forward (from the starting material) and backward (from the target compound) thinking.

SKILLS TO MASTER

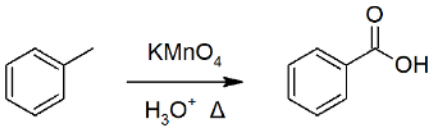
- Skill 16.1 Write detailed electrophilic aromatic substitution mechanisms (halogentation, nitration, sulfonation, Friedel-Crafts alkyation and acylation).
- Skill 16.2 Write detailed mechanisms for formation of reactive electrophiles.
- Skill 16.3 Predict and explain rearrangements that can occur during Friedel-Crafts alkylation.
- Skill 16.4 Explain activation and deactivation of aromatic rings toward electrophilic aromatic substitution.
- Skill 16.5 Explain ortho, para vs. meta directing during electrophilic aromatic substitution reactions.
- Skill 16.6 Combine activation and deactivation and directing effects to predict products of reactions of substituted aromatic molecules.
- Skill 16.7 Write detailed nucleophilic aromatic substitution mechanisms through addition-elimination.
- Skill 16.8 Write detailed nucleophilic aromatic substitution mechanisms through benzyne elimination-addition.
- Skill 16.9 Draw products of oxidation of aromatic molecules.
- Skill 16.10 Draw products of reduction of aromatic side-chains.
- Skill 16.11 Draw mechanisms for reduction of aromatic rings.
- Skill 16.12 Solve multistep synthesis problems incorporating directing effects and side-chain reactions.

SUMMARY OF REACTIONS

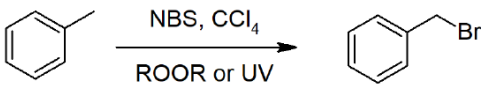
Reduction of Nitro Group



Oxidation of Alkylbenzene

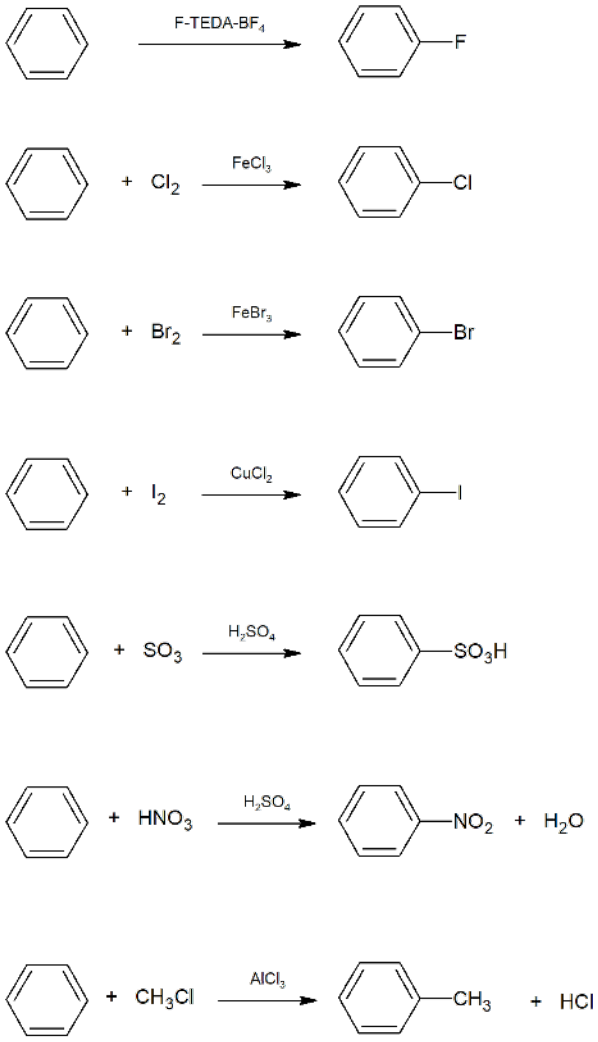


Benzylic Bromination of Alkylbenzene

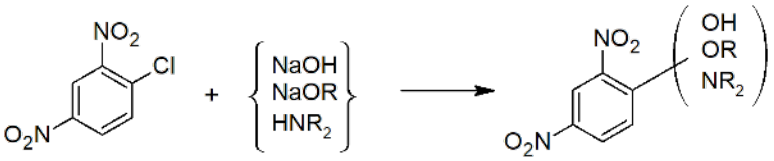


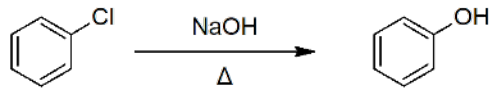
Reduction of Aromatic Compounds

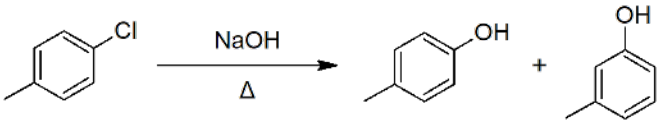
Electrophilic Aromatic Substitution



Nucleophilic Aromatic Substitution









CONTRIBUTORS

- Layne Morsch (University of Illinois Springfield)
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

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5.8: Racemic Mixtures and the Resolution of Enantiomers

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4.3: Stability of Cycloalkanes - Ring Strain

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