

CHE 201: ORGANIC CHEMISTRY I



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CHAPTER OVERVIEW

1: Introduction to Organic Chemistry

- 1.1: Organic Compounds
- 1.2: The Functional Group
- 1.3: Covalent Bonds
- 1.4: Bonding in Organic Molecules
- 1.5: Structural Isomerism in Organic Molecules
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1.1: Organic Compounds

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from “organized” (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.



Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today organic chemistry is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Formally, Organic chemistry is the study of the chemistry of carbon compounds. Carbon is singled out because it has a chemical diversity unrivaled by any other chemical element. Its diversity is based on the following:

- Carbon atoms bond reasonably strongly with other carbon atoms.
- Carbon atoms bond reasonably strongly with atoms of other elements.
- Carbon atoms make a large number of covalent bonds (four).

Curiously, elemental carbon is not particularly abundant. It does not even appear in the list of the most common elements in Earth’s crust (Table 2.1.1). Nevertheless, all living things consist of organic compounds. Most organic chemicals are covalent compounds, which is why we introduce organic chemistry here. By convention, compounds containing carbonate ions and bicarbonate ions, as well as carbon dioxide and carbon monoxide, are not considered part of organic chemistry, even though they contain carbon.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 1.1.1.

Table 1.1.1: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane	Inorganic	NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table 1.1.1 also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C₆H₁₄), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table 1.1.1.

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1.2: The Functional Group

Learning Objectives

- Define *functional group*.
- Identify the functional group(s) present in organic compounds.

With over twenty million known organic compounds in existence, it would be very challenging to memorize chemical reactions for each one. Fortunately, molecules with similar functional groups tend to undergo similar reactions. A **functional group** is defined as an atom or group of atoms within a molecule that has similar chemical properties whenever it appears in various compounds. Even if other parts of the molecule are quite different, certain functional groups tend to react in certain ways.

We've already looked at alkanes, but they are generally unreactive. We primarily use alkanes as a source of energy when they are combusted. While the majority of functional groups involve atoms other than carbon and hydrogen, we will also look at some that include only carbon and hydrogen. Some of the most common functional groups are presented in the following sections.

Organic molecules vary greatly in size and when focusing on functional groups, we want to direct our attention to the atoms involved in the functional group. As a result, the abbreviation **R** is used in some examples. The letter **R** is used in molecular structures to represent the "**R**est of the molecule". It consists of a group of carbon and hydrogen atoms of any size. It is used as an abbreviation since a group of carbon and hydrogen atoms does not affect the functionality of the compound. In some molecules, you will see **R**, **R'**, or **R''** which indicates that the R groups in the molecule can be different from one another. For example, R might be $-\text{CH}_2\text{CH}_3$ while R' is $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

The structure of capsaicin, the compound responsible for the heat in peppers, incorporates several functional groups, labeled in the figure below and explained throughout this section.

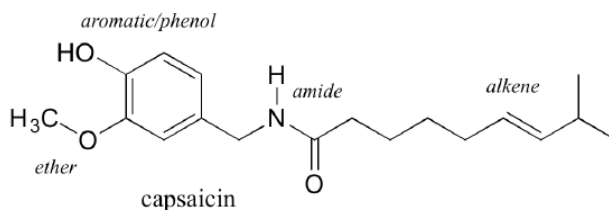


Figure 1.2.1 The structure of capsaicin

The table below summarizes the structures that will be discussed in this chapter:

Table 1.2.1 Selected Organic Functional Groups

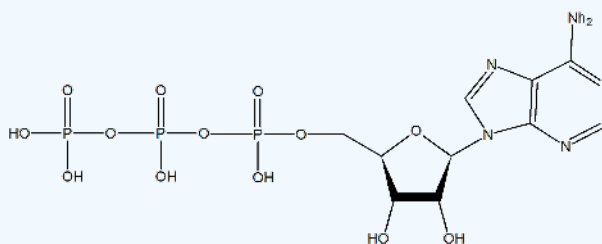
Functional group name	Structural feature	Description	Functional group name	Structural feature	Description
Alkane	$R-CH_2-CH_3$	Only single bonds between carbons (C-C) and hydrogens (C-H)	Aldehyde	$R-\overset{\overset{O}{\parallel}}{C}-H$	Contains a carbonyl group (C=O) at the end of a carbon chain, bonded to at least one hydrogen.
Alkene	$R-CH=CH_2$	Contains at least one C=C double bond	Ketone	$R-\overset{\overset{O}{\parallel}}{C}-R$	Contains a carbonyl group (C=O) bonded to two carbons (never at the chain end).
Alkyne	$R-C\equiv CH$	Contains at least one C≡C triple bond	Carboxylic acid	$R-\overset{\overset{O}{\parallel}}{C}-OH$	Has a carbonyl (C=O) plus a hydroxyl (-OH) on the same carbon; written as -COOH.
Aromatic		Ring of 6 carbons with alternating double bonds	Ester	$R-\overset{\overset{O}{\parallel}}{C}-O-R$	Similar to acids but the -OH is replaced by -OR
Alcohol	$R-OH$	Has a -OH (hydroxyl) group attached to a carbon	Amine	$R-NH_2$	Contains nitrogen attached to carbon(s)
Ether	$R-O-R$	Oxygen bridges two carbons (C-O-C); no hydroxyl group	Amide	$R-\overset{\overset{O}{\parallel}}{C}-NH-R$	Contains a carbonyl (C=O) directly bonded to nitrogen

R = carbon chain of any length

Figure 1.2.1

✓ Example 1.2.1

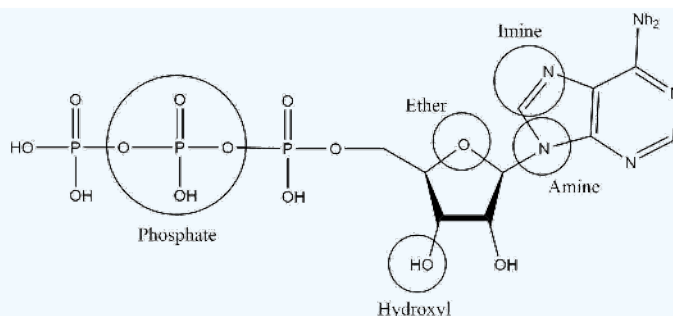
Identify the common functional groups for ATP.



Example 1.2.1

Solution

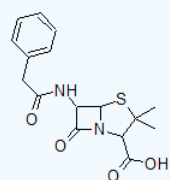
The common functional groups for ATP are **hydroxyl**, **ether** and **amine**. The other functional groups are covered in higher organic chemistry courses.



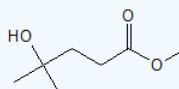
Example 1.2.1 ATP

? Exercise 1.2.1

Identify the functional groups (other than alkanes) in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.



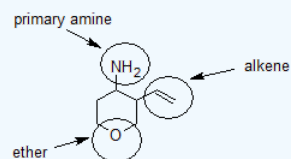
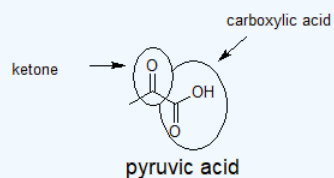
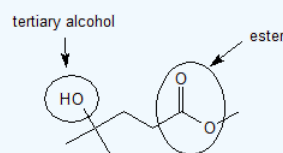
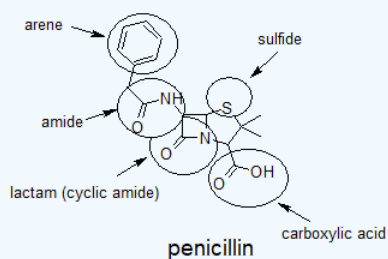
penicillin



pyruvic acid



Answer



Summary

- Functional groups consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). It can determine the chemical reactivity of a molecule under a given set of conditions
- The major families of organic compounds are characterized by their functional groups.

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1.3: Covalent Bonds

Learning Objectives

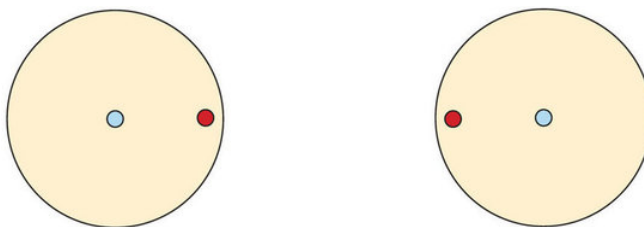
- To describe how a covalent bond forms.
- To apply the octet rule to covalent compounds

You have already seen examples of substances that contain covalent bonds. One substance mentioned previously was water (H_2O). You can tell from its formula that it is not an ionic compound; it is not composed of a metal and a nonmetal. Consequently, its properties are different from those of ionic compounds.

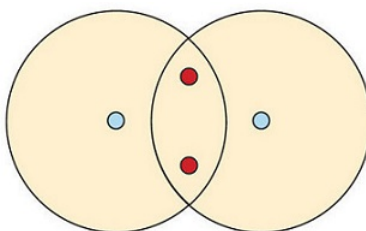
Electron Sharing

Previously, we discussed **ionic bonding** where electrons can be transferred from one atom to another so that both atoms have an energy-stable outer electron shell. Because most filled electron shells have eight electrons in them, chemists called this tendency the octet rule. However, there is another way an atom can achieve a full valence shell: atoms can *share* electrons.

This concept can be illustrated by using two hydrogen atoms, each of which has a single electron in its valence shell. (For small atoms such as hydrogen atoms, the valence shell will be the first shell, which holds only two electrons.) We can represent the two individual hydrogen atoms as follows:



In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:



By sharing their valence electrons, both hydrogen atoms now have two electrons in their respective valence shells. Because each valence shell is now filled, this arrangement is more stable than when the two atoms are separate. The sharing of electrons between atoms is called a covalent bond, and the two electrons that join atoms in a covalent bond are called a bonding pair of electrons. A discrete group of atoms connected by covalent bonds is called a molecule—the smallest part of a compound that retains the chemical identity of that compound.

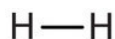
Chemists frequently use Lewis diagrams to represent covalent bonding in molecular substances. For example, the Lewis diagrams of two separate hydrogen atoms are as follows:



The Lewis diagram of two hydrogen atoms sharing electrons looks like this:



This depiction of molecules is simplified further by using a dash to represent a covalent bond. The hydrogen molecule is then represented as follows:



Remember that the dash, also referred to as a single bond, represents a *pair* of electrons.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-11} m, or 74 picometers (pm; $1 \text{ pm} = 1 \times 10^{-12} \text{ m}$). This particular bond length represents a balance between several forces: the attractions between oppositely charged electrons and nuclei, the repulsion between two negatively charged electrons, and the repulsion between two positively charged nuclei. If the nuclei were closer together, they would repel each other more strongly; if the nuclei were farther apart, there would be less attraction between the positive and negative particles.

Fluorine is another element whose atoms bond together in pairs to form *diatomic* (two-atom) molecules. Two separate fluorine atoms have the following electron dot diagrams:

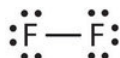


Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the **octet** rule:



Two F's with two dots in between them, and two dots on the top, left/right side, and bottoms of each F.

The circles show that each fluorine atom has eight electrons around it. As with hydrogen, we can represent the fluorine molecule with a dash in place of the bonding electrons:



Two F's with a long dash in between them, and two dots on the top, left/right side, and bottoms of each F.

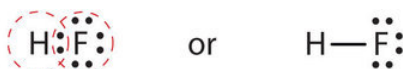
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called nonbonding pairs (or lone pairs) of electrons.

Covalent Bonds between Different Atoms

Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:



Each atom needs one additional electron to complete its valence shell. By each contributing one electron, they make the following molecule:



An H and F connected by two dots, and the F has 2 dots on the top, right, and bottom. It also shows the same combination but with a long dash in between the H and F rather than two dots.

In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the valence electron shells are filled for both atoms.

✓ Example 1.3.1

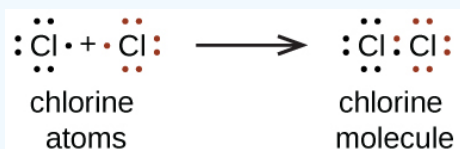
Use Lewis diagrams to indicate the formation of the following:

- Cl_2
- HBr

Solution

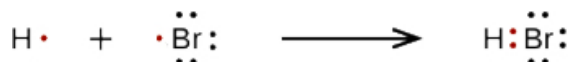
a. When two chlorine atoms form a chlorine molecule, they share one pair of electrons. In Cl_2 molecule, each chlorine atom is surrounded by an **octet** number of electrons.

The Lewis diagram for a Cl_2 molecule is similar to the one for F_2 (shown above).



Cl with 7 dots surrounding it plus Cl with 7 dots surrounding it means they are chlorine atoms. To turn into a chlorine molecule, have two dots in between each Cl and 6 dots surrounding each Cl on the sides that aren't connected.

b. When a hydrogen atom and a bromine atom form HBr, they share one pair of electrons. In the HBr molecule, H achieves a full valence of two electrons (**duet**) while Br achieves an **octet**. The Lewis diagram for HBr is similar to that for HF shown above.



H with one dot plus Br with 7 dots turns into H connected to Br by two dots, with 6 other dots surrounding Br.

? Exercise 1.3.1

Draw the Lewis diagram for each compound.

- a molecule composed of one chlorine atom and one fluorine atom
- a molecule composed of one hydrogen atom and one iodine atom

Answer a:

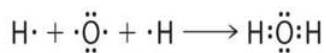


Answer b:



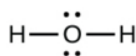
Covalent Bonds in Larger Molecules

The formation of a water molecule from two hydrogen atoms and an oxygen atom can be illustrated using Lewis dot symbols (shown below).



H with one dot + O with 6 dots + H with one dot turns into H connected to O with two dots connected to H with two dots. O also has two dots on top and top dots on bottom.

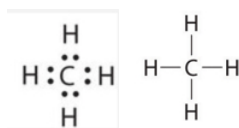
The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O . With two bonding pairs and two lone pairs, the oxygen atom has now completed its **octet**. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown (below).



Water

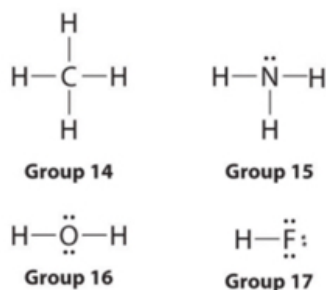
Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane (CH_4), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis

structures below. Again, sharing electrons between C and H atoms results in C achieving an octet while H achieving a duet number of electrons.



How Many Covalent Bonds Are Formed?

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons). In the Lewis structure, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For example, each atom of a **group 4A** (14) element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming **four covalent bonds**, as illustrated here for carbon in CH₄ (methane). **Group 5A** (15) elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form **three covalent bonds**, as in NH₃ (ammonia). Oxygen and other atoms in **group 6A** (16) obtain an octet by forming **two covalent bonds**. Fluorine and the other halogens in **group 7A** (17) have seven valence electrons and can obtain an octet by forming **one covalent bond**.



Typically, the atoms of group 4A form 4 covalent bonds; group 5A form 3 bonds; group 6A form 2 bonds; and group 7A form one bond. The number of electrons required to obtain an octet determines the number of covalent bonds an atom can form. This is summarized in the table below. In each case, the sum of the number of bonds and the number of lone pairs is 4, which is equivalent to eight (octet) electrons.

This table shows atoms and their group numbers, and how many bonds and lone pairs each has.

Atom (Group number)	Number of Bonds	Number of Lone Pairs
Carbon (Group 14 or 4A)	4	0
Nitrogen (Group 15 or 5A)	3	1
Oxygen (Group 16 or 6A)	2	2
Fluorine (Group 17 or 7A)	1	3

Because hydrogen only needs two electrons to fill its valence shell, it follows the duet rule. It is an **exception to the octet rule**. Hydrogen only needs to form one bond. This is the reason why H is always a terminal atom and never a central atom. Figure 1.3.1 shows the number of covalent bonds various atoms typically form.

The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.

✓ Example 1.3.2

$$\begin{array}{c} \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot\text{F} & -\text{O}- & \text{F}\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \end{array}$$

Solution

1.3.2 Exercise

$$\begin{array}{c} \text{:}\ddot{\text{Cl}}-\ddot{\text{N}}-\ddot{\text{Cl}}\text{:} \\ | \\ \text{:}\ddot{\text{Cl}}\text{:} \end{array}$$

Answer

Key Takeaways

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1.4: Bonding in Organic Molecules



Figure 1.4.1: (Public Domain; Priit Kallas (Wikimedia: Pk2000) via Wikipedia)

Do you recognize this plant?

If we were walking on the beach, the plants shown above would look very different. They would be short and sticking out of the sand. When we see them this way, we may not immediately recognize them as beach plants. Often, we need to look at the world around us in different ways to understand things better.

Hybrid Orbitals - sp^3

The bonding scheme described by valence bond theory must account for molecular geometries as predicted by VSEPR theory. To do that, we must introduce the concept of hybrid orbitals.

sp^3 Hybridization

Unfortunately, overlap of existing atomic orbitals (s , p , etc.) is not sufficient to explain some of the bonding and molecular geometries that are observed. Consider the element carbon and the methane (CH_4) molecule. A carbon atom has the electron configuration of $1s^2 2s^2 2p^2$, meaning that it has two unpaired electrons in its $2p$ orbitals, as shown in the figure below.

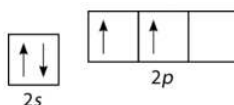


Figure 1.4.2: Orbital configuration for carbon atom. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

According to the description of valence bond theory so far, carbon would be expected to form only two bonds, corresponding to its two unpaired electrons. However, methane is a common and stable molecule, with four equivalent C-H bonds. To account for this, one of the $2s$ electrons is promoted to the empty $2p$ orbital (see figure below).

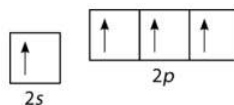


Figure 1.4.3: Promotion of carbon s electron to empty p orbital. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

Now, four bonds are possible. The promotion of the electron "costs" a small amount of energy, but recall that the process of bond formation is accompanied by a decrease in energy. The two extra bonds that can now be formed results in a lower overall energy, and thus greater stability to the CH_4 molecule. Carbon normally forms four bonds in most of its compounds.

The number of bonds is now correct, but the geometry is wrong. The three p orbitals, (p_x , p_y , and p_z), are oriented at 90° relative to one another. However, as seen in VSEPR theory, the observed H-C-H bond angle in the tetrahedral CH_4 molecule is actually 109.5° . Therefore, the methane molecule cannot be adequately represented by simple overlap of the $2s$ and $2p$ orbitals of carbon with the $1s$ orbitals of each hydrogen atom.

To explain the bonding in methane, it is necessary to introduce the concept of hybridization and hybrid atomic orbitals. **Hybridization** is the mixing of the atomic orbitals in an atom to produce a set of hybrid orbitals. When hybridization occurs, it must do so as a result of the mixing of nonequivalent orbitals. In other words, s and p orbitals can hybridize, but p orbitals cannot hybridize with other p orbitals. **Hybrid orbitals** are the atomic orbitals obtained when two or more nonequivalent orbitals from the

same atom combine in preparation for bond formation. In the current case of carbon, the single $2s$ orbital hybridizes with the three $2p$ orbitals to form a set of four hybrid orbitals, called sp^3 hybrids (see figure below).

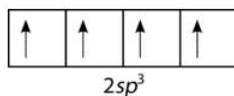


Figure 1.4.4: Carbon sp^3 hybrid orbitals. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

The sp^3 hybrids are all equivalent to one another. Spatially, the hybrid orbitals point towards the four corners of a tetrahedron (see figure below).

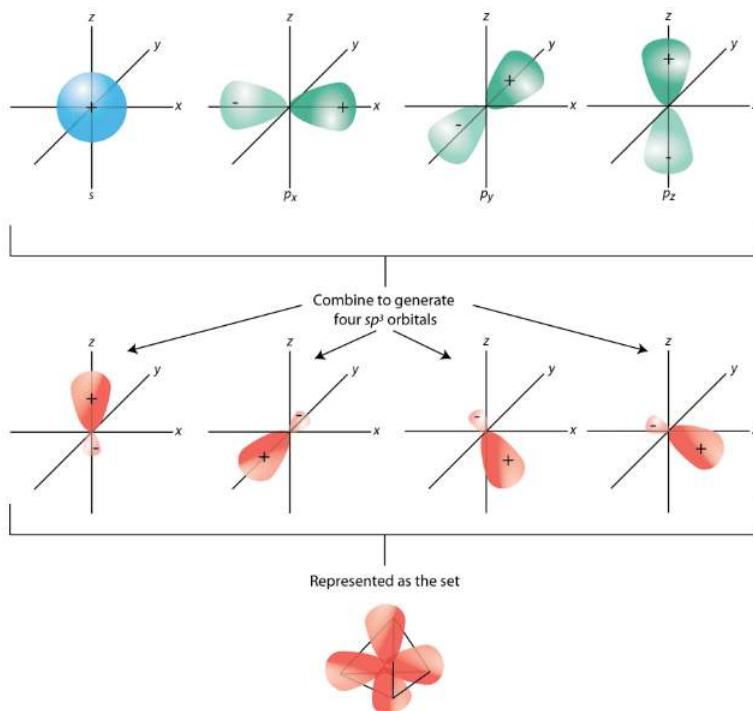


Figure 1.4.5: The process of sp^3 hybridization is the mixing of an s orbital with a set of three p orbitals to form a set of four sp^3 hybrid orbitals. Each large lobe of the hybrid orbitals points to one corner of a tetrahedron. The four lobes of each of the sp^3 hybrid orbitals then overlap with the normal unhybridized $1s$ orbitals of each hydrogen atom to form the tetrahedral methane molecule. (CC BY-NC 3.0; Jodi So via CK-12 Foundation)





Summary

- Electrons hybridize in order to form covalent bonds.
- Nonequivalent orbitals mix to form hybrid orbitals.

Review

- Why is carbon expected to form only two covalent bonds?
- How many covalent bonds does carbon actually form?
- What needs to happen to allow carbon to form four bonds?

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1.5: Structural Isomerism in Organic Molecules

This page explains what structural isomerism is, and looks at some of the various ways that structural isomers can arise.

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.

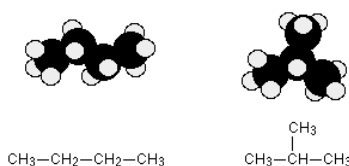


There are also endless other possible ways that this molecule could twist itself. There is completely free rotation around all the carbon-carbon single bonds. If you had a model of a molecule in front of you, you would have to take it to pieces and rebuild it if you wanted to make an isomer of that molecule. 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. Structural isomers could be chain isomers, position isomers, and functional group isomers. The difference 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 don't matter all that much, but you must be aware of the different possibilities when you come to draw isomers. Some other forms of isomerism (stereoisomers) will be discussed later.

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.

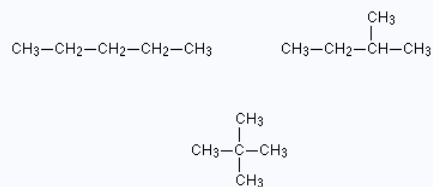


You could easily see this with a model. This is the example we've already used at the top of this page.



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.

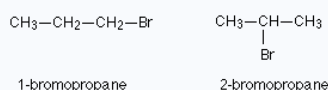


Position isomerism

In position isomerism, the basic carbon skeleton remains unchanged, but important groups are moved around on that skeleton.

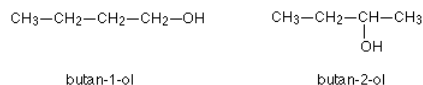
Example 2: Positional Isomers in C_5H_{12}

For example, there are two structural isomers with the molecular formula $\text{C}_3\text{H}_7\text{Br}$. In one of them the bromine atom is on the end of the chain, whereas in the other it's attached in the middle.



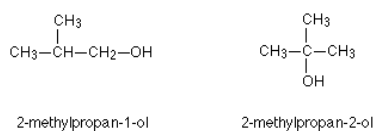
If you made a model, there is no way that you could twist one molecule to turn it into the other one. You would have to break the bromine off the end and re-attach it in the middle. At the same time, you would have to move a hydrogen from the middle to the end.

Another similar example occurs in alcohols such as $\text{C}_4\text{H}_9\text{OH}$

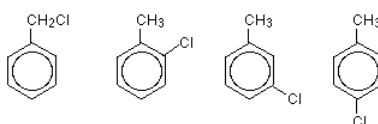


These are the only two possibilities provided you keep to a four carbon chain, but there is no reason why you should do that. You can easily have a mixture of chain isomerism and position isomerism - you aren't restricted to one or the other.

So two other isomers of butanol are:



You can also get position isomers on benzene rings. Consider the molecular formula $\text{C}_7\text{H}_7\text{Cl}$. There are four different isomers you could make depending on the position of the chlorine atom. In one case it is attached to the side-group carbon atom, and then there are three other possible positions it could have around the ring - next to the CH_3 group, next-but-one to the CH_3 group, or opposite the CH_3 group.

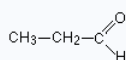


Functional group isomerism

In this variety of structural isomerism, the isomers contain different functional groups - that is, they belong to different families of compounds (different homologous series).

Example 3: Isomers in C_3H_6O

A molecular formula C_3H_6O could be either propanal (an aldehyde) or propanone (a ketone).

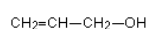


propanal

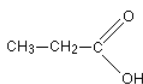


propanone

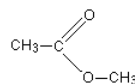
There are other possibilities as well for this same molecular formula - for example, you could have a carbon-carbon double bond (an alkene) and an -OH group (an alcohol) in the same molecule.



Another common example is illustrated by the molecular formula $C_3H_6O_2$. Amongst the several structural isomers of this are propanoic acid (a carboxylic acid) and methyl ethanoate (an ester).



propanoic acid



methyl ethanoate

Contributors

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1.6: How to Draw Organic Molecules

This page explains the various ways that organic molecules can be represented on paper or on screen - including molecular formulae, and various forms of structural formulae.

Molecular formula

A molecular formula simply counts the numbers of each sort of atom present in the molecule, but tells you nothing about the way they are joined together. For example, the molecular formula of butane is C_4H_{10} , and the molecular formula of ethanol is C_2H_6O .

Molecular formulae are very rarely used in organic chemistry, because they do not give useful information about the bonding in the molecule. About the only place where you might come across them is in equations for the [combustion of simple hydrocarbons](#), for example:

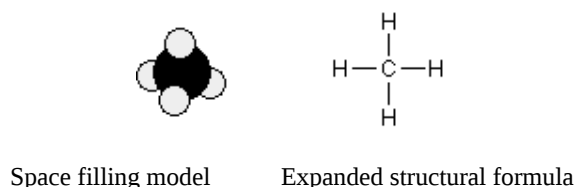


In cases like this, the bonding in the organic molecule isn't important.

Structural formula

A structural formula shows how the various atoms are bonded. There are various ways of drawing this and you will need to be familiar with all of them.

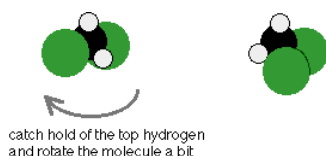
An expanded structural formula shows all the bonds in the molecule as individual lines. You need to remember that each line represents a pair of shared electrons. For example, this is a model of methane together with its displayed formula:



Notice that the way the methane is drawn bears no resemblance to the actual shape of the molecule. Methane isn't flat with 90° bond angles. This mismatch between what you draw and what the molecule actually looks like can lead to problems if you aren't careful. For example, consider the simple molecule with the molecular formula CH_2Cl_2 . You might think that there were two different ways of arranging these atoms if you drew a displayed formula.



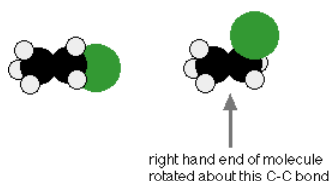
The chlorines could be opposite each other or at right angles to each other. But these two structures are actually exactly the same. Look at how they appear as models.



One structure is in reality a simple rotation of the other one. Consider a slightly more complicated molecule, $\text{C}_2\text{H}_5\text{Cl}$. The displayed formula could be written as either of these:

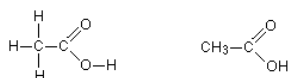


But, again these are exactly the same. Look at the models.



The commonest way to draw structural formulas

For anything other than the most simple molecules, drawing a fully displayed formula is a bit of a bother - especially all the carbon-hydrogen bonds. You can simplify the expanded formula by writing, for example, CH_3 or CH_2 instead of showing all these bonds. For example, ethanoic acid would be shown in an expanded structural formula and a condensed structural formula as:

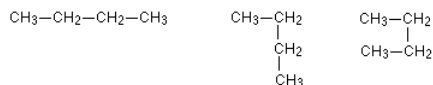


Expanded structural formula Condensed structural formula

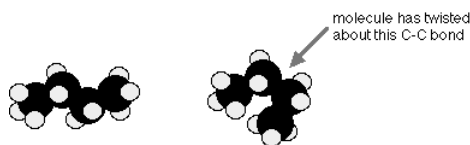
In other words, in a condensed structural formula all hydrogen atoms are "condensed" into a "molecular formula" by adding them to the corresponding carbon atom attached to all the hydrogens. You could even condense it further to CH_3COOH , and would probably do this if you had to write a simple chemical equation involving ethanoic acid. You do, however, lose something by condensing the acid group in this way, because you can't immediately see how the bonding works. You still have to be careful in drawing structures in this way. Remember from above that these two structures both represent the same molecule:



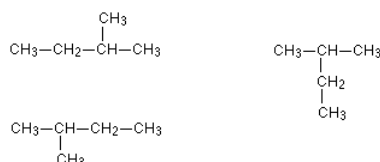
The next three condensed structural formulas represent butane:



All of these are just versions of four carbon atoms joined up in a line. The only difference is that there has been some rotation about some of the carbon-carbon bonds. You can see this in a couple of models.

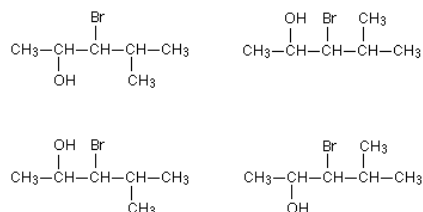


Not one of the structural formulae accurately represents the shape of butane (as we will discuss later). The convention is that we draw it with all the carbon atoms in a straight line - as in the first of the structures above. This is even more important when you start to have branched chains of carbon atoms. The following structures again all represent the same molecule - 2-methylbutane.



The two structures on the left are fairly obviously the same - all we've done is flip the molecule over. The other one isn't so obvious until you look at the structure in detail. There are four carbons joined up in a row, with a CH_3 group attached to the next-to-end one. That's exactly the same as the other two structures. If you had a model, the only difference between these three diagrams is that you have rotated some of the bonds and turned the model around a bit.

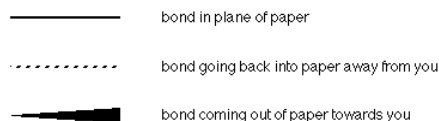
To overcome this possible confusion, the convention is that you always look for the longest possible chain of carbon atoms, and then draw it horizontally. Anything else is simply hung off that chain. It does not matter in the least whether you draw any side groups pointing up or down. All of the following represent exactly the same molecule.



If you made a model of one of them, you could turn it into any other one simply by rotating one or more of the carbon-carbon bonds.

How to draw structural formulae in 3-dimensions

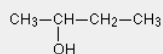
There are occasions when it is important to be able to show the precise 3-D arrangement in parts of some molecules. To do this, the bonds are shown using conventional symbols:



For example, you might want to show the 3-D arrangement of the groups around the carbon which has the $-\text{OH}$ group in butan-2-ol.

Example 1: 2-butanol

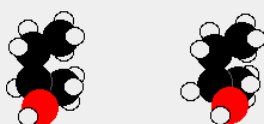
2-Butanol has the structural formula:



Using conventional bond notation, you could draw it as, for example:



The only difference between these is a slight rotation of the bond between the centre two carbon atoms. This is shown in the two models below. Look carefully at them - particularly at what has happened to the lone hydrogen atom. In the left-hand model, it is tucked behind the carbon atom. In the right-hand model, it is in the same plane. The change is very slight.

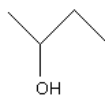
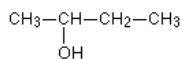


It doesn't matter in the least which of the two arrangements you draw. You could easily invent other ones as well. Choose one of them and get into the habit of drawing 3-dimensional structures that way. My own habit (used elsewhere on this site) is to draw two bonds going back into the paper and one coming out - as in the left-hand diagram above.

Notice that no attempt was made to show the whole molecule in 3-dimensions in the structural formula diagrams. The CH_2CH_3 group was left in a simple form. Keep diagrams simple - trying to show too much detail makes the whole thing amazingly difficult to understand!

Skeletal formulae

In a skeletal formula, all the hydrogen atoms are removed from carbon chains, leaving just a carbon skeleton with functional groups attached to it. For example, we've just been talking about 2-butanol. The normal structural formula and the skeletal formula look like this:



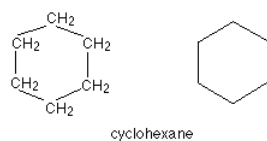
Condensed structural formula Skeletal formula

In a skeletal diagram of this sort

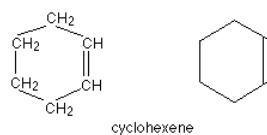
- there is a carbon atom at each junction between bonds in a chain and at the end of each bond (unless there is something else there already - like the -OH group in the example);
- there are enough hydrogen atoms attached to each carbon to make the total number of bonds on that carbon up to 4.

Beware! Diagrams of this sort take practice to interpret correctly - and may well not be acceptable to your examiners (see below).

There are, however, some very common cases where they are frequently used. These cases involve rings of carbon atoms which are surprisingly awkward to draw tidily in a normal structural formula. Cyclohexane, C_6H_{12} , is a ring of carbon atoms each with two hydrogens attached. This is what it looks like in both a structural formula and a skeletal formula.



And this is cyclohexene, which is similar but contains a double bond:



Deciding which sort of formula to use

There's no easy, all-embracing answer to this problem. It depends more than anything else on experience - a feeling that a particular way of writing a formula is best for the situation you are dealing with.

Don't worry about this - as you do more and more organic chemistry, you will probably find it will come naturally. You'll get so used to writing formulae in reaction mechanisms, or for the structures for isomers, or in simple chemical equations, that you won't even think about it.

Contributors

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CHAPTER OVERVIEW

2: Alkanes and Cycloalkanes

- 2.1: Structures and Names of Alkanes
- 2.2: Branched-Chain Alkanes
- 2.3: Condensed Structural and Skeletal Formulas
- 2.4: IUPAC Nomenclature
- 2.5: Halogenated Hydrocarbons
- 2.6: Conformations of Ethane
- 2.7: Conformations of Other Alkanes
- 2.8: Source of hydrocarbons- crude oil and natural gas
- 2.9: Cycloalkanes
- 2.10: Naming Cycloalkanes
- 2.11: Stability of Cycloalkanes - Ring Strain
- 2.12: Cis-Trans Isomerism in Cycloalkanes
- 2.13: Conformations of Cyclohexane
- 2.14: Axial and Equatorial Bonds in Cyclohexane
- 2.15: Conformations of Monosubstituted Cyclohexanes
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- 2.17: Physical Properties of Alkanes
- 2.18: Reactions of Alkanes
- 2.19: Reaction Mechanism for Free-Radical Halogenation of Alkanes

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2.1: Structures and Names of Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

Hydrocarbons

We begin our study of organic chemistry with the **hydrocarbons**, the simplest organic compounds, **which are composed of carbon and hydrogen atoms only**. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding ((Figure 2.1.1). Hydrocarbons are classified as aliphatic or aromatic. Aromatic hydrocarbons contain a particular structural feature, which the aromatic ring. Aliphatic hydrocarbons do not contain the aromatic ring.



Aromatic ring

Saturated hydrocarbons have no double or triple bonds in the molecules. Unsaturated hydrocarbons contain carbon-to-carbon double bonds ($C=C$) or carbon-carbon triple bonds ($C\equiv C$).

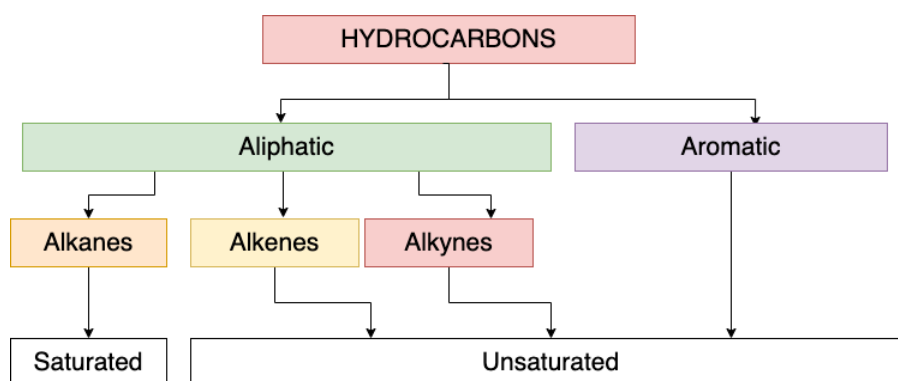


Figure 2.1.1. Classification of hydrocarbons

The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds ($C=C$).

Alkanes

Hydrocarbons with only carbon-to-carbon single bonds ($C-C$) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible. We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure 2.1.2.

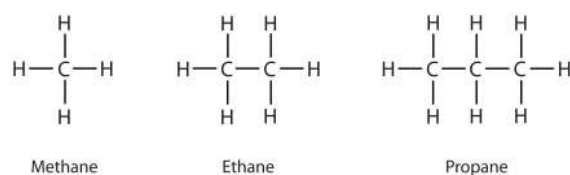


Figure 2.1.2: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure 2.1.3).

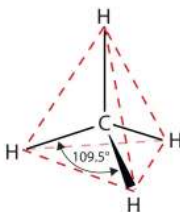


Figure 2.1.3: The Tetrahedral Methane Molecule

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table 2.1.1.

Table 2.1.1: The First 10 Straight-Chain Alkanes

Name	Molecular Formula ($\text{C}_n\text{H}_{2n+2}$)	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$\text{CH}_3\text{CH}_2\text{CH}_3$	—
butane	C_4H_{10}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	2
pentane	C_5H_{12}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	3
hexane	C_6H_{14}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	5
heptane	C_7H_{16}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	9
octane	C_8H_{18}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	18
nonane	C_9H_{20}	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	35
decane	$\text{C}_{10}\text{H}_{22}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	75

Consider the series in Figure 2.1.4. The sequence starts with C_3H_8 , and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

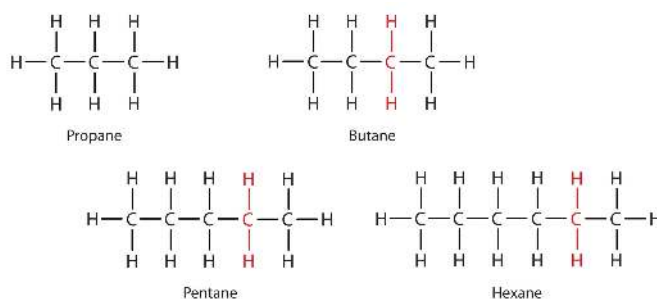


Figure 2.1.4: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2} . Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8) + 2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

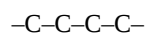
2.1: Structures and Names of Alkanes is shared under a [CC BY-NC-SA 4.0](https://creativecommons.org/licenses/by-nc-sa/4.0/) license and was authored, remixed, and/or curated by LibreTexts.

2.2: Branched-Chain Alkanes

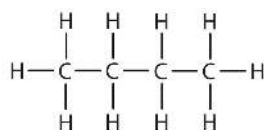
Learning Objectives

- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

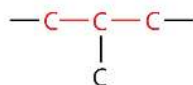
We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,



and then adding enough hydrogen atoms to give each carbon atom four bonds:



The compound butane has this structure, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then branch the fourth one off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds.

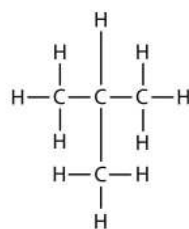


Figure 2.2.1).

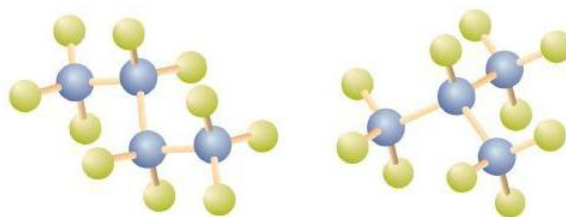
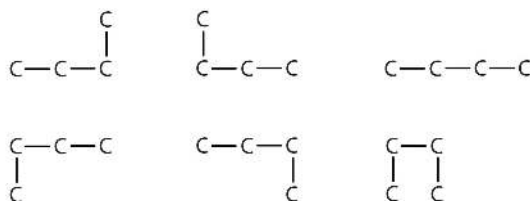


Figure 2.2.1: Butane and Isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10} .

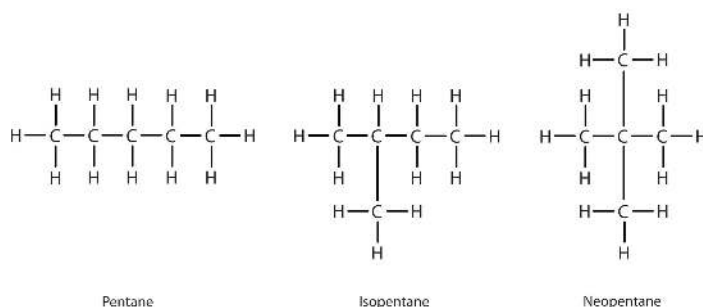
Notice that C_4H_{10} is depicted with a bent chain in Figure 2.2.1. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure 2.2.1).

Unlike C_4H_{10} , the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12} . (Table 12.1.1 from the previous section has a column identifying the number of possible isomers for the first 10 straight-chain alkanes.) The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning “new”). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, $36.1^\circ C$; isopentane, $27.7^\circ C$; and neopentane, $9.5^\circ C$.



A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

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- 12.3: Branched-Chain Alkanes by Anonymous is licensed CC BY-NC-SA 3.0. Original source: <https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological/>.

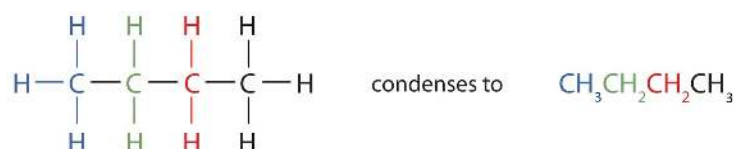
2.3: Condensed Structural and Skeletal Formulas

Learning Objectives

- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and isobutane. An expanded structural formula shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms.

Unfortunately, expanded structural formulas are difficult to type/write and take up a lot of space. Chemists often use condensed structural formulas to alleviate these problems. The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:



The ultimate condensed formula is the skeletal formula (sometimes known as a line-angle formula), in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) and isopentane $[(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3]$ as follows:



Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Key Takeaways

- Condensed structural chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Skeletal formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

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2.4: IUPAC Nomenclature

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

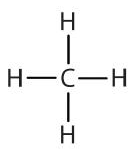
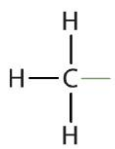
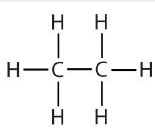
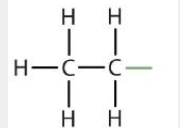
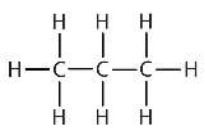
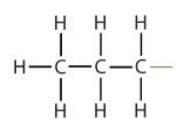
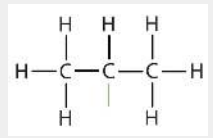
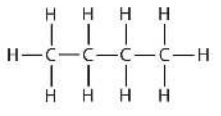
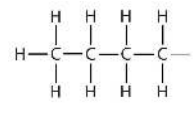
As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.) A stem name (Table 2.4.1) indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers. For now, we will consider only those substituents called alkyl groups.

Table 2.4.1: Stems That Indicate the Number of Carbon Atoms in Organic Molecules

Stem	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the -CH_3 group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table 2.4.2. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

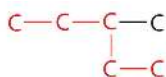
Table 2.4.2: Common Alkyl Groups

Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		CH ₃ –
ethane		ethyl		CH ₃ CH ₂ –
propane		propyl		CH ₃ CH ₂ CH ₂ –
		isopropyl		(CH ₃) ₂ CH–
butane		butyl*		CH ₃ CH ₂ CH ₂ CH ₂ –

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 2.4.1).

- Name alkanes according to the LCC (longest continuous chain) of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.
- If the hydrocarbon is branched, number the carbon atoms of the LCC.** Numbers are assigned in the direction that gives the lowest numbers to the carbon atoms with attached substituents. Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other. (The LCC need not be written in a straight line; for example, the LCC in the following has five carbon atoms.)



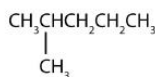
- Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the *di-* is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

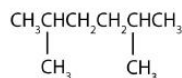
Example 2.4.1

Name each compound.

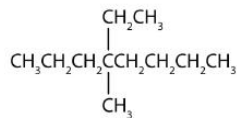
1.



2.



3.



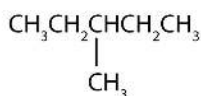
Solution

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.
2. The LCC has six carbon atoms, so the parent compound is hexane (rule 1). Methyl groups (rule 2) are attached to the second and fifth carbon atoms. The name is 2,5-dimethylhexane.
3. The LCC has eight carbon atoms, so the parent compound is octane (rule 1). There are methyl and ethyl groups (rule 2), both attached to the fourth carbon atom (counting from the *right* gives this carbon atom a lower number; rule 3). The correct name is thus 4-ethyl-4-methyloctane.

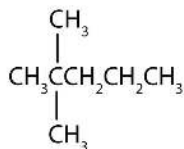
Exercise 2.4.1

Name each compound.

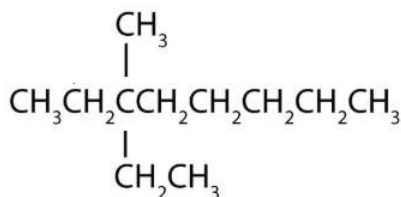
1.



2.



3.



Example 2.4.2

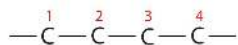
Draw the structure for each compound.

- a. 2,3-dimethylbutane
- b. 4-ethyl-2-methylheptane

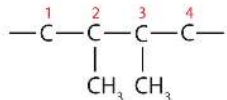
Solution

In drawing structures, always start with the parent chain.

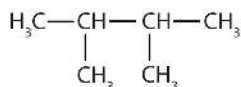
- a. The parent chain is butane, indicating four carbon atoms in the LCC.



Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (CH_3) groups, one on the second carbon atom and one on the third.

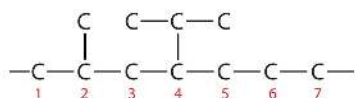


Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.

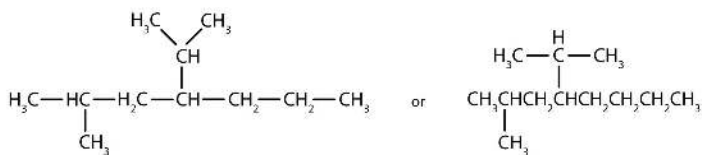


- b. The parent chain is heptane in this case, indicating seven carbon atoms in the LCC. —C—C—C—C—C—C—C—

Adding the groups at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas:



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

Exercise 2.4.2

Draw the structure for each compound.

- 4-ethyloctane
- 3-ethyl-2-methylpentane
- 3,3,5-trimethylheptane

Key Takeaway

- Alkanes have both common names and systematic names, specified by IUPAC.

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2.5: Halogenated Hydrocarbons

Learning Objectives

- 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 previously, 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). 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 $\text{CH}_3\text{CH}_2\text{Cl}$ 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 2.5.1

Give the common and IUPAC names for each compound.

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
- $(\text{CH}_3)_2\text{CHCl}$

Solution

- The alkyl group $(\text{CH}_3\text{CH}_2\text{CH}_2-)$ 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.
- The alkyl group $[(\text{CH}_3)_2\text{CH}-]$ 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.

? Exercise 2.5.1

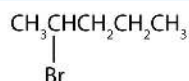
Give common and IUPAC names for each compound.

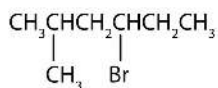
- $\text{CH}_3\text{CH}_2\text{I}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{F}$

✓ Example 2.5.2

Give the IUPAC name for each compound.

1.





2.

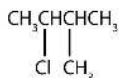
Solution

1. 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.
2. 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.

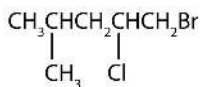
? Exercise 2.5.2

Give the IUPAC name for each compound.

a.



b.



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 2.5.1, along with some of their uses.

Table 2.5.1: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH₄			
CH ₃ Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH ₂ Cl 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 ₃ F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl ₂ F ₂	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH₃CH₃			
CH ₃ CH ₂ Cl	ethyl chloride	chloroethane	local anesthetic
ClCH ₂ CH ₂ Cl	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl ₃ CH 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 (CCl₄), 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 (COCl₂) gas, which makes the use of CCl₄ 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.

To Your Health: Chlorofluorocarbons and the Ozone Layer

Alkanes substituted with both fluorine (F) and chlorine (Cl) atoms have been used as the dispersing gases in aerosol cans, as foaming agents for plastics, and as refrigerants. Two of the best known of these chlorofluorocarbons (CFCs) are listed in Table 2.5.1.

Chlorofluorocarbons contribute to the greenhouse effect in the lower atmosphere. They also diffuse into the stratosphere, where they are broken down by ultraviolet (UV) radiation to release Cl atoms. These in turn break down the ozone (O₃) molecules that protect Earth from harmful UV radiation. Worldwide action has reduced the use of CFCs and related compounds. The CFCs and other Cl- or bromine (Br)-containing ozone-destroying compounds are being replaced with more benign substances. Hydrofluorocarbons (HFCs), such as CH₂FCF₃, which have no Cl or Br to form radicals, are one alternative. Another is

hydrochlorofluorocarbons (HCFCs), such as CHCl_2CF_3 . HCFC molecules break down more readily in the troposphere, and fewer ozone-destroying molecules reach the stratosphere.

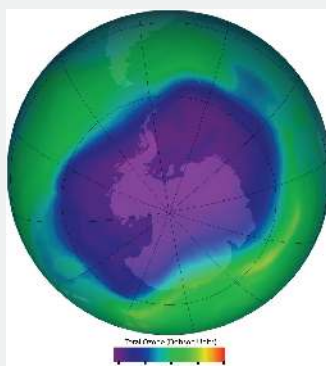


Figure 2.5.1: Ozone in the upper atmosphere shields Earth's surface from UV radiation from the sun, which can cause skin cancer in humans and is also harmful to other animals and to some plants. Ozone "holes" in the upper atmosphere (the gray, pink, and purple areas at the center) are large areas of substantial ozone depletion. They occur mainly over Antarctica from late August through early October and fill in about mid-November. Ozone depletion has also been noted over the Arctic regions. The largest ozone hole ever observed occurred on 24 September 2006. Source: Image courtesy of NASA, [Ozone watch \(opens in new window\)](#) [ozonewatch.gsfc.nasa.gov].

Key Takeaway

- The replacement of an hydrogen atom on an alkane by a halogen atom—F, Cl, Br, or I—forms a halogenated compound.

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2.6: 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 structural isomerism.
3. draw the conformers of ethane using 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)
- dihedral angle
- eclipsed conformation
- Newman projection
- staggered conformation
- strain energy
- torsional strain (eclipsing strain)

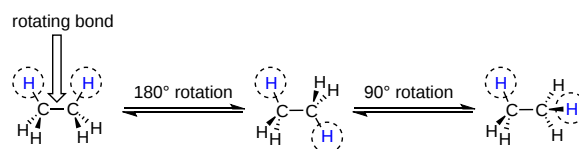
Study Notes

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 clearly draw the rear hydrogens exactly behind the front ones. This is an inherent limitation associated with representing a 3-D structure in two dimensions.

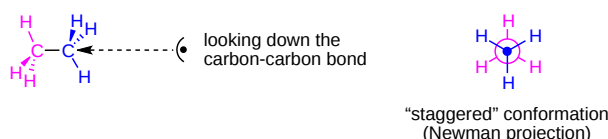
Conformational isomerism involves rotation about sigma bonds, and does not involve any differences in the connectivity of the atoms or geometry of bonding. Two or more structures that are categorized as conformational isomers, or **conformers**, are really just two of the exact same molecule that differ only in rotation of 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.



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.

Figure 3.6.1: A 3D Model of Staggered Ethane.

The lowest energy conformation of ethane, shown in the figure above, is called the 'staggered' conformation. In the staggered conformation, all of the C-H bonds on the front carbon are positioned at an angle of 60° relative to the C-H bonds on the back carbon. This angle between a sigma bond on the front carbon compared to a sigma bond on the back carbon is called the **dihedral angle**. In this conformation, the distance between the bonds (and the electrons in them) is maximized. Maximizing the distance between the electrons decreases the electrostatic repulsion between the electrons and results in a more stable structure.

If we now rotate the front CH_3 group 60° clockwise, the molecule is in the highest energy 'eclipsed' conformation, and the hydrogens on the front carbon are as close as possible to the hydrogens on the back carbon.



This is the highest energy conformation because of unfavorable electrostatic repulsion between the electrons in the front and back C-H bonds. The energy of the eclipsed conformation is approximately 3 kcal/mol (12 kJ/mol) higher than that of the staggered conformation. **Torsional strain** (or eclipsing strain) is the name given to the energy difference caused by the increased electrostatic repulsion of eclipsing bonds.

Another 60° rotation returns the molecule to a second staggered 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. We will focus on the staggered and eclipsed conformers since they are, respectively, the lowest and highest energy conformers.

Unhindered (Free) Rotations Do Not Exist in Ethane

The carbon-carbon bond is not *completely* free to rotate – the 3 kcal/mol torsional strain in ethane creates a barrier to rotation that must be overcome for the bond to rotate from one staggered conformation to another. This rotational barrier is not large enough to prevent rotation except at extremely cold temperatures. So at normal temperatures, the carbon-carbon bond is constantly rotating. 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 conformer. The potential energy associated with the various conformations of ethane varies with the dihedral angle of the bonds, as shown in Figure 3.6.2.

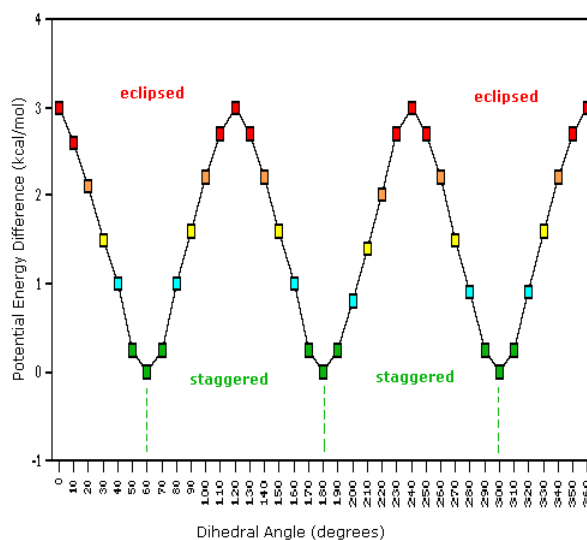


Figure 3.6.2: The potential energy associated with the various conformations of ethane varies with the dihedral angle of the bonds. Valleys in the graph represent the low energy staggered conformers, while peaks represent the higher energy eclipsed conformers.

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

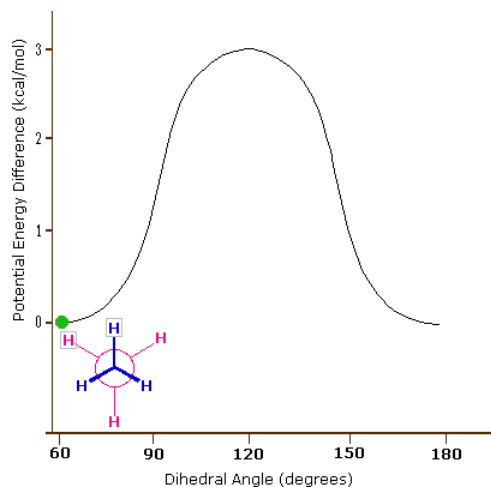


Figure 3.6.2: Animation of potential energy vs. dihedral angle in ethane

Exercises

1) What is the most stable rotational conformation of ethane and explain why it is preferred over the other conformation?

Solutions

1) 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.

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2.7: Conformations of Other Alkanes

Objectives

After completing this section, you should be able to

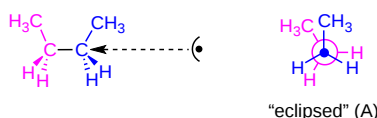
1. depict the staggered and eclipsed conformers of propane (or a similar compound) using sawhorse representations and Newman projections.
2. sketch a graph of energy versus bond rotation for propane (or a similar compound) and discuss the graph in terms of torsional strain.
3. depict the anti, gauche, 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 (strain)

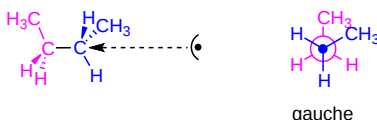
In butane, there are three rotating carbon-carbon sigma bonds to consider, but we will focus on the middle bond between C₂ and C₃. Below are two representations of butane in a conformation which puts the two CH₃ groups (C₁ and C₄) in the eclipsed position.



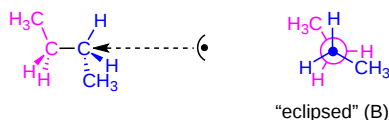
Eclipsed interaction	Energy (kcal/mol)	Energy (kJ/mol)
H-H	1.0	4.0
H-CH ₃	1.4	6.0
CH ₃ -CH ₃	2.6	11.0

The CH₃-CH₃ groups create the significantly larger eclipsed interaction of 11.0 kJ/mol. There are also two H-H eclipsed interactions at 4.0 kJ/mol each to create a total of 2(4.0 kJ/mol) + 11.0 kJ/mol = 19.0 kJ/mol of strain. This is the highest energy conformation for butane, due to torsional strain caused by the electrostatic repulsion of electrons in the eclipsed bonds, but also because of another type of strain called '**steric repulsion**', between the two rather bulky methyl groups. Steric strain comes about when two large groups, such as two methyl groups, try to occupy the same space. What results is a repulsive non-covalent interaction caused by their respective electron densities.

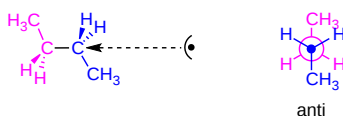
If we rotate the front, (blue) carbon by 60° clockwise, the butane molecule is now in a staggered conformation.



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.



The anti conformation is the lowest energy conformation for butane. The diagram below summarizes the relative energies for the various eclipsed, staggered, and gauche conformations.

Figure 2.7.1: A 3D Structure of the Anti Butane Conformer.

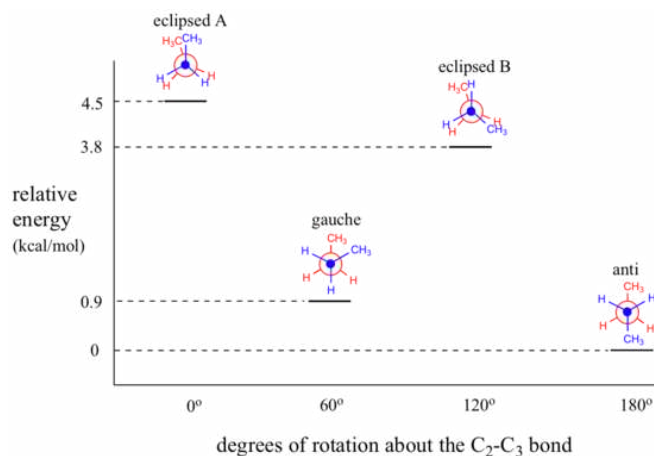


Figure 2.7.2: Potential curve vs dihedral angle of the C_2-C_3 bond of butane.

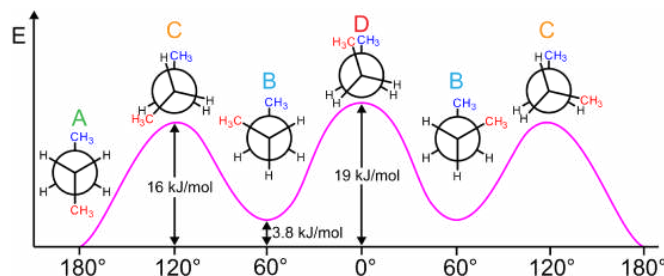
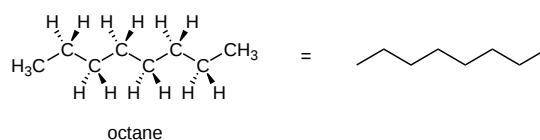


Figure 2.7.2: Newman projections of butane conformations & their relative energy differences (not total energies). Conformations form when butane rotates about one of its single covalent bond. Torsional/dihedral angle is shown on x-axis. Conformation names (according to IUPAC): **A**: anti-periplanar, 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; Keminsti).

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 the anti conformation at all carbon-carbon bonds. For example octane is commonly drawn as:



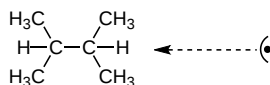
Drawing Newman Projections

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.

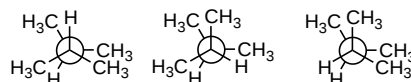
First draw the molecule and locate the indicated bond:



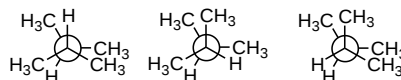
Because the question asks for the least stable conformation, focus on the three possible eclipsed Newman projections. Draw out three eclipsed Newman projections as a template. Because it is difficult to draw a true staggered Newman projection, it is common to show the bonds slightly askew.



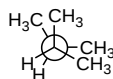
Place the substituents attached to the second carbon (C_3) on the back bonds of all three Newman projections. In this example they are 2 CH_3 s and an H. Place the substituents in the same position on all three Newman projections.



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_3 s 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.



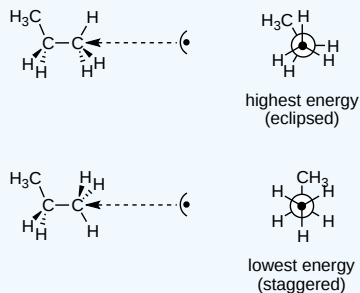
Compare the Newman projections by looking the eclipsed interactions. Remember that the order of torsional strain interactions are CH_3 - $CH_3 > CH_3$ -H $>$ H-H. The third structure has two CH_3 - CH_3 torsional interactions which will make it the least stable conformer of 2,3 dimethyl butane.



✓ Example 2.7.1

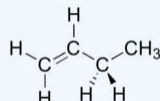
Draw Newman projections of the eclipsed and staggered conformations of propane, as if viewed down the C₁-C₂ bond.

Answer

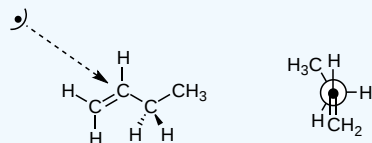


✓ Example 2.7.2

Draw a Newman projection, looking down the C₂-C₃ bond, of 1-butene in the conformation shown below.



Answer



Exercises

Questions

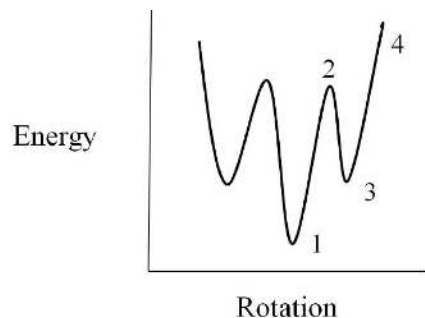
Q3.7.1

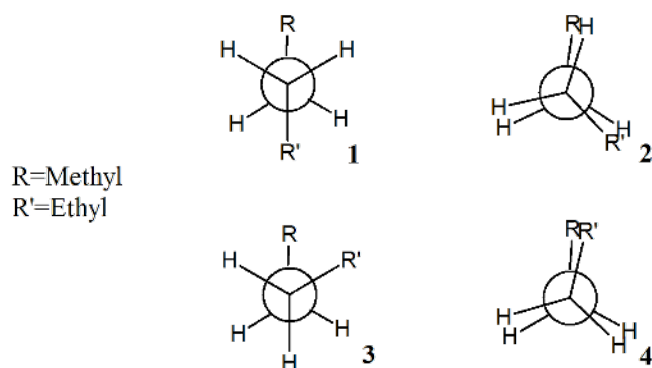
Draw the energy diagram for the rotation of the bond highlighted in pentane.



Solutions

S3.7.1





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2.8: Source of hydrocarbons- crude oil and natural gas

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)

Petroleum and fossil fuels

Most hydrocarbons are extracted from crude oil and natural gas. The petroleum that is pumped out of the ground 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 abundance of the components vary depending on the source - 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.

Crude oil and natural gas are a type of fossil fuels. A fossil fuel is a fuel formed by natural processes, such as anaerobic decomposition of buried dead organisms. Although fossil fuels are continually formed by natural processes, they are generally classified as **non-renewable resources** because they take millions of years to form and known viable reserves are being depleted much faster than new ones are generated. The use of fossil fuels raises serious environmental concerns, since The burning of fossil fuels produces around 35 billion tonnes of carbon dioxide (CO₂) per year. United States, European Union, and China are the main consumers of fossil fuels per capita.

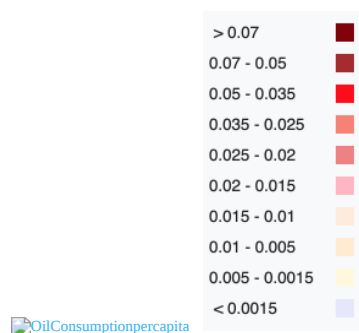


Figure 2.8.1. A map of world oil consumption in barrels a day per capita, 2007. Image by [GRock at the English-language Wikipedia](#), [CC BY-SA 3.0](#), via Wikimedia Commons.

Gasoline

Petroleum is converted to useful products such as gasoline in three steps: distillation, cracking, and reforming. Distillation separates compounds on the basis of their relative volatility, which is usually inversely proportional to their boiling points. Part (a) in Figure

2.8.2 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) and becomes 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 2.8.2 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.

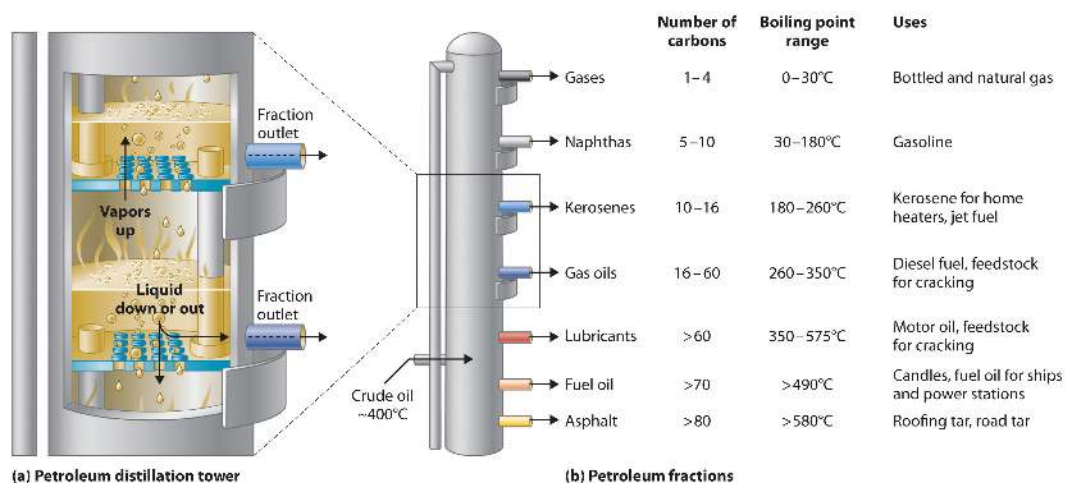


Figure 2.8.2: The Distillation of Petroleum. (a) This is a diagram of a distillation column used for separating petroleum fractions. (b) Petroleum fractions condense at different temperatures, depending on the number of carbon atoms in the molecules, and are drawn off from the column. The most volatile 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 are 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 2.8.3, 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.

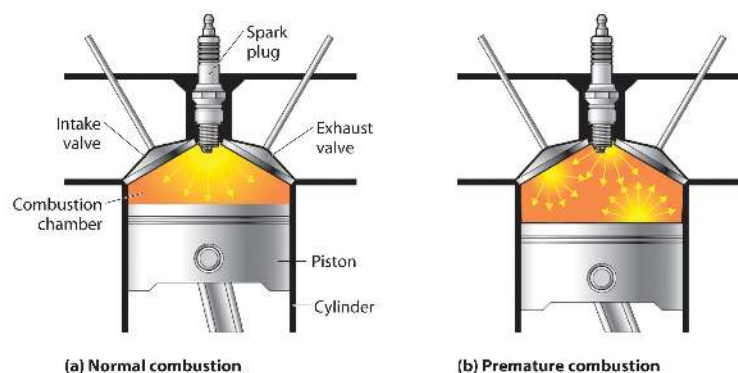


Figure 2.8.3 The Burning of Gasoline in an Internal Combustion Engine. (a) Normally, fuel is ignited by the spark plug, and combustion spreads uniformly outward. (b) Gasoline with an octane rating that is too low for the engine can ignite prematurely, resulting in uneven burning that causes knocking 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:

$$0.89(100) + 0.11(0) = 89 \quad (3.8.1)$$

As shown in Figure 2.8.3, many compounds that are now available have octane ratings greater than 100, which means they are better fuels than pure isooctane. In addition, anti-knock agents, also called octane enhancers, have been developed. One of the most widely used for many years was tetraethyl lead $[(C_2H_5)_4Pb]$, 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.

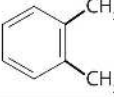
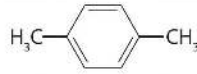
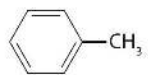
Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
n-heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	0	o-xylene		107
n-hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	25	ethanol	CH_3CH_2OH	108
n-pentane	$CH_3CH_2CH_2CH_2CH_3$	62	t-butyl alcohol	$(CH_3)_3COH$	113
isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	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

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- Wikipedia contributors. (2021, May 12). Fossil fuel. In *Wikipedia, The Free Encyclopedia*. Retrieved 15:11, May 20, 2021, from https://en.wikipedia.org/w/index.php?title=Fossil_fuel&oldid=1022720849

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2.9: Cycloalkanes

Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The hydrocarbons we have encountered so far have been composed of molecules with open-ended chains of carbon atoms. When a chain contains three or more carbon atoms, the atoms can join to form *ring* or *cyclic* structures. The simplest of these cyclic hydrocarbons has the formula C_3H_6 . Each carbon atom has two hydrogen atoms attached (Figure 2.9.1) and is called cyclopropane.

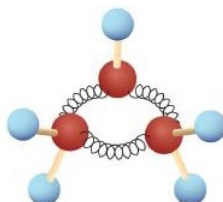
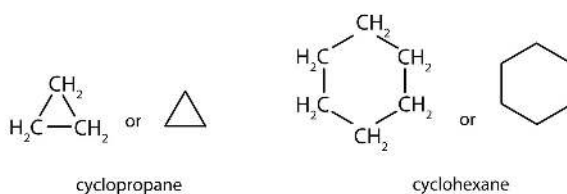


Figure 2.9.1: Ball-and-Spring Model of Cyclopropane. The springs are bent to join the carbon atoms.

To Your Health: Cyclopropane as an Anesthetic

With its boiling point of -33°C , cyclopropane is a gas at room temperature. It is also a potent, quick-acting anesthetic with few undesirable side effects in the body. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



Some cyclic compounds have substituent groups attached. Example 2.9.1 interprets the name of a cycloalkane with a single substituent group.

✓ Example 2.9.1

Draw the structure for each compound.

- cyclopentane
- methylcyclobutane

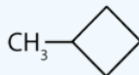
Solution a

The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



Solution b

The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH₃ group attached.

**? Exercise 2.9.1**

Draw the structure for each compound.

- cycloheptane
- ethylcyclohexane

The properties of cyclic hydrocarbons are generally quite similar to those of the corresponding open-chain compounds. So cycloalkanes (with the exception of cyclopropane, which has a highly strained ring) act very much like noncyclic alkanes. Cyclic structures containing five or six carbon atoms, such as cyclopentane and cyclohexane, are particularly stable. We will see later that some carbohydrates (sugars) form five- or six-membered rings in solution.

The cyclopropane ring is strained because the C–C–C angles are 60°, and the preferred (tetrahedral) bond angle is 109.5°. (This strain is readily evident when you try to build a ball-and-stick model of cyclopropane; see Figure 2.9.1.) Cyclopentane and cyclohexane rings have little strain because the C–C–C angles are near the preferred angles.

Key Takeaway

- Many organic compounds have cyclic structures.

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2.10: Naming Cycloalkanes

Objectives

After completing this section, you should be able to:

- Name a substituted or unsubstituted cycloalkane, given its Kekulé structure, shorthand structure or condensed structure.
- Draw the Kekulé, shorthand or condensed structure for a substituted or unsubstituted cycloalkane, given its IUPAC name.

Key Terms

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

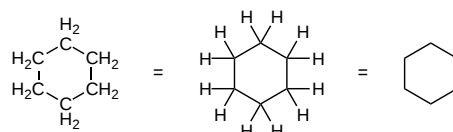
- cycloalkane

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.

Many organic compounds found in nature contain rings of carbon atoms. These compounds are known as **cycloalkanes**. Cycloalkanes only contain carbon-hydrogen bonds and carbon-carbon single bonds. The simplest examples of this class consist of a single, un-substituted carbon ring, and these form a homologous series similar to the unbranched alkanes.

Like alkanes, cycloalkane molecules are often drawn as skeletal structures in which each intersection between two lines is assumed to have a carbon atom with its corresponding number of hydrogens. Cyclohexane, one of the most common cycloalkanes is shown below as an example.



Cyclic hydrocarbons have the prefix "cyclo-". The IUPAC names, molecular formulas, and skeleton structures of the cycloalkanes with 3 to 10 carbons are given in Table 2.10.1. Note that the general formula for a cycloalkane composed of *n* carbons is **C_nH_{2n}**, and not **C_nH_{2n+2}** as for alkanes. Although a cycloalkane has two fewer hydrogens than the equivalent alkane, each carbon is bonded to four other atoms so are still considered to be **saturated** with hydrogen.

Table 2.10.1: Examples of Simple Cycloalkanes

Cycloalkane	Molecular Formula	Skeleton 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

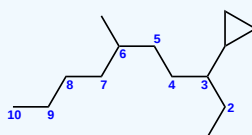
The naming of substituted cycloalkanes follows the same basic steps used in naming alkanes.

1. Determine the parent chain.
2. Number the substituents of the ring beginning at one substituent so that the nearest substituent is numbered the lowest possible.
If there are multiple choices that are still the same, go to the next substituent and give it the lowest number possible.
3. Name the substituents and place them in alphabetical order.

More specific rules for naming substituted cycloalkanes with examples are given below.

1. Determine the cycloalkane to use as the parent. 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. Cycloalkanes substituents have an ending "-yl". If there are two cycloalkanes in the molecule, use the cycloalkane with the higher number of carbons as the parent.

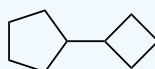
✓ Example 2.10.1



The longest straight chain contains 10 carbons, compared with cyclopropane, which only contains 3 carbons. The parent chain in this molecule is decane and cyclopropane is a substituent. The name of this molecule is 3-cyclopropyl-6-methyldecane.

✓ Example 2.10.2

Name the cycloalkane structure.



Solution

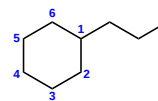
There are two different cycloalkanes in this molecule. Because it contains more carbons, the cyclopentane ring will be named as the parent chain. The smaller ring, cyclobutane, is named as a substituent on the parent chain. The name of this molecule is cyclobutylcyclopentane.

2. When there is only one substituent on the ring, the ring carbon attached to the substituent is automatically carbon #1. Indicating the number of the carbon with the substituent in the name is optional.

✓ Example 2.10.3



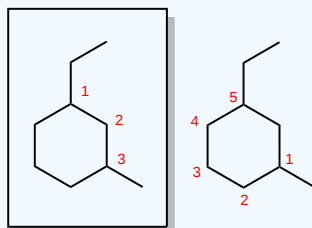
1-chlorocyclobutane or chlorocyclobutane



1-propylcyclohexane or propylcyclohexane

3. If there are multiple substituents on the ring, number the carbons of the cycloalkane so that the carbons with substituents 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.
4. When naming the cycloalkane, the substituents must be placed in alphabetical order. Remember the prefixes di-, tri-, etc. , are not used for alphabetization.

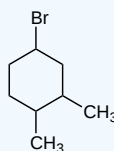
✓ Example 2.10.4



In this example, the ethyl or the methyl substituent could be attached to carbon one. The ethyl group attachment is assigned carbon 1 because ethyl comes before methyl alphabetically. After assigning carbon 1 the cyclohexane ring can be numbered going clockwise or counterclockwise. When looking at the numbers produced going clockwise produces lower first substituent numbers (1,3) than when numbered counterclockwise (1,5). So the correct name is 1-ethyl-3-methylcyclohexane.

✓ Example 2.10.5

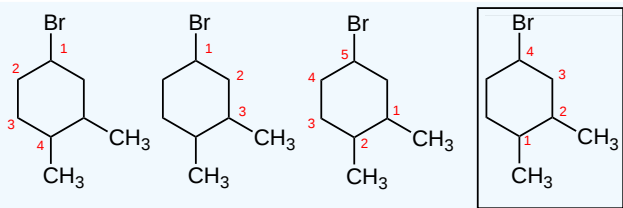
Name the following structure using IUPAC rules.



Solution

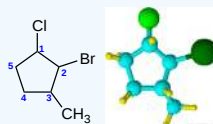
Remember when dealing with cycloalkanes with more than two substituents, finding the lowest possible 2nd substituent numbering takes precedence. Consider a numbering system with each substituent attachment point as being carbon one. Compare them and whichever produces the lowest first point of difference will be correct.

The first structure would have 1,4 for the relationship between the first two groups. The next structure would have 1,3. The final 2 structures both have 1,2 so those are preferable to the first two. Now we have to determine which is better between the final 2 structures. The 3rd substituent on structure 3 would be at the 5 position leading to 1,2,5 while in the final structure the 3rd methyl group is on carbon 4 leading to 1,2,4. This follows the rules of giving the lowest numbers at the first point of difference.



The correct name for the molecule is 4-Bromo-1,2-dimethylcyclohexane.

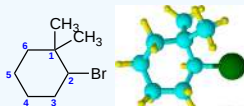
✓ Example 2.10.6



2-bromo-1-chloro-3-methylcyclopentane

Notice that "b" of bromo alphabetically precedes the "m" of methyl. Also, notice that the chlorine attachment point is assigned carbon 1 because it comes first alphabetically and the overall sum of numbers would be the same if the methyl attachment carbon was assigned as 1 and the chlorine attachment as 3.

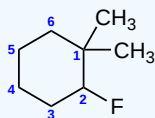
✓ Example 2.10.7



(2-bromo-1,1-dimethylcyclohexane)

Although "di" alphabetically precedes "f", "di" is not used in determining the alphabetical order.

✓ Example 2.10.8



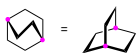
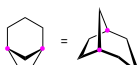
2-fluoro-1,1,-dimethylcyclohexane **NOT** 1,1-dimethyl-2-fluorocyclohexane also 2-fluoro-1,1,-dimethylcyclohexane **NOT** 1-fluoro-2,2-dimethylcyclohexane (as that would give a larger number to the first point of difference)

Although "di" alphabetically precedes "f", "di" is not used in determining the alphabetical order of the substituents. Notice that the attachment point of the two methyl groups is assigned carbon 1 despite the fact that fluorine comes first alphabetically. This is because this assignment allows for a lower overall numbering of substituents, so assigning alphabetical priority is not necessary.

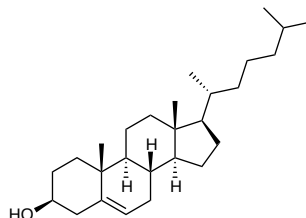
Polycyclic Compounds

Hydrocarbons having more than one ring are common, and are referred to as **bicyclic** (two rings), **tricyclic** (three rings) and in general, **polycyclic compounds**. The molecular formulas of such compounds have H/C ratios that decrease with the number of rings. In general, for a hydrocarbon composed of n carbon atoms associated with m rings the formula is: $C_nH_{2n+2-2m}$. The structural relationship of rings in a polycyclic compound can vary. They may be separate and independent, or they may share one or two common atoms. Some examples of these possible arrangements are shown in the following table.

Table 2.10.2: Examples of Isomeric C_8H_{14} Bicycloalkanes

Isolated Rings	Spiro Rings	Fused Rings	Bridged Rings
No common atoms	One common atom	One common bond	Two common atoms
 	 	 	 

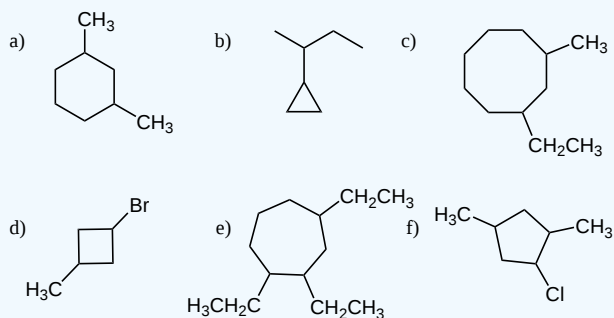
Polycyclic compounds, like cholesterol shown below, are biologically important and typically have common names accepted by IUPAC. However, the common names do not generally follow the basic IUPAC nomenclature rules, and will not be covered here.



Cholesterol (polycyclic)

? Exercise 2.10.1

Give the IUPAC names for the following cycloalkane structures.



Answer

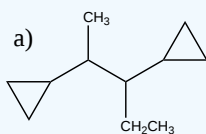
- 1,3-Dimethylcyclohexane
- 2-Cyclopropylbutane
- 1-Ethyl-3-methylcyclooctane
- 1-Bromo-3-methylcyclobutane
- 1,2,4-Triethylcycloheptane
- 1-Chloro-2,4-dimethylcyclopentane

? Exercise 2.10.2

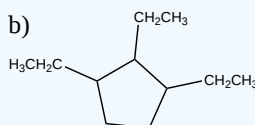
Draw the structures for the IUPAC names below.

- 2,3-dicyclopropylpentane
- 1,2,3-triethylcyclopentane
- 3-cyclobutyl-2-methylhexane
- 2-bromo-1-chloro-4-methylcyclohexane
- 1-bromo-5-propylcyclododecane

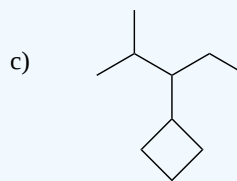
Answer



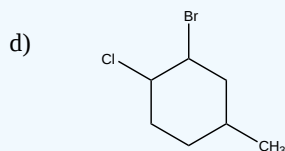
2,3-dicyclopropylpentane



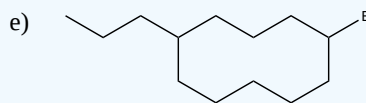
1,2,3-triethylcyclopentane



3-cyclobutyl-2-methylhexane



2-bromo-1-chloro-4-methylcyclohexane



1-bromo-5-propylcyclodecane

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2.11: Stability of Cycloalkanes - Ring Strain

Objectives

After completing this section, you should be able to:

- Describe the Baeyer strain theory.
- Describe how the measurement of heats of combustion provides information about the amount of strain present in a cycloalkane ring.
- Determine the relative stability of cyclic compounds, by assessing such factors as angle strain, torsional strain and steric strain.

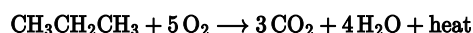
Key Terms

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

- angle strain
- steric strain
- torsional strain
- ring strain
- heat of combustion

Heat of Combustion as a Measure of Bond Strength

The combustion of carbon compounds, especially hydrocarbons, has been the most important source of heat energy for human civilizations throughout recorded history. The practical importance of this reaction cannot be denied, but the massive and uncontrolled chemical changes that take place in combustion make it difficult to deduce mechanistic paths. Using the combustion of propane as an example, we see from the following equation that every covalent bond in the reactants has been broken and an entirely new set of covalent bonds have formed in the products. No other common reaction involves such a profound and pervasive change, and the mechanism of combustion is so complex that chemists are just beginning to explore and understand some of its elementary features.



Since all the covalent bonds in the reactant molecules are broken, the quantity of heat evolved in this reaction, and any other combustion reaction, is related to the strength of these bonds (and, of course, the strength of the bonds formed in the products). Precise heat of combustion measurements can provide useful information about the structure of molecules and their relative stability.

For example, heat of combustion is useful in determining the relative stability of isomers. Pentane has a heat of combustion of -782 kcal/mol, while that of its isomer, 2,2-dimethylpropane (neopentane), is -777 kcal/mol. These values indicate that 2,3-dimethylpentane is 5 kcal/mol more stable than pentane, since it has a lower heat of combustion.

Ring Strain

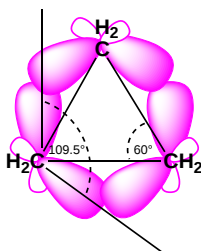
Table 2.11.1 lists the heat of combustion data for some simple cycloalkanes. These cycloalkanes do not have the same molecular formula, so the heat of combustion per each CH₂ unit present in each molecule is calculated (the fourth column) to provide a useful comparison. From the data, cyclopropane and cyclobutane have significantly higher heats of combustion per CH₂, while cyclohexane has the lowest heat of combustion. This indicates that cyclohexane is more stable than cyclopropane and cyclobutane, and in fact, that cyclohexane has a same relative stability as long chain alkanes that are not cyclic. This difference in stability is seen in nature where six membered rings are by far the most common. What causes the difference in stability or the strain in small cycloalkanes?

Table 2.11.1: Heats of combustion of select hydrocarbons

Cycloalkane (CH ₂) _n	CH ₂ Units n	ΔH^{25° kcal/mol	ΔH^{25° per CH ₂ Unit	Ring Strain kcal/mol
Cyclopropane	n = 3	468.7	156.2	27.6
Cyclobutane	n = 4	614.3	153.6	26.4
Cyclopentane	n = 5	741.5	148.3	6.5
Cyclohexane	n = 6	882.1	147.0	0.0
Cycloheptane	n = 7	1035.4	147.9	6.3
Cyclooctane	n = 8	1186.0	148.2	9.6
Cyclononane	n = 9	1335.0	148.3	11.7
Cyclodecane	n = 10	1481	148.1	11.0
CH ₃ (CH ₂) _m CH ₃	m = large	—	147.0	0.0

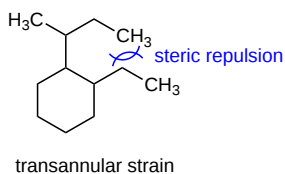
The Baeyer Theory on the Strain in Cycloalkane Rings

In 1890, the famous German organic chemist, A. Baeyer, suggested that cyclopropane and cyclobutane are less stable than cyclohexane, because the the smaller rings are more "strained". There are many different types of strain that contribute to the overall ring strain in cycloalkanes, including angle strain, torsional strain, and steric strain. **Torsional strain** and **steric strain** were previously defined in the discussion of conformations of butane. **Angle Strain** occurs when the sp³ hybridized carbons in cycloalkanes do not have the expected ideal bond angle of 109.5°, causing an increase in the potential energy. An example of angle strain can be seen in the diagram of cyclopropane below in which the bond angle is 60° between the carbons. The compressed bond angles causes poor overlap of the hybrid orbitals forming the carbon-carbon sigma bonds which in turn creates destabilization.

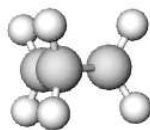


The C-C-C bond angles in cyclopropane (diagram above) (60°) and cyclobutane (90°) are much different than the ideal bond angle of 109.5°. This bond angle causes cyclopropane and cyclobutane to be less stable than molecules such as cyclohexane and cyclopentane, which have a much lower ring strain because the bond angle between the carbons is much closer to 109.5°. Changes in chemical reactivity as a consequence of angle strain are dramatic in the case of cyclopropane, and are also evident for cyclobutane.

In addition to angle strain, there is also steric (transannular) strain and torsional strain in many cycloalkanes. Transannular strain exists when there is steric repulsion between atoms.

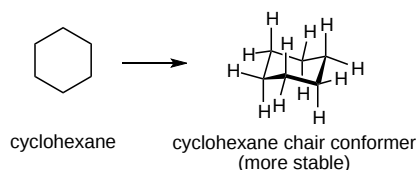


Because cycloalkane lack the ability to freely rotate, torsional (eclipsing) strain exists when a cycloalkane is unable to adopt a staggered conformation around a C-C bond. Torsional strain is especially prevalent in small cycloalkanes, such as cyclopropane, whose structures are nearly planar.



The Eclipsed C-H Bonds in Cyclopropane

Larger rings like cyclohexane, deal with torsional strain by forming conformers in which the rings are not planar. 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, which decreases the angle and torsional strain in the ring. The non-planar structures of cyclohexane are very stable compared to cyclopropane and cyclobutane, and will be discussed in more detail in the next section.



The Types of Strain Which Contribute to Ring Strain in Cycloalkanes

- Angle Strain - The strain caused by the increase or reduction of bond angles
- Torsional Strain - The strain caused by eclipsing bonds on adjacent atoms
- Steric Strain - The strain caused by the repulsive interactions of atoms trying to occupy the same space

Exercise 2.11.1

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 2.11.2

Cyclobutane has more torsional strain than cyclopropane. Explain this observation.

Answer

Cyclobutane has 4 CH₂ groups while cyclopropane only has 3. More CH₂ groups means cyclobutane has more eclipsing H-H interactions and therefore has more torsional strain.

Exercises

1. *Trans*-1,2-Dimethylcyclobutane is more stable than *cis*-1,2-dimethylcyclobutane. Explain this observation.
2. 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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2.12: Cis-Trans Isomerism in Cycloalkanes

Objectives

After completing this section, you should be able to

- draw structural formulas that distinguish between *cis* and *trans* disubstituted cycloalkanes.
- construct models of *cis* and *trans* disubstituted cycloalkanes using ball-and-stick molecular models.

Key Terms

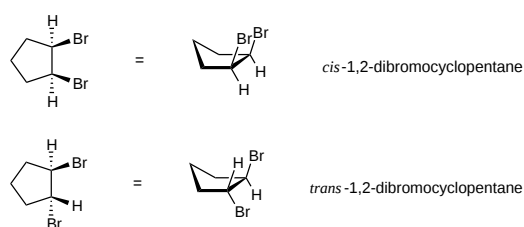
Make certain that you can define, and use in context, the key terms below.

- constitutional isomer
- stereoisomer
- *cis-trans* isomers

Previously, constitutional isomers have been defined as molecules that have the same molecular formula, but different atom connectivity. In this section, a new class of isomers, stereoisomers, will be introduced. **Stereoisomers** are molecules that have the same molecular formula, the same atom connectivity, but they differ in the relative spatial orientation of the atoms.

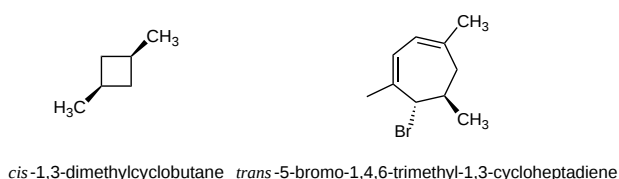
Cycloalkanes are similar to open-chain alkanes in many respects. They both tend to be nonpolar and relatively inert. One important difference, is that cycloalkanes have much less freedom of movement than open-chain alkanes. As discussed in Sections 3.6 and 3.7, open-chain alkanes are capable of rotation around their carbon-carbon sigma bonds. The ringed structures of cycloalkanes prevent such free rotation, causing them to be more rigid and somewhat planar.

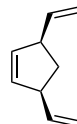
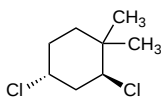
Di-substituted cycloalkanes are one class of molecules that exhibit stereoisomerism. 1,2-dibromocyclopentane can exist as two different stereoisomers: *cis*-1,2-dibromocyclopentane and *trans*-1,2-dibromocyclopentane. The *cis*-1,2-dibromocyclopentane and *trans*-1,2-dibromocyclopentane stereoisomers of 1,2-dibromocyclopentane are shown below. Both molecules have the same molecular formula and the same atom connectivity. They differ only in the relative spatial orientation of the two bromines on the ring. In *cis*-1,2-dibromocyclopentane, both bromine atoms are on the same "face" of the cyclopentane ring, while in *trans*-1,2-dibromocyclopentane, the two bromines are on opposite faces of the ring. Stereoisomers require an additional nomenclature prefix be added to the IUPAC name in order to indicate their spatial orientation. Di-substituted cycloalkane stereoisomers are designated by the nomenclature prefixes *cis* (Latin, meaning on this side) and *trans* (Latin, meaning across).



Representing 3D Structures

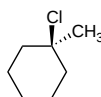
By convention, chemists use heavy, wedge-shaped bonds to indicate a substituent located above the plane of the ring (coming out of the page), a dashed line for bonds to atoms or groups located below the ring (going back into the page), and solid lines for bonds in the plane of the page.





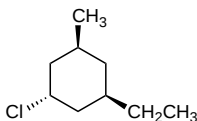
trans-2,4-dichloro-1,1-dimethylcyclohexane *cis*-3,5-divinylcyclopentene

In general, if any two sp^3 carbons in a ring have two different substituent groups (not counting other ring atoms) *cis/trans* stereoisomerism is possible. However, the *cis/trans* designations are not used if both groups are on the same carbon. For example, the chlorine and the methyl group are on the same carbon in 1-chloro-1-methylcyclohexane and the *trans* prefix should not be used.



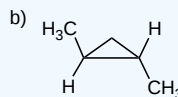
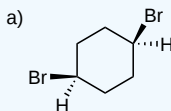
1-chloro-1-methylcyclohexane

If more than two ring carbons have substituents, the stereochemical notation distinguishing the various isomers becomes more complex and the prefixes *cis* and *trans* cannot be used to formally name the molecule. However, the relationship of any two substituents can be informally described using *cis* or *trans*. For example, in the tri-substituted cyclohexane below, the methyl group is *cis* to the ethyl group, and also *trans* to the chlorine. However, the entire molecule cannot be designated as either a *cis* or *trans* isomer. Later sections will describe how to name these more complex molecules ([5.5: Sequence Rules for Specifying Configuration](#))



✓ Example 2.12.1

Name the following cycloalkanes:



Solution

These two examples represent the two main ways of showing spatial orientation in cycloalkanes.

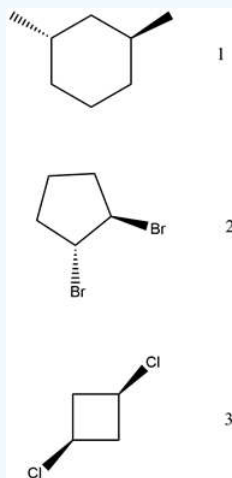
- In example "a" the cycloalkane is shown as being flat and in the plane of the page. The positioning of the substituents is shown by using dash-wedge bonds. *Cis/trans* positioning can be determined by looking at the type of bonds attached to the substituents. If the substituents are both on the same side of the ring (*Cis*) they would both have either dash bonds or wedge bonds. If the substituents are on opposite side of the ring (*Trans*) one substituent would have a dash bond and the other a wedge bond. Because both bromine substituents have a wedge bond they are on the same side of the ring and are *cis*. The name of this molecule is *cis*-1,4-Dibromocyclohexane.
- Example "b" shows the cycloalkane ring roughly perpendicular to the plane of the page. When this is done, the upper and lower face of the ring is defined and each carbon in the ring will have a bond on the upper face and a bond on the lower face. *Cis* substituents will either both be on the upper face or the lower face. *Trans* substituents will have one on the upper face and one on the lower face. In example "b", one of the methyl substituents is on the upper face of the ring and one is on the lower face which makes them *trans* to each other. The name of this molecule is *trans*-1,2-Dimethylcyclopropane.

? Exercise 2.12.2

Draw the following molecules:

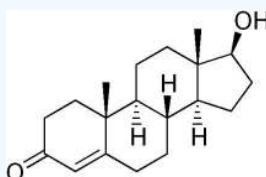
1. *trans*-1,3-dimethylcyclohexane
2. *trans*-1,2-dibromocyclopentane
3. *cis*-1,3-dichlorocyclobutane

Answer



? Exercise 2.12.3

Cis/Trans nomenclature can be used to describe the relative positioning of substituents on molecules with more complex ring structures. The molecule below is testosterone, 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?

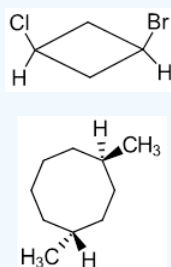


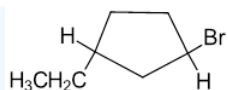
Answer

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 2.12.4

Name the following compounds:





Answer

Cis-1-Bromo-3-Chlorocyclobutane

Trans-1,4-Dimethylcyclooctane

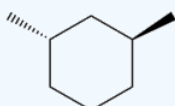
Trans-1-Bromo-3-ethylcyclopentane

? Exercise 2.12.5

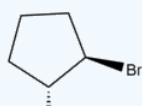
Draw the following molecules:

- trans*-1,3-dimethylcyclohexane
- trans*-1,2-dibromocyclopentane
- cis*-1,3-dichlorocyclobutane

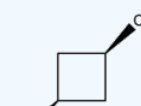
Answer



1



2



3

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- 4.2: Cis-Trans Isomerism in Cycloalkanes by Dietmar Kennepohl, Kelly Matthews, Krista Cunningham, Steven Farmer is licensed [CC BY-SA 4.0](#).

2.13: Conformations of Cyclohexane

Objectives

After completing this section, you should be able to

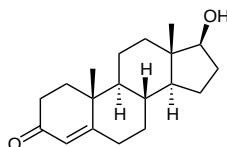
1. explain why cyclohexane rings are free of angular strain.
2. draw the structure of a cyclohexane ring in the chair conformation.

Key Terms

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

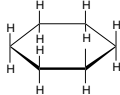
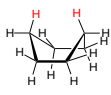
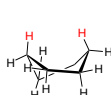
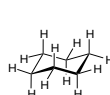
- chair conformation
- twist-boat conformation

We will find that cyclohexanes tend to have the least angle strain and consequently are the most common cycloalkanes found in nature. A wide variety of compounds including, hormones, pharmaceuticals, and flavoring agents have substituted cyclohexane rings.



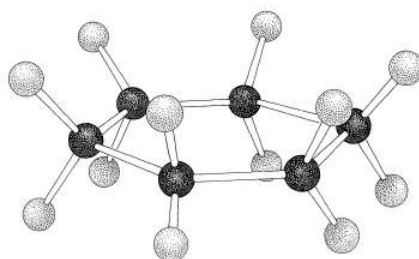
testosterone, which contains three cyclohexane rings and one cyclopentane ring

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). Cyclohexane has the possibility of forming multiple conformations each of which have structural differences which lead to different amounts of ring strain.

 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
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Conformations of Cyclohexane

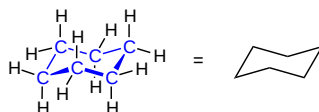
A planar structure for cyclohexane is clearly improbable. The bond angles would necessarily be 120° , 10.5° larger than the ideal tetrahedral angle. Also, every carbon-hydrogen bond in such a structure would be eclipsed. The resulting angle and eclipsing strains would severely destabilize this structure. The ring strain of planar cyclohexane is in excess of 84 kJ/mol so it rarely discussed other than in theory.



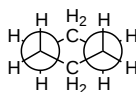
Cyclohexane in the strained planar configuration showing how the hydrogens become eclipsed.

Chair Conformation of Cyclohexane

The flexibility of cyclohexane allows for a conformation which is almost free of ring strain. If two carbon atoms on opposite sides of the six-membered ring are bent out of the plane of the ring, a shape is formed that resembles a reclining beach chair. This **chair conformation** is the lowest energy conformation for cyclohexane with an overall ring strain of 0 kJ/mol. In this conformation, the carbon-carbon ring bonds are able to assume bonding angles of $\sim 111^\circ$ which is very near the optimal tetrahedral 109.5° so angle strain has been eliminated.

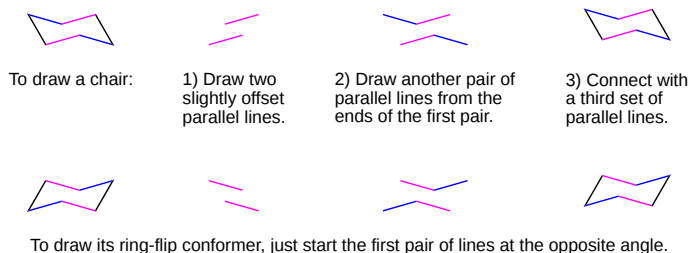


Also, the C-H ring bonds are staggered so torsional strain has also been eliminated. This is clearly seen when looking at a Newman projection of chair cyclohexane sighted down the two central C-C bonds.



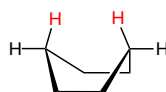
Newman projection of cyclohexane

How to Draw the Chair Conformation



Boat Conformation of Cyclohexane

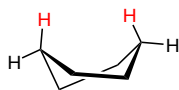
The **Boat Conformation** of cyclohexane is created when two carbon atoms on opposite sides of the six-membered ring are both lifted up out of the plane of the ring creating a shape which slightly resembles a boat. The boat conformation is less stable than the chair form for two major reasons. The boat conformation has unfavorable steric interactions between a pair of 1,4 hydrogens (the so-called "flagpole" hydrogens) that are forced to be very close together ($1.83\text{\AA}$). This steric hindrance creates a repulsion energy of about 12 kJ/mol. An additional cause of the higher energy of the boat conformation is that adjacent hydrogen atoms on the 'bottom of the boat' are forced into eclipsed positions. For these reasons, the boat conformation about 30 kJ/mol less stable than the chair conformation.



A boat structure of cyclohexane (the interfering "flagpole" hydrogens are shown in red)

Twist-Boat Conformation of Cyclohexane

The boat form is quite flexible and by twisting it at the bottom created the **twist-boat conformer**. This conformation reduces the strain which characterized the boat conformer. The flagpole hydrogens move farther apart (the carbons they are attached to are shifted in opposite directions, one forward and one back) and the eight hydrogens along the sides become largely but not completely staggered. Though more stable than the boat conformation, the twist-boat (sometimes skew-boat) conformation is roughly 23 kJ/mol less stable than the chair conformation.



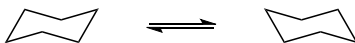
A twist-boat structure of cyclohexane

Half Chair Conformation of Cyclohexane

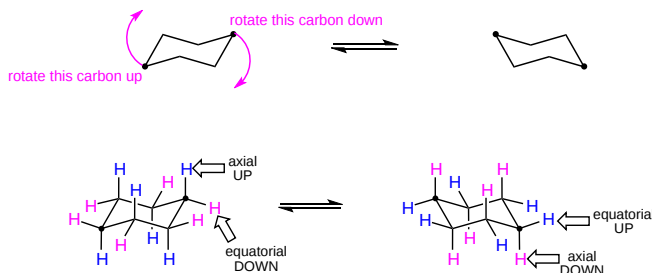
Cyclohexane can obtain a partially plane conformation called "half chair" but with only with excessive amounts of ring strain. The half chair conformation is formed by taking planar cyclohexane and lifting one carbon out of the plane of the ring. The half chair conformation has much of the same strain effects predicted by the fully planar cyclohexane. In the planar portion of half chair cyclohexane the C-C bond angles are forced to 120° which creates significant amounts of angle strain. Also, the corresponding C-H bonds are fully eclipsed which create torsional strain. The out-of-plane carbon allows for some of the ring's bond angles to reach 109.5° and for some of C-H bonds to not be fully eclipsed. Overall, the half chair conformation is roughly 45 kJ/mol less stable than the chair conformation.

Conformation Changes in Cyclohexane - "Ring Flips"

Cyclohexane is rapidly rotating between the two most stable conformations known as the chair conformations in what is called the "ring flip" shown below. The importance of the ring flip will be discussed in the next section.



"Ring flip" describes the rapid equilibrium of cyclohexane rings between the two chair conformations



It is important to note that one chair does not immediately become the other chair, rather the ring must travel through the higher energy conformations as transitions. At room temperature the energy barrier created by the half chair conformation is easily overcome allowing for equilibration between the two chair conformation on the order of 80,000 times per second. Although cyclohexane is continually converting between these different conformations, the stability of the chair conformation causes it to comprises more than 99.9% of the equilibrium mixture at room temperature.

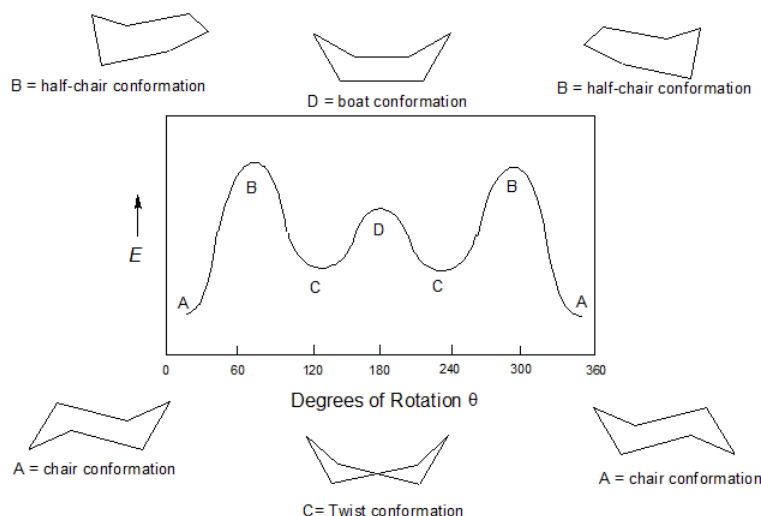


Image of energy diagram of cyclohexane conformations

Exercises

1) Consider the conformations of cyclohexane: half chair, chair, boat, twist boat. Order them in increasing ring strain in the molecule.

Solutions

1) Chair < Twist Boat < Boat < half chair (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)

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- 4.5: Conformations of Cyclohexane by Dietmar Kennepohl, Krista Cunningham, Layne Morsch, Robert Bruner, Steven Farmer, William Reusch is licensed [CC BY-SA 4.0](#).

2.14: Axial and Equatorial Bonds in Cyclohexane

Objectives

After completing this section, you should be able to

1. Draw the chair conformation 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.

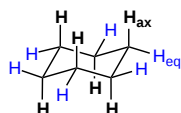
Key Terms

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

- axial position
- equatorial position
- ring flip

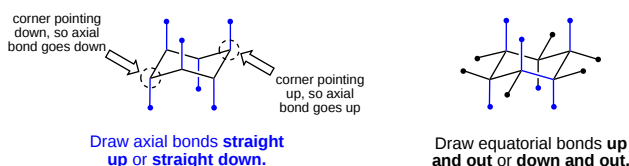
Axial and Equatorial Positions in Cyclohexane

Careful examination of the chair conformation of cyclohexane, shows 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.

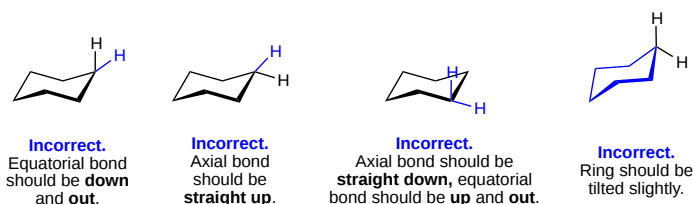


In the figure above, the equatorial hydrogens are colored blue, and the axial hydrogens are black. Since there are two equivalent chair conformations of cyclohexane in rapid equilibrium, all twelve hydrogens have 50% equatorial and 50% axial character.

How To Draw Axial and Equatorial Bonds



How **not** to draw the chair:



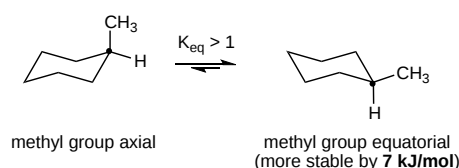
Aside from drawing the basic chair, the key points are:

- Axial bonds alternate up and down, and are shown "vertical".
- Equatorial groups are approximately horizontal, but actually somewhat distorted from that (slightly up or slightly down), so that the angle from the axial group is a bit more than a right angle -- reflecting the common 109.5° bond angle.
- Each carbon has an axial and an equatorial bond.
- Each face of the cyclohexane ring has three axial and three equatorial bonds.

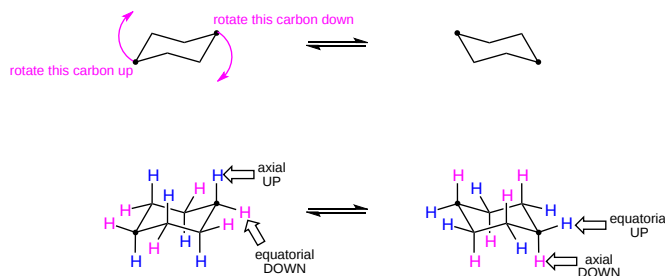
- Each face alternates between axial and equatorial bonds. Then looking at the "up" bond on each carbon in the cyclohexane ring they will alternate axial-equatorial-axial ect.
- When looking down at a cyclohexane ring:
 - the equatorial bonds will form an "equator" around the ring.
 - The axial bonds will either face towards you or away. These will alternate with each axial bond. The first axial bond will be coming towards with the next going away. There will be three of each type.
- Note! The terms cis and trans in regards to the stereochemistry of a ring are not directly linked to the terms axial and equatorial. It is very common to confuse the two. It typically best not to try and directly inter convert the two naming systems.

Axial vs. Equatorial Substituents

When a substituent is added to cyclohexane, the ring flip allows for two distinctly different conformations. One will have the substituent in the axial position while the other will have the substituent in the equatorial position. In the next section will discuss the energy differences between these two possible conformations. Below are the two possible chair conformations of methylcyclohexane created by a ring-flip. Although the conformation which places the methyl group in the equatorial position is more stable by 7 kJ/mol, the energy provided by ambient temperature allows the two conformations to rapidly interconvert.

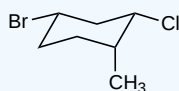


The figure below illustrates how to convert a molecular model of cyclohexane between two different chair conformations - this is something that you should practice with models. Notice that a 'ring flip' causes equatorial groups to become axial, and vice-versa.



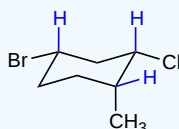
✓ Example 2.14.1

For the following please indicate if the substituents are in the axial or equatorial positions.



Solution

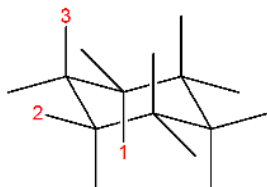
Due to the large number of bonds in cyclohexane it is common to only draw in the relevant ones (leaving off the hydrogens unless they are involved in a reaction or are important for analysis). It is still possible to determine axial and equatorial positioning with some thought. With problems such as this it is important to remember that each carbon in a cyclohexane ring has one axial and one equatorial bond. Also, remember that axial bonds are perpendicular with the ring and appear to be going either straight up or straight down. Equatorial bonds will be roughly in the plane of the cyclohexane ring (only slightly up or down). Sometimes it is valuable to draw in the additional bonds on the carbons of interest.



With this it can be concluded that the bromine and chlorine substituents are attached in equatorial positions and the CH_3 substituent is attached in an axial position.

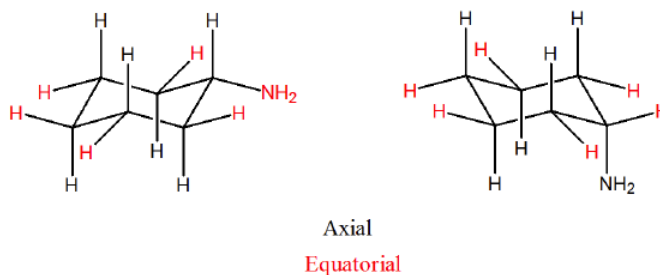
Exercises

- 1) Draw two conformations of cyclohexyl amine ($\text{C}_6\text{H}_{11}\text{NH}_2$). Indicate axial and equatorial positions.
- 2) Draw the two isomers of 1,4-dihydroxycyclohexane, identify which are equatorial and axial.
- 3) In the following molecule, label which are equatorial and which are axial, then draw the chair flip (showing labels 1,2,3).

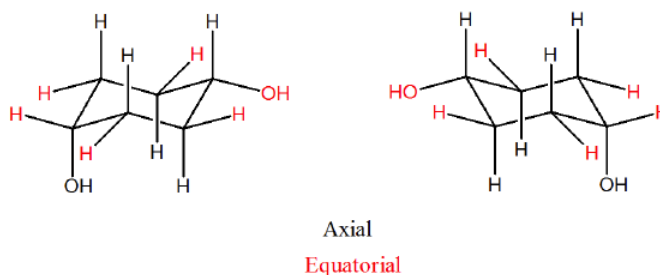


Solutions

1)

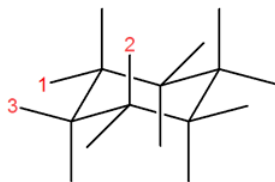


2)



3) Original conformation: 1 = axial, 2 = equatorial, 3 = axial

Flipped chair now looks like this.



Questions

Q4.6.1

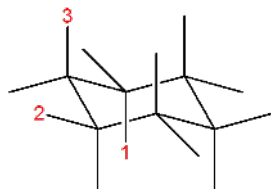
Draw two conformations of cyclohexyl amine ($\text{C}_6\text{H}_{11}\text{NH}_2$). Indicate axial and equatorial positions.

Q4.6.2

Draw the two isomers of 1,4-dihydroxycyclohexane, identify which are equatorial and axial.

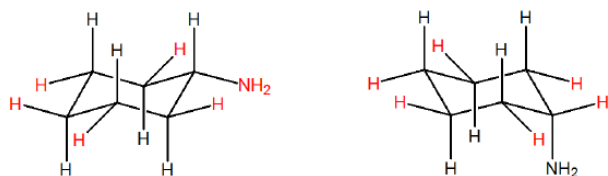
Q4.6.3

In the following molecule, label which are equatorial and which are axial, then draw the chair flip (showing labels 1,2,3).



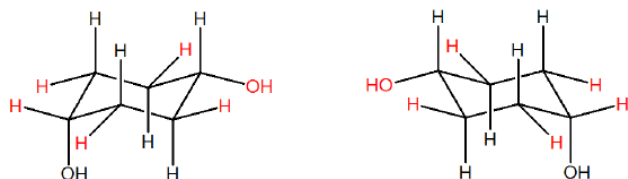
Solutions

S4.6.1



Axial
Equatorial

S4.6.2

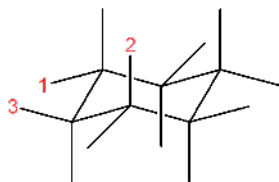


Axial
Equatorial

S4.6.3

Original conformation: 1 = axial, 2 = equatorial, 3 = axial

Flipped chair now looks like this.



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2.15: 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

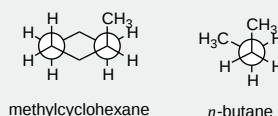
Make certain that you can define, and use in context, the key term below.

- 1,3-diaxial interaction

Study Notes

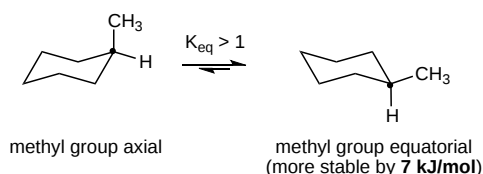
1,3-Diaxial interactions are steric interactions between an axial substituent located on carbon atom 1 of a cyclohexane ring and the hydrogen atoms (or other substituents) located on carbon atoms 3 and 5.

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.

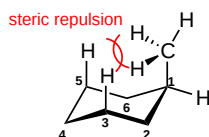


Newman projections of methylcyclohexane and *n*-butane

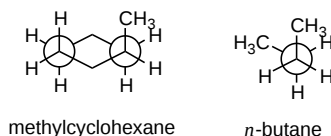
When a substituent is added to a cyclohexane ring, the two possible chair conformations created during a ring flip are not equally stable. In the example of methylcyclohexane the conformation where the methyl group is in the equatorial position is more stable than the axial conformation by 7.6 kJ/mol at 25° C. The percentages of the two different conformations at equilibrium can be determined by solving the following equation for *K* (the equilibrium constant): $\Delta E = -RT \ln K$. In this equation ΔE is the energy difference between the two conformations, *R* is the gas constant (8.314 J/mol•K), *T* is the temperature in Kelvin, and *K* is the equilibrium constant for the ring flip conversion. Using this equation, we can calculate a *K* value of 21 which means about 95% methylcyclohexane molecules have the methyl group in the equatorial position at 25° C.



The energy difference between the two conformations comes from strain, called 1,3-diaxial interactions, created when the axial methyl group experiences steric crowding with the two axial hydrogens located on the same side of the cyclohexane ring. Because axial bonds are parallel to each other, substituents larger than hydrogen experience greater steric crowding when they are oriented axial rather than equatorial. Consequently, **substituted cyclohexanes will preferentially adopt conformations in which the larger substituents are in the equatorial orientation**. When the methyl group is in the equatorial position this strain is not present which makes the equatorial conformer more stable and favored in the ring flip equilibrium.



Actually, 1,3-diaxial steric strain is directly related to the steric strain created in the gauche conformer of butane discussed in Section: 3-7. When butane is in the gauche conformation 3.8 kJ/mol of strain was created due the steric crowding of two methyl group with a 60° dihedral angle. When looking at the a Newman projection of axial methylcyclohexane the methyl group is at a 60° dihedral angle with the ring carbon in the rear. This creates roughly the same amount of steric strain as the gauche conformer of butane. Given that there is actually two such interactions in axial methylcyclohexane, it makes sense that there is $2(3.8 \text{ kJ/mol}) = 7.6 \text{ kJ/mol}$ of steric strain in this conformation. The Newman projection of equatorial methylcyclohexane shows no such interactions and is therefore more stable.



Newman projections of methyl cyclohexane and butane showing similarity of 1,3-diaxial and gauche interactions.

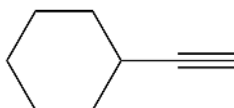
Strain values for other cyclohexane substituents can also be considered. The relative steric hindrance experienced by different substituent groups oriented in an axial versus equatorial location on cyclohexane determined the amount of strain generated. The strain generated can be used to evaluate the 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.

Table 4.7.1: A Selection of ΔG° Values for the Change from Axial to Equatorial Orientation of Substituents for Monosubstituted Cyclohexanes

Substituent	$-\Delta G^\circ$ (kcal/mol)	Substituent	$-\Delta G^\circ$ (kcal/mol)
CH_3-	1.7	$\text{O}_2\text{N}-$	1.1
CH_2H_5-	1.8	$\text{N}\equiv\text{C}-$	0.2
$(\text{CH}_3)_2\text{CH}-$	2.2	$\text{CH}_3\text{O}-$	0.5
$(\text{CH}_3)_3\text{C}-$	≥ 5.0	$\text{HO}_2\text{C}-$	0.7
$\text{F}-$	0.3	$\text{H}_2\text{C}=\text{CH}-$	1.3
$\text{Cl}-$	0.5	C_6H_5-	3.0
$\text{Br}-$	0.5		
$\text{I}-$	0.5		

Exercises

1) In the molecule, cyclohexyl ethyne there is little steric strain, why?



2) Calculate the energy difference between the axial and equatorial conformations of bromocyclohexane?

3) Using your answer from Question 2) estimate the percentages of axial and equatorial conformations of bromocyclohexane at 25°C .



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.

Solutions

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.

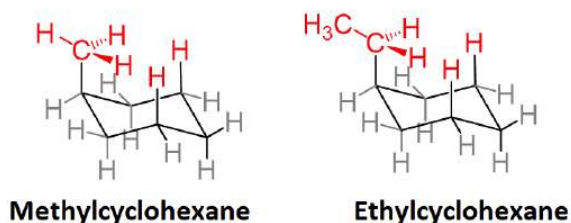


2) The equatorial conformation of bromocyclohexane will have two 1,3 diaxial interactions. The table above states that each interaction accounts for 1.2 kJ/mol of strain. The total strain in equatorial bromocyclohexane will be $2(1.2 \text{ kJ/mol}) = 2.4 \text{ kJ/mol}$.

3) Remembering that the axial conformation is higher in energy, the energy difference between the two conformations is $\Delta E = (E_{\text{equatorial}} - E_{\text{axial}}) = (0 - 2.4 \text{ kJ/mol}) = -2.4 \text{ kJ/mol}$. After converting $^{\circ}\text{C}$ to Kelvin and kJ/mol to J/mol we can use the equation $\Delta E = -RT \ln K$ to find that $-\Delta E/RT = \ln K$ or $(2.4 \times 10^3 \text{ J/mol}) / (8.313 \text{ J/mol K} \cdot 298 \text{ K}) = \ln K$. From this we calculate that $K = 2.6$. Because the ring flip reaction is an equilibrium we can say that $K = [\text{Equatorial}] / [\text{Axial}]$. If assumption is made that $[\text{Equatorial}] = X$ then $[\text{Axial}]$ 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. $2.6 = [X] / [1-X] \rightarrow 2.6 - 2.6X = X \rightarrow 2.6 = 3.6X \rightarrow 2.6/3.6 = X = 0.72$. This means that bromocyclohexane is in the equatorial position 72% of the time and in the axial position 28% of the time.



4) The fact that C-C sigma bonds can freely rotate allows the ethyl substituent 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.



Exercises

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.



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2.16: 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

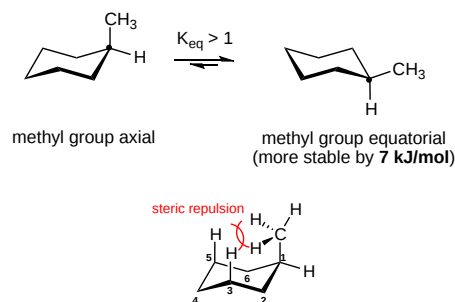
Study Notes

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.



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.

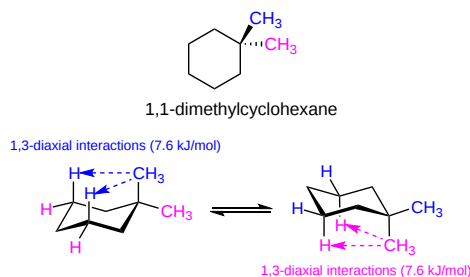
In this section, the effect of conformations on the relative stability of disubstituted cyclohexanes is examined using the two principles:

- Substituents prefer equatorial rather than axial positions in order to minimize the steric strain created of 1,3-diaxial interactions.
- The more stable conformation will place the larger substituent in the equatorial position.

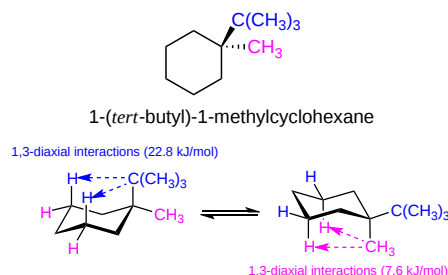
1,1-Disubstituted Cyclohexanes

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.

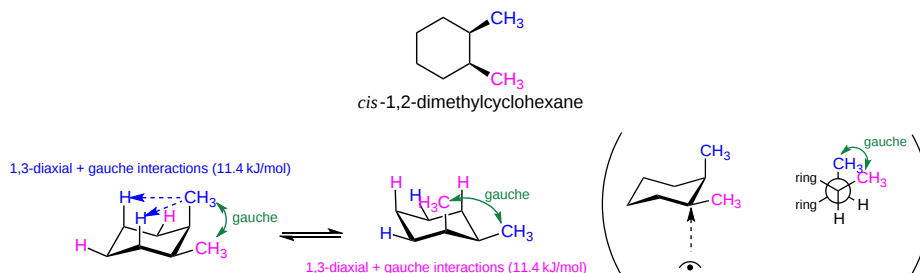


However, if the two groups are different, as in 1-*tert*-butyl-1-methylcyclohexane, then the equilibrium favors the conformer in which the larger group (*tert*-butyl in this case) is in the more stable equatorial position. The energy cost of having one *tert*-butyl group axial (versus equatorial) can 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 than 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.

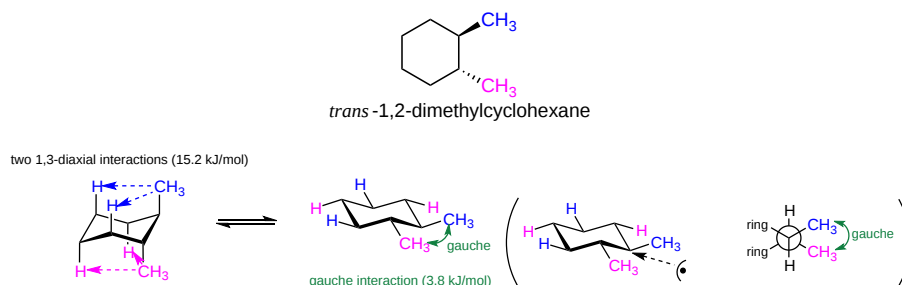


Cis and *trans* stereoisomers of 1,2-dimethylcyclohexane

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.

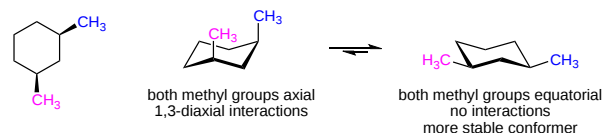


In *trans*-1,2-dimethylcyclohexane, one chair conformer has both methyl groups axial and the other conformer has both methyl groups equatorial. The conformer with both methyl groups equatorial has no 1,3-diaxial interactions however there is still 3.8 kJ/mol of strain created by a gauche interaction. The conformer with both methyl groups axial has four 1,3-Diaxial interactions which creates 2×7.6 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.

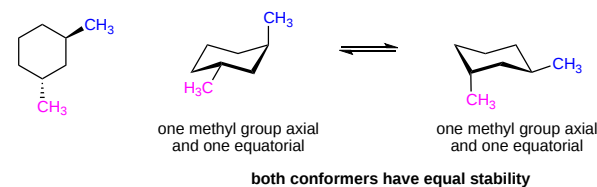


Cis and *trans* stereoisomers of 1,3-dimethylcyclohexane

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 Disubstituted 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.

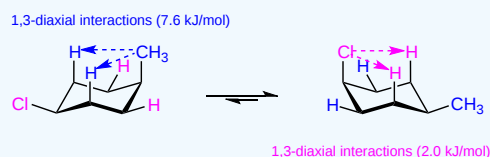
Substitution type	Chair Conformation Relationship
<i>cis</i> -1,2-disubstituted cyclohexanes	AE/EA
<i>trans</i> -1,2-disubstituted cyclohexanes	AA/EE
<i>cis</i> -1,3-disubstituted cyclohexanes	AA/EE
<i>trans</i> -1,3-disubstituted cyclohexanes	AE/EA
<i>cis</i> -1,4-disubstituted cyclohexanes	AE/EA
<i>trans</i> -1,4-disubstituted cyclohexanes	AA/EE

✓ Example 2.16.1

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-disubstituted 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.



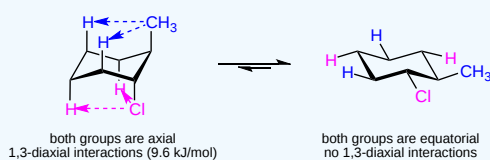
As predicted, each chair conformer places one of the substituents in the axial position. Because the methyl group is larger and has a greater 1,3-diaxial interaction than the chloro, the most stable conformer will place it in the equatorial position, as shown in the structure on the right. Using the 1,3-diaxial energy values given in the previous sections we can calculate that the conformer on the right is $(7.6 \text{ kJ/mol} - 2.0 \text{ kJ/mol})$ 5.6 kJ/mol more stable than the other.

✓ Example 2.16.2

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-disubstituted 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.



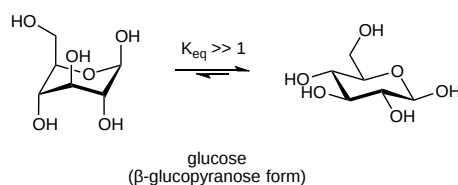
As predicted, one chair conformer places both substituents in the axial position and other places both substituents equatorial. The more stable conformer will place both substituents in the equatorial position, as shown in the structure on the right. Using

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

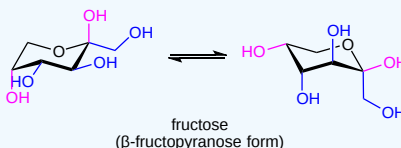
Cyclohexane can have more than two substituents. Also, there are multiple six membered rings which contain atoms other than carbon. All of these systems usually form chair conformations and follow the same steric constraints discussed in this section. Because the most commonly found rings in nature are 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 membered 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-flip chair conformations, one has all of the substituents axial and the other has all the substituents 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.



✓ Example 2.16.3

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?

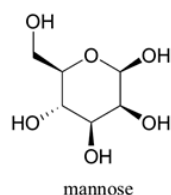


Solution

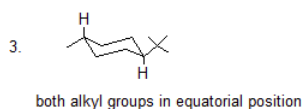
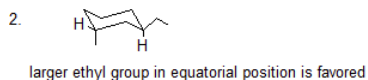
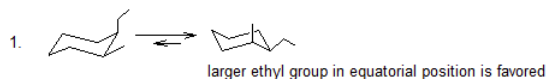
The lower energy chair conformation is the one with three of the five substituents (including the bulky $-\text{CH}_2\text{OH}$ group) in the equatorial position (pictured on the right). The left structure has 3 equatorial substituents while the structure on the right only has two equatorial substituents.

Exercises

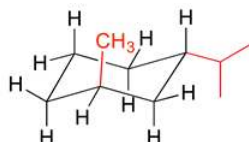
1. Draw the two chair conformations for *cis*-1-ethyl-2-methylcyclohexane using bond-line structures and indicate the more energetically favored conformation.
2. Draw the most stable conformation for *trans*-1-ethyl-3-methylcyclohexane using bond-line structures.
3. Draw the most stable conformation for *trans*-1-*t*-butyl-4-methylcyclohexane using bond-line structures.
4. Draw the most stable conformation for *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.



Solutions



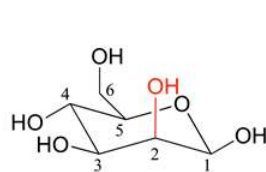
4.



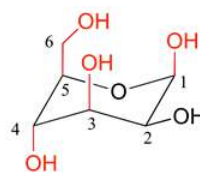
The bulkier isopropyl group is in the equatorial position.

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

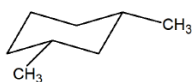
S4.8.1

1 – The most stable conformation would be to have the methyl groups equatorial reducing steric interaction

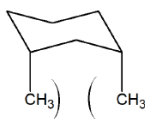
2 – The most stable conformation would be to have the groups equatorial this would reduce the strain if they were axial



1



2



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2.17: Physical Properties of Alkanes

Learning Objectives

- To identify the physical properties of alkanes and describe trends in these properties.

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let's consider their physical properties first.

Table 2.17.1 describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H₂O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table 2.17.1: Physical Properties of Some Alkanes

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH ₄	−182	−164	0.668 g/L	gas
ethane	C ₂ H ₆	−183	−89	1.265 g/L	gas
propane	C ₃ H ₈	−190	−42	1.867 g/L	gas
butane	C ₄ H ₁₀	−138	−1	2.493 g/L	gas
pentane	C ₅ H ₁₂	−130	36	0.626 g/mL	liquid
hexane	C ₆ H ₁₄	−95	69	0.659 g/mL	liquid
octane	C ₈ H ₁₈	−57	125	0.703 g/mL	liquid
decane	C ₁₀ H ₂₂	−30	174	0.730 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.



Figure 2.17.1: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, <http://www.nasa.gov/topics/earth/features/oilspill/oil-20100519a.html>.

Looking Closer: Gas Densities and Fire Hazards

Table 2.17.1 indicates that the first four members of the alkane series are gases at ordinary temperatures. Natural gas is composed chiefly of methane, which has a density of about 0.67 g/L. The density of air is about 1.29 g/L. Because natural gas is less dense than air, it rises. When a natural-gas leak is detected and shut off in a room, the gas can be removed by opening an upper window. On the other hand, bottled gas can be either propane (density 1.88 g/L) or butanes (a mixture of butane and isobutane; density about 2.5 g/L). Both are much heavier than air (density 1.2 g/L). If bottled gas escapes into a building, it collects near the floor. This presents a much more serious fire hazard than a natural-gas leak because it is more difficult to rid the room of the heavier gas.

Also shown in Table 2.17.1 are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

Looking Closer: An Alkane Basis for Properties of Other Compounds

An understanding of the physical properties of the alkanes is important in that petroleum and natural gas and the many products derived from them—gasoline, bottled gas, solvents, plastics, and more—are composed primarily of alkanes. This understanding is also vital because it is the basis for describing the properties of other organic and biological compound families. For example, large portions of the structures of lipids consist of nonpolar alkyl groups. Lipids include the dietary fats and fatlike compounds called [phospholipids](#) and [sphingolipids](#) that serve as structural components of living tissues. These compounds have both polar and nonpolar groups, enabling them to bridge the gap between water-soluble and water-insoluble phases. This characteristic is essential for the selective permeability of cell membranes.

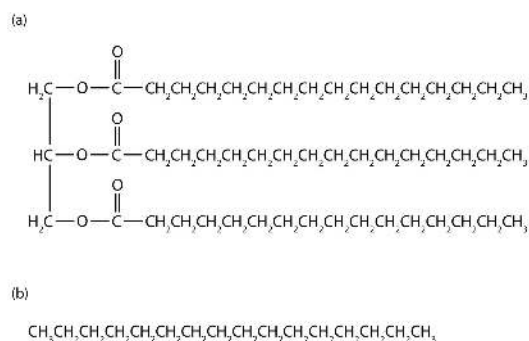


Figure 2.17.2: Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms.

Concept Review Exercises

1. Without referring to a table, predict which has a higher boiling point—hexane or octane. Explain.
2. If 25 mL of hexane were added to 100 mL of water in a beaker, which of the following would you expect to happen? Explain.
 - a. Hexane would dissolve in water.
 - b. Hexane would not dissolve in water and would float on top.
 - c. Hexane would not dissolve in water and would sink to the bottom of the container.

Answers

1. octane because of its greater molar mass
2. b; hexane is insoluble in water and less dense than water.

Key Takeaway

- Alkanes are nonpolar compounds that are low boiling and insoluble in water.

Exercises

- Without referring to a table or other reference, predict which member of each pair has the higher boiling point.
 - pentane or butane
 - heptane or nonane
- For which member of each pair is hexane a good solvent?
 - pentane or water
 - sodium chloride or soybean oil

Answer

- pentane
 - nonane

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2.18: Reactions of Alkanes

Alkanes (the most basic of all organic compounds) undergo very few reactions. The two reactions of more importance are combustion and halogenation, (i.e., substitution of a single hydrogen on the alkane for a single halogen) to form a haloalkane. The halogen reaction is very important in organic chemistry because it opens a gateway to further chemical reactions.

Combustion

Complete combustion (given sufficient oxygen) of any hydrocarbon produces carbon dioxide and water. It is quite important that you can write properly balanced equations for these reactions, because they often come up as a part of thermochemistry calculations. Some are easier than others. For example, with alkanes, the ones with an even number of carbon atoms are marginally harder than those with an odd number!

✓ Example 2.18.1: Propane Combustion

For example, with propane (C_3H_8), you can balance the carbons and hydrogens as you write the equation down. Your first draft would be:



Counting the oxygens leads directly to the final version:



✓ Example 2.18.2: Butane Combustion

With butane (C_4H_{10}), you can again balance the carbons and hydrogens as you write the equation down.



Counting the oxygens leads to a slight problem - with 13 on the right-hand side. The simple trick is to allow yourself to have "six-and-a-half" O_2 molecules on the left.



If that offends you, double everything:



The hydrocarbons become harder to ignite as the molecules get bigger. This is because the bigger molecules don't vaporize so easily - the reaction is much better if the oxygen and the hydrocarbon are well mixed as gases. If the liquid is not very volatile, only those molecules on the surface can react with the oxygen. Bigger molecules have greater Van der Waals attractions which makes it more difficult for them to break away from their neighbors and turn to a gas.

Provided the combustion is complete, all the hydrocarbons will burn with a blue flame. However, combustion tends to be less complete as the number of carbon atoms in the molecules rises. That means that the bigger the hydrocarbon, the more likely you are to get a yellow, smoky flame. Incomplete combustion (where there is not enough oxygen present) can lead to the formation of carbon or carbon monoxide. As a simple way of thinking about it, the hydrogen in the hydrocarbon gets the first chance at the oxygen, and the carbon gets whatever is left over! The presence of glowing carbon particles in a flame turns it yellow, and black carbon is often visible in the smoke. Carbon monoxide is produced as a colorless poisonous gas.

📌 Note: Why carbon monoxide is poisonous

Oxygen is carried around the blood by hemoglobin, which unfortunately binds to exactly the same site on the hemoglobin that oxygen does. The difference is that carbon monoxide binds irreversibly (or very strongly) - making that particular molecule of

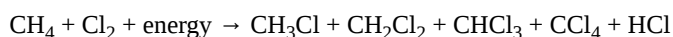
hemoglobin useless for carrying oxygen. If you breath in enough carbon monoxide you will die from a sort of internal suffocation.

Halogenation of Alkanes

Halogenation is the replacement of one or more hydrogen atoms in an organic compound by a halogen (fluorine, chlorine, bromine or iodine). Unlike the complex transformations of combustion, the halogenation of an alkane appears to be a simple **substitution reaction** in which a C-H bond is broken and a new C-X bond is formed. The chlorination of methane, shown below, provides a simple example of this reaction.

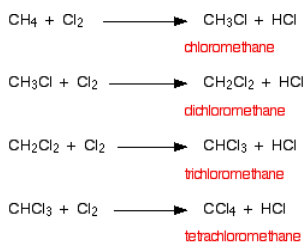


Since only two covalent bonds are broken (C-H & Cl-Cl) and two covalent bonds are formed (C-Cl & H-Cl), this reaction seems to be an ideal case for mechanistic investigation and speculation. However, one complication is that all the hydrogen atoms of an alkane may undergo substitution, resulting in a mixture of products, as shown in the following unbalanced equation. The relative amounts of the various products depend on the proportion of the two reactants used. In the case of methane, a large excess of the hydrocarbon favors formation of methyl chloride as the chief product; whereas, an excess of chlorine favors formation of chloroform and carbon tetrachloride.



In the presence of a flame, the reactions are rather like the fluorine one - producing a mixture of carbon and the hydrogen halide. The violence of the reaction drops considerably as you go from fluorine to chlorine to bromine. The interesting reactions happen in the presence of ultra-violet light (sunlight will do). These are photochemical reactions that happen at room temperature. We'll look at the reactions with chlorine, although the reactions with bromine are similar, but evolve more slowly.

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.

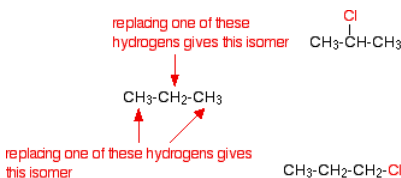


The original mixture of a colorless and a green gas would produce steamy fumes of hydrogen chloride and a mist of organic liquids. All of the organic products are liquid at room temperature with the exception of the chloromethane which is a gas.

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. One would not 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.

Larger alkanes and chlorine

You would again get a mixture of substitution products, but it is worth just looking briefly at what happens if only one of the hydrogen atoms gets substituted (monosubstitution) - just to show that things aren't always as straightforward as they seem! For example, with propane, you could get one of two isomers:



If chance was the only factor, you would expect to get three times as much of the isomer with the chlorine on the end. There are 6 hydrogens that could get replaced on the end carbon atoms compared with only 2 in the middle. In fact, you get about the same amount of each of the two isomers. If you use bromine instead of chlorine, the great majority of the product is where the bromine is attached to the center carbon atom.

Cycloalkanes

The reactions of the cycloalkanes are generally just the same as the alkanes, with the exception of the very small ones - particularly cyclopropane. In the presence of UV light, cyclopropane will undergo substitution reactions with chlorine or bromine just like a non-cyclic alkane. However, it also has the ability to react in the dark. In the absence of UV light, cyclopropane can undergo addition reactions in which the ring is broken. For example, with bromine, cyclopropane gives 1,3-dibromopropane.



This can still happen in the presence of light - but you will get substitution reactions as well. The ring is broken because cyclopropane suffers badly from ring strain. The bond angles in the ring are 60° rather than the normal value of about 109.5° when the carbon makes four single bonds. The overlap between the atomic orbitals in forming the carbon-carbon bonds is less good than it is normally, and there is considerable repulsion between the bonding pairs. The system becomes more stable if the ring is broken.

Contributors and Attributions

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Introduction

$$\text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{heat or light}} \text{CH}_3\text{Cl} + \text{HCl}$$
$$\Delta H = (\text{Energy put into reaction}) - (\text{Energy given off from reaction})$$

The diagram shows Energy on the y-axis and Reaction Coordinate on the x-axis. A solid black curve represents an exothermic reaction, starting at a reactant energy level, rising to a peak, and then falling to a lower product energy level. A dashed red curve represents an endothermic reaction, starting at a reactant energy level, rising to a peak, and then falling to a higher product energy level. Vertical red arrows indicate the enthalpy change (ΔH) for each reaction, with the exothermic ΔH being negative and the endothermic ΔH being positive.

$$\Delta H = \sum \Delta H^\circ \text{ of bonds broken} - \sum \Delta H^\circ \text{ of bonds formed} \quad (2.19.1)$$

Bonds Broken **Bonds Formed**

$\text{CH}_3\text{---}\overset{\text{105}}{\text{H}} + \text{CH}_3\text{---}\overset{\text{58}}{\text{Cl}}$	$\rightarrow$	$\text{CH}_3\text{---}\overset{\text{85}}{\text{Cl}} + \text{H---}\overset{\text{103}}{\text{Cl}}$
---	---------------	--

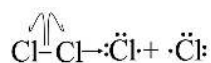
Since, the ΔH for the chlorination of methane is negative, the reaction is exothermic. Energetically this reaction is favorable. In order to better understand this reaction, we need to look at the mechanism (a detailed step by step look at the reaction showing how it occurs) by which the reaction occurs.

Radical Chain Mechanism

The reaction proceeds through the free radical chain mechanism. A free radical is a compound that contains an unpaired valence electron (indicated as a single dot in a Lewis structure). Because of their incomplete octet, **free radicals are very unstable and chemically reactive** (there are a few minor exceptions). Reaction mechanisms involving free radicals are characterized by three steps: **initiation**, **propagation**, and **termination**. Initiation requires an input of energy (usually light or UV radiation) to generate the initial free radical, but after this initial free radical is generated, 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 indefinitely. This is why the mechanism is said to be a "**chain reaction**:" once the initiation step has started, the reaction will continue until the termination step is completed.

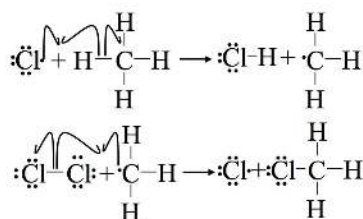
Step 1: Initiation

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. Therefore, the reaction needs some form of energy such as heat or UV radiation to act as a catalyst. 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.

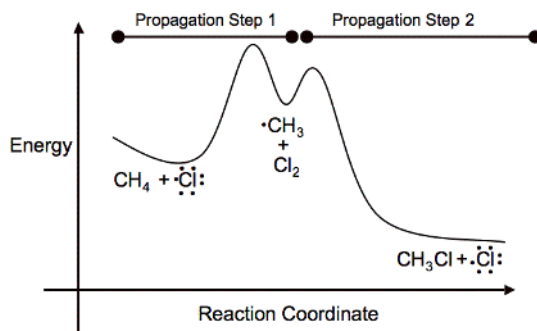


Step 2: Propagation

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.

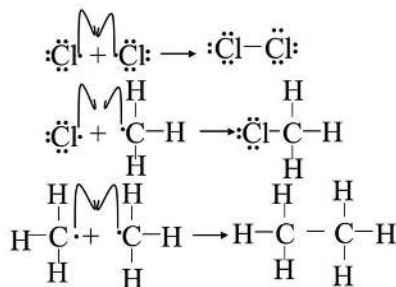


The first propagation step is endothermic, meaning it takes in heat (requires 2 kcal/mol) and is not energetically favorable. In contrast the second propagation step is exothermic, releasing 27 kcal/mol. Once the reaction is initiated, the exothermic energy released from the second propagation step provides the activation energy for the first propagation step creating a cyclic chain reaction following Le Chatelier's principle until termination.



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).



Limitations of the Chlorination

The chlorination of methane or any other alkane 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 or other alkane 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.

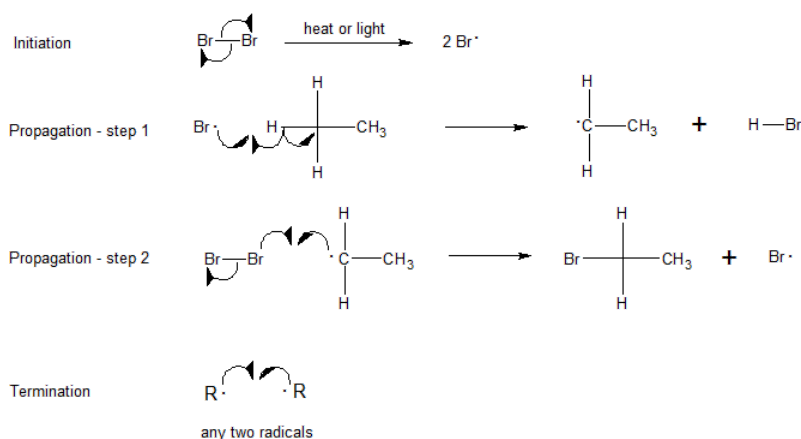
Exercises

1. Compounds other than chlorine and methane can react via free-radical halogenation. Write out the complete mechanism for the monobromination of ethane.
2. Explain how the energetically unfavorable first propagation step can continue to occur without the input of energy from an external source.
3. Which step of the radical chain mechanism requires outside energy? What can be used as this energy?
4. Use the table provided below to calculate the change in enthalpy for the monobromination of ethane.

Compound	Bond Dissociation Energy (kcal/mol)
$\text{CH}_3\text{CH}_2\text{-H}$	101
$\text{CH}_3\text{CH}_2\text{-Br}$	70
H-Br	87
Br_2	46

Solutions

- 1.



2. The exothermic energy released from the second propagation step provides the activation energy for the first propagation step creating a cyclic chain reaction following Le Chatelier's principle until termination.

3. The initiation step requires energy from heat or light. For maximum photoefficiency, the wavelength of light is correlated with bond being homolytically cleaved.

4. $\Delta H = (101 + 46) - (70 + 87) \text{ kcal/mol}$

References

- Matyjaszewski, Krzysztof, Wojciech Jakubowski, Ke Min, Wei Tang, Jinyu Huang, Wade A. Braunecker, and Nicolay V. Tsarevsky. "Diminishing Catalyst Concentration in Atom Transfer Radical Polymerization with Reducing Agents." *Science* 72 (1930): 379-90.
- Phillips, Francis C. "# Researches upon the Chemical Properties of Gases." *Researches upon the Chemical Properties of Gases* 17 (1893): 149-236.

Outside Links

- Video of Mechanism: <http://www.jbpub.com/organic-online/movies/chlormet.htm>
- Wikipedia of Radical Chain Mechanism: en.Wikipedia.org/wiki/Free_radical_halogenation
- Wikipedia of Le Chatelier's Principle: en.Wikipedia.org/wiki/Le_Chatelier%27s_principle#Concentration

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CHAPTER OVERVIEW

3: Unsaturated Hydrocarbons

- 3.1: Alkenes- Structures and Names
- 3.2: Bonding in Ethene
- 3.3: Cis-Trans Isomers (Geometric Isomers)
- 3.4: Physical Properties of Alkenes
- 3.5: Chemical Properties of Alkenes
- 3.6: Alkene Asymmetry and Markovnikov's Rule
- 3.7: Polymerization
- 3.8: Polymerization Mechanism
- 3.9: Alkynes
- 3.10: Bonding in Ethyne
- 3.11: Physical Properties of Alkynes
- 3.12: Chemical properties of Alkynes

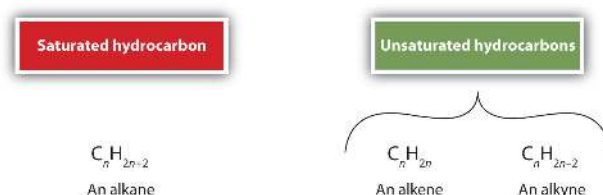
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3.1: Alkenes- Structures and Names

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C=CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds ($R-C\equiv C-R$). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

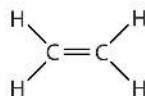


Some representative alkenes—their names, structures, and physical properties—are given in Table 3.1.1.

Table 3.1.1: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2=CH_2$	−169	−104
propene	C_3H_6	$CH_2=CHCH_3$	−185	−47
1-butene	C_4H_8	$CH_2=CHCH_2CH_3$	−185	−6
1-pentene	C_5H_{10}	$CH_2=CH(CH_2)_2CH_3$	−138	30
1-hexene	C_6H_{12}	$CH_2=CH(CH_2)_3CH_3$	−140	63
1-heptene	C_7H_{14}	$CH_2=CH(CH_2)_4CH_3$	−119	94
1-octene	C_8H_{16}	$CH_2=CH(CH_2)_5CH_3$	−102	121

We used only condensed structural formulas in Table 3.1.1. Thus, $CH_2=CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4 , whereas that for ethane is C_2H_6 .

The first two alkenes in Table 3.1.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 3.1.1). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

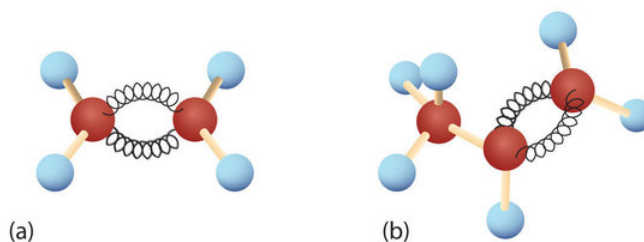
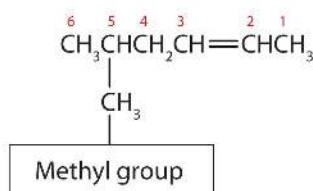


Figure 3.1.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8 .

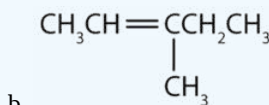
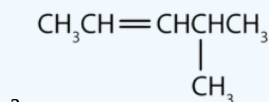
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound $CH_2=CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers. The compound $CH_3CH=CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



✓ Example 3.1.1

Name each compound.

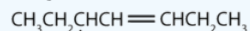
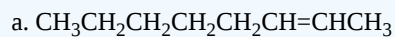


Solution

- a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
- b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

? Exercise 3.1.1

Name each compound.

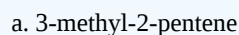


Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

✓ Example 3.1.2

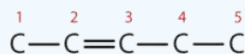
Draw the structure for each compound.



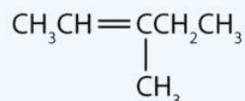
Solution

a.

First write the parent chain of five carbon atoms: $\text{C}-\text{C}-\text{C}-\text{C}-\text{C}$. Then add the double bond between the second and third carbon atoms:

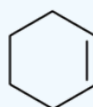


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



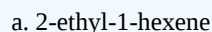
b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



? Exercise 3.1.2

Draw the structure for each compound.



Key Takeaway

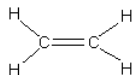
- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

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3.2: Bonding in Ethene

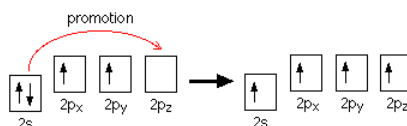
At a simple level, you will have drawn ethene showing two bonds between the carbon atoms. Each line in this diagram represents one pair of shared electrons. Ethene is actually much more interesting than this.



Ethene is built from hydrogen atoms ($1s^1$) and carbon atoms ($1s^2 2s^2 2p_x^1 2p_y^1$). The carbon atom doesn't have enough unpaired electrons to form the required number of bonds, so it needs to promote one of the $2s^2$ pair into the empty $2p_z$ orbital. This is exactly the same as happens whenever carbon forms bonds - whatever else it ends up joined to.

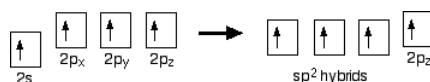
Promotion of an electron

There is only a small energy gap between the $2s$ and $2p$ orbitals, and an electron is promoted from the $2s$ to the empty $2p$ to give 4 unpaired electrons. The extra energy released when these electrons are used for bonding more than compensates for the initial input. The carbon atom is now said to be in an *excited state*.

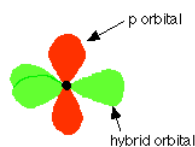


Hybridization

In the case of ethene, there is a difference from, say, methane or ethane, because each carbon is only joining to three other atoms rather than four. When the carbon atoms hybridize their outer orbitals before forming bonds, this time they only hybridize *three* of the orbitals rather than all four. They use the $2s$ electron and two of the $2p$ electrons, but leave the other $2p$ electron unchanged.



The new orbitals formed are called sp^2 hybrids, because they are made by an s orbital and two p orbitals reorganizing themselves. sp^2 orbitals look rather like sp^3 orbitals that you have already come across in the bonding in methane, except that they are shorter and fatter. The three sp^2 hybrid orbitals arrange themselves as far apart as possible - which is at 120° to each other in a plane. The remaining p orbital is at right angles to them.



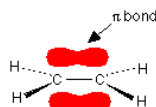
The two carbon atoms and four hydrogen atoms would look like this before they joined together:



The various atomic orbitals which are pointing towards each other now merge to give molecular orbitals, each containing a bonding pair of electrons. These are **sigma bonds** - just like those formed by end-to-end overlap of atomic orbitals in, say, ethane.



The p orbitals on each carbon are not pointing towards each other, and so we'll leave those for a moment. In the diagram, the black dots represent the nuclei of the atoms. Notice that the p orbitals are so close that they are overlapping sideways.



This sideways overlap also creates a molecular orbital, but of a different kind. In this one the electrons aren't held on the line between the two nuclei, but above and below the plane of the molecule. A bond formed in this way is called a π bond.

For clarity, the sigma bonds are shown using lines - each line representing one pair of shared electrons. The various sorts of line show the directions the bonds point in. An ordinary line represents a bond in the plane of the screen (or the paper if you've printed it), a broken line is a bond going back away from you, and a wedge shows a bond coming out towards you.

Be clear about what a π bond is. It is a region of space in which you can find the two electrons which make up the bond. Those two electrons can live anywhere within that space. It would be quite misleading to think of one living in the top and the other in the bottom. The π bond dominates the chemistry of ethene. It is very vulnerable to attack - a very negative region of space above and below the plane of the molecule. It is also somewhat distant from the control of the nuclei and so is a weaker bond than the sigma bond joining the two carbons. All double bonds (whatever atoms they might be joining) will consist of a sigma bond and a pi bond.

The shape of Ethene

The shape of ethene is controlled by the arrangement of the sp^2 orbitals. Notice two things about them:

- They all lie in the same plane, with the other p orbital at right angles to it. When the bonds are made, all of the sigma bonds in the molecule must also lie in the same plane. Any twist in the molecule would mean that the p orbitals wouldn't be parallel and touching any more, and you would be breaking the π bond.

There is no free rotation about a carbon-carbon double bond. Ethene is a planar molecule.

- The sp^2 orbitals are at 120° to each other. When the molecule is constructed, the bond angles will also be 120° . That is approximate though; there will be a slight distortion because you are joining 2 hydrogens and a carbon atom to each carbon, rather than 3 identical groups.

Contributors

Jim Clark (Chemguide.co.uk)

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3.3: Cis-Trans Isomers (Geometric Isomers)

Learning Objectives

- Recognize that alkenes can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure 3.3.1.

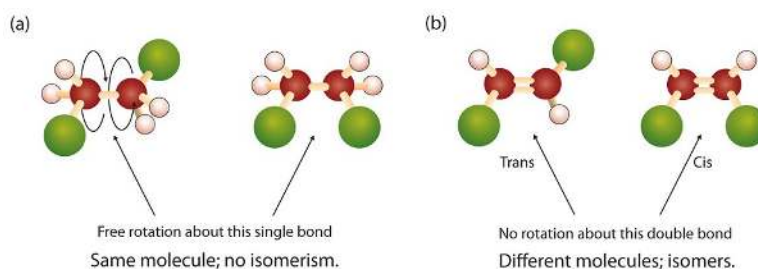


Figure 3.3.1: Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.

In 1,2-dichloroethane (part (a) of Figure 3.3.1), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:



In 1,2-dichloroethene (Figure 3.3.1b), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the *cis* isomer (Latin *cis*, meaning “on this side”) and is named *cis*-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the *trans* isomer (Latin *trans*, meaning “across”) and is named *trans*-1,2-dichloroethene. These two compounds are *cis-trans* isomers (or *geometric isomers*), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $\text{CH}_3\text{CH}=\text{CHCH}_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in *cis-trans* isomerism (Figure 3.3.2).

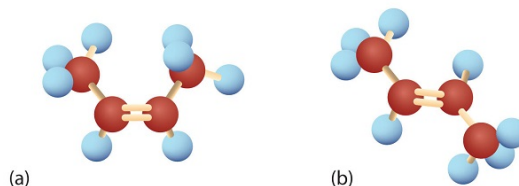


Figure 3.3.2: Ball-and-Spring Models of (a) *Cis*-2-Butene and (b) *Trans*-2-Butene. *Cis-trans* isomers have different physical, chemical, and physiological properties.

Cis-2-butene has both methyl groups on the same side of the molecule. *Trans*-2-butene has the methyl groups on opposite sides of the molecule. Their structural formulas are as follows:

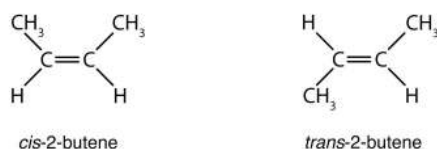


Figure 3.3.3: Models of (left) *Cis*-2-Butene and (right) *Trans*-2-Butene.

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure 3.3.4). We can draw two *seemingly* different propenes:



Figure 3.3.4: Different views of the propene molecule (flip vertically). These are not isomers.

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups on each** doubly bonded carbon atom.

In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $C=CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C=CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type $R-CH=CH-R$ can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

Advanced Note: E/Z Isomerization

If a molecule has a $C=C$ bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature described above is enough to describe it. However, if you have three different groups (or four), then the cis/trans approach is insufficient to describe the different isomers, since we do not know which two of the three groups are being described. For example, if you have a $C=C$ bond, with a methyl group and a bromine on one carbon, and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl. This is addressed with a more advanced [E,Z Convention](#) [E] [E] [E] discussed elsewhere.

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon-carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring.



✓ Example 3.3.1

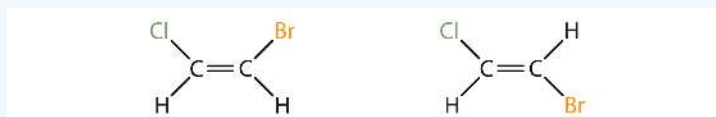
Which compounds can exist as cis-trans (geometric) isomers? Draw them.

1. $\text{CHCl}=\text{CHBr}$
2. $\text{CH}_2=\text{CBrCH}_3$
3. $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_3$
4. $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$

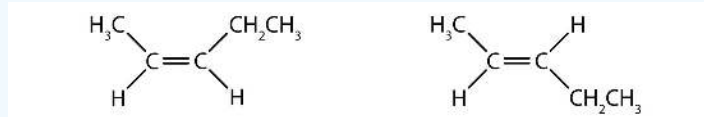
Solution

All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:



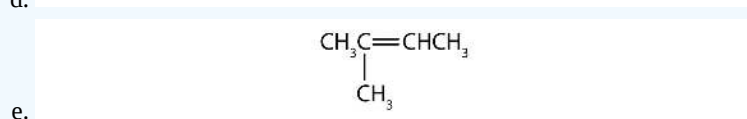
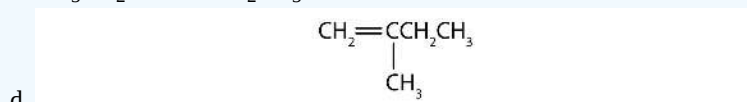
2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl (CH_3) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:



? Exercise 3.3.1

Which compounds can exist as cis-trans isomers? Draw them.

- a. $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$
- b. $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$
- c. $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$



Key Takeaway

- Cis-trans (geometric) isomerism exists when there is restricted rotation in a molecule and there are two nonidentical groups on *each* doubly bonded carbon atom.

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3.4: Physical Properties of Alkenes

Alkenes contain a carbon-carbon double bond. This carbon-carbon double bond changes the physical properties of alkenes. At room temperature, alkenes exist in all three phases, solid, liquids, and gases. Melting and boiling points of alkenes are similar to that of alkanes, however, isomers of cis alkenes have lower melting points than that of trans isomers. Alkenes display a weak dipole-dipole interaction due to the electron-attracting sp^2 carbon.

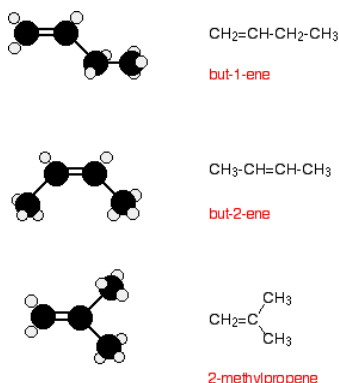
Alkenes are a family of hydrocarbons (compounds containing carbon and hydrogen only) containing a carbon-carbon double bond. The first two are:

- ethene (C_2H_4)
- propene (C_3H_6)

You can work out the formula of any of them using: C_nH_{2n} . The list is limited to the first two, because after that there are isomers which affect the names.

Structural Isomerism

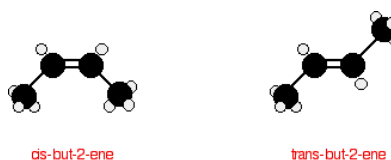
All the alkenes with 4 or more carbon atoms in them show structural isomerism. This means that there are two or more different structural formulae that you can draw for each molecular formula. For example, with C_4H_8 , it isn't too difficult to come up with these three structural isomers:



There is, however, another isomer. But-2-ene also exhibits geometric isomerism.

Geometric (cis-trans) Isomerism

The carbon-carbon double bond doesn't allow any rotation about it. That means that it is possible to have the CH_3 groups on either end of the molecule locked either on one side of the molecule or opposite each other. These are called cis-but-2-ene (where the groups are on the same side) or trans-but-2-ene (where they are on opposite sides).



Cis-but-2-ene is also known as (Z)-but-2-ene; trans-but-2-ene is also known as (E)-but-2-ene. For an explanation of the two ways of naming these two compounds.

Physical state

Ethene, Propene, and Butene exist as colorless gases. Members of the 5 or more carbons such as Pentene, Hexene, and Heptene are liquids, and members of the 15 carbons or more are solids.

Density

Alkenes are lighter than water and are insoluble in water due to their non-polar characteristics. Alkenes are only soluble in nonpolar solvents.

Solubility

Alkenes are virtually insoluble in water, but dissolve in organic solvents. The reasons for this are exactly the same as for the alkanes.

Boiling Points

The boiling point of each alkene is very similar to that of the alkane with the same number of carbon atoms. Ethene, propene and the various butenes are gases at room temperature. All the rest that you are likely to come across are liquids. Boiling points of alkenes depends on more molecular mass (chain length). The more intermolecular mass is added, the higher the boiling point. Intermolecular forces of alkenes gets stronger with increase in the size of the molecules.

Table 1: *Meting Points and Boiling Points of common Alkenes*

Compound	Melting Points (°C)	Boiling points (°C)
Ethene	-169	-104
Propene	-185	-47
Trans-2-Butene	-105.5	0.9
Cis-2-butene	-138.9	3.7
Trans 1,2-dichlorobutene		155
Cis 1,2-dichlorobutene		152
1-Pentene	-165	30
Trans-2-Pentene	-135	36
Cis-2-Pentene	-180	37
1-Heptene	-119	115
3-Octene	-101.9	122
3-Nonene	-81.4	147
5-Decene	-66.3	170

In each case, the alkene has a boiling point which is a small number of degrees lower than the corresponding alkane. The only attractions involved are Van der Waals dispersion forces, and these depend on the shape of the molecule and the number of electrons it contains. Each alkene has 2 fewer electrons than the alkane with the same number of carbons.

Melting Points

Melting points of alkenes depends on the packaging of the molecules. Alkenes have similar melting points to that of alkanes, however, in cis isomers molecules are package in a U-bending shape, therefore, will display a lower melting points to that of the trans isomers.

Polarity

Chemical structure and functional groups can affect the polarity of alkenes compounds. The sp^2 carbon is much more electron-withdrawing than the sp^3 hybridized orbitals, therefore, creates a weak dipole along the substituent weak alkenyl carbon bond. The two individual dipoles together form a net molecular dipole. In trans-substituted alkenes, the dipole cancel each other out. In cis-substituted alkenes there is a net dipole, therefore contributing to higher boiling in cis-isomers than trans-isomers.

References

1. Vollhardt, K. P.C. & Shore, N. (2007). Organic Chemistry (5th Ed.). New York: W. H. Freeman (453-454)
2. Vollhardt, K. P.C. & Shore, N (2007) Organic Chemistry: Study Guide and Solution Manual (5th Ed.). New York: W.H Freeman (200-202)

Problems

1. Compound containing carbon-carbon double bonds are called:

- (a) Alkanes
- (b) Alkynes
- (c) Alkenes
- (d) Alcohols

2. Cis-alkenes exhibit a weak net dipole-dipole interactions:

- True
- False

3. Which has a lower melting point

- (a) 5-Decene
- (b) 3-Octene
- (c) cis-2-Pentene
- (d) 1-Pentene

Contributors

- Trung Nguyen
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3.5: Chemical Properties of Alkenes

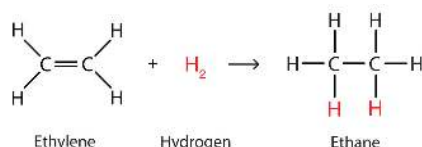
Skills to Develop

- To write equations for the addition reactions of alkenes with hydrogen, halogens, and water

Contrary to alkanes, alkenes are very reactive. Alkenes are valued mainly for **addition reactions**, in which one of the bonds in the double bond is broken. Each of the carbon atoms in the bond can then attach another atom or group while remaining joined to each other by a single bond.

Hydrogenation

Perhaps the simplest addition reaction is hydrogenation—a reaction with hydrogen (H_2) in the presence of a catalyst such as nickel (Ni) or platinum (Pt).



The product is an alkane having the same carbon skeleton as the alkene.

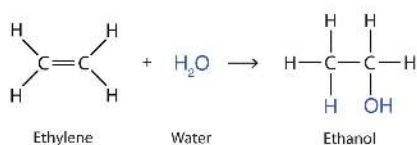
Halogenation

Alkenes also readily undergo halogenation—the addition of halogens. Indeed, the reaction with bromine (Br_2) can be used to test for alkenes. Bromine solutions are brownish red. When we add a Br_2 solution to an alkene, the color of the solution disappears because the alkene reacts with the bromine:



Hydration

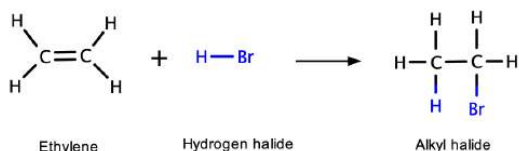
Another important addition reaction is that between an alkene and water to form an alcohol. This reaction, called hydration, requires a catalyst—usually a strong acid, such as sulfuric acid (H_2SO_4):



The hydration reaction is discussed later, where we deal with this reaction in the synthesis of alcohols.

Addition of hydrogen halides (HX)

Alkenes can also react with a hydricid (HX, where X = F, Cl, Br or I) to produce an alkyl halide (halogen-substituted alkane)



Example 3.5.1

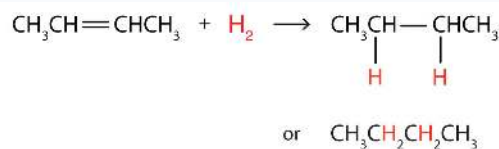
Write the equation for the reaction between $\text{CH}_3\text{CH}=\text{CHCH}_3$ and each substance.

- H_2 (Ni catalyst)
- Br_2
- H_2O (H_2SO_4 catalyst)

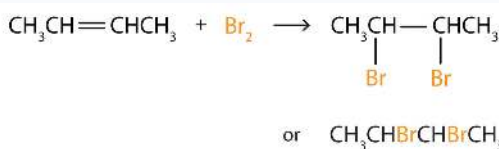
SOLUTION

In each reaction, the reagent adds across the double bond.

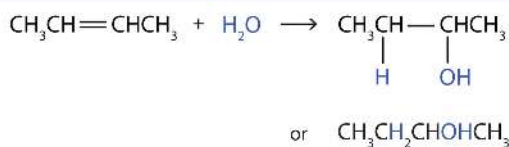
a.



b.



c.



Exercise 3.5.1

Write the equation for each reaction.

- $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ with H_2 (Ni catalyst)
- $\text{CH}_3\text{CH}=\text{CH}_2$ with Cl_2
- $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$ with H_2O (H_2SO_4 catalyst)

Concept Review Exercises

- What is the principal difference in properties between alkenes and alkanes? How are they alike?
- If $\text{C}_{12}\text{H}_{24}$ reacts with HBr in an addition reaction, what is the molecular formula of the product?

Answers

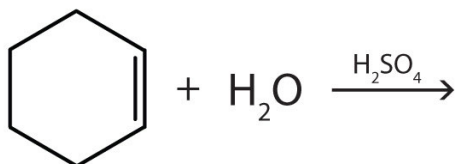
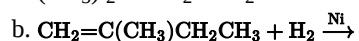
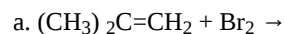
- Alkenes undergo addition reactions; alkanes do not. Both burn.
- $\text{C}_{12}\text{H}_{24}\text{Br}_2$

Key Takeaway

- Alkenes undergo addition reactions, adding such substances as hydrogen, bromine, and water across the carbon-to-carbon double bond.

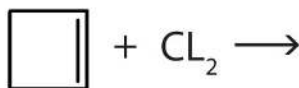
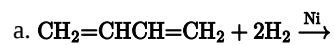
Exercises

1. Complete each equation.



c.

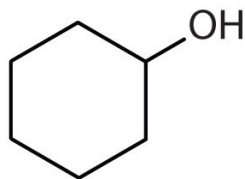
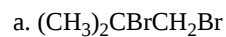
2. Complete each equation.



c.

Answer

1.



c.

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3.6: Alkene Asymmetry and Markovnikov's Rule

Learning Objective

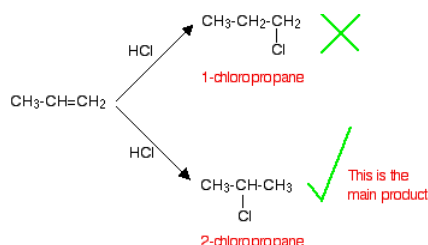
- predict the products/specify the reagents for EAR of hydrohalic acids (HX) with asymmetrical alkenes using Markovnikov's Rule for Regioselectivity
- apply the principles of regioselectivity and stereoselectivity to the addition reactions of alkenes

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 of asymmetric reactants, such as H_2O and HX , across the double bond.

Markovnikov's Rule

If an asymmetric reactant, such as 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 according to Markovnikov's Rule.



Markovnikov's Rule: When an symmetric reactant is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already.

Applying Markovnikov's Rule to the reaction above, the hydrogen bonds with 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.

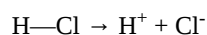
This type of reaction is called **regioselective**, because the breaking of the double bond favors one direction over another, resulting in a specific isomer as the major product (2-chloropropane is obtained with a larger yield compared to 1-chloropropane, instead of the expected 50:50 mixture between these two possible products)

Markovnikov's Rule - a closer look

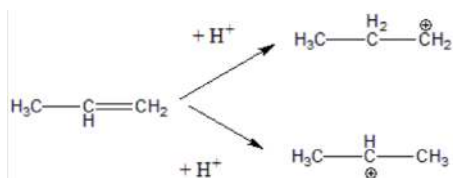
To understand the bases of Markovnikov's Rule, we need to consider the reaction mechanism for the addition of HX or water to the double bond. A **reaction mechanism** is the step-by-step sequence of elementary reactions by which overall chemical change occurs.

The mechanism for this reaction consists of three steps

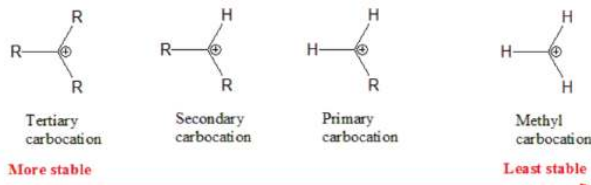
Step 1. The acid HX dissociates into H^+ and X^-



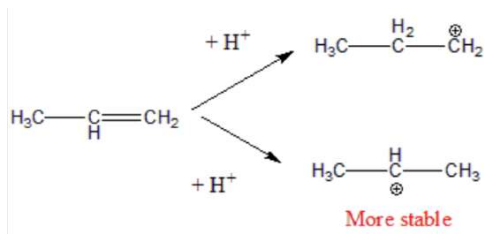
Step 2. The H^+ (an electrophile) to the double bond (a nucleophile). This generates a carbon atom with a positive charge known as a **carbocation**. Two possible carbocation intermediates can be formed from propene:



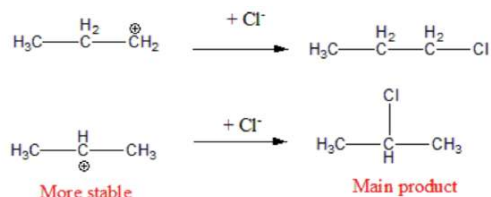
Not all carbocations have the same stability. The stability order for carbocation decreases as shown:



Therefore, during this second step, the formation of a secondary carbocation is favored (more stable than the primary carbocation):



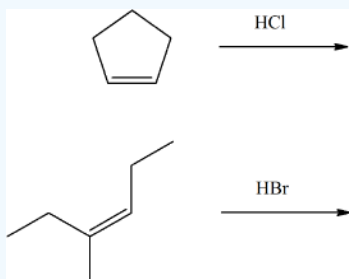
Step 3. The carbocation is very reactive intermediate, and it combines with the halide X^- anion forming the final addition product. The major product derives from the most stable carbocation.



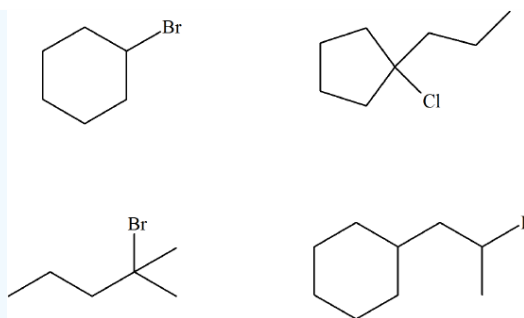
Preferred formation of the most stable carbocation intermediate is the basis for Markovnikov's Rule and the regioselectivity of this reaction. Remember that something very similar occurs with the addition of H_2O in the presence of an acid catalyst. In this case, the acid catalyst is responsible for initiation step 1 in the mechanism.

Exercises

1. Predict the product(s) for the following reactions:

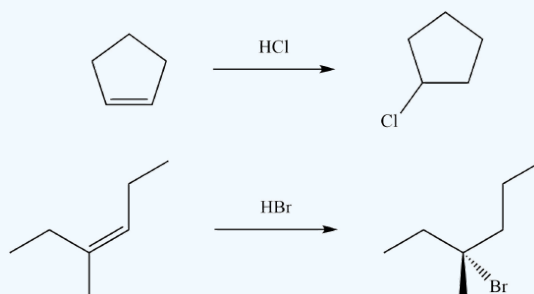


2. In each case, suggest an alkene that would give the product shown.

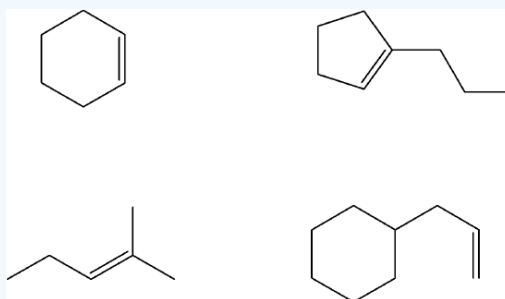


Answers

1.



2.



Citations, Contributors and Attributions

Alkene Asymmetry and Markovnikov's Rule. (2020, May 30). Retrieved May 20, 2021, from <https://chem.libretexts.org/@go/page/110139>

Wikipedia contributors. (2021, January 2). Regioselectivity. In *Wikipedia, The Free Encyclopedia*. Retrieved 16:14, May 20, 2021, from <https://en.wikipedia.org/w/index.php?title=Regioselectivity&oldid=997903090>

Wikipedia contributors. (2021, March 14). Reaction mechanism. In *Wikipedia, The Free Encyclopedia*. Retrieved 16:14, May 20, 2021, from https://en.wikipedia.org/w/index.php?title=Reaction_mechanism&oldid=1012125264

Wikipedia contributors. (2021, January 7). Markovnikov's rule. In *Wikipedia, The Free Encyclopedia*. Retrieved 16:15, May 20, 2021, from https://en.wikipedia.org/w/index.php?title=Markovnikov%27s_rule&oldid=998882337

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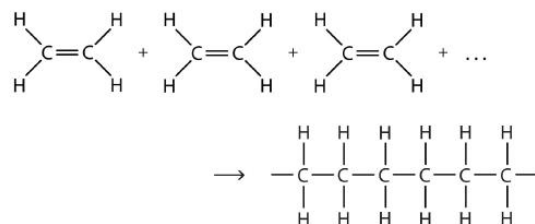
3.7: Polymerization

Learning Objectives

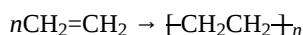
- To draw structures for monomers that can undergo addition polymerization and for four-monomer-unit sections of an addition polymer.

The most important commercial reactions of alkenes are *polymerizations*, reactions in which small molecules, referred to in general as monomers (from the Greek *monos*, meaning “one,” and *meros*, meaning “parts”), are assembled into giant molecules referred to as polymers (from the Greek *poly*, meaning “many,” and *meros*, meaning “parts”). A polymer is as different from its monomer as a long strand of spaghetti is from a tiny speck of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene—a gas.

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers. Ethylene molecules are joined together in long chains. The polymerization can be represented by the reaction of a few monomer units:



The bond lines extending at the ends in the formula of the product indicate that the structure extends for many units in each direction. Notice that all the atoms—two carbon atoms and four hydrogen atoms—of each monomer molecule are incorporated into the polymer structure. Because displays such as the one above are cumbersome, the polymerization is often abbreviated as follows:



Many natural materials—such as proteins, cellulose and starch, and complex silicate minerals—are polymers. Artificial fibers, films, plastics, semisolid resins, and rubbers are also polymers. More than half the compounds produced by the chemical industry are synthetic polymers.

Some common addition polymers are listed in Table 3.7.1. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table 3.7.1: Some Addition Polymers

Monomer	Polymer	Polymer Name	Some Uses
$\text{CH}_2=\text{CH}_2$	$\sim\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
$\text{CH}_2=\text{CHCH}_3$	$\begin{array}{c} \sim\text{CH}_2\text{CHCH}_2\text{CHCH}_2\text{CH}\sim \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	polypropylene	carpeting, bottles, luggage, exercise clothing
$\text{CH}_2=\text{CHCl}$	$\begin{array}{c} \sim\text{CH}_2\text{CHCH}_2\text{CHCH}_2\text{CH}\sim \\ \quad \quad \\ \text{Cl} \quad \text{Cl} \quad \text{Cl} \end{array}$	polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$\text{CF}_2=\text{CF}_2$	$\sim\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\sim$	polytetrafluoroethylene	nonstick coatings, electrical insulation

Medical Uses of Polymers

An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers.

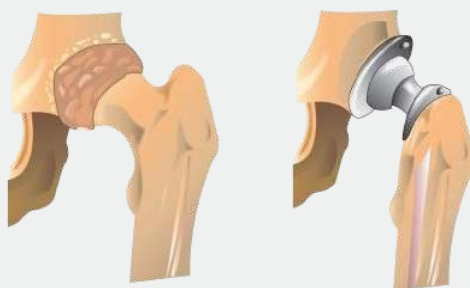


Figure 3.7.1: Hip Joint Replacement. Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup.

Key Takeaway

- Molecules having carbon-to-carbon double bonds can undergo addition polymerization.

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3.8: Polymerization Mechanism

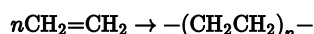
We reap the benefits of using Styrofoam containers, but don't often consider where they end up. Styrofoam materials do not break down quickly under exposure to the elements. When buried in a landfill, styrofoam will remain intact for a long time. The good news is that there is not a lot of this pollutant found in landfills (maybe about **0.5%** by weight of the total mass of garbage). There is no good way to recycle Styrofoam at present, but in the future, a creative scientist may change that.

Polymerization - Addition Polymers

Polymers are very different from the other kinds of organic molecules that you have seen so far. Whereas other compounds are of relatively low molar mass, polymers are giant molecules of very high molar mass. Polymers are the primary components of all sorts of plastics and related compounds. A **polymer** is a large molecule formed of many smaller molecules covalently bonded in a repeating pattern. The small molecules which make up the polymer are called **monomers**. Polymers generally form either from an addition reaction or a condensation reaction.

Addition Polymers

An **addition polymer** is a polymer formed by chain addition reactions between monomers that contain a double bond. Molecules of ethene can polymerize with each other under the right conditions to form the polymer called polyethylene.



The letter ***n*** stands for the number of monomers that are joined in repeated fashion to make the polymer, and can have a value in the hundreds or even thousands.

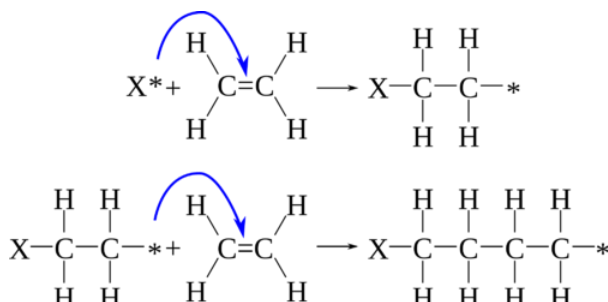


Figure 3.8.1: Polyethylene synthesis.

The reactions above show the basic steps to form an addition polymer:

1. Initiation - a free radical initiator (***X****) attacks the carbon-carbon double bond (first step above). The initiator can be something like hydrogen peroxide. This material can easily split to form two species with a free electron attached to each: **$\text{H}-\text{O}-\text{O}-\text{H} \rightarrow 2\text{H}-\text{O}\cdot$** . This free radical attacks a carbon-carbon double bond. One of the pi electrons forms a single bond with the initiator while the other pi electron forms a new free radical on the carbon atom.
2. Propagation - the new free radical compound interacts with another alkane, continuing the process of chain growth (second step above).
3. Termination occurs whenever two free radicals come in contact with one another (not shown). The two free electrons form a covalent bond and the free radical on each molecule no longer exists.

Polyethylene can have different properties depending on the length of the polymer chains, and on how efficiently they pack together. Some common products made from different forms of polyethylene include plastic bottles, plastic bags, and harder plastic objects such as milk crates.

Several other kinds of unsaturated monomers can be polymerized, and are components in common household products. Polypropylene is stiffer than polyethylene, and is in plastic utensils and some other types of containers.

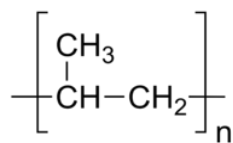


Figure 3.8.2: Polypropylene structure.

Polystyrene is used in insulation and in molded items such as coffee cups.

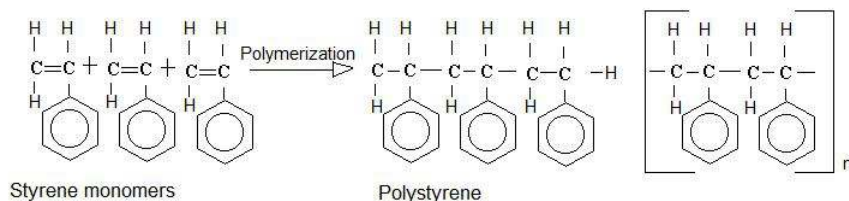


Figure 3.8.3: Polystyrene synthesis and structure.

Polyvinyl chloride (PVC) is extensively used for plumbing pipes.

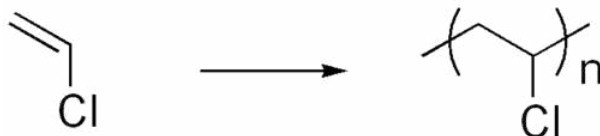


Figure 3.8.4: Polyvinyl chloride.

Polyisoprene is a polymer of isoprene and is better known as rubber. It is produced naturally by rubber trees, but several variants have been developed which demonstrate improvements on the properties of natural rubber.

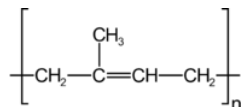


Figure 3.8.5: Polyisoprene.

Summary

- A polymer is a large molecule formed of many smaller molecules covalently bonded in a repeating pattern; they are the primary components of all sorts of plastics and related compounds.
- The small molecules which make up polymers are called monomers.
- Polymers generally form either from an addition reaction or a condensation reaction.
- An addition polymer is a polymer formed by chain addition reactions between monomers that contain a double bond.
- The basic steps to form an addition polymer are: (1) initiation, (2) propagation, (3) termination

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3.9: Alkynes

Learning Objectives

- Describe the general physical and chemical properties of alkynes.
- Name alkynes given formulas and write formulas for alkynes given names.

The simplest alkyne—a hydrocarbon with carbon-to-carbon triple bond—has the molecular formula C_2H_2 and is known by its common name—acetylene (Figure 3.9.1). Its structure is $H-C\equiv C-H$.

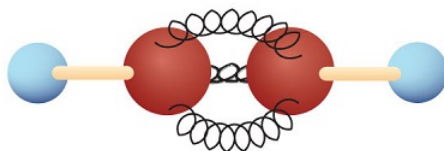


Figure 3.9.1: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Alkynes are similar to alkenes in both physical and chemical properties. For example, alkynes undergo many of the typical addition reactions of alkenes.

Nomenclature

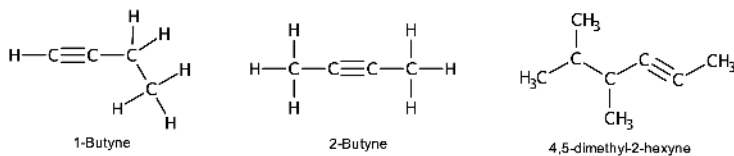
The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *-yne* rather than *-ene*. The IUPAC name for acetylene is ethyne. The names of other alkynes are illustrated in the following exercises.

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.

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.

Examples:



Concept Review Exercises

- Briefly identify the important differences between an alkene and an alkyne. How are they similar?
- The alkene $(CH_3)_2CHCH_2CH=CH_2$ is named 4-methyl-1-pentene. What is the name of $(CH_3)_2CHCH_2C\equiv CH$?
- Do alkynes show cis-trans isomerism? Explain.

Answers

1. Alkenes have double bonds; alkynes have triple bonds. Both undergo addition reactions.
2. 4-methyl-1-pentyne
3. No; a triply bonded carbon atom can form only one other bond. It would have to have two groups attached to show cis-trans isomerism.

Key Takeaway

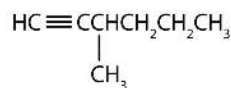
- Alkynes are hydrocarbons with carbon-to-carbon triple bonds and properties much like those of alkenes.

Exercises

1. Draw the structure for each compound.
 - a. acetylene
 - b. 3-methyl-1-hexyne
2. Draw the structure for each compound.
 - a. 4-methyl-2-hexyne
 - b. 3-octyne
3. Name each alkyne.
 - a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$
 - b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3$

Answers

1. a. $\text{H}-\text{C}\equiv\text{C}-\text{H}$



b.

3. a. 1-pentyne
b. 2-hexyne

Attributions and citations

Naming Alkynes. (2021, February 15). Retrieved May 20, 2021, from <https://chem.libretexts.org/@go/page/31481>

Alkynes. (2020, August 17). Retrieved May 20, 2021, from <https://chem.libretexts.org/@go/page/16058>

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3.10: Bonding in Ethyne

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 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 orbital

Study Notes

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

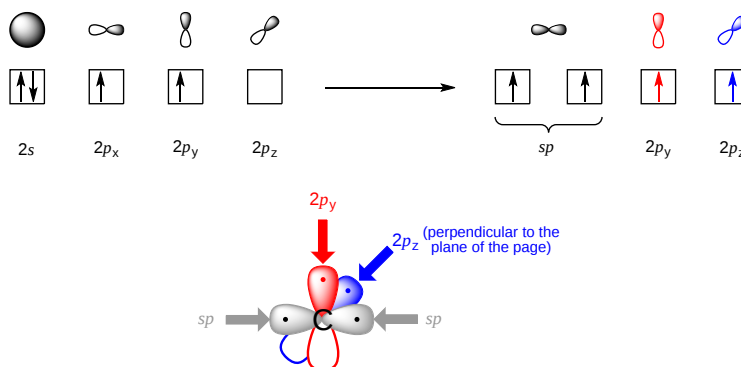
Bonding in acetylene

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



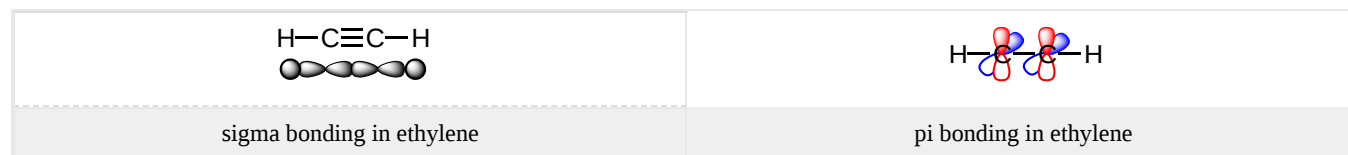
ethyne
(acetylene)

This molecule is linear: all four atoms lie in a straight line. The carbon-carbon triple bond is only $1.20\text{\AA}$ long. In the hybrid orbital picture of acetylene, both carbons are **sp -hybridized**. In an sp -hybridized carbon, the $2s$ 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 non-hybridized, and are oriented perpendicularly along the y and z axes, respectively.

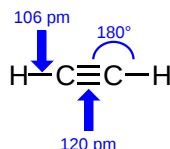


The C-C sigma bond is formed by the overlap of one sp orbital from each of the carbons, while the two C-H sigma bonds are formed by the overlap of the second sp orbital on each carbon with a $1s$ orbital on a hydrogen. Each carbon atom still has two half-

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).



Acetylene is said to have three sigma bonds and two pi bonds. The carbon-carbon triple bond in acetylene is the shortest (120 pm) and the strongest (965 kJ/mol) of the carbon-carbon bond types. Because each carbon in acetylene has two electron groups, VSEPR predicts a linear geometry and an H-C-C bond angle of 180° .

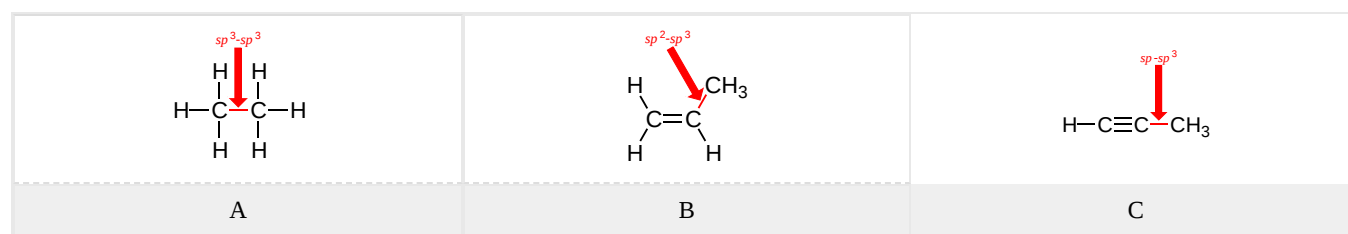


Comparison of C-C bonds Ethane, Ethylene, and Acetylene

Molecule	Bond	Bond Strength (kJ/mol)	Bond Length (pm)
Ethane, CH_3CH_3	$(sp^3)\text{C}-\text{C}(sp^3)$	376	154
Ethylene, $\text{H}_2\text{C}=\text{CH}_2$	$(sp^2)\text{C}=\text{C}(sp^2)$	728	134
Acetylene, $\text{HC}\equiv\text{CH}$	$(sp)\text{C}\equiv\text{C}(sp)$	965	120

Notice that as the bond order increases the bond length decreases and the bond strength increases.

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.



In propene (B), however, the carbon-carbon single bond is the result of overlap between an sp^2 orbital and an sp^3 orbital, while in propyne (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 single 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, $2s$ orbitals are smaller, and hold electrons closer and 'tighter' to the nucleus, compared to $2p$ 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^3 overlap (as in alkane A) are the longest and weakest of the group, because of the 75% ' p ' character of the hybrids.

Hybridization Summary

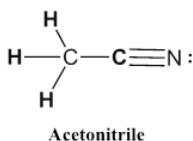
- A single bond is a sigma bond.
- A double bond is made up of a sigma bond and a pi bond.
- A triple bond is made up of a sigma bond and two pi bonds.
- Sigma bonds are made by the overlap of two hybrid orbitals or the overlap of a hybrid orbital and a s orbital from hydrogen.
- Pi bonds are made by 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	$\text{—C}\equiv$	Linear	180°
3	sp^2	$\text{C}=\text{C}$	Trigonal Planar	120°
4	sp^3	C	Tetrahedral	109.5°

Exercises

1) For the molecule acetonitrile:



- How many sigma and pi bonds does it have?
- What orbitals overlap to form the C-H sigma bonds?
- What orbitals overlap to form the C-C sigma bond?
- What orbitals overlap to form the C-N sigma bond?
- What orbitals overlap to form the C-N pi bonds?
- What orbital contains the lone pair electrons on nitrogen?

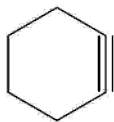
Solutions

- 5 sigma and 2 pi
 - An sp^3 hybrid orbital from carbon and an s orbital from hydrogen.
 - An sp^3 hybrid orbital from one carbon and an sp^3 orbital from the other carbon.
 - An sp hybrid orbital from carbon and an sp orbital from nitrogen.
 - An p_y and p_z orbital from carbon and an p_y and p_z orbital from nitrogen.
 - 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° .

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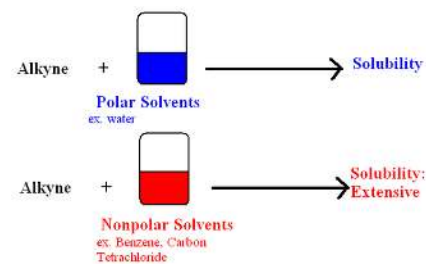
- [1.9: sp Hybrid Orbitals and the Structure of Acetylene](#) by Dietmar Kennepohl, Krista Cunningham, Steven Farmer, Tim Soderberg, William Reusch is licensed [CC BY-SA 4.0](#).

3.11: Physical Properties of Alkynes

The characteristic of the triple bond helps to explain the properties and bonding in the alkynes. Hybridization due to triple bonds allows the uniqueness of alkyne structure. This triple bond contributes to the nonpolar bonding strength, linear, and the acidity of alkynes.

Solubility

Physical Properties include nonpolar due to slight solubility in polar solvents and insoluble in water. This solubility in water and polar solvents is a characteristic feature to alkenes as well. Alkynes dissolve in organic solvents.



Boiling Points

Compared to alkanes and alkenes, alkynes have a slightly higher boiling point. Ethane has a boiling point of $-88.6\text{ }^{\circ}\text{C}$, while Ethene is $-103.7\text{ }^{\circ}\text{C}$ and Ethyne has a higher boiling point of $-84.0\text{ }^{\circ}\text{C}$. That is because the triple bonds concentrate more electron density, making alkynes more polarizable and increasing the intensity of the London Dispersion forces (more polarizable electrons means easier to form temporary dipoles). Increasing the number of carbon atoms results in higher boiling points.

Boiling points for selected compounds	
Compound	Boiling point ($^{\circ}\text{C}$)
Ethane	-88.6
Ethene	-103.7
Ethyne	-84
1-Butyne	8.08

Outside links

- <http://www.ucc.ie/academic/chem/dolc...t/alkynes.html>
- <http://www.cliffsnotes.com/WileyCDA/...eId-22631.html>

References

- Bloch, D.R. Organic chemistry demystified, New York : McGraw-Hill, 2006.
- Vollhardt. Schore, Organic Chemistry Structure and Function Fifth Edition, New York: W.H. Freeman and Company, 2007.

Problems

- What is the carbon-carbon, carbon-hydrogen bond length for alkyne? Is it shorter or longer than alkane and alkene?
- Which is the most acidic and most stable, alkane, alkene, or alkyne? And depends on what?
- How many pi bonds and sigma bonds are involved in the structure of ethyne?

4. Why is the carbon-hydrogen bond so short?
5. What is the alkyne triple bond characterizes by? How is this contribute to the weakness of the pi bonds?
6. How is heat of hydrogenation effects the stability of the alkyne?

Contributors

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3.12: Chemical properties of Alkynes

Objectives

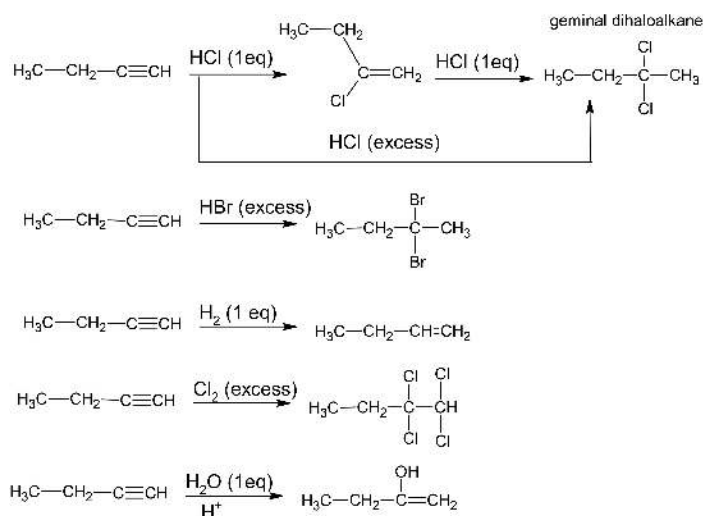
After completing this section, you should be able to

1. explain the reactivity of alkynes based on the known strengths of carbon-carbon single, double and triple bonds.
2. 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).
3. draw the structure of the product formed when an alkyne reacts with one equivalent of the halogens and halogen acids
4. 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.

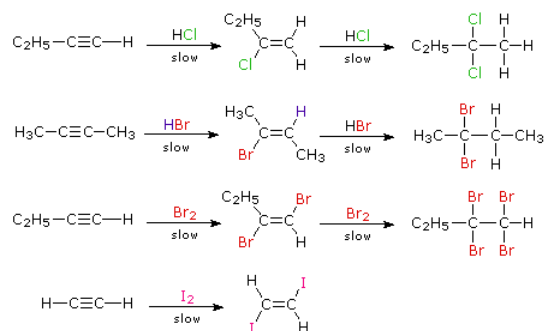
Addition by Electrophilic Reagents

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.

Although these electrophilic additions to alkynes are sluggish, they do take place and generally display **Markovnikov's Rule regioselectivity**. Depending on the proportion of each reactant used, the product can be an alkene or an alkane. Here are a few examples:



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.



Addition of Hydrogen Halide to an Alkyne

Summary: Reactivity order of hydrogen halides: $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

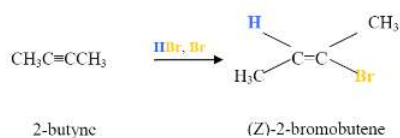
Follows Markovnikov's rule:

- Hydrogen adds to the carbon with the greatest number of hydrogens, the halogen adds to the carbon with fewest hydrogens.
- Protonation 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 HX to an Alkyne

For example, HBr herefore attacks the double bond in 2-butyne to generate 2-bromobutene, as shown below.

Figure 2



Now, what if you have excess HBr? Due to Markovnikov's rule, the addition of HX in excess yields a geminal dihaloalkane

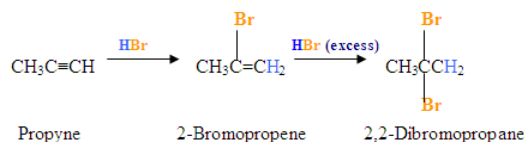
Figure 3



Addition of HX to Terminal Alkyne

- Here is an addition of HBr to an asymmetric molecule. Now, what if you have excess HBr? Due to Markovnikov's rule, the addition of HX in excess yields a geminal dihaloalkane

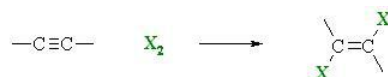
Figure 5



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.

Reaction: Addition of Halogens (Cl_2 , Br_2 , I_2)

Summary:



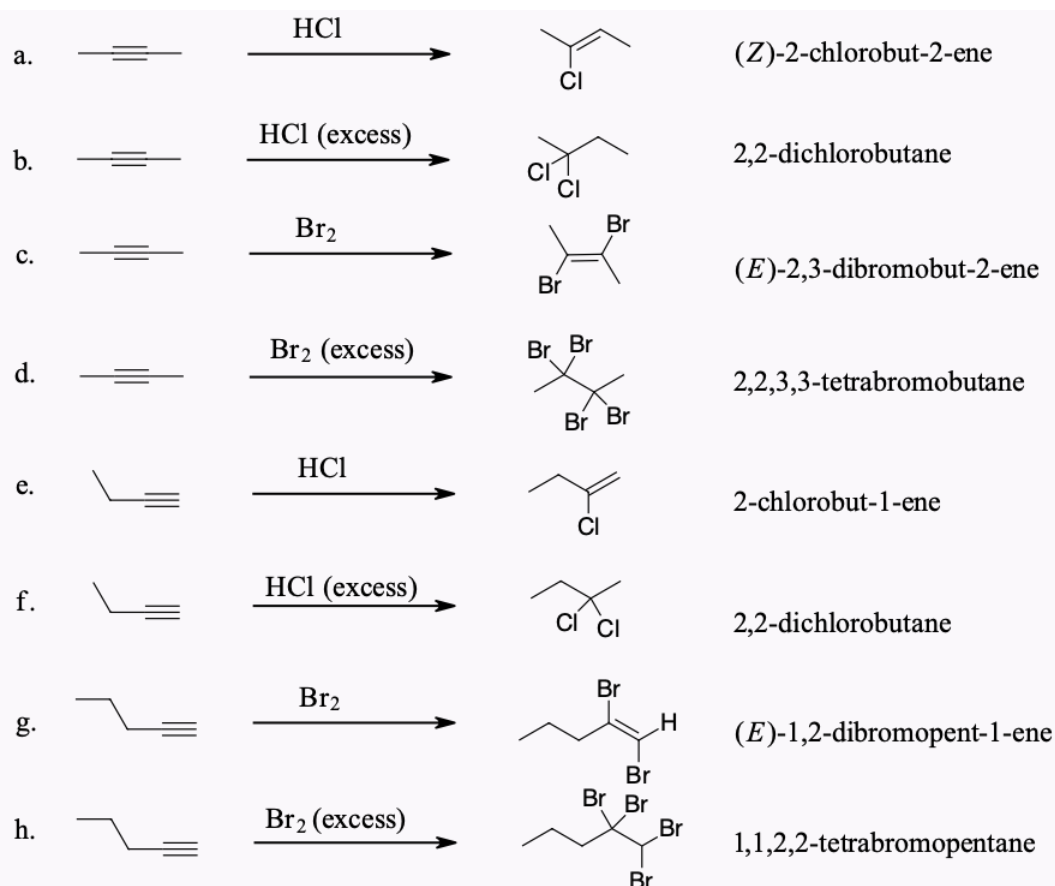
The addition of halogen to an alkyne is analogous to adding to an alkene. The trans-alkene is obtained first. The use of halogen in excess results in a tetrahalogenated alkane.

Exercise 3.12.1

Draw the structure and give the IUPAC name of the product formed in each of the reactions listed below:



Answer



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- Jim Clark ([Chemguide.co.uk](#))
- Layne Morsch (University of Illinois Springfield)

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CHAPTER OVERVIEW

4: Aromatic Compounds (Arenes)

4.1: Aromatic Compounds- Benzene

4.2: Aromaticity

4.3: Bonding and Physical Properties of Arenes

4.4: Nomenclature of Aromatic Compounds

4.5: Polycyclic Aromatics

4.6: Carbon Nanomaterials

4.7: Chemical Properties of Aromatic Compounds

4.8: General Mechanism for Electrophilic Substitution Reactions of Benzene

4.9: Halogenation, Sulfonation, and Nitration of Aromatic Compounds

4.10: Alkylation and Acylation of Aromatic Rings - The Friedel-Crafts Reaction

4.11: Electrophilic Aromatic Substitution Reactions of Benzene Derivatives

4.12: Heterocyclic Aromatic Compounds

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4.1: Aromatic Compounds- Benzene

Learning Objectives

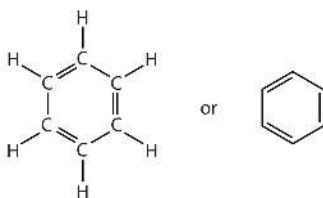
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14} —eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Benzene is a liquid that smells like gasoline, boils at $80^\circ C$, and freezes at $5.5^\circ C$. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

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4.2: Aromaticity

Aromaticity is a property of conjugated cycloalkenes in which the stabilization of the molecule is enhanced due to the ability of the electrons in the π orbitals to delocalize. This act as a framework to create a planar molecule.

Introduction

Why do we care if a compound is aromatic or not? Because we encounter aromatics every single day of our lives. Without aromatic compounds, we would not only be lacking many material necessities, our bodies would also not be able to function. Aromatic compounds are essential in industry; about 35 million tons of aromatic compounds are produced in the world every year to produce important chemicals and polymers, such as polyester and nylon. Aromatic compounds are also vital to the biochemistry of all living things. Three of the twenty [amino acids](#) used to form proteins ("the building blocks of life") are aromatic compounds and all five of the nucleotides that make up [DNA](#) and RNA sequences are all aromatic compounds. Needless to say, aromatic compounds are vital to us in many aspects.

The three general requirements for a compound to be aromatic are:

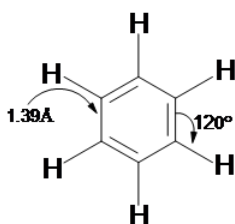
1. The compound must be cyclic
2. Each element within the ring must have a p-orbital that is *perpendicular* to the ring, hence the molecule is planar.
3. The compound must follow Hückel's Rule (the ring has to contain $4n+2$ p-orbital electrons).

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.

Basic Structure of Benzene

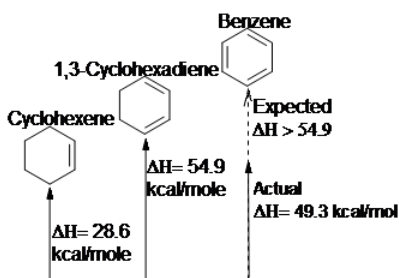


Because of the aromaticity of benzene, the resulting molecule is planar in shape with each C-C bond being 1.39 Å in length and each bond angle being 120° . You might ask yourselves how it's possible to have all of the bonds to be the same length if the ring is conjugated with both single (1.47 Å) and 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.

Evidence of Aromaticity: Heats of Hydrogenation

One of the ways to test the relative amounts of resonance energy in a molecule is to compare the heats of hydrogenation between similar compounds. For instance, if we compare cyclohexene, 1,3-cyclohexadiene, and benzene, we would expect that their heats of hydrogenation will increase since the number of double bonds increases respectively. However, experimental evidence suggests that the actual heat of hydrogenation for benzene is actually 49.3 kcal/mole, making it even more stable than the 1,3-cyclohexadiene even though it has two double bonds, compared to benzene's three double bonds. This characteristic can be attributed to the aromaticity of benzene which delocalizes the electrons of the six pi orbitals.



References

1. P. Schleyer, "Aromaticity (Editorial)", Chemical Reviews, 2001.
2. P. Schleyer, "Introduction: Delocalization-? and ? (Editorial)", Chemical Reviews, 2005.
3. Vollhardt, K. Peter C., and Neil E. Schore. Organic Chemistry: Structure and Function. New York: W.H. Freeman and Company, 2007.

Problems

1. What is the hybridization of each carbon and the overall shape of benzene?
2. What is the resonance energy of benzene?
3. Place the following compounds in order of heats of hydrogenation from smallest to greatest : Benzene, 1,3-Cyclohexadiene, and Cyclohexene.

Answers

1. All six carbons are sp^2 hybridized and the aromaticity of the benzene creates a planar molecule.
2. 29.6 kcal/mol
3. Cyclohexene < Benzene < 1,3-Cyclohexadiene.

Contributors

- Ramie Hosein

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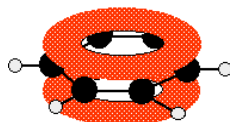
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4.3: Bonding and Physical Properties of Arenes

Arenes are aromatic hydrocarbons. The term "aromatic" originally referred to the pleasant smells given off by arenes, but now implies a particular type of delocalized bonding (see below). The arenes you are likely to encounter at this level are based on benzene rings. The simplest of these arenes is benzene itself, C_6H_6 . The next simplest arene is methylbenzene (common name: toluene), which has one of the hydrogen atoms attached to the ring replaced by a methyl group - $C_6H_5CH_3$.

The structure of Benzene

The structure of benzene is covered in detail on two pages in the organic bonding section of this site. It is important to understand the structure of benzene thoroughly to understand benzene and methylbenzene chemistry. Unless you have read these pages recently, you should spend some time on them now before you go any further on this page.

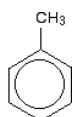


This diagram shows one of the molecular orbitals containing two of the delocalized electrons, which may be found anywhere within the two "doughnuts". The other molecular orbitals are almost never drawn.

- 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.
- The presence of the delocalized electrons makes benzene particularly stable.
- Benzene resists addition reactions because those reactions would involve breaking the delocalization and losing that stability.
- Benzene is represented by this symbol, where the circle represents the delocalized electrons, and each corner of the hexagon has a carbon atom with a hydrogen attached.

The structure of methylbenzene (toluene)

Methylbenzene has a methyl group attached to the benzene ring replacing one of the hydrogen atoms.



Attached groups are often drawn at the top of the ring, but you may occasionally find them drawn in other places with the ring rotated.

Physical properties

Boiling points

In benzene, the only attractions between the neighbouring molecules are the van der Waals dispersion forces. There is no permanent dipole on the molecule. Benzene boils at $80^\circ C$, which is higher than other hydrocarbons of similar molecular size (pentane and hexane, for example). The higher boiling point is presumably due to the ease with which temporary dipoles can be set up involving the delocalized electrons.

Methylbenzene boils at $111^\circ C$. Methylbenzene is a larger molecule, thus, the van der Waals dispersion forces will be increased. Methylbenzene also has a small permanent dipole; thus, there will be dipole-dipole attractions as well as dispersion forces. The dipole is due to the CH_3 group's tendency to "push" electrons away from itself. This also affects the reactivity of methylbenzene (see below).

Melting points

You might have expected that methylbenzene's melting point would be higher than benzene's as well, but it isn't - it is much lower! Benzene melts at 5.5°C; methylbenzene at -95°C.

Molecules must pack efficiently in the solid if they are to optimize their intermolecular forces. Benzene is a tidy, symmetrical molecule and packs very efficiently. The methyl group that protrudes from the methylbenzene structure tends to disrupt the closeness of the packing. If the molecules are not as closely packed, the intermolecular forces don't work as well, causing the melting point to decrease.

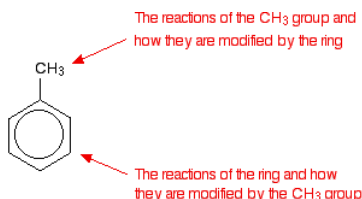
Solubility in water

The arenes are insoluble in water. Benzene is quite large compared with a water molecule. For benzene to dissolve, it would have to break a significant number of the existing hydrogen bonds between the water molecules. In addition, the quite strong van der Waals dispersion forces between the benzene molecules would require breaking; both of these processes require energy. The only new forces between the benzene and the water would be van der Waals dispersion forces. These forces are not as strong as hydrogen bonds (or the original dispersion forces in the benzene), therefore, only a limited amount of energy is released when they form. It simply isn't energetically profitable for benzene to dissolve in water. It would, of course, be even worse for larger arene molecules.

Reactivity

Benzene is resistant to addition reactions. Adding something new to the ring would require that some of the delocalized electrons form bonds with the substituent being added, resulting in a major loss of stability because the delocalization is broken. Instead, benzene primarily undergoes substitution reactions - replacing one or more of the hydrogen atoms with a new substituent, preserving the delocalized electrons as they were.

The reactivity of a compound like methylbenzene must be considered in two distinct parts:



For example, if you explore other pages in this section, you will find that alkyl groups attached to a benzene ring are oxidized by alkaline potassium manganate(VII) solution. This oxidation does not occur in the absence of the benzene ring. The tendency of the CH₃ group to "push" electrons away from itself also has an effect on the ring, making methylbenzene react more quickly than benzene itself. You will find this explored in other pages in this section as well.

Contributors

- Jim Clark (Chemguide.co.uk)

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4.4: Nomenclature of Aromatic Compounds

Learning Objectives

- Recognize aromatic compounds from structural formulas.
- Name aromatic compounds given formulas.
- Write formulas for aromatic compounds given their names.

Historically, benzene-like substances were called aromatic hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table 4.4.1, where the benzene ring is represented as C_6H_5 .

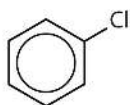
Table 4.4.1: Some Representative Aromatic Compounds

Name	Structure	Typical Uses
aniline	$C_6H_5-NH_2$	starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
benzoic acid	C_6H_5-COOH	food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
bromobenzene	C_6H_5-Br	starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
nitrobenzene	$C_6H_5-NO_2$	starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
phenol	C_6H_5-OH	disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
toluene	$C_6H_5-CH_3$	solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

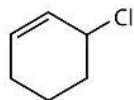
✓ Example 4.4.1

Which compounds are aromatic?

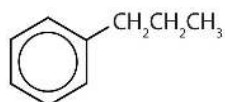
1.



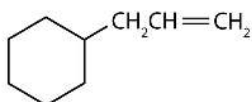
2.



3.



4.



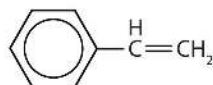
Solution

1. The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen atoms); it is aromatic.
2. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.
3. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic.
4. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.

? Exercise 4.4.1

Which compounds are aromatic?

1.



2.



3.



In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure 4.4.1 shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent.

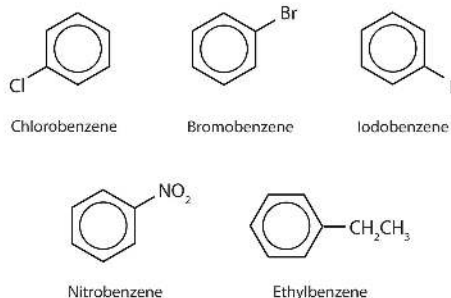
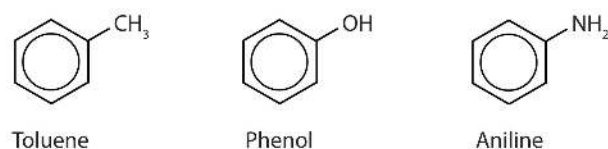


Figure 4.4.1: Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, NO₂ as nitro, and CH₃CH₂ as ethyl.

Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table 4.4.1.



When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure 4.4.2). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path.

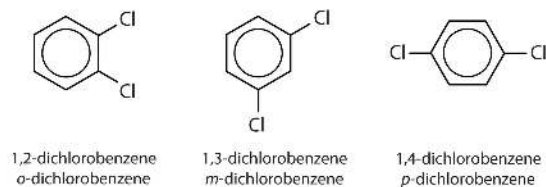
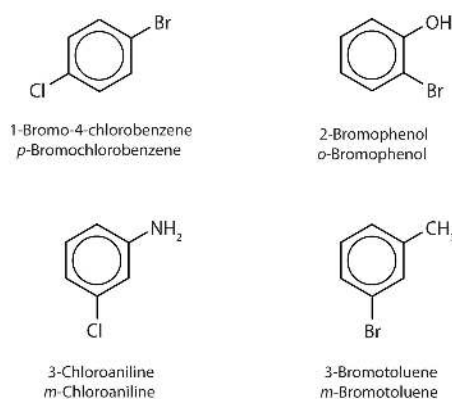


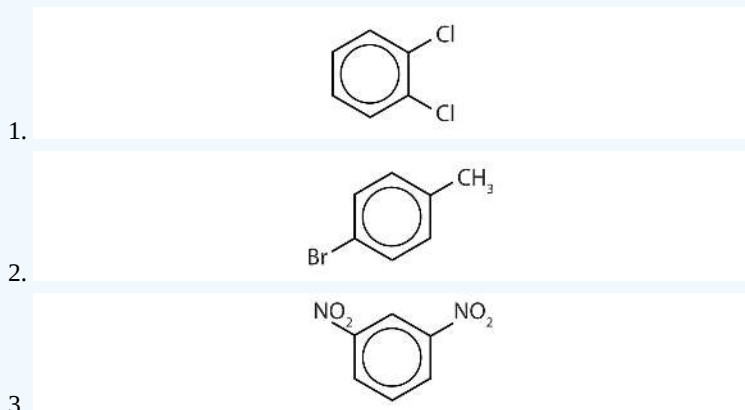
Figure 4.4.2: The Three Isomeric Dichlorobenzenes

In Figure 4.4.2, common names are also used: the prefix *ortho* (*o*-) for 1,2-disubstitution, *meta* (*m*-) for 1,3-disubstitution, and *para* (*p*-) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1:



✓ Example 4.4.2

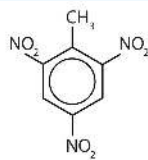
Name each compound using both the common name and the IUPAC name.



Solution

1. The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene or 1,2-dichlorobenzene.
2. The benzene ring has a methyl (CH_3) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.
3. The benzene ring has two nitro (NO_2) groups in the first and third positions. It is *m*-dinitrobenzene or 1,3-dinitrobenzene.

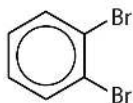
4. Note: The nitro (NO_2) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).



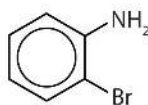
? Exercise 4.4.2

Name each compound using both the common name and the IUPAC name.

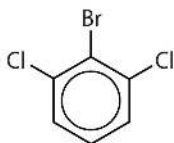
1.



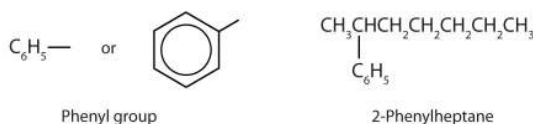
2.



3.



- Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene (C_6H_6) by removing one hydrogen atom (C_6H_5) and is called a *phenyl* group, from *pheno*, an old name for benzene.



Polycyclic Aromatic Hydrocarbons

Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs).



The three examples shown here are colorless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odor and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure.

To Your Health: Polycyclic Aromatic Hydrocarbons and Cancer

The intense heating required for distilling coal tar results in the formation of PAHs. For many years, it has been known that workers in coal-tar refineries are susceptible to a type of skin cancer known as tar cancer. Investigations have shown that a number of PAHs

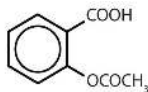
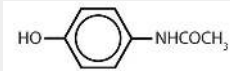
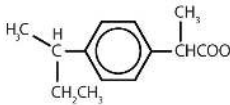
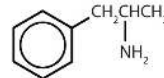
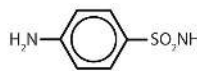
are carcinogens. One of the most active carcinogenic compounds, benzopyrene, occurs in coal tar and has also been isolated from cigarette smoke, automobile exhaust gases, and charcoal-broiled steaks. It is estimated that more than 1,000 t of benzopyrene are emitted into the air over the United States each year. Only a few milligrams of benzopyrene per kilogram of body weight are required to induce cancer in experimental animals.

Biologically Important Compounds with Benzene Rings

Substances containing the benzene ring are common in both animals and plants, although they are more abundant in the latter. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and tryptophan (essential amino acids) and vitamins K, B₂ (riboflavin), and B₉ (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table 4.4.2, also feature a benzene ring.

So far we have studied only aromatic compounds with carbon-containing rings. However, many cyclic compounds have an element other than carbon atoms in the ring. These compounds, called *heterocyclic compounds*, are discussed later. Some of these are heterocyclic aromatic compounds.

Table 4.4.2: Some Drugs That Contain a Benzene Ring

Name	Structure
aspirin	
acetaminophen	
ibuprofen	
amphetamine	
sulfanilamide	

Key Takeaway

- Aromatic compounds contain a benzene ring or have certain benzene-like properties; for our purposes, you can recognize aromatic compounds by the presence of one or more benzene rings in their structure.

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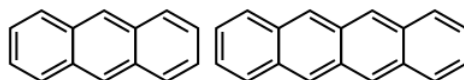
- 13.8: Structure and Nomenclature of Aromatic Compounds by Anonymous is licensed CC BY-NC-SA 3.0. Original source: <https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological>.

4.5: Polycyclic Aromatics

Polycyclic aromatics are compounds containing two or more fused aromatic rings. These fused benzene rings share two carbon atoms between them. These are also called polycyclic benoid or polycyclic aromatic hydrocarbons (PAHs). Many PAHs are carcinogenic and highly toxic.

Naming

The naming system for PAHs is quite complex. A series of fused benzene rings that occur in a linear manner are called acenes.



Anthracene Tetracene

Another form of fusion of benzene rings is angular fusion, or "annulation", which is, as its name implies, an angled fusion of the benzene rings.

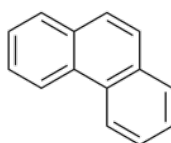


Figure 1: Phenanthrene

Naphthalene

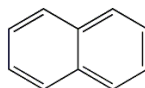


Figure 2: Naphthalene

Naphthalene is the simplest polycyclic aromatic hydrocarbon since it is only a bicyclic molecule made up of two aromatic benzenes. The pi electrons in this molecule are even more delocalized than those in the simpler benzene molecule. Naphthalene is also planar and has $4n + 2$ pi electrons (10) giving it the stabilizing and resonating aromatic properties shared with benzene.

Most Fused Benzenoid Hydrocarbons are aromatic

Aromaticity is a property that the majority of fused benzenoid hydrocarbons share. The extent to which each polycyclic molecule is aromatic varies. As shown above, the structural isomers of anthracene and phenanthrene are very similar molecules made up of three benzene rings. Anthracene is fused linearly, whereas phenanthrene is fused at an angle. This difference in fusions causes the phenanthrene to have five resonance structures which is one more than anthracene. This extra resonance makes the phenanthrene around 6 kcal per mol more stable.

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. "17.10 Polynuclear Aromatic Hydrocarbons." Organic Chemistry. Daley. 5 July 2005. 26 Feb. 2009.

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4.6: Carbon Nanomaterials

Nanomaterials: Fullerenes and Nanotubes

Fullerenes

Carbon-60 (C_{60}) is probably the most studied individual type of nanomaterial. The spherical shape of C_{60} is constructed from twelve pentagons and twenty hexagons and resembles a soccer ball (Figure 4.6.1a). The next stable higher fullerene is C_{70} (Figure 4.6.1b) that is shaped like a rugby or American football. The progression of higher fullerenes continues in the sequence C_{74} , C_{76} , C_{78} , etc. The structural relationship between each involves the addition of six membered rings. Mathematically (and chemically) two principles define the existence of a stable fullerene, i.e., Euler's theorem and isolated pentagon rule (IPR). Euler's theorem states that for the closure of each spherical network, n ($n \geq 2$) hexagons and 12 pentagons are required while the IPR says no two pentagons may be connected directly with each other as destabilization is caused by two adjacent pentagons.

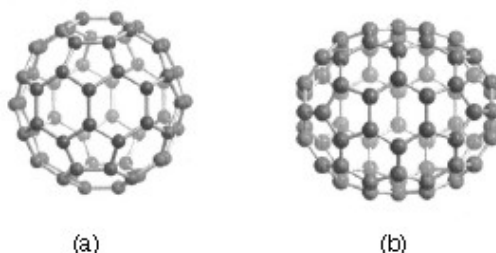


Figure 4.6.1: Molecular structures of (a) C_{60} and (b) C_{70} .

Although fullerenes are composed of sp^2 carbons in a similar manner to graphite, fullerenes are soluble in various common organic solvents. Due to their hydrophobic nature, fullerenes are most soluble in CS_2 ($C_{60} = 7.9$ mg/mL) and toluene ($C_{60} = 2.8$ mg/mL). Although fullerenes have a conjugated system, their aromaticity is distinctive from benzene that has all C-C bonds of equal lengths, in fullerenes two distinct classes of bonds exist. The shorter bonds are at the junctions of two hexagons ([6, 6] bonds) and the longer bonds at the junctions of a hexagon and a pentagon ([5,6] bonds). This difference in bonding is responsible for some of the observed reactivity of fullerenes.

Synthesis of fullerenes

The first observation of fullerenes was in molecular beam experiments at Rice University. Subsequent studies demonstrated that C_{60} it was relatively easy to produce grams of fullerenes. Although the synthesis is relatively straightforward fullerene purification remains a challenge and determines fullerene's commercial price. The first method of production of measurable quantities of fullerenes used laser vaporization of carbon in an inert atmosphere, but this produced microscopic amounts of fullerenes. Laboratory scales of fullerene are prepared by the vaporization of carbon rods in a helium atmosphere. Commercial production ordinarily employs a simple ac or dc arc. The fullerenes in the black soot collected are extracted in toluene and purified by liquid chromatography. The magenta C_{60} comes off the column first, followed by the red C_{70} , and other higher fullerenes. Even though the mechanism of a carbon arc differs from that of a resistively heated carbon rod (because it involves a plasma) the He pressure for optimum C_{60} formation is very similar.

A ratio between the mass of fullerenes and the total mass of carbon soot defines fullerene yield. The yields determined by UV-Vis absorption are approximately 40%, 10-15%, and 15% in laser, electric arc, and solar processes. Interestingly, the laser ablation technique has both the highest yield and the lowest productivity and, therefore, a scale-up to a higher power is costly. Thus, fullerene commercial production is a challenging task. The world's first computer controlled fullerene production plant is now operational at the MER Corporation, who pioneered the first commercial production of fullerene and fullerene products.

Carbon nanotubes

A key breakthrough in carbon nanochemistry came in 1993 with the report of needle-like tubes made exclusively of carbon. This material became known as carbon nanotubes (CNTs). There are several types of nanotubes. The first discovery was of multi walled

tubes (MWNTs) resembling many pipes nested within each other. Shortly after MWNTs were discovered single walled nanotubes (SWNTs) were observed. Single walled tubes resemble a single pipe that is potentially capped at each end. The properties of single walled and multi walled tubes are generally the same, although single walled tubes are believed to have superior mechanical strength and thermal and electrical conductivity; it is also more difficult to manufacture them.

Single walled carbon nanotubes (SWNTs) are by definition fullerene materials. Their structure consists of a graphene sheet rolled into a tube and capped by half a fullerene (Figure 4.6.6). The carbon atoms in a SWNT, like those in a fullerene, are sp^2 hybridized. The structure of a nanotube is analogous to taking this graphene sheet and rolling it into a seamless cylinder. The different types of SWNTs are defined by their diameter and chirality. Most of the presently used single-wall carbon nanotubes have been synthesized by the pulsed laser vaporization method, however, increasingly SWNTs are prepared by vapor liquid solid catalyzed growth.

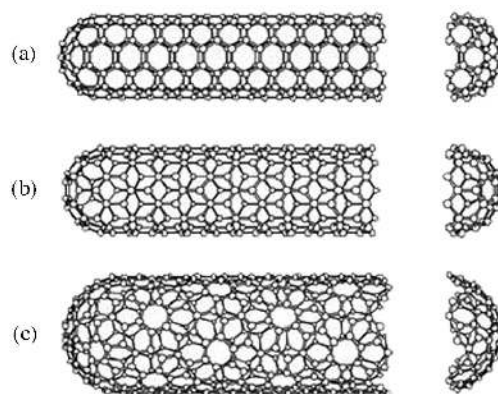


Figure 4.6.6: Structure of single walled carbon nanotubes (SWNTs) with (a) armchair, (b) zig-zag, and (c) chiral chirality.

The physical properties of SWNTs have made them an extremely attractive material for the manufacturing of nano devices. SWNTs have been shown to be stronger than steel as estimates for the Young's modulus approaches 1 Tpa. Their electrical conductance is comparable to copper with anticipate current densities of up to 10^{13} A/cm² and a resistivity as low as 0.34×10^{-4} Ω .cm at room temperatures. Finally, they have a high thermal conductivity (3000 - 6000 W.m/K).

The electronic properties of a particular SWNT structure are based on its chirality or twist in the structure of the tube which is defined by its n,m value. The values of n and m determine the chirality, or "twist" of the nanotube. The chirality in turn affects the conductance of the nanotube, its density, its lattice structure, and other properties. A SWNT is considered metallic if the value $n-m$ is divisible by three. Otherwise, the nanotube is semi-conducting. The external environment also has an effect on the conductance of a tube, thus molecules such as O₂ and NH₃ can change the overall conductance of a tube, while the presence of metals have been shown to significantly effect the opto-electronic properties of SWNTs.

Multi walled carbon nanotubes (MWNTs) range from double walled NTs, through many-walled NTs (Figure 4.6.7) to carbon nanofibers. Carbon nanofibers are the extreme of multi walled tubes (Figure 4.6.8) and they are thicker and longer than either SWNTs or MWNTs, having a cross-sectional of ca. 500 Å² and are between 10 to 100 μ m in length. They have been used extensively in the construction of high strength composites.

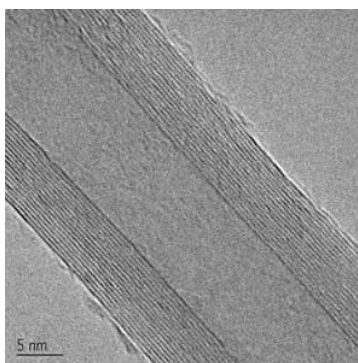


Figure 4.6.7: TEM image of an individual multi walled carbon nanotube (MWNTs). Copyright of Nanotech Innovations.

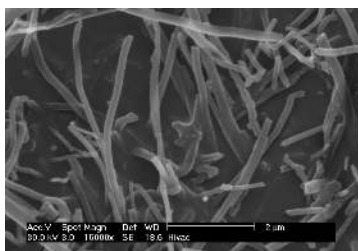


Figure 4.6.8: SEM image of vapor grown carbon nanofibers.

Synthesis of carbon nanotubes

A range of methodologies have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high pressure carbon monoxide (HiPco), and vapor liquid solid (VLS) growth. All these processes take place in vacuum or at low pressure with a process gases, although VLS growth can take place at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making SWNTs more commercially viable.

Chemical functionalization of carbon nanotubes

The limitation of using carbon nanotubes in any practical applications has been its solubility; for example SWNTs have little to no solubility in most solvent due to the aggregation of the tubes. Aggregation/roping of nanotubes occurs as a result of the high van der Waals binding energy of *ca.* 500 eV per mm of tube contact. The van der Waals force between the tubes is so great, that it take tremendous energy to pry them apart, making it very to make combination of nanotubes with other materials such as in composite applications. The functionalization of nanotubes, i.e., the attachment of “chemical functional groups” provides the path to overcome these barriers. Functionalization can improve solubility as well as processibility, and has been used to align the properties of nanotubes to those of other materials. The clearest example of this is the ability to solubilize nanotubes in a variety of solvents, including water. It is important when discussing functionalization that a distinction is made between covalent and non-covalent functionalization.

Various applications of nanotubes require different, specific modification to achieve desirable physical and chemical properties of nanotubes. In this regard, covalent functionalization provides a higher degree of fine-tuning the chemistry and physics of SWNTs than non-covalent functionalization. Until now, a variety of methods have been used to achieve the functionalization of nanotubes (Figure 4.6.9).

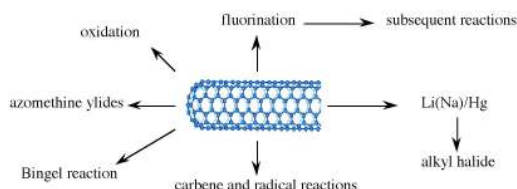


Figure 4.6.9: Schematic description of various covalent functionalization strategies for SWNTs.

Bibliography

- S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, and R. B. Weisman, *Science*, 2002, **298**, 2361.
- D. S. Bethune, C. H. Klang, M. S. deVries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, *Nature*, 1993, **363**, 605.
- J. J. Brege, C. Gallaway, and A. R. Barron, *J. Phys. Chem., C*, 2007, **111**, 17812.
- C. A. Dyke and J. M. Tour, *J. Am. Chem. Soc.*, 2003, **125**, 1156.
- Z. Ge, J. C. Duchamp, T. Cai, H. W. Gibson, and H. C. Dorn, *J. Am. Chem. Soc.*, 2005, **127**, 16292.
- L. A. Girifalco, M. Hodak, and R. S. Lee, *Phys. Rev. B*, 2000, **62**, 13104.
- T. Guo, P. Nikolaev, A. G. Rinzler, D. Tománek, D. T. Colbert, and R. E. Smalley, *J. Phys. Chem.*, 1995, **99**, 10694.
- J. H. Hafner, M. J. Bronikowski, B. R. Azamian, P. Nikolaev, A. G. Rinzler, D. T. Colbert, K. A. Smith, and R. E. Smalley, *Chem. Phys. Lett.*, 1998, **296**, 195.

- A. Hirsch, *Angew. Chem. Int. Ed.*, 2002, **40**, 4002.
- S. Iijima and T. Ichihashi, *Nature*, 1993, **363**, 603.
- H. R. Jafry, E. A. Whitsitt, and A. R. Barron, *J. Mater. Sci.*, 2007, **42**, 7381.
- H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, 1985, **318**, 162.
- F. Liang, A. K. Sadana, A. Peera, J. Chattopadhyay, Z. Gu, R. H. Hauge, and W. E. Billups, *Nano Lett.*, 2004, **4**, 1257.
- D. Ogrin and A. R. Barron, *J. Mol. Cat. A: Chem.*, 2006, **244**, 267.
- D. Ogrin, J. Chattopadhyay, A. K. Sadana, E. Billups, and A. R. Barron, *J. Am. Chem. Soc.*, 2006, **128**, 11322.
- R. E. Smalley, *Acc. Chem. Res.*, 1992, **25**, 98.
- M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, *Nature*, 1996, **381**, 678.
- E. A. Whitsitt and A. R. Barron, *Nano Lett.*, 2003, **3**, 775.
- J. Yang and A. R. Barron, *Chem. Commun.*, 2004, 2884.
- L. Zeng, L. B. Alemany, C. L. Edwards, and A. R. Barron, *Nano Res.*, 2008, **1**, 72.

Graphene

Introduction

Graphene is a one-atom-thick planar sheet of sp^2 -bonded carbon atoms that are densely packed in a honeycomb crystal lattice (Figure 4.6.11). The name comes from “graphite” and “alkene”; graphite itself consists of many graphene sheets stacked together.

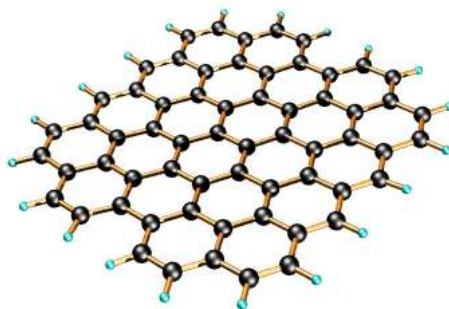


Figure 4.6.11: Idealized structure of a single graphene sheet.

Single-layer graphene nanosheets were first characterized in 2004, prepared by mechanical exfoliation (the “scotch-tape” method) of bulk graphite. Later graphene was produced by epitaxial chemical vapor deposition on silicon carbide and nickel substrates. Most recently, graphene nanoribbons (GNRs) have been prepared by the oxidative treatment of carbon nanotubes and by plasma etching of nanotubes embedded in polymer films.

Physical properties of graphene

Graphene has been reported to have a Young’s modulus of 1 TPa and intrinsic strength of 130 GP; similar to single walled carbon nanotubes (SWNTs). The electronic properties of graphene also have some similarity with carbon nanotubes. Graphene is a zero-bandgap semiconductor. Electron mobility in graphene is extraordinarily high ($15,000 \text{ cm}^2/\text{V.s}$ at room temperature) and ballistic electron transport is reported to be on length scales comparable to that of SWNTs. One of the most promising aspects of graphene involves the use of GNRs. Cutting an individual graphene layer into a long strip can yield semiconducting materials where the bandgap is tuned by the width of the ribbon.

While graphene’s novel electronic and physical properties guarantee this material will be studied for years to come, there are some fundamental obstacles yet to overcome before graphene based materials can be fully utilized. The aforementioned methods of graphene preparation are effective; however, they are impractical for large-scale manufacturing. The most plentiful and inexpensive source of graphene is bulk graphite. Chemical methods for exfoliation of graphene from graphite provide the most realistic and scalable approach to graphene materials.

Graphene layers are held together in graphite by enormous van der Waals forces. Overcoming these forces is the major obstacle to graphite exfoliation. To date, chemical efforts at graphite exfoliation have been focused primarily on intercalation, chemical derivatization, thermal expansion, oxidation-reduction, the use of surfactants, or some combination of these.

Graphite oxide

Probably the most common route to graphene involves the production of graphite oxide (GO) by extremely harsh oxidation chemistry. The methods of Staudenmeier or Hummers are most commonly used to produce GO, a highly exfoliated material that is dispersible in water. The structure of GO has been the subject of numerous studies; it is known to contain epoxide functional groups along the basal plane of sheets as well as hydroxyl and carboxyl moieties along the edges (Figure 4.6.12). In contrast to other methods for the synthesis of GO, the *m*-peroxybenzoic acid (*m*-CPBA) oxidation of microcrystalline synthetic graphite at room temperature yields graphite epoxide in high yield, without significant additional defects.

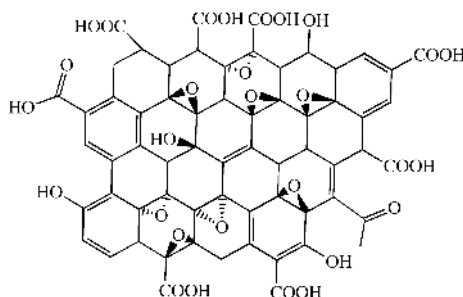


Figure 4.6.12: Idealized structure proposed for graphene oxide (GO). Adapted from C. E. Hamilton, PhD Thesis, Rice University (2009).

As graphite oxide is electrically insulating, it must be converted by chemical reduction to restore the electronic properties of graphene. Chemically converted graphene (CCG) is typically reduced by hydrazine or borohydride. The properties of CCG can never fully match those of graphene for two reasons:

1. Oxidation to GO introduces defects.
2. Chemical reduction does not fully restore the graphitic structure.

As would be expected, CCG is prone to aggregation unless stabilized. Graphene materials produced from pristine graphite avoid harsh oxidation to GO and subsequent (incomplete) reduction; thus, materials produced are potentially much better suited to electronics applications.

A catalytic approach to the removal of epoxides from fullerenes and SWNTs has been applied to graphene epoxide and GO. Treatment of oxidized graphenes with methyltrioxorhenium (MeReO₃, MTO) in the presence of PPh₃ results in the oxygen transfer, to form O=PPh₃ and allow for quantification of the C:O ratio.

Homogeneous graphene dispersions

An alternate approach to producing graphene materials involves the use of pristine graphite as starting material. The fundamental value of such an approach lies in its avoidance of oxidation to GO and subsequent (incomplete) reduction, thereby preserving the desirable electronic properties of graphene. There is precedent for exfoliation of pristine graphite in neat organic solvents without oxidation or surfactants. It has been reported that *N,N*-dimethylformamide (DMF) dispersions of graphene are possible, but no detailed characterization of the dispersions were reported. In contrast, Coleman and coworkers reported similar dispersions using *N*-methylpyrrolidone (NMP), resulting in individual sheets of graphene at a concentration of ≤ 0.01 mg/mL. NMP and DMF are highly polar solvents, and not ideal in cases where reaction chemistry requires a nonpolar medium. Further, they are hygroscopic, making their use problematic when water must be excluded from reaction mixtures. Finally, DMF is prone to thermal and chemical decomposition.

Recently, dispersions of graphene has been reported in *ortho*-dichlorobenzene (ODCB) using a wide range of graphite sources. The choice of ODCB for graphite exfoliation was based on several criteria:

1. ODCB is a common reaction solvent for fullerenes and is known to form stable SWNT dispersions.
2. ODCB is a convenient high-boiling aromatic, and is compatible with a variety of reaction chemistries.
3. ODCB, being aromatic, is able to interact with graphene *via* π - π stacking.
4. It has been suggested that good solvents for graphite exfoliation should have surface tension values of 40 – 50 mJ/m². ODCB has a surface tension of 36.6 mJ/m², close to the proposed range.

Graphite is readily exfoliated in ODCB with homogenization and sonication. Three starting materials were successfully dispersed: microcrystalline synthetic, thermally expanded, and highly ordered pyrolytic graphite (HOPG). Dispersions of microcrystalline synthetic graphite have a concentration of 0.03 mg/mL, determined gravimetrically. Dispersions from expanded graphite and HOPG are less concentrated (0.02 mg/mL).

High resolution transmission electron microscopy (HRTEM) shows mostly few-layer graphene ($n < 5$) with single layers and small flakes stacked on top (Figure 4.6.13). Large graphitic domains are visible; this is further supported by selected area electron diffraction (SAED) and fast Fourier transform (FFT) in selected areas. Atomic force microscope (AFM) images of dispersions sprayed onto silicon substrates shows extremely thin flakes with nearly all below 10 nm. Average height is 7 - 10 nm. The thinnest are less than 1 nm, graphene monolayers. Lateral dimensions of nanosheets range from 100 – 500 nm.

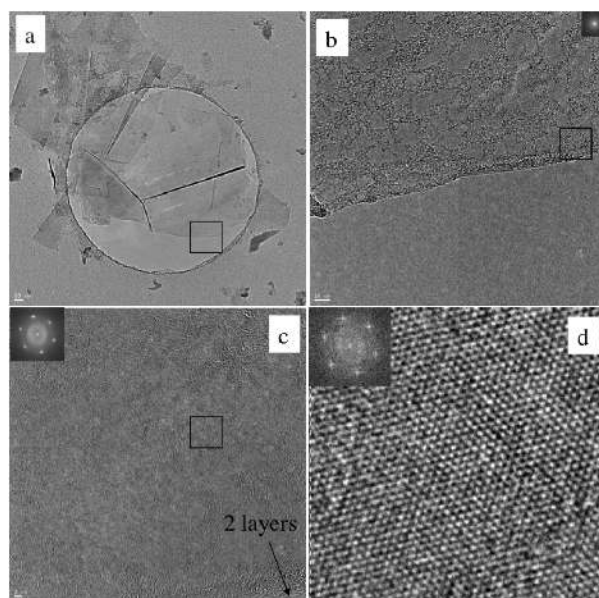


Figure 4.6.13: TEM images of single layer graphene from HOPG dispersion. (a) monolayer and few layer of graphene stacked with smaller flakes; (b) selected edge region from (a), (c) selected area from (b) with FFT inset, (d) HRTEM of boxed region in (c) showing lattice fringes with FFT inset. Adapted from C. E. Hamilton, PhD Thesis, Rice University (2009).

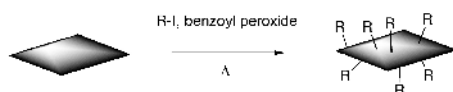
As-deposited films cast from ODCB graphene show poor electrical conductivity, however, after vacuum annealing at 400 °C for 12 hours the films improve vastly, having sheet resistances on the order of 60 Ω /sq. By comparison, graphene epitaxially grown on Ni has a reported sheet resistance of 280 Ω /sq.

Covalent functionalization of graphene and graphite oxide

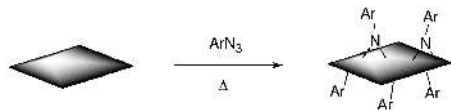
The covalent functionalization of SWNTs is well established. Some routes to covalently functionalized SWNTs include esterification/ amidation, reductive alkylation (Billups reaction), and treatment with azomethine ylides (Prato reaction), diazonium salts, or nitrenes. Conversely, the chemical derivatization of graphene and GO is still relatively unexplored.

Some methods previously demonstrated for SWNTs have been adapted to GO or graphene. GO carboxylic acid groups have been converted into acyl chlorides followed by amidation with long-chain amines. Additionally, the coupling of primary amines and amino acids via nucleophilic attack of GO epoxide groups has been reported. Yet another route coupled isocyanates to carboxylic acid groups of GO. Functionalization of partially reduced GO by aryldiazonium salts has also been demonstrated. The Billups reaction has been performed on the intercalation compound potassium graphite (C_8K), as well as graphite fluoride, and most recently GO. Graphene alkylation has been accomplished by treating graphite fluoride with alkyl lithium reagents.

ODCB dispersions of graphene may be readily converted to covalently functionalize graphene. Thermal decomposition of benzoyl peroxide is used to initiate radical addition of alkyl iodides to graphene in ODCB dispersions.



Additionally, functionalized graphene with nitrenes generated by thermal decomposition of aryl azides



Bibliography

- P. Blake, P. D. Brimicombe, R. R. Nair, T. J. Booth, D. Jiang, F. Schedin, L. A. Ponomarenko, S. V. Morozov, H. F. Gleeson, E. W. Hill, A. K. Geim, and K. S. Novoselov, *Nano Lett.*, 2008, **8**, 1704.
- J. Chattopadhyay, A. Mukherjee, C. E. Hamilton, J.-H. Kang, S. Chakraborty, W. Guo, K. F. Kelly, A. R. Barron, and W. E. Billups, *J. Am. Chem. Soc.*, 2008, **130**, 5414.
- G. Eda, G. Fanchini, and M. Chhowalla, *Nat. Nanotechnol.*, 2008, **3**, 270.
- M. Y. Han, B. Ozyilmaz, Y. Zhang, and P. Kim, *Phys. Rev. Lett.*, 2008, **98**, 206805.
- Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchinson, V. Scardaci, A. C. Ferrari, and J. N. Coleman, *Nat. Nanotechnol.*, 2008, **3**, 563.
- W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- L. Jiao, L. Zhang, X. Wang, G. Diankov, and H. Dai, *Nature*, 2009, **458**, 877.
- D. V. Kosynkin, A. L. Higginbotham, A. Sinitskii, J. R. Lomeda, A. Dimiev, B. K. Price, and J. M. Tour, *Nature*, 2009, **458**, 872.
- D. Li, M. B. Mueller, S. Gilje, R. B. Kaner, and G. G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101.
- S. Niyogi, E. Bekyarova, M. E. Itkis, J. L. McWilliams, M. A. Hamon, and R. C. Haddon, *J. Am. Chem. Soc.*, 2006, **128**, 7720.
- Y. Si and E. T. Samulski, *Nano Lett.*, 2008, **8**, 1679.
- L. Staudenmaier, *Ber. Dtsch. Chem. Ges.*, 1898, **31**, 1481.

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4.7: Chemical Properties of Aromatic Compounds

Objective

After completing this section, you should be able to identify electrophilic substitution as the single most important reaction of aromatic compounds.

Key Terms

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

- acylation
- alkylation
- electrophilic substitution
- halogenation
- nitration
- sulfonation

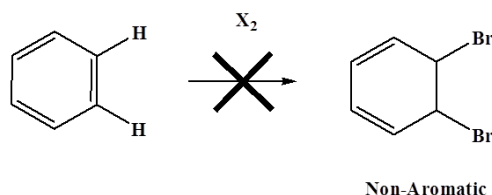
Study Notes

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.

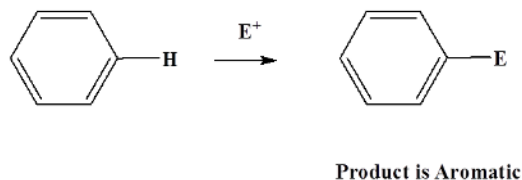
 benzene converts to phenol

It is important that you recognize the similarities between these reactions to minimize the amount you must memorize.

Benzene and aromatic rings in general are especially stable. This means that the aromaticity must be retained during reactions. Because of this, benzene does not undergo addition like other unsaturated hydrocarbons.



Benzene can undergo electrophilic aromatic substitution because aromaticity is maintained.



Other Examples of Electrophilic 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 ₆ H ₆	+ Cl ₂ & heat FeCl ₃ catalyst	————>	C ₆ H ₅ Cl + HCl Chlorobenzene	Cl ⁽⁺⁾ or Br ⁽⁺⁾
Nitration:	C ₆ H ₆	+ HNO ₃ & heat H ₂ SO ₄ catalyst	————>	C ₆ H ₅ NO ₂ + H ₂ O Nitrobenzene	NO ₂ ⁽⁺⁾
Sulfonation:	C ₆ H ₆	+ H ₂ SO ₄ + SO ₃ & heat	————>	C ₆ H ₅ SO ₃ H + H ₂ O Benzenesulfonic acid	SO ₃ H ⁽⁺⁾
Alkylation: Friedel-Crafts	C ₆ H ₆	+ R-Cl & heat AlCl ₃ catalyst	————>	C ₆ H ₅ -R + HCl An Arene	R ⁽⁺⁾
Acylation: Friedel-Crafts	C ₆ H ₆	+ RCOCl & heat AlCl ₃ catalyst	————>	C ₆ H ₅ COR + HCl An Aryl Ketone	RCO ⁽⁺⁾

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- William Reusch, Professor Emeritus ([Michigan State U.](#)), Virtual Textbook of Organic Chemistry

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4.8: General Mechanism for Electrophilic Substitution Reactions of Benzene

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

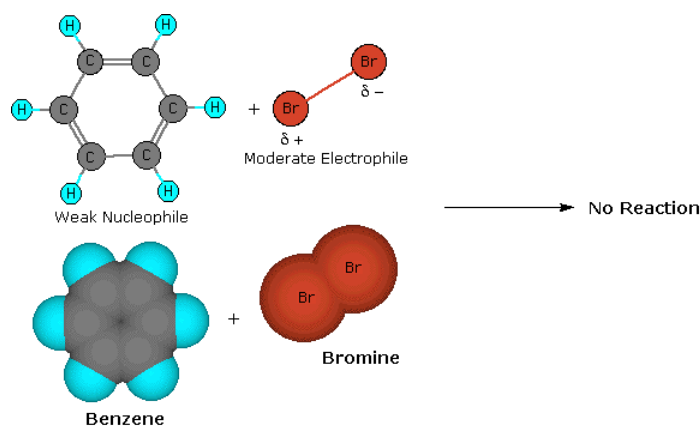
The Mechanism for Electrophilic Substitution Reactions of Benzene is the key to understanding electrophilic aromatic substitution. You will see similar equations written for nitration, sulphonation, acylation, etc., with the major difference being the identity of the electrophile in each case.

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.

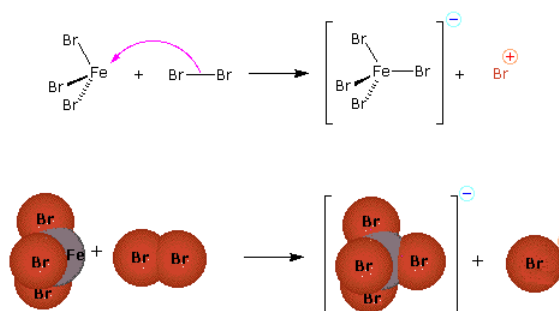
Halogenation is an example of electrophilic aromatic substitution. In electrophilic aromatic substitutions, a benzene is attacked by an electrophile which results in substitution of hydrogens. However, halogens are not electrophilic enough to break the aromaticity of benzenes, which require a catalyst 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 **arenium 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.

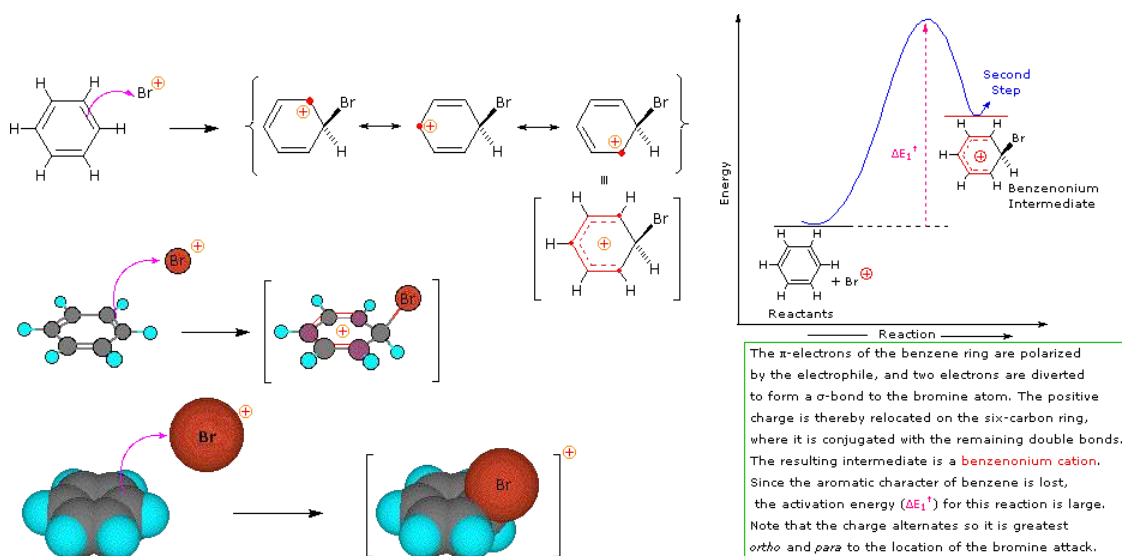


The bromine molecule is polarized so that one end is electrophilic and the other nucleophilic. Although the electrophilic end reacts easily with simple alkenes and dienes, it fails to react with the more stable and weaker nucleophilic π -electron system of benzene.

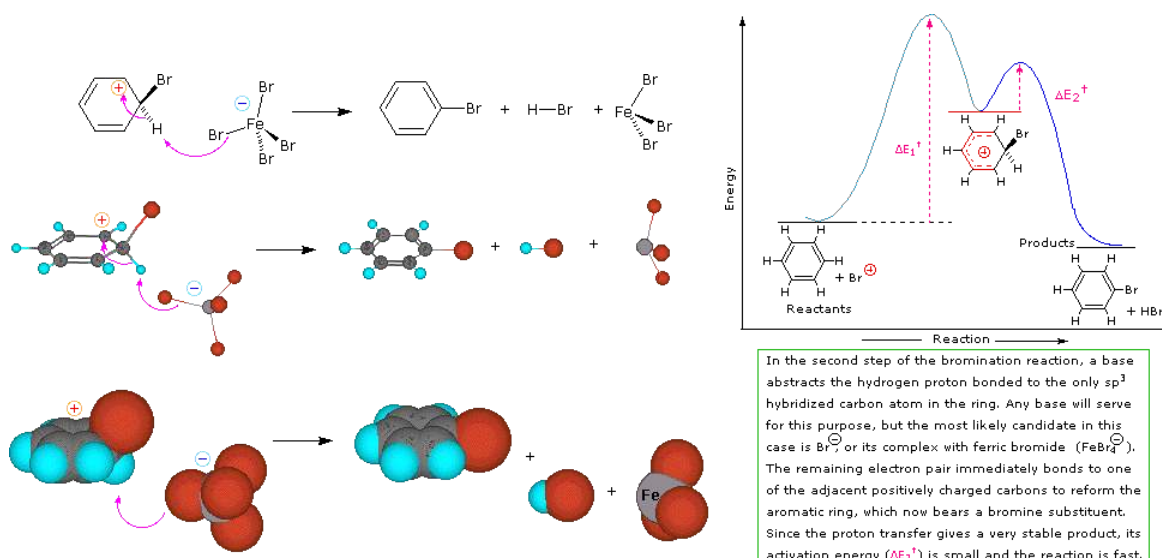


Ferric bromide and other Lewis acids enhance the electrophilic strength of bromine by forming a complex anion, in this case FeBr₄⁻. At the same time, this complexation creates the strongly electrophilic bromine cation, which reacts with nucleophiles.

Preliminary step: Formation of the strongly electrophilic bromine cation



Step 1: The electrophile forms a sigma-bond to the benzene ring, generating a positively charged benzenonium intermediate



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 $\text{S}_{\text{N}}1$ and $\text{E}1$ 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:

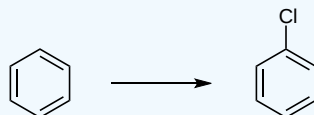
1. The cation may bond to a nucleophile to give a substitution or addition product.
2. The cation may transfer a proton to a base, giving a double bond product.
3. The cation may rearrange to a more stable carbocation, and then react by mode #1 or #2.

$\text{S}_{\text{N}}1$ and $\text{E}1$ 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 arenium 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 4.8.1

What reagents would you need to get the given product?

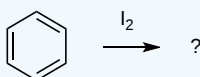


Answer

Cl_2 and AlCl_3 or Cl_2 and FeCl_3

? Exercise 4.8.2

What product would result from the given reagents?

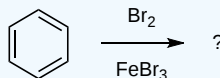


Answer

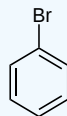
No Reaction

? Exercise 4.8.3

What is the major product given the reagents below?



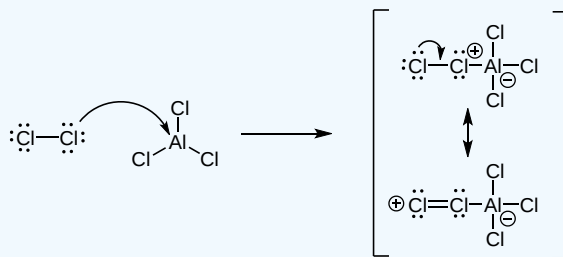
Answer



? Exercise 4.8.4

Draw the formation of Cl^+ from AlCl_3 and Cl_2 .

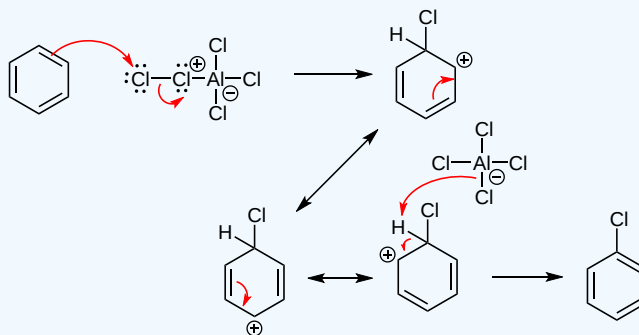
Answer



? Exercise 4.8.5

Draw the mechanism of the reaction between Cl^+ and a benzene.

Answer



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4.9: Halogenation, Sulfonation, and Nitration of Aromatic Compounds

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.

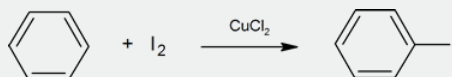
Key Terms

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

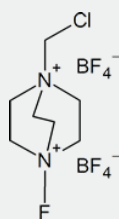
- nitronium ion, (NO^{+2})

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 I_2 is oxidized to the more electrophilic species I^+ .



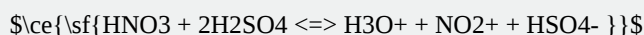
In contrast, fluorine is too reactive, so it cannot be used directly for aromatic fluorination. However, fluorinating agents like 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane ditetrafluoroborate (also known as F-TEDA- BF_4) sold commercially as Sectfluor® offer convenient sources of “ F^+ ” for this type of reaction.



F-TEDA- BF_4

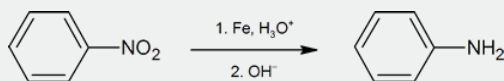


The overall equation for the formation of nitronium ions by the action of sulfuric acid on nitric acid is



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.)

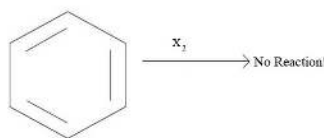


Halogenation of Benzene

Halogenation is an example of electrophilic aromatic substitution. In electrophilic aromatic substitutions, a benzene is attacked by an electrophile which results in substitution of hydrogens. However, halogens are not electrophilic enough to break the aromaticity of benzenes, which require a catalyst to activate.

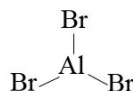
Activation of Halogen

(where X= Br or Cl, we will discuss further in detail later why other members of the halogen family Fluorine and Iodine are not used in halogenation of benzenes)

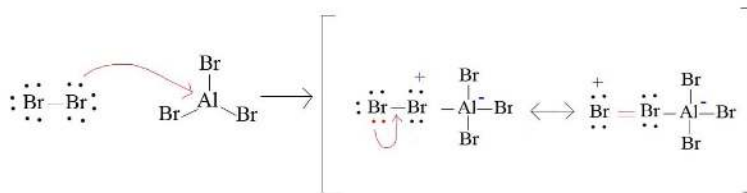


Hence, Halogen needs the help and aid of Lewis Acidic Catalysts to activate it to become a very strong electrophile. Examples of these activated halogens are Ferric Halides (FeX_3) Aluminum Halides (AlX_3) where X= Br or Cl. In the following examples, the halogen we will look at is Bromine.

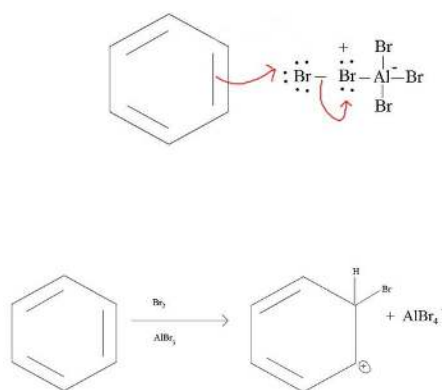
In the example of bromine, in order to make bromine electrophilic enough to react with benzene, we use the aid of an aluminum halide such as aluminum bromide.



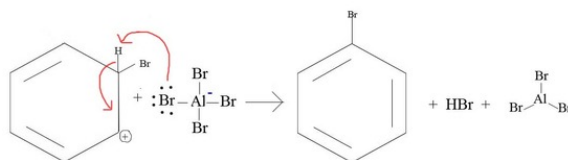
With aluminum bromide as a Lewis acid, we can mix Br_2 with AlBr_3 to give us Br^+ . The presence of Br^+ is a much better electrophile than Br_2 alone. Bromination is achieved with the help of AlBr_3 (Lewis acid catalysts) as it polarizes the Br-Br bond. The polarization causes the bromine atoms within the Br-Br bond to become more electrophilic. The presence of Br^+ compared to Br_2 alone is a much better electrophile that can then react with benzene.



As the bromine has now become more electrophilic after activation of a catalyst, an electrophilic attack by the benzene occurs at the terminal bromine of $\text{Br}-\text{Br}-\text{AlBr}_3$. This allows the other bromine atom to leave with the AlBr_3 as a good leaving group, AlBr_4^- .



After the electrophilic attack of bromine 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.

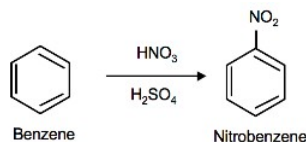
Dissociation Energies of Halogens and its Effect on Halogenation of Benzenes

The electrophilic bromination of benzenes is an exothermic reaction. Considering the exothermic rates of aromatic halogenation decreasing down the periodic table in the Halogen family. Fluorination is the most exothermic and Iodination would be the least. Being so exothermic, a reaction of fluorine with benzene is explosive! For iodine, electrophilic iodination is generally endothermic, hence a reaction is often not possible. Similar to bromine, chlorination would require the aid of an activating presence such as Aluminium 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.

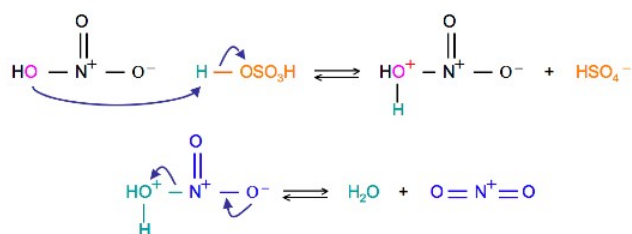
Nitration of Benzene

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.



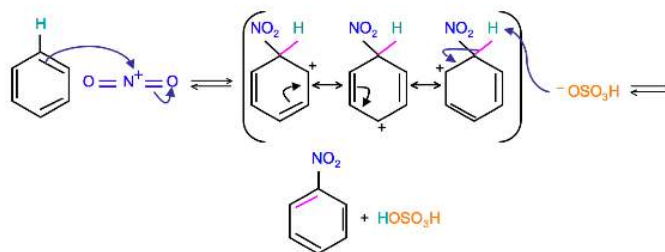
Sulfuric Acid Activation of Nitric Acid

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.

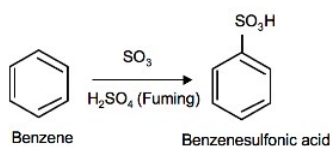
Mechanism



(Resonance forms of the intermediate can be seen in the generalized electrophilic aromatic substitution)

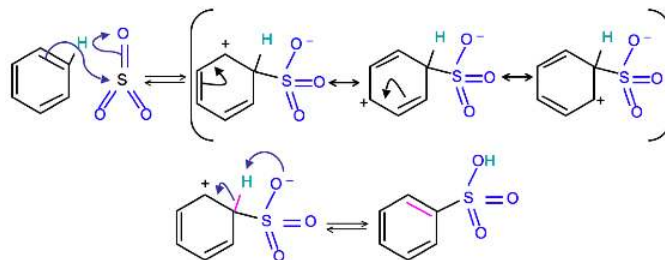
Sulfonation of Benzene

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.



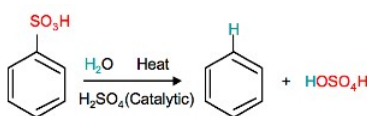
Mechanism

To produce benzenesulfonic acid from benzene, fuming sulfuric acid and sulfur trioxide are added. Fuming sulfuric acid, also referred 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. Benzenesulfonyl Chloride is a precursor to sulfonamides, which are used in chemotherapy.

Exercises

? Exercise 4.9.1

1. What is/are the required reagent(s) for the following reaction:

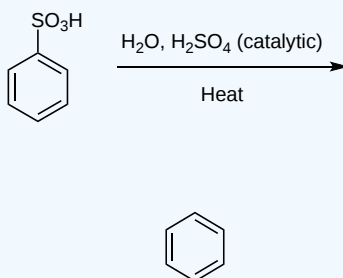


Answer

SO_3 and H_2SO_4 (fuming)

? Exercise 4.9.2

What is the product of the following reaction:



Answer



? Exercise 4.9.3

Why is it important that the nitration of benzene by nitric acid occurs in sulfuric acid?

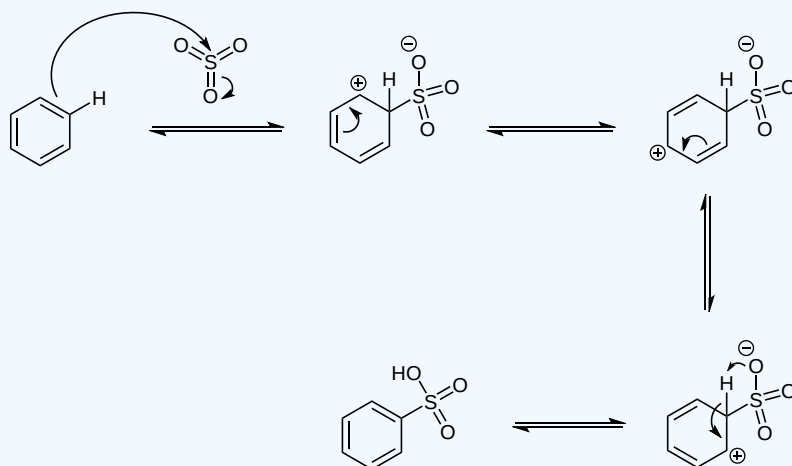
Answer

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 4.9.4

Write a detailed mechanism for the sulfonation of benzene, including all resonance forms.

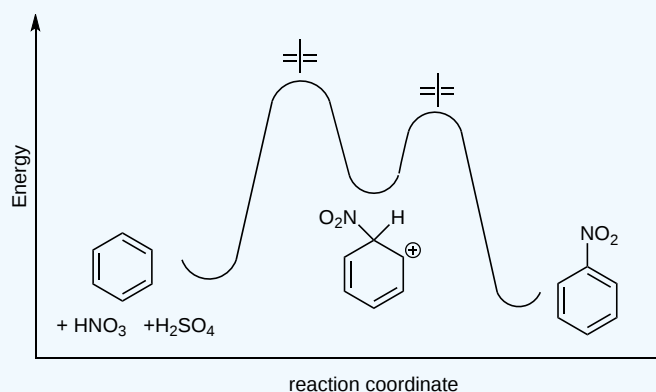
Answer



? Exercise 4.9.5

Draw an energy diagram for the nitration of benzene. Draw the intermediates, starting materials, and products. Label the transition states.

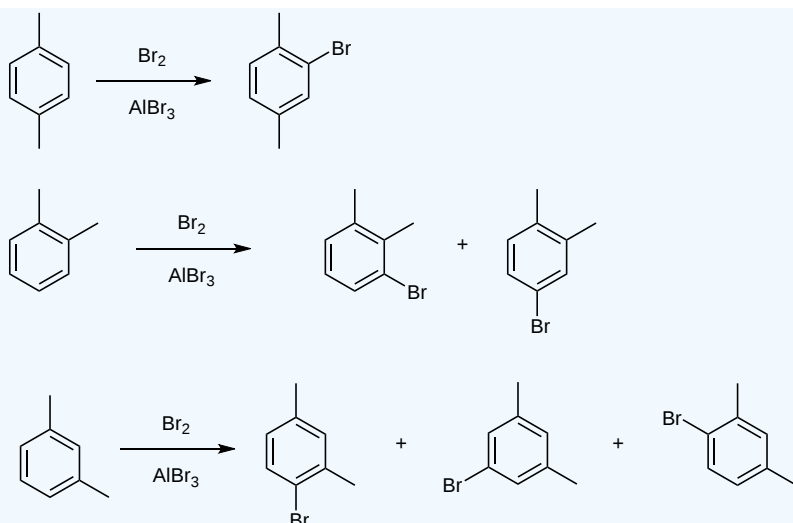
Answer



? Exercise 4.9.6

In each case, how many products would be possible for the bromination of *p*-xylene, *o*-xylene, and *m*-xylene?

Answer

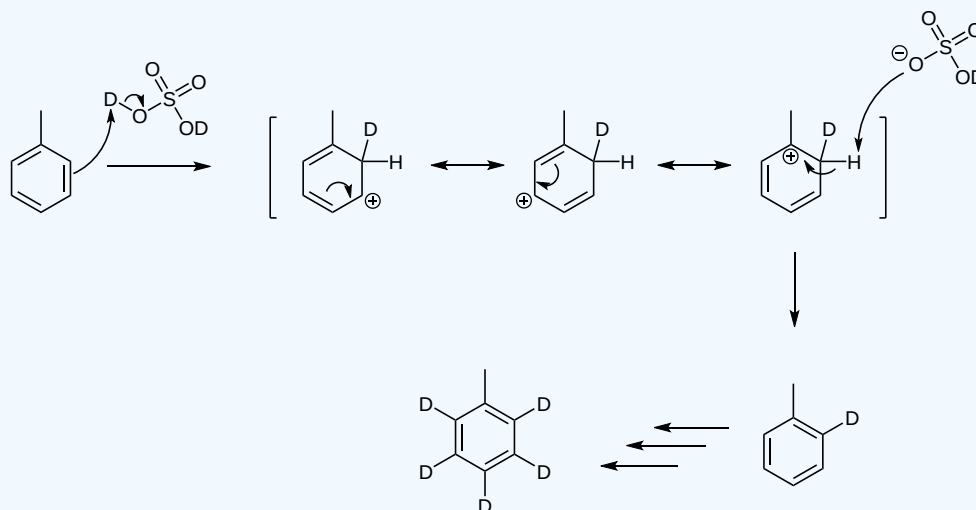


? Exercise 4.9.7

If toluene is treated with D₂SO₄ 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. Gettvert. “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.

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- [16.2: Other Aromatic Substitutions](#) by Catherine Nguyen, Dietmar Kennepohl, James Kabrhel, Steven Farmer, William Reusch is licensed CC BY-SA 4.0.

4.10: Alkylation and Acylation of Aromatic Rings - The Friedel-Crafts Reaction

Objectives

After completing this section, you should be able to

- write the equation for the preparation of an alkylbenzene by a Friedel-Crafts alkylation reaction.
- identify the product formed from the Friedel-Crafts alkylation of a given aromatic compound.
- identify the aromatic compound needed to prepare a given arene by a Friedel-Crafts alkylation.
- identify the alkyl halide and catalyst needed to form a specified arene from a given aromatic compound.
- 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.
- show how alkyl halides and acylhalides can be used as alkylating agents in Friedel-Crafts alkylation reactions.
- 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.
- write an equation for a typical Friedel-Crafts acylation.
- write the detailed mechanism of the Friedel-Crafts acylation reaction.
- identify the product formed by the Friedel-Crafts acylation of a given aromatic compound.
- identify the aromatic compound, and the reagent and catalyst needed to prepare a given ketone through a Friedel-Crafts acylation reaction.
- Explain the following laws within the Ideal Gas Law

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 is attacked by a pi bond from 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.

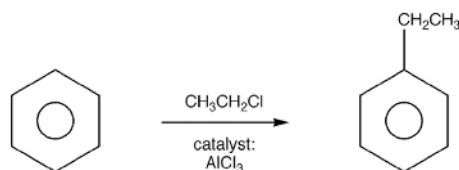
The four limitations on the use of Friedel-Crafts alkylations are as follows:

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 ($\text{C}=\text{O}$) into the aromatic ring through an electrophilic aromatic substitution mechanism. Such reactions are Friedel-Crafts acylation reactions.

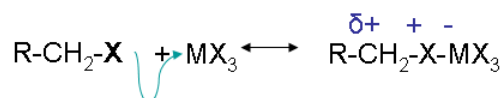
Friedel-Crafts Alkylation

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 effectiveness.



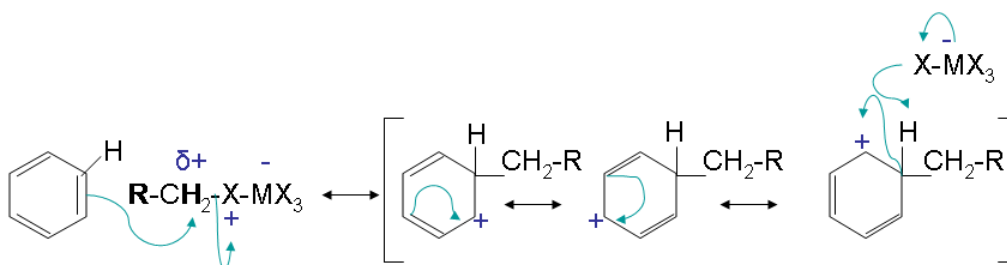
The mechanism takes place as follows:

Step 1:



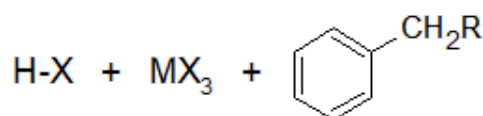
Step one creates a carbocation that acts as the electrophile in the reaction. This step activates the haloalkane. Secondary and tertiary halides only form the free carbocation in this step.

Steps 2 and 3:



Step 2 has an electron pair from the aromatic ring attack the carbocation forming a new C-C bond. The arenium ion intermediate results with stabilization from multiple resonance forms. The loss of a proton then gives the neutral alkylated substitution product.

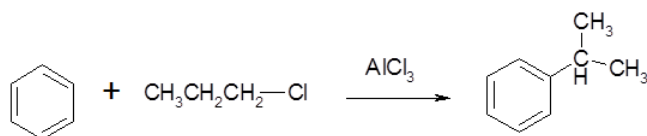
Final Products



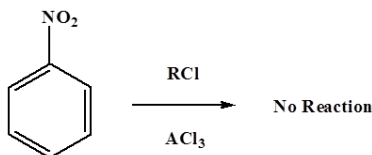
The reactivity of haloalkanes increases as you move up the periodic table and increase polarity. This means that an RF haloalkane is most reactive followed by RCl then RBr and finally RI. This means that the Lewis acids used as catalysts in Friedel-Crafts Alkylation reactions tend have similar halogen combinations such as BF₃, SbCl₅, AlCl₃, SbCl₅, and AlBr₃, all of which are commonly used in these reactions.

Some limitations of Friedel-Crafts Alkylation

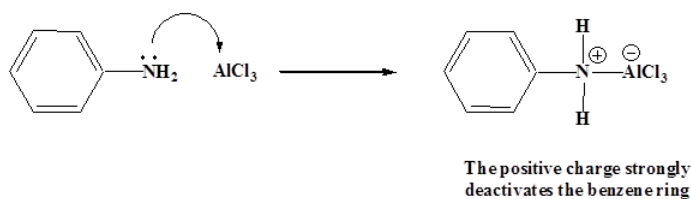
There are possibilities of carbocation rearrangements when you are trying to add a carbon chain greater than two carbons. The rearrangements occur due to hydride shifts and methyl shifts. For example, the product of a Friedel-Crafts Alkylation will show an iso rearrangement when adding a three carbon chain as a substituent. One way to resolve these problems is through Friedel-Crafts Acylation.



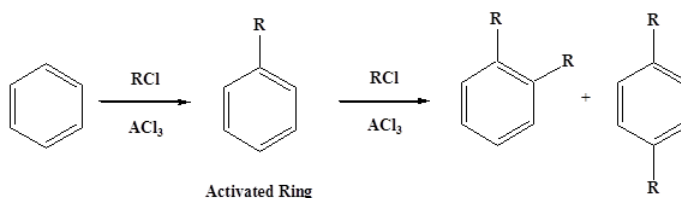
Also, the reaction will only work if the ring you are adding a substituent to is not deactivated. Friedel-Crafts fails when used with compounds such as nitrobenzene and other strong deactivating systems.



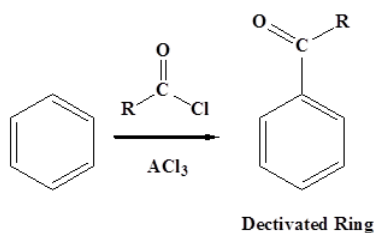
Friedel-Crafts reactions cannot be performed then the aromatic ring contains a NH_2 , NHR , or NR_2 substituent. The lone pair electrons on the amines react with the Lewis acid AlCl_3 . This places a positive charge next to the benzene ring, which is so strongly activating that the Friedel-Crafts reaction cannot occur.



Lastly, Friedel-Crafts alkylation can undergo polyalkylation. The reaction adds an electron donating alkyl group, which activates the benzene ring to further alkylation.

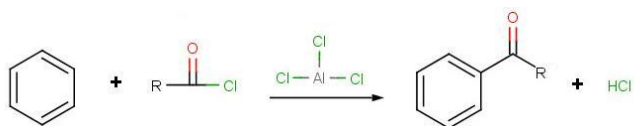


This problem does not occur during Friedel-Crafts Acylation because an acyl group is deactivating, thus prevents further acylations.

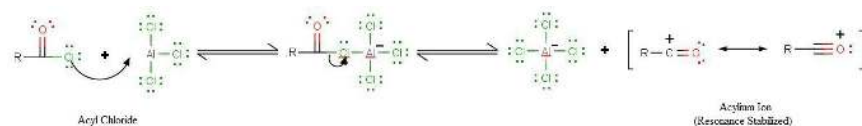


Friedel-Crafts Acylation

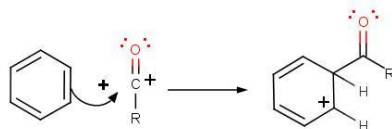
The goal of the reaction is the following:



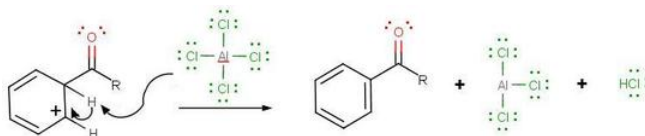
The very first step involves the formation of the acylium ion which will later react with benzene:



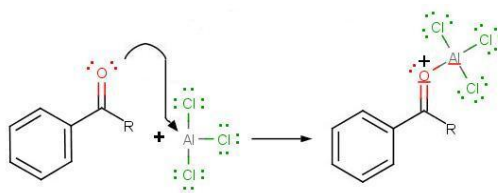
The second step involves the attack of the acylium ion on benzene as a new electrophile to form one complex:



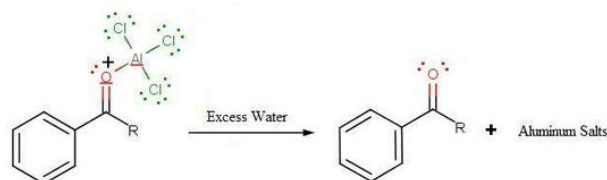
The third step involves the departure of the proton to reform aromaticity:



During the third step, AlCl_3 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. This 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 (unlike in Friedel-Crafts Alkylation reactions - see Limitation 1 above). Also, because of the deactivation of the product, it is no longer susceptible to electrophilic attack and hence, no longer goes into further reactions (Limitation 3 above from Friedel-Crafts Alkylation reactions). However, as not all is perfect, Limitation 2 still prevails where Friedel-Crafts Acylation fails with strong deactivating rings.

Exercises

? Exercise 4.10.1

Which of the following will NOT undergo a rearrangement in a Friedel-Crafts reaction?

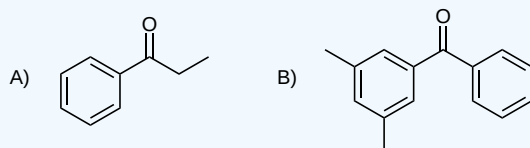
- A) CH_3Cl B) C)
- D) E)

Answer

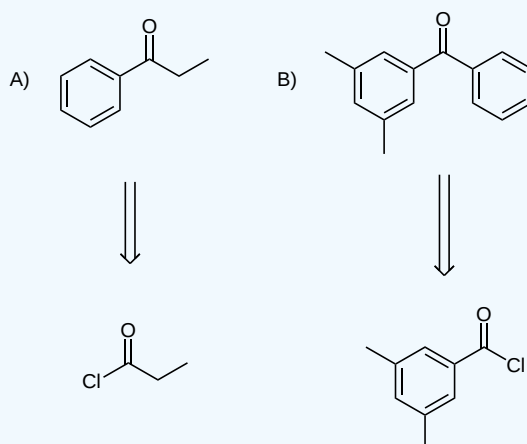
A and E will not undergo a rearrangement.

? Exercise 4.10.2

Suggest an acyl chloride that was used to make the following compounds:



Answer

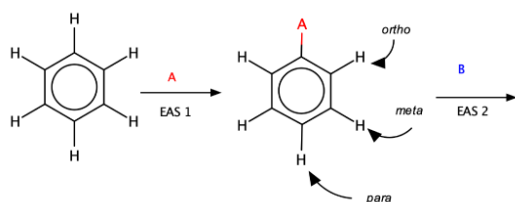


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4.11: Electrophilic Aromatic Substitution Reactions of Benzene Derivatives

Once the aromatic ring has undergone an electrophilic aromatic substitution (EAS1), the monosubstituted benzene can also undergo a second electrophilic aromatic substitution (EAS 2)

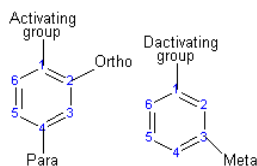


However, in this case, the second substituent B could enter the aromatic ring in position *ortho*, *meta*, or *para*. How can we determine the most likely position? To answer this question, we need to consider the electron effects of the already existing substituent (A) in the electron density of the aromatic ring.

Substituted aromatic rings are divided into two groups based on the type of the substituent that the ring carries (A):

- **Activated rings:** the substituents on the ring are groups that donate electrons. These substituents undergo electrophilic aromatic substitution faster than benzene.
- **Deactivated rings:** the substituents on the ring are groups that withdraw electrons. These substituents undergo electrophilic aromatic substitution slower than benzene.

The activating group directs the reaction to the *ortho* or *para* position, which means the electrophile substitutes the hydrogen that is on carbon 2 or carbon 4. The deactivating group directs the reaction to the *meta* position, which means the electrophile substitutes 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 or mesomeric 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. These effects can increase or decrease the electron density on the aromatic, activating or deactivating it. Substituted rings are divided into two groups based on the type of the substituent that the ring carries:

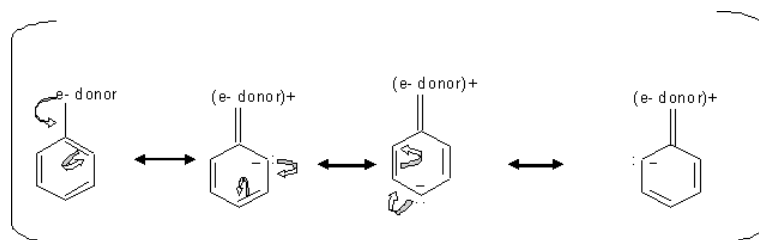
- **Activated rings:** the substituents on the ring are groups that donate electrons. These substituents undergo electrophilic aromatic substitution faster than benzene.
- **Deactivated rings:** the substituents on the ring are groups that withdraw electrons. These substituents undergo electrophilic aromatic substitution slower than benzene.

At the same time, not every carbon atom in the aromatic ring is activated or deactivated at the same level. As a consequence, the introduction of a second substituent in the aromatic can occur in position *ortho*, *meta*, or *para* depending on the electron effects induced by the previously existing substituent.

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 makes these substituents stronger activators, since this resonance effect directs the electron toward the ring. In cases where the

substituents is esters or amides, they are less activating because they form resonance structure that pull the electron density away from the ring.

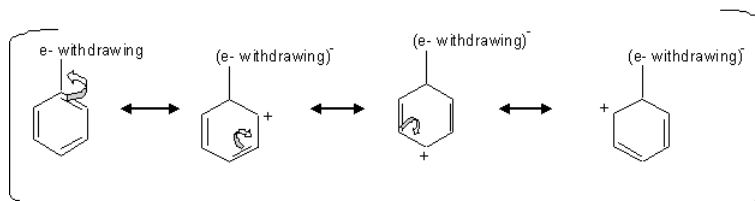


By looking at the mechanism above, we can see how groups donating electron direct the ortho, para electrophilic substitution. Since the electrons locatinn transfer between the ortho and para carbons, then the electrophile prefer attacking the carbon that has the free electron.

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.

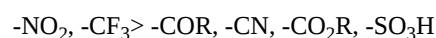
Classification of Substituents according to their influence in the reactivity of aromatic rings

- Examples of **activating groups** in the relative order from the most activating group to the least activating:



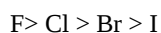
with R as alkyl groups ($\text{C}_n\text{H}_{2n+1}$)

- Examples of **deactivating groups** in the relative order from the most deactivating to the least deactivating:



with R as alkyl groups

The order of reactivity among Halogens from the more reactive (least deactivating substituent) to the least reactive (most deactivating substituent) halogen is:



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 electronegative 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.

Figure 4.11.1. can help you predict the position of the second substituent and the reactivity of the aromatic compared to benzene.

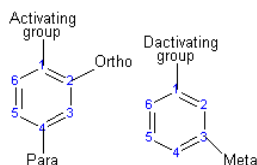
Meta- directing substituents	Ortho, para- directing substituents
-NO ₂ , -CF ₃ , -COR, -CN, -CO ₂ R, -SO ₃ H < I < Br < Cl < F	<-R< -NHCOR< -OH, -OR<-NH ₂ , -NR ₂
Deactivating substituents	Activating substituents

Reactivity towards EAS →

Figure 4.11.1. Effect of the substituent in Electrophilic aromatic substitution

In summary

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.



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.

References

- Schore, N.E. and P.C. Vollhardt. 2007. *Organic Chemistry, structure and function*, 5th ed. New York, NY: W.H. Freeman and Company.
- Fryhle, C.B. and G. Solomons. 2008. *Organic Chemistry*, 9th ed. Danvers, MA: Wiley.
- Substitution Reactions of Benzene Derivatives. (2020, September 13). Retrieved May 20, 2021, from <https://chem.libretexts.org/@go/page/933>

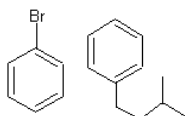
Outside Links

- 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

Problems

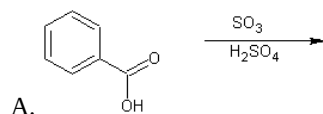
1. Predict the direction of the electrophile substitution on these rings:



2. Which nitration product is going to form faster?

nitration of aniline or nitration of nitrobenzene?

3. Predict the product of the following two sulfonation reactions:



4. Classify these two groups as activating or deactivating groups:

A. alcohol (-OH)

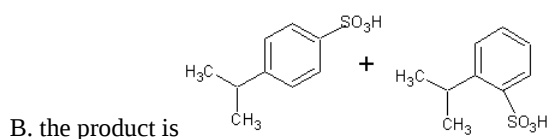
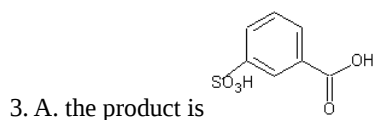
B. ester (-CO₂R)

5. By which effect does trichloride effect a monosubstituted ring?

Answers

1. The first substitution is going to be ortho and/or para substitution since we have a halogen substituent. The second substitution is going to be ortho and/or para substitution also since we have an alkyl substituent.

2. The nitration of aniline is going to be faster than the **nitration** of nitrobenzene, since the aniline is a ring with NH₂ substituent and nitrobenzene is a ring with NO₂ substituent. As described above NH₂ is an activating group which speeds up the reaction and NO₂ is deactivating group that slows down the reaction.



4. A. alcohol is an activating group.

B. ester is a deactivating group.

5. Trichloride deactivate a monosubstituted ring by inductive effect.

Contributors

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4.12: Heterocyclic Aromatic Compounds

Aromaticity in compounds other than benzene

The concept of aromaticity can be extended to other cyclic compounds that contain atoms other than carbon and hydrogen. The structural requirement for these compounds is to contain one or more rings with pi electrons delocalized all the way around them. In **heterocyclic aromatic compounds**, at least one carbon atom is replaced by one of the heteroatoms **oxygen**, **nitrogen**, or **sulfur**. Examples of heterocyclic aromatic compounds are **furan**, a heterocyclic compound with a five-membered ring that includes a single oxygen atom, and **pyridine**, a heterocyclic compound with a six-membered ring containing one nitrogen atom. Many of these heterocyclic aromatic compounds are components of important biological molecules, such as the bases of DNA and RNA, and medicinal drugs.

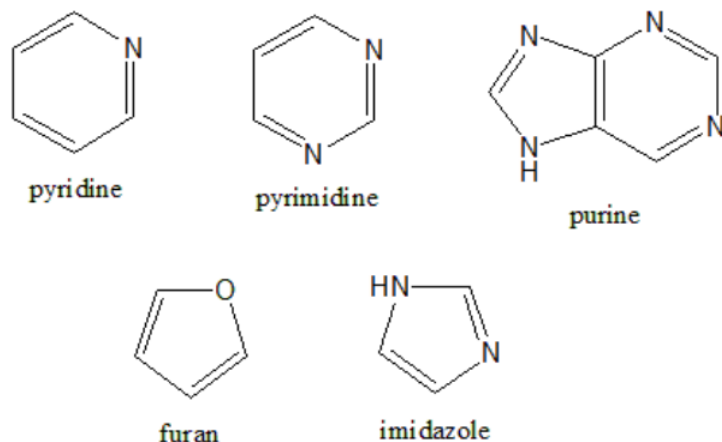


Figure 1. Examples of Heterocyclic Aromatic Compounds.

For a compound (or ion) to be considered aromatic, the molecule must be cyclic, planar, and must have $4n + 2$ electrons in a conjugated system of p orbitals (usually on sp^2 -hybridized atoms. This is known as Hückel's rule.

Sources

- [Aromatic compounds](#) on Wikipedia. Retrieved on Oct 16, 2020. Content adapted under [Creative Commons Attribution-ShareAlike License](#).
- [Hückel's rule](#) on Wikipedia. Retrieved on Oct 16, 2020. Content adapted under [Creative Commons Attribution-ShareAlike License](#).

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CHAPTER OVERVIEW

5: Stereochemistry

Learning Objectives

After reading this chapter and completing the exercises and homework, a student can be able to:

- recognize and classify molecules as chiral or achiral and identify planes of symmetry - refer to section 6.1
- draw, interpret, and convert between perspective formulae and Fischer projections for chiral compounds - refer to section 6.2
- name chiral compounds using (R) & (S) nomenclature - refer to section 6.3
- recognize and classify diastereomers and meso compounds - refer to section 6.4 and 6.5 respectively
- explain how physical properties differ for different types of stereoisomers - refer to section 6.6
- distinguish and discern the structural and chemical relationships between isomeric compounds - refer to section 6.6
- define and explain the lack of optical activity of racemic mixtures - refer to section 6.7
- determine the percent composition of an enantiomeric mixture from polarimetry data and the for specific rotation formula - refer to section 6.7
- explain how to resolve (separate) a pair of enantiomers - refer to section 6.8
- interpret the stereoisomerism of compounds with three or more chiral centers - refer to section 6.9
- compare and contrast absolute configuration with relative configuration - refer to section 6.10
- interpret the stereoisomerism of compounds with nitrogen, phosphorus, or sulfur as chiral centers - refer to section 6.11
- recognize and explain biochemical applications of chirality - refer to section 6.12
- describe Jean Baptiste Biot and Louis Pasteur's contributions to the understanding of optical isomers - refer to section 6.13

[5.1: Chirality](#)

[5.2: Fischer Projections to communicate Chirality](#)

[5.3: Absolute Configuration and the \(R\) and \(S\) System](#)

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5.1: Chirality

Learning Objective

- recognize and classify molecules as chiral or achiral and identify planes of symmetry

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 existence of these molecules are determined by concept known as [chirality](#).

Introduction

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 1).

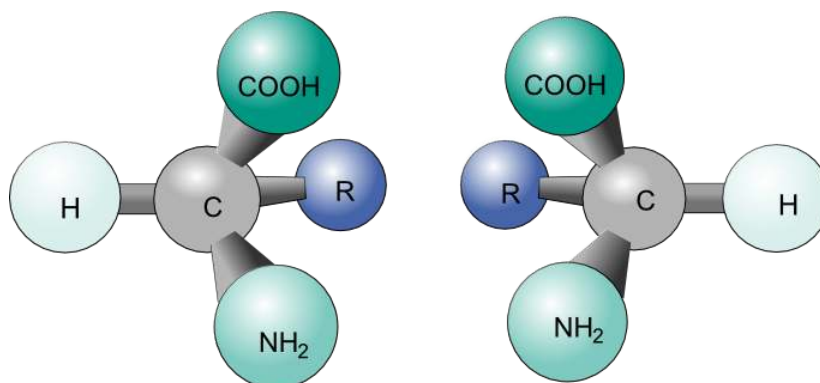


Figure 1: Two enantiomers of a tetrahedral complex.

The concepts of stereoisomerism 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 enantiomer 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.

The Many Synonyms of the Chiral Carbon

Be aware - all of the following terms can be used to describe a chiral carbon.

chiral carbon = asymmetric carbon = optically active carbon = stereo carbon

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.

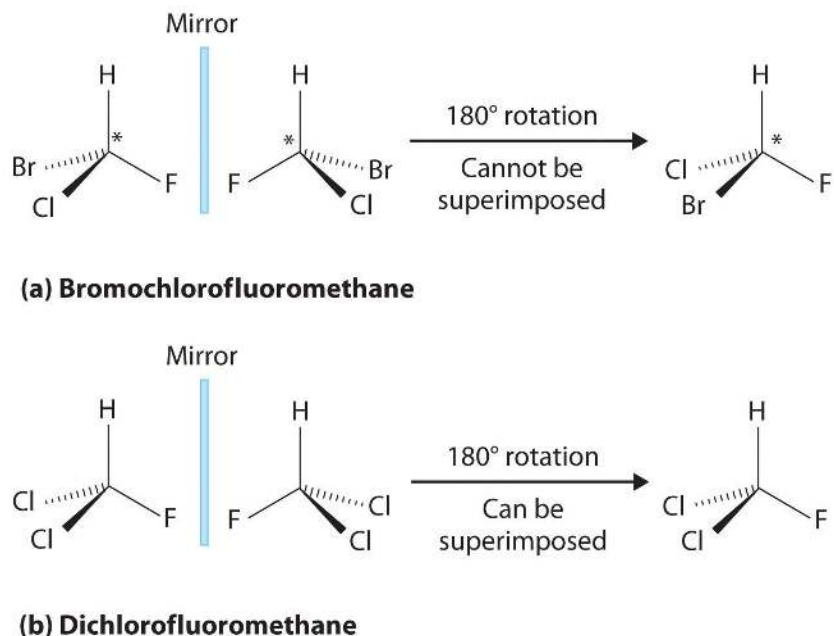


Figure 2: Comparison of Chiral and Achiral Molecules. (a) Bromochlorofluoromethane is a chiral molecule whose stereocenter is designated with an asterisk. Rotation of its mirror image does not generate the original structure. To superimpose the mirror images, bonds must be broken and reformed. (b) In contrast, dichlorofluoromethane and its mirror image can be rotated so they are superimposable.

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 4 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 4).

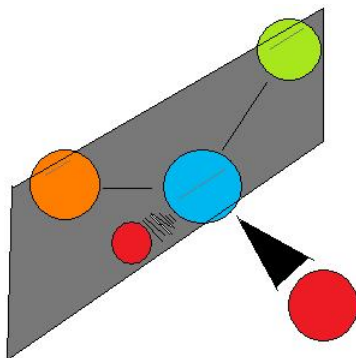


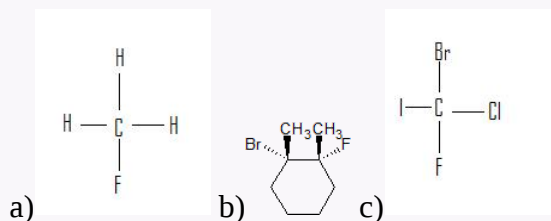
Figure 4.

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 deprived 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 chirality in relation to modern organic chemistry.

Exercise 1

Identify the following as either a constitutional isomer or stereoisomer. If stereoisomer, determine if it is an enantiomer or diastereomer. Explain the reason behind the answer. Also mark chirality for each molecule.



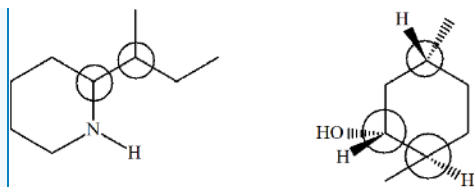
Solutions

- a) achiral
- b) chiral
- c) chiral

Exercise 2

Identify the chiral centers in each of the following:

Solutions



References

1. Anslyn, Eric V. and Dougherty, Dennis A. Modern Physical Organic Chemistry. Chicago, IL.: University Science. 2005
2. Hick, Janice M. The Physical Chemistry of Chirality. New York, N.Y.: An American Chemical Society Publication. 2001.
3. Vollhardt, K. Peter C. and Schore, Neil E. Organic Chemistry: Structure and Function. Fifth Edition. New York, N.Y.: W. H. Freeman Company, 2007.

Contributors and Attributions

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- Jonathan Mooney (McGill University)

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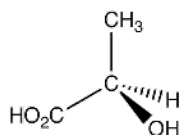
5.2: Fischer Projections to communicate Chirality

Learning Objective

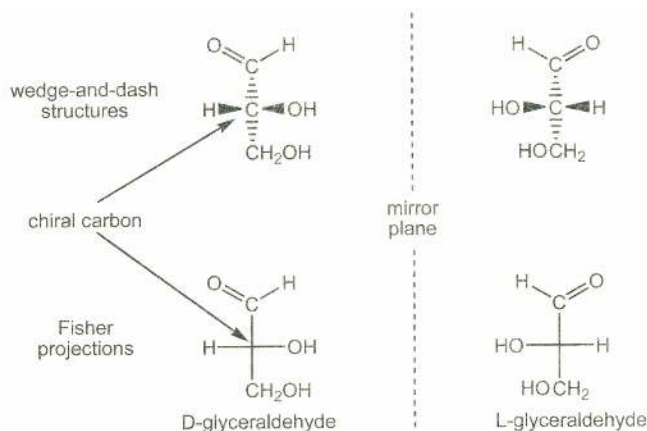
- draw, interpret, and convert between perspective formulae and Fischer projections for chiral compounds

Perspective Formulas and Fischer Projections

So far, we have communicated the stereochemical orientation of compounds using the wedges and dashes of perspective formulas. For example, the perspective formula for (*R*)-Lactic acid is shown below.



A Fischer projection is a convention used to depict stereochemistry in two dimensions. The horizontal bonds are seen as wedges and the vertical bonds are seen as dashed lines as shown below in the example below for glyceraldehyde.

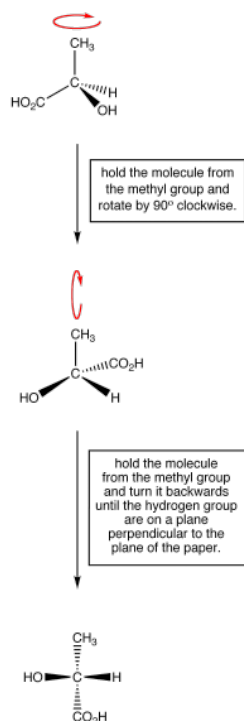


Converting between Perspective and Fischer Formulas

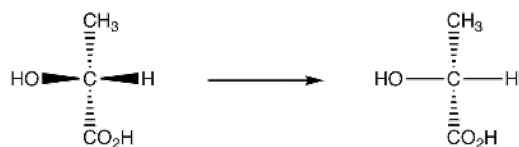
It can be useful to convert between perspective formulas and Fischer projections. Below is one approach using (*R*)-lactic acid as an example..

Step 1: Hold the molecule so that

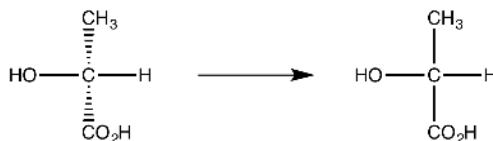
- the chiral center is on the plane of the paper,
- two bonds are coming out of the plane of the paper and are on a horizontal plane,
- the two remaining bonds are going into the plane of the paper and are on a vertical plane



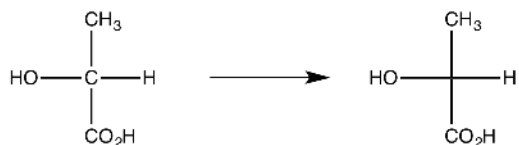
Step 2: Push the two bonds coming out of the plane of the paper onto the plane of the paper.



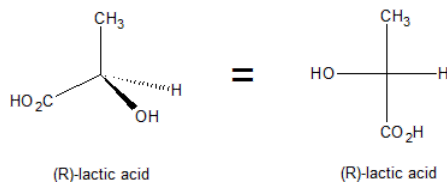
Step 3: Pull the two bonds going into the plane of the paper onto the plane of the paper.



Step 4: Omit the chiral atom symbol for convenience. This is the Fischer Projection of (*R*)-Lactic acid.

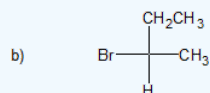
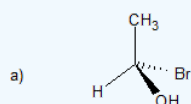


The stereochemical formula for (*R*)-lactic acid can be drawn using either method. To build this skill, we begin by drawing the structures and converting them step wise. Models can also be helpful. Eventually, we will be able to mentally conversion between these two structures.

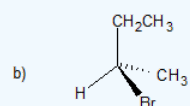
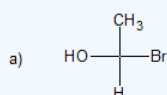


Exercise 1

1. Convert each compound into the alternate stereochemical structure (Perspective $\longleftrightarrow$ Fischer).



Answer



Other representations are possible. If you are not sure, use a molecular model kit to make a model for each structure and then compare the models.

See also [D,L-convention](#).

Contributors and Attributions

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5.3: Absolute Configuration and the (R) and (S) System

Learning Objective

- name chiral compounds using (R) & (S) nomenclature

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.

If you have a modeling kit use it as you read through this section and work the practice problems.

Introduction and the Cahn-Ingold-Prelog rules of Priority

To name the enantiomers of a compound unambiguously, their names must include the "handedness" of the molecule. The letters "R" and "S" are determined by applying the Cahn-Ingold-Prelog (CIP) rules. The optical activity (+/-) can also be communicated in the name, but must be empirically derived. There are also biochemical conventions for carbohydrates (sugars) and amino acids (the building blocks of proteins).

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 CIP system, there are two ways of experimentally determining the absolute configuration of an enantiomer:

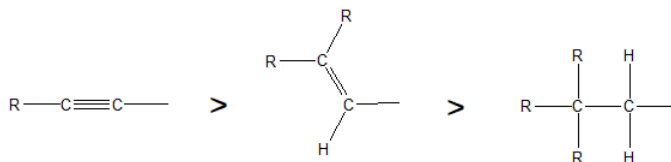
1. **X-ray diffraction** analysis. Note that there is no correlation between the sign of rotation and the structure of a particular enantiomer.
2. Chemical correlation with a molecule whose structure has already been determined via X-ray diffraction.

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.

The **Cahn-Ingold-Prelog** rules of priority are based on the atomic numbers of the atoms of interest. For chirality, the atoms of interest are the atoms bonded to the chiral carbon.

1. The atom with higher atomic number has higher priority ($I > Br > Cl > S > P > F > O > N > C > H$).
2. When comparing isotopes, the atom with the higher mass number has higher priority [$^{18}O > ^{16}O$ or $^{15}N > ^{14}N$ or $^{13}C > ^{12}C$ or $T(^3H) > D(^2H) > H$].
3. When there is a tie in (2) above, establish relative priority by proceeding to the next atom(s) along the chain until the first difference is observed.

Multiple bonds are treated as if each bond of the multiple bond is bonded to a unique atom. For example, the ethenyl group ($CH_2=CH$) has higher priority than the ethyl group (CH_3CH_2). The ethenyl carbon priority is "two" bonds to carbon atoms and one bond to a hydrogen atom compared with the ethyl carbon that has only one bond to a carbon atom and two bonds to two hydrogen atoms. Similarly, the carbon-carbon triple bond of acetylene would give it higher CIP priority than the ethenyl group as summarized below.



Relative Priority according to the Cahn-Ingold-Prelog Rules

Stereocenters are labeled R or S

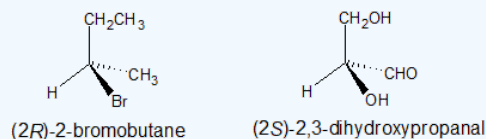
The "right hand" and "left hand" nomenclature is used to name the enantiomers of a chiral compound. The stereocenters are labeled as R or S.



Consider the diagram above on the left: a curved arrow is drawn counter-clockwise (c-cw) from the highest priority substituent (1) to the lowest priority substituent (4) in the **S-configuration** ("Sinister" → Latin= "left"). The counterclockwise direction can be recognized by the movement left when leaving the 12 o' clock position. Now consider the diagram above on the right where a curved arrow is drawn clockwise (cw) from the highest priority substituent (1) to the lowest priority substituent (4) in the R configuration ("Rectus" → Latin= "right"). The **R** or **S** is then added as a prefix, in parenthesis, to the name of the enantiomer of interest. A locator number is required if there is more than one chiral center. Otherwise, the person reading the name is expected to recognize the chiral center.

Example 1

The two chiral compounds below are drawn to emphasize the chiral carbon with the full chemical name below each structure.



Absolute Configurations of Perspective Formulas

Chemists need a convenient way to distinguish one stereoisomer from another. The **Cahn-Ingold-Prelog system** is a set of rules that allows us to unambiguously define the stereochemical configuration of any stereocenter, using the designations '**R**' (from the Latin *rectus*, meaning right-handed) or '**S**' (from the Latin *sinister*, meaning left-handed).

The rules for this system of stereochemical nomenclature are, on the surface, fairly simple.

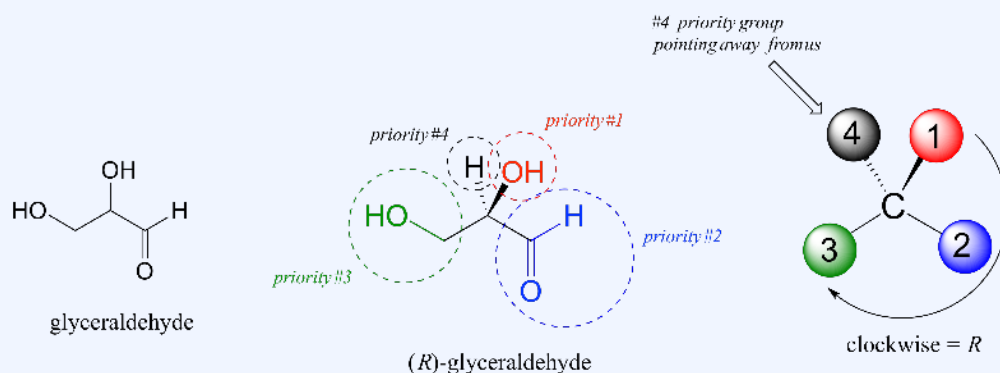
Rules for assigning an R/S designation to a chiral center

- 1: Assign priorities to the four substituents, with #1 being the highest priority and #4 the lowest. Priorities are based on the atomic number.
- 2: Trace a circle from #1 to #2 to #3.
- 3: Determine the orientation of the #4 priority group. If it is oriented into the plane of the page (away from you), go to step 4a. If it is oriented out of the plane of the page (toward you) go to step 4b.
- 4a: (*#4 group pointing away from you*): a clockwise circle in part 2 corresponds to the **R** configuration, while a counterclockwise circle corresponds to the **S** configuration.
- 4b: (*#4 group pointing toward you*): a clockwise circle in part 2 corresponds to the **S** configuration, while a counterclockwise circle corresponds to the **R** configuration.

We'll use the 3-carbon sugar glyceraldehyde as our first example. The first thing that we must do is to assign a **priority** to each of the four substituents bound to the chiral center. We first look at the atoms that are directly bonded to the chiral center:

these are H, O (in the hydroxyl), C (in the aldehyde), and C (in the CH₂OH group).

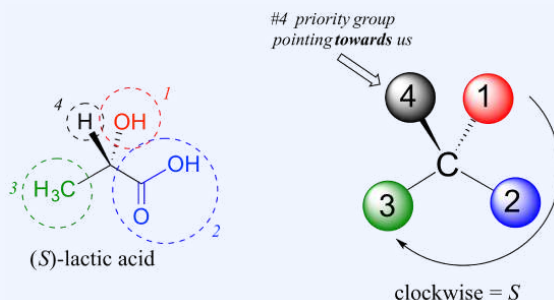
Assigning R/S configuration to glyceraldehyde:



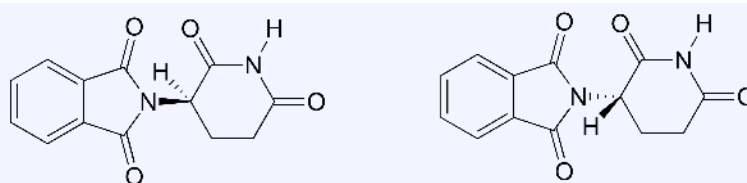
Two priorities are easy: hydrogen, with an atomic number of 1, is the lowest (#4) priority, and the hydroxyl oxygen, with atomic number 8, is priority #1. Carbon has an atomic number of 6. Which of the two 'C' groups is priority #2, the aldehyde or the CH₂OH? To determine this, we move one more bond away from the chiral center: for the aldehyde we have a *double* bond to an oxygen, while on the CH₂OH group we have a *single* bond to an oxygen. If the atom is the same, double bonds have a higher priority than single bonds. Therefore, the aldehyde group is assigned #2 priority and the CH₂OH group the #3 priority.

With our priorities assigned, we look next at the #4 priority group (the hydrogen) and see that it is pointed back away from us, into the plane of the page - thus step 4a from the procedure above applies. Then, we trace a circle defined by the #1, #2, and #3 priority groups, in increasing order. The circle is clockwise, which by step 4a tells us that this carbon has the '*R*' configuration, and that this molecule is (*R*)-glyceraldehyde. Its enantiomer, by definition, must be (*S*)-glyceraldehyde.

Next, let's look at one of the enantiomers of lactic acid and determine the configuration of the chiral center. Clearly, H is the #4 substituent and OH is #1. Owing to its three bonds to oxygen, the carbon on the acid group takes priority #2, and the methyl group takes #3. The #4 group, hydrogen, happens to be drawn pointing *toward* us (out of the plane of the page) in this figure, so we use step 4b: The circle traced from #1 to #2 to #3 is clockwise, which means that the chiral center has the *S* configuration.

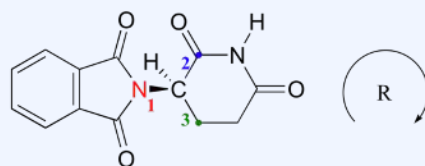


The drug thalidomide is an interesting - but tragic - case study in the importance of stereochemistry in drug design. First manufactured by a German drug company and prescribed widely in Europe and Australia in the late 1950's as a sedative and remedy for morning sickness in pregnant women, thalidomide was soon implicated as the cause of devastating birth defects in babies born to women who had taken it. Thalidomide contains a chiral center, and thus exists in two enantiomeric forms. It was marketed as a **racemic mixture**: in other words, a 50:50 mixture of both enantiomers.



two enantiomers of thalidomide

Let's try to determine the stereochemical configuration of the enantiomer on the left. Of the four bonds to the chiral center, the #4 priority is hydrogen. The nitrogen group is #1, the carbonyl side of the ring is #2, and the $-\text{CH}_2$ side of the ring is #3.



(R)-thalidomide

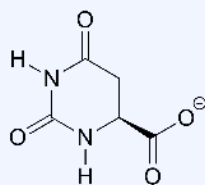
The hydrogen is shown pointing away from us, and the prioritized substituents trace a clockwise circle: this is the *R* enantiomer of thalidomide. The other enantiomer, of course, must have the *S* configuration.

Although scientists are still unsure today how thalidomide works, experimental evidence suggests that it was actually the *R* enantiomer that had the desired medical effects, while the *S* enantiomer caused the birth defects. Even with this knowledge, however, pure (*R*)-thalidomide is not safe, because enzymes in the body rapidly convert between the two enantiomers - we will see how that happens in chapter 12.

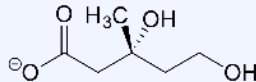
As a historical note, thalidomide was never approved for use in the United States. This was thanks in large part to the efforts of Dr. Frances Kelsey, a Food and Drug officer who, at peril to her career, blocked its approval due to her concerns about the lack of adequate safety studies, particularly with regard to the drug's ability to enter the bloodstream of a developing fetus. Unfortunately, though, at that time clinical trials for new drugs involved widespread and unregulated distribution to doctors and their patients across the country, so families in the U.S. were not spared from the damage caused.

Very recently a close derivative of thalidomide has become legal to prescribe again in the United States, with strict safety measures enforced, for the treatment of a form of blood cancer called multiple myeloma. In Brazil, thalidomide is used in the treatment of leprosy - but despite safety measures, children are still being born with thalidomide-related defects.

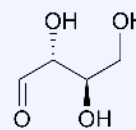
Exercise 1.: Determine the stereochemical configurations of the chiral centers in the biomolecules shown below.



dihydroorotate

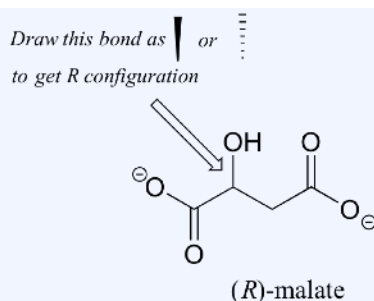


mevalonate



(D)-erythrose

Exercise 2.: Should the (*R*) enantiomer of malate have a solid or dashed wedge for the C-O bond in the figure below?



Exercise 3.: Using solid or dashed wedges to show stereochemistry, draw the (R) enantiomer of ibuprofen and the (S) enantiomer of 2-methylerythritol-4-phosphate (structures are shown earlier in this chapter without stereochemistry).

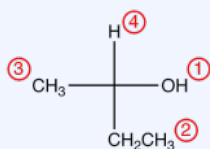
[Solutions to exercises](#)

Absolute Configurations of Fischer Projections

To determine the absolute configuration of a chiral center in a Fischer projection, use the following two-step procedure.

Step 1

Assign priority numbers to the four ligands (groups) bonded to the chiral center using the CIP priority system.



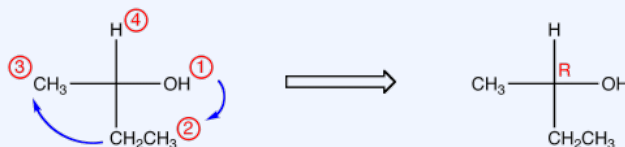
Step 2 - vertical option

If the lowest priority ligand is on a Vertical bond, then it is pointing away from the viewer.

Trace the three highest-priority ligands starting at the highest-priority ligand (① → ② → ③) in the direction that will give a Very correct answer.

direction of ① → ② → ③	absolute configuration
clockwise	R
counterclockwise	S

In the compound below, the movement is clockwise indicating an R-configuration. The complete IUPAC name for this compound is (R)-butan-2-ol.



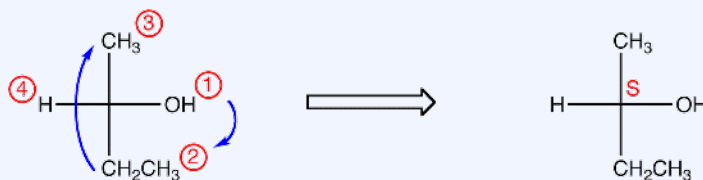
Step 2 - horizontal option

If the lowest-priority ligand is on a Horizontal bond, then it is pointing toward the viewer.

Trace the three highest-priority ligands starting at the highest-priority ligand (① → ② → ③) in the direction that will give a Horribly wrong answer. Note in the table below that the configurations are reversed from the first example.

direction of ① → ② → ③	absolute configuration
clockwise	S
counterclockwise	R

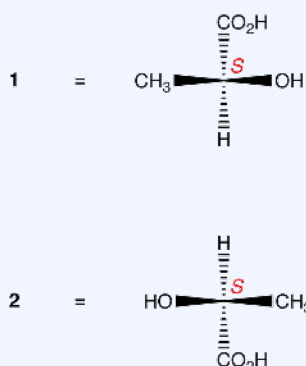
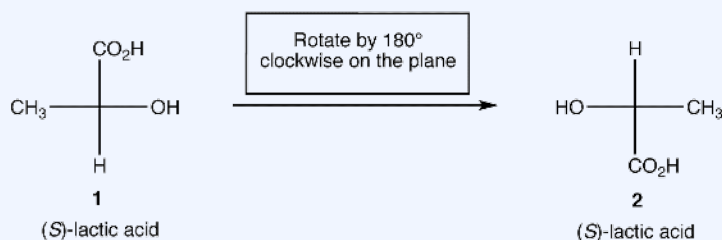
In the compound below, the movement is clockwise (R) which is Horribly wrong, so the actual configuration is S. The complete IUPAC name for this compound is (S)-butan-2-ol.



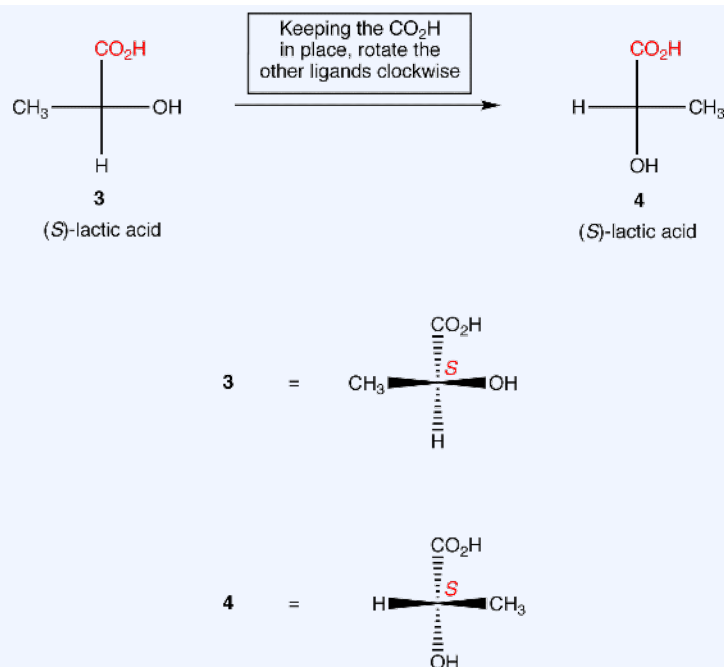
Manipulating Fischer Projections with NO Change to Configuration

A Fischer projection restricts a three-dimensional molecule into two dimensions. Consequently, there are limitations as to the operations that can be performed on a Fischer projection without changing the absolute configuration at chiral centers. The operations that do not change the absolute configuration at a chiral center in a Fischer projections can be summarized as two rules.

Rule 1: Rotation of the Fischer projection by 180° in either direction without lifting it off the plane of the paper does not change the absolute configuration at the chiral center.



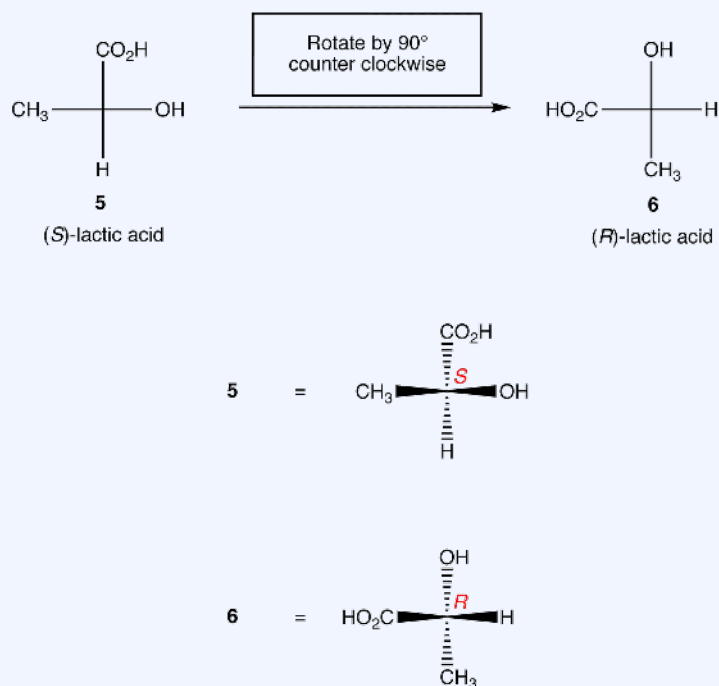
Rule 2: Rotation of three ligands on the chiral center in either direction, keeping the remaining ligand in place, does not change the absolute configuration at the chiral center.



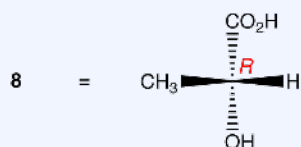
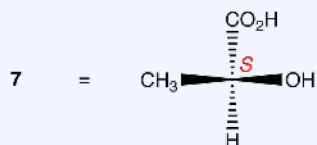
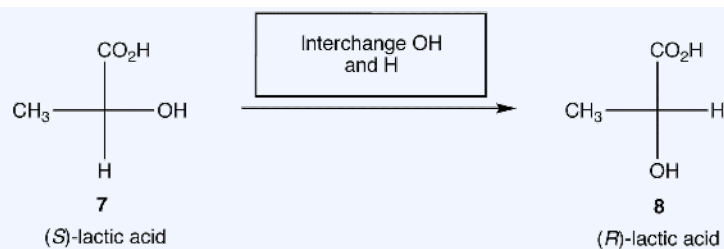
Manipulating Fischer Projections with Change to Configuration

The operations that do change the absolute configuration at a chiral center in a Fischer projection can be summarized as two rules.

Rule 1: Rotation of the Fischer projection by 90° in either direction changes the absolute configuration at the chiral center.



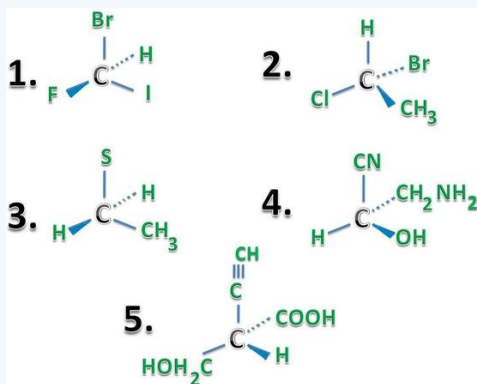
Rule 2: Interchanging any two ligands on the chiral center changes the absolute configuration at the chiral center.



The above rules assume that the Fischer projection under consideration contains only one chiral center. However, with care, they can be applied to Fischer projections containing any number of chiral centers.

Exercise 1

Classify the following compounds as R or S?



Solution

- S:** I > Br > F > H. The lowest priority substituent, H, is already going towards the back. It turns left going from I to Br to F, so it's a S.
- R:** Br > Cl > CH₃ > H. You have to switch the H and Br in order to place the H, the lowest priority, in the back. Then, going from Br to Cl, CH₃ is turning to the right, giving you a R.
- Neither R or S:** This molecule is achiral. Only chiral molecules can be named R or S.
- R:** OH > CN > CH₂NH₂ > H. The H, the lowest priority, has to be switched to the back. Then, going from OH to CN to CH₂NH₂, you are turning right, giving you a R.
- (S) S:** -COOH > -CH₂OH > C≡CH > H. Then, going from -COOH to -CH₂OH to -C≡CH you are turning left, giving you a S configuration.

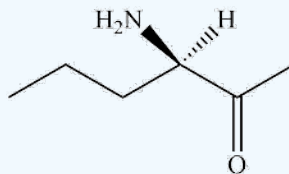
Exercises

6. Orient the following so that the least priority (4) atom is paced behind, then assign stereochemistry (*R* or *S*).



7. Draw (*R*)-2-bromobutan-2-ol.

8. Assign *R/S* to the following molecule.



Solutions

6.



A = *S*; B = *R*

7.

8. The stereo center is *R*.

Other Resources

[Kahn Academy video tutorial on the R-S naming system](#)

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.

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5.4: The E/Z System for alkenes

Learning Objective

- recognize and classify the stereochemistry of alkenes using the cis/trans and E/Z systems
- give the IUPAC names for alkenes given their structure & vice versa including E/Z isomers

E/Z Nomenclature in Alkenes

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 for chirality 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.

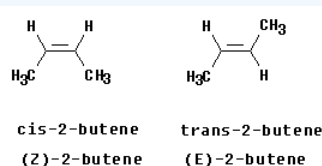
The priority rules are often called the Cahn-Ingold-Prelog (CIP) rules, after the chemists who developed the system.

The general strategy of the E-Z system is to analyze the two groups at each end of the double bond. For each vinyl carbon, rank the two groups using the CIP priority rules. Determine 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 Zee Zame Zide") or on **opposite** sides (E, from German entgegen = opposite) of the double bond.

Example 5.4.1

The figure below 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.

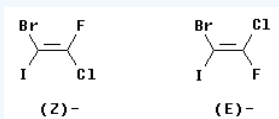


E/Z will work -- even when cis/trans fails

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 5.4.1

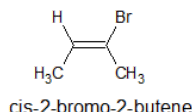
The following figure shows two isomers of an alkene with four different groups on the double bond, 1-bromo-2-chloro-2-fluoro-1-iodoethene.



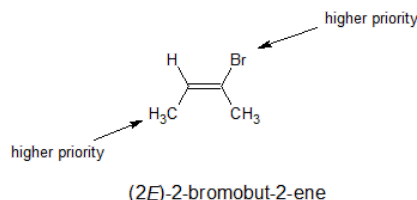
It should be apparent that the two structures shown are distinct chemicals. However, it is impossible to name them as cis or trans. On the other hand, the E-Z system works fine... Consider the left hand structure. On C1 (the left end of the double bond), the two atoms attached to the double bond are 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

There are also molecules for which the E/Z system will not agree with the cis/trans system. Let's use 2-bromo-2-butene to explore this option. Is this compound cis or trans? This molecule is clearly cis. The two methyl groups are on the same side. More rigorously, the "parent chain" is cis.



Is this compound 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 -CH₃ (left) and -Br (right). Thus the two priority groups are on opposite sides = entgegen = E.

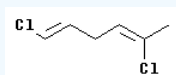


This example should convince you that cis and Z are not synonyms. Cis/trans and E,Z are determined by distinct criteria. There may seem to be a simple correspondence, but it is not a rule. Be sure to determine cis/trans or E,Z separately, as needed.

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 5.4.3

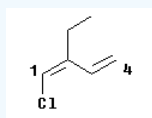


The configuration at the left hand double bond is E; at the right hand double bond it is Z. Thus this compound is (1E,4Z)-1,5-dichloro-1,4-hexadiene.

The double-bond rule in determining priorities

Example 5.4.4

Consider the compound below

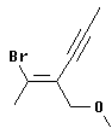


This is 1-chloro-2-ethyl-1,3-butadiene -- ignoring, for the moment, the geometric isomerism. There is no geometric isomerism at the second double bond, at 3-4, because it has 2 H at its far end.

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 $-\text{CH}_2\text{-CH}_3$ (an ethyl group) and $-\text{CH}=\text{CH}_2$ (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.



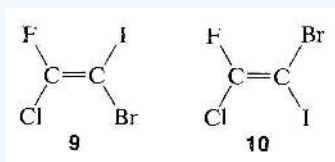
To illustrate this, consider the molecule at the left. Is the double bond here E or Z? At the left end of the double bond, $\text{Br} > \text{H}$. But the right end of the double bond requires a careful analysis.

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 $-\text{Br}$) and "down" on the right end (the $-\text{CH}_2\text{-O-CH}_3$). This means that the isomer shown is opposite = entgegen = E. And what is the name? The "name" feature of ChemSketch says it is (2E)-2-(1-bromoethylidene)pent-3-ynyl methyl ether.

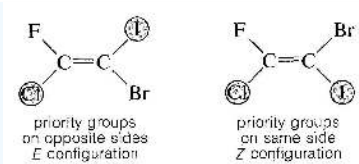
Example 5.4.1

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:

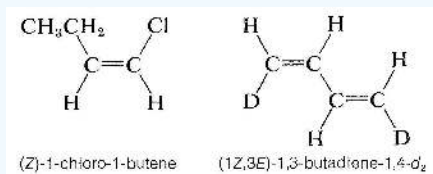


A system that is easy to use and which is based on the sequence rules already described for the R,S system works as follows:

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, $\text{Cl} > \text{F}$
 - at carbon atom 2, $\text{I} > \text{Br}$
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:

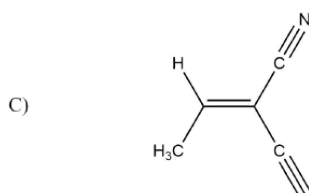
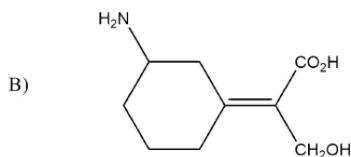
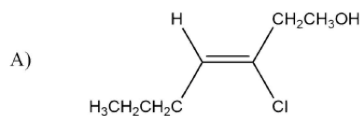


Exercises

1. Order the following in increasing priority.

- A) -H , -Cl , -OH
 B) -CH_3 , $\text{-CH}_2\text{OH}$, $\text{-CH}_2\text{CH}_3$
 C) $\text{-C}\equiv\text{CH}$, -CH=CH_2 , -CH=O

2. Label the following as E or Z conformations.



Answer

1. A) $\text{-H} < \text{-OH} < \text{-Cl}$ (highest priority)

B) $\text{-CH}_3 < \text{-CH}_2\text{CH}_3 < \text{-CH}_2\text{OH}$ (highest priority)

C) $\text{-CH=CH}_2 < \text{-C}\equiv\text{CH} < \text{-CH=O}$ (highest priority)

2. A) Z B) Z C) E

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>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."

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5.5: Diastereomers - more than one chiral center

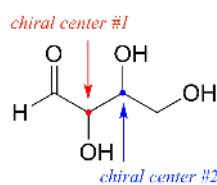
Learning Objective

- recognize and classify diastereomers

Diastereomers are stereoisomers with two or more chiral centers that are not enantiomers. Diastereomers have different physical properties (melting points, boiling points, and densities). Depending on the reaction mechanism, diastereomers can produce different stereochemical products.

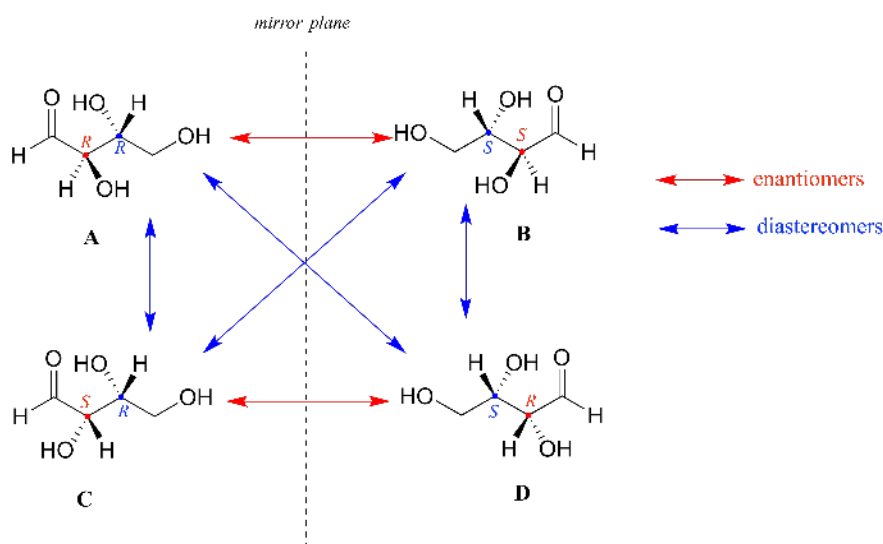
Introduction

So far, we have been analyzing compounds with a single chiral center. Next, we turn our attention to those which have multiple chiral centers. We'll start with some stereoisomeric four-carbon sugars with two chiral centers.



To avoid confusion, we will simply refer to the different stereoisomers by capital letters.

Look first at compound A below. Both chiral centers in have the *R* configuration (you should confirm this for yourself!). The mirror image of Compound A is compound B, which has the *S* configuration at both chiral centers. If we were to pick up compound A, flip it over and put it next to compound B, we would see that they are *not* superimposable (again, confirm this for yourself with your models!). A and B are nonsuperimposable mirror images: in other words, enantiomers.



Now, look at compound C, in which the configuration is *S* at chiral center 1 and *R* at chiral center 2. Compounds A and C are stereoisomers: they have the same molecular formula and the same bond connectivity, but a different arrangement of atoms in space (recall that this is the definition of the term 'stereoisomer'). However, they are *not* mirror images of each other (confirm this with your models!), and so they are *not* enantiomers. By definition, they are **diastereomers** of each other.

Notice that compounds C and B also have a diastereomeric relationship, by the same definition.

So, compounds A and B are a pair of enantiomers, and compound C is a diastereomer of both of them. Does compound C have its own enantiomer? Compound D is the mirror image of compound C, and the two are not superimposable. Therefore, C and D are a pair of enantiomers. Compound D is also a diastereomer of compounds A and B.

This can also seem very confusing at first, but there are some simple shortcuts to analyzing stereoisomers:

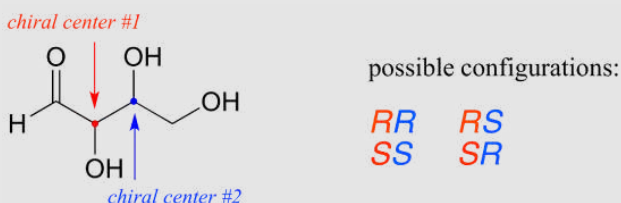
Stereoisomer shortcuts

If **all** of the chiral centers are of opposite R/S configuration between two stereoisomers, they are enantiomers.

If **at least one, but not all** of the chiral centers are opposite between two stereoisomers, they are diastereomers.

(Note: these shortcuts do not take into account the possibility of additional stereoisomers due to alkene groups: we will come to that later)

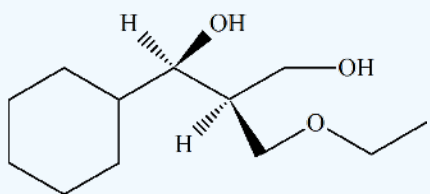
Here's another way of looking at the four stereoisomers, where one chiral center is associated with red and the other blue. Pairs of enantiomers are stacked together.



We know, using the shortcut above, that the enantiomer of **RR** must be **SS** - both chiral centers are different. We also know that **RS** and **SR** are diastereomers of **RR**, because in each case one - but not both - chiral centers are different.

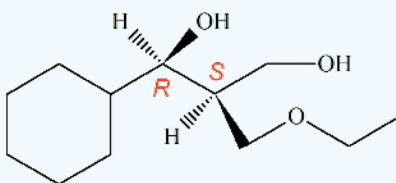
Exercises

1. Determine the stereochemistry of the following molecule:



Answer

1.



Contributors and Attributions

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5.6: Meso Compounds

Learning Objective

- recognize and classify 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.

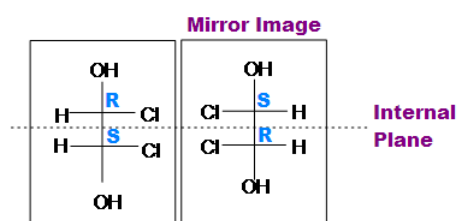
Introduction

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.

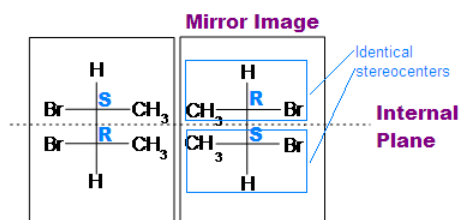
Identification

If A is a meso compound, it should have two or more stereocenters, an internal plane, and the stereochemistry should be R and S.

- Look for an internal plane, or internal mirror, that lies in between the compound.
- 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.

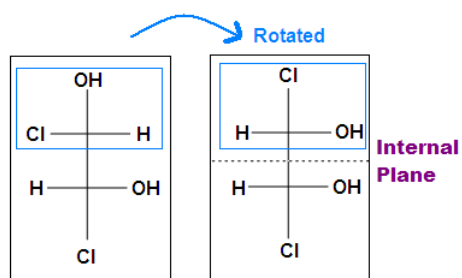


trans-1,2-dichloro-1,2-ethanediol

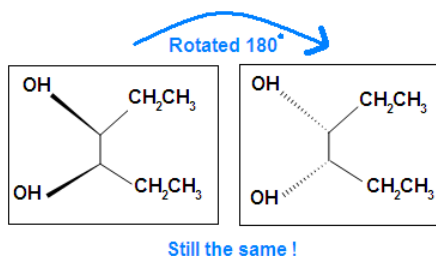


(meso)-2,3-dibromobutane

Tips: An interesting thing about single bonds or sp³-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:

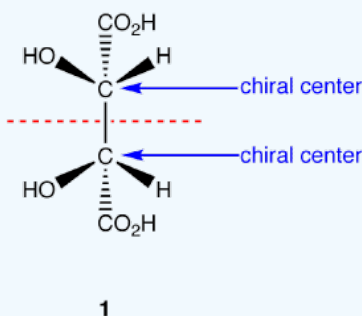


Another case is when we rotate the whole molecule by 180 degree. Both molecules below are still meso.



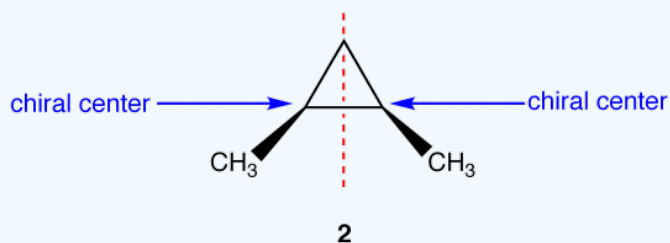
Remember the internal plane here is depicted on two dimensions. However, in reality, it is three dimensions, so be aware of it when we identify the internal mirror.

Example 5.6.1:



1 has a plane of symmetry (the horizontal plane going through the red broken line) and, therefore, is achiral; 1 has chiral centers. Thus, 1 is a meso compound.

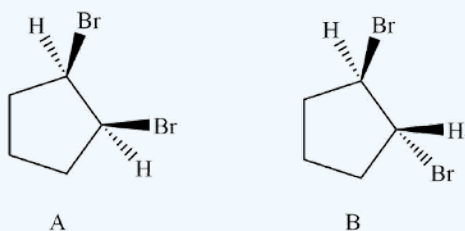
Example 5.6.2:



This molecule 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 two chiral centers. Thus, it is a meso compound.

Exercise 5.6.1

Which of the following are meso-compounds:



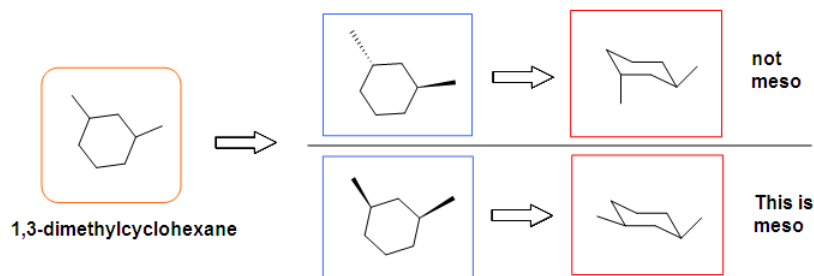
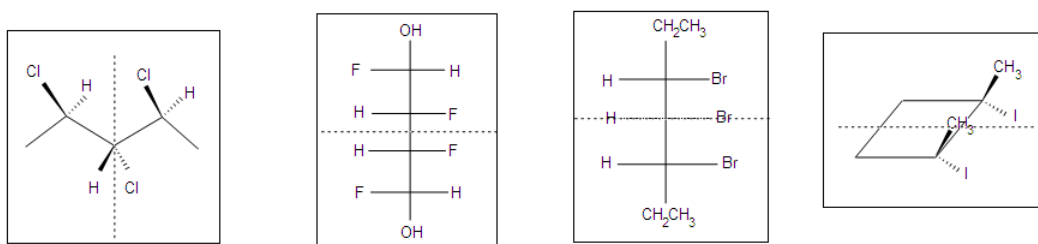
- b. C – 2,3-dibromobutane
- c. D – 2,3-dibromopentane

Answer

Compounds A and C are meso.

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.

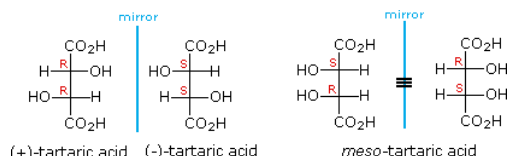


The chiral centers in the preceding examples have all been different. In the case of 2,3-dihydroxybutanedioic acid, known as tartaric acid, the two chiral centers have the same four substituents and are equivalent. As a result, two of the four possible stereoisomers of this compound are identical due 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:	$[\alpha]_D = +13^\circ$	m.p. 172 °C
(-)-tartaric acid:	$[\alpha]_D = -13^\circ$	m.p. 172 °C
meso-tartaric acid:	$[\alpha]_D = 0^\circ$	m.p. 140 °C

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 180° in the plane.



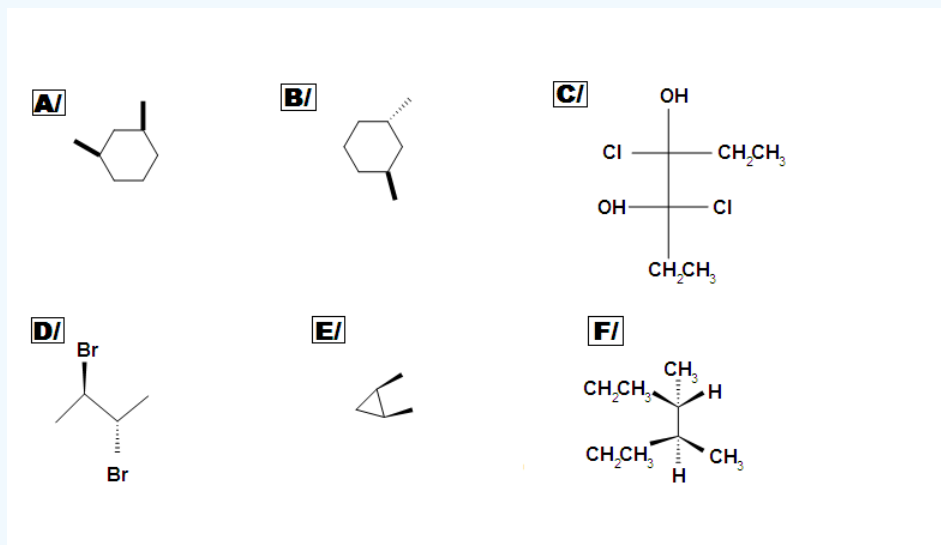
Optical Activity Analysis

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 dextrorotatory (+).

Achiral Diastereomers (meso-Compounds)

Exercise 5.6.1

Beside meso, there are also other types of molecules: enantiomer, **diastereomer**, and identical. Determine if the following molecules are meso.



Answer

A C, D, E are meso compounds.

Contributors and Attributions

- Duy Dang
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- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
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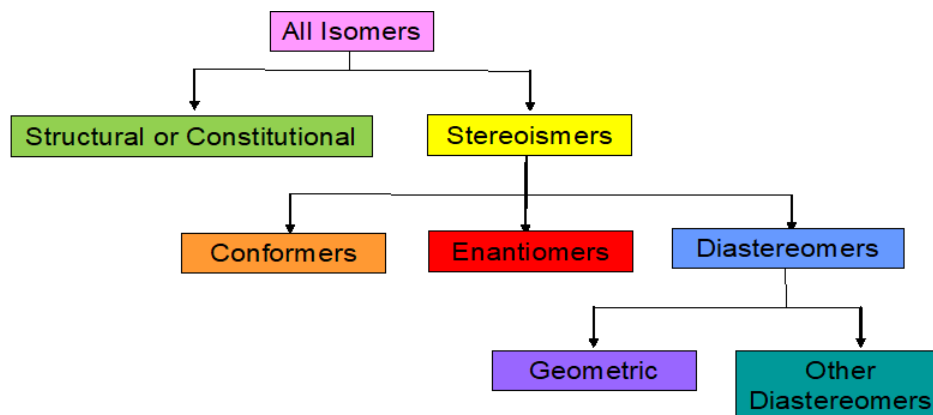
5.6: [Meso Compounds](#) is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

5.7: Isomerism Summary

Learning Objective

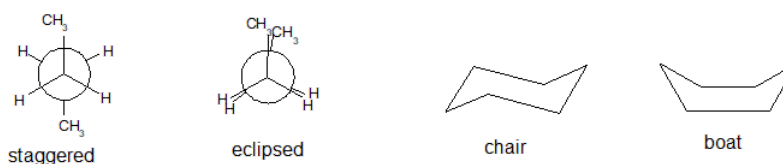
- distinguish and discern the structural and chemical relationships between isomeric compounds

The various types of isomers have been introduced and explored over several chapters. It can be helpful to review, compare, and contrast all of the forms of isomerism to build our skills of discernment. A brief review of each type of isomerism follows the summary diagram. See the respective chapter for a complete explanation.



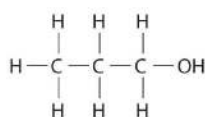
Conformational Isomers

The rotation of C–C single bonds both carbon chains creates conformers (the same compound shown in different rotations). 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). While complete rotation of C–C single bonds is not possible in rings. The freedom of bond movement does allow the rings to assume different conformations, such as the chair and boat for 6-membered rings.

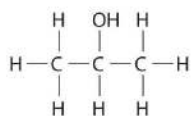


Structural (Constitutional) Isomers

Unlike conformational isomers, structural isomers differ in connectivity, as illustrated below 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 creating a unique compounds with differences in their physical and chemical properties.

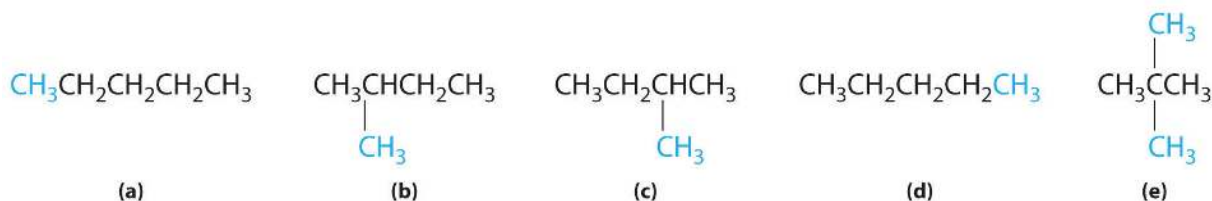


1-Propanol (*n*-propanol)



2-Propanol (isopropanol)

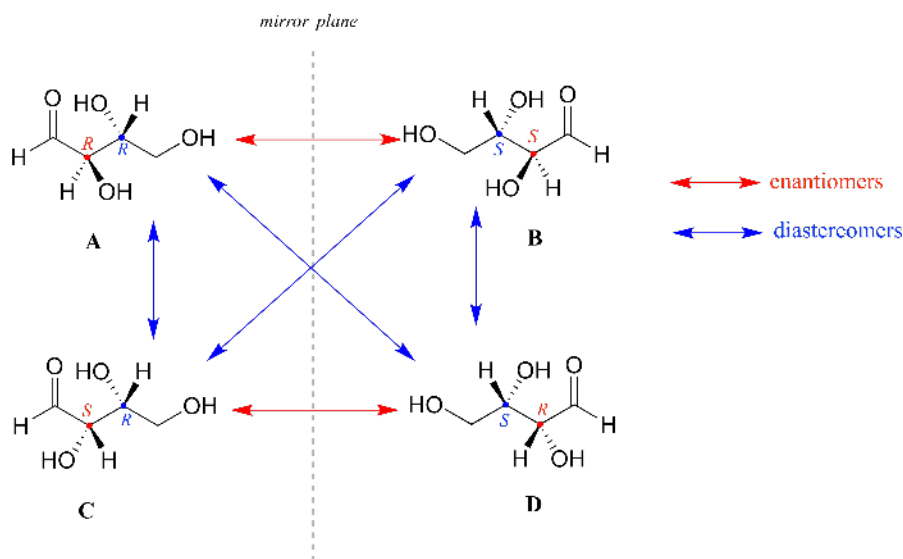
Consider, for example, the following five structures represented by the formula C_5H_{12} . In the conversion of one structural isomer to another, at least one bond must be broken and reformed at a different position in the molecule.



Structures (a) and (d) above represent the same compound, *n*-pentane. Structures (b) and (c) represent the same compound, 2-methylbutane. No bonds need to be broken and reformed to convert between (a) and (d) or between (b) and (c). The molecules are simply rotated 180° about a vertical axis. Structure (e) is named 2,2-dimethylpropane. There are only three structural isomers possible with the chemical formula C_5H_{12} : *n*-pentane, 2-methylbutane, and 2,2-dimethylpropane. Structural isomers have distinct physical and chemical properties.

Stereoisomers

Enantiomers are pairs of compounds that are non-superimposable images. When there are two or more chiral centers in a compound, the diastereomers can exist. Diastereomers are stereoisomers that are NOT enantiomers. Enantiomers share all physical properties except for their interaction with plane polarized light. Diastereomers have different physical properties (melting points and boiling points and densities).



Exercise

1. What kind of isomers are the following pairs? Note: It can be difficult to answer this question directly from the names. It can be helpful to draw the structures.

- a. (R)-5-chlorohexene and 6-chlorohexene
- b. (2R,3R)-dibromohexane and (2R,3S)-dibromohexane

Answer

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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5.8: Optical Activity, Racemic Mixtures, and Separation of Chiral Compounds

Learning Objective

- define and explain the lack of optical activity of racemic mixtures
- determine the percent composition of an enantiomeric mixture from polarimetry data and the for specific rotation formula

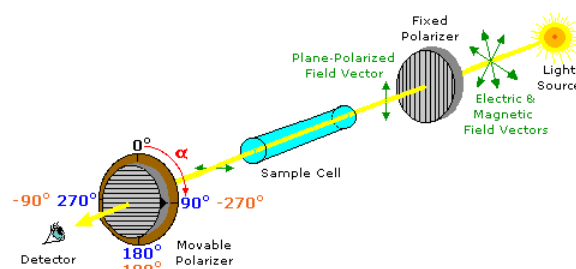
Racemic Mixtures (Racimates)

A *racemic mixture* is a 50:50 mixture of two enantiomers. Racemic mixtures were an interesting experimental discovery because two optically active samples can be combined in a 1:1 ratio to create an optically INACTIVE sample. Polarimetry is used to measure optical activity. The history and theoretical foundation are discussed below.

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.



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 ($\alpha = 0^\circ$). If the analyzer is turned 90° 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 $+90^\circ$, 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 -90° or $+270^\circ$ rather than $+90^\circ$. If the sample concentration is reduced by 10%, then the

positive rotation would change to $+81^\circ$ (or $+243^\circ$) while the negative rotation would change to -81° , 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:

$$[\alpha]_D = \frac{\alpha}{lc} \quad (5.3.1)$$

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: $[\alpha]_D = +62.5^\circ$	this isomer may be referred to as (+)-carvone or <i>d</i> -carvone
Carvone from spearmint: $[\alpha]_D = -62.5^\circ$	this isomer may be referred to as (–)-carvone or <i>l</i> -carvone
Lactic acid from muscle tissue: $[\alpha]_D = +2.5^\circ$	this isomer may be referred to as (+)-lactic acid or <i>d</i> -lactic acid
Lactic acid from sour milk: $[\alpha]_D = -2.5^\circ$	this isomer may be referred to as (–)-lactic acid or <i>l</i> -lactic acid

A 50:50 mixture of enantiomers has no observable optical activity. Such mixtures are called **racemates** or racemic modifications, and are designated $(\pm)$. 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%.

$$\% \text{ optical purity} = \frac{\text{specific rotation of mixture}}{\text{specific rotation of pure enantiomer}} \times 100$$

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:

$$ee = \frac{(\% \text{ more abundant enantiomer} - 50) \times 100}{50}$$

For example, a mixture containing 60% *R* enantiomer (and 40% *S* enantiomer) has a 20% enantiomeric excess of *R*: $((60-50) \times 100) / 50 = 20\%$.

Example

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?

Solution

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.

$$\text{Rotation (R/S Mix)} = [\text{Fraction(S)} \times \text{Rotation (S)}] + [\text{Fraction(R)} \times \text{Rotation (R)}]$$

Let Fraction (*S*) = *x*, therefore Fraction (*R*) = 1 – *x*

$$\text{Rotation (R/S Mix)} = x[\text{Rotation (S)}] + (1 - x)[\text{Rotation (R)}]$$

$$-23 = x(+61) + (1 - x)(-61)$$

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.

$$\begin{aligned} ee &= [(\% \text{ more abundant enantiomer} - 50) \times 100] / 50 \\ &= [68.9 - 50] \times 100 / 50 = 37.8\% \end{aligned}$$

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 an enantiomerically pure carboxylic acid, the result is a mixture of diastereomers: in this case, because the pure (*R*) enantiomer 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. This technique is known as 'Moscher's esters', after Harry Stone Moscher, a chemist who pioneered the method at Stanford University.

Exercise 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 $[\alpha]_D$?

Solution

$$5 \text{ cm} = 0.5 \text{ dm}$$

$$[\alpha]_D = \alpha / (c \times l) = +1.52 / (0.3 \times 0.5) = +10.1^\circ$$

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5.9: RESOLUTION (SEPARATION) OF ENANTIOMERS

Learning Objective

- explain how to resolve (separate) a pair of enantiomers

INTRODUCTION AND OVERVIEW

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.

CHIRAL RESOLUTION

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 an enantiomerically pure carboxylic acid, the result is a mixture of diastereomers: in this case, because the pure (R) enantiomer 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 'Mosher's esters', after Harry Stone Mosher, 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.

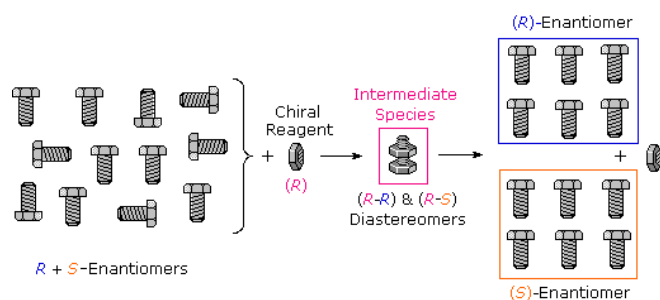


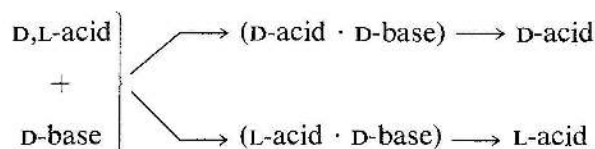
Figure 5.8.1:

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.

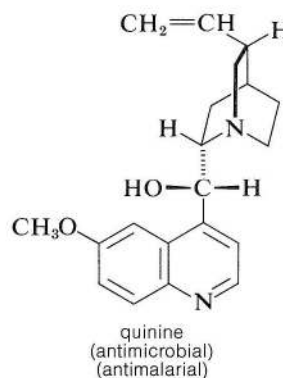
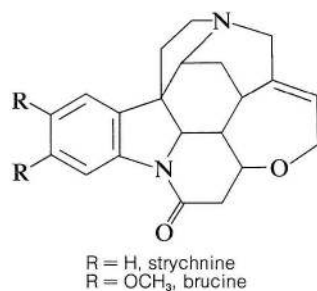
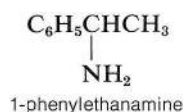
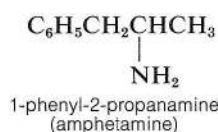
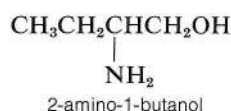
Because the physical properties of enantiomers are identical, they seldom can be separated by simple physical methods, such as fractional crystallization or distillation. It is only under the influence of another chiral substance that enantiomers behave differently, and almost all methods of resolution 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:

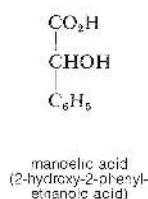
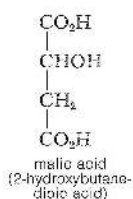
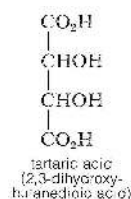


Resolution of chiral acids through the formation of diastereomeric salts requires adequate supplies of suitable chiral bases. Brucine, strychnine, and quinine frequently are used for this purpose because they are readily available, naturally occurring chiral bases. Simpler amines of synthetic origin, such as 2-amino-1-butanol, amphetamine, and 1-phenylethanamine, also can be used, but first they must be resolved themselves.



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.

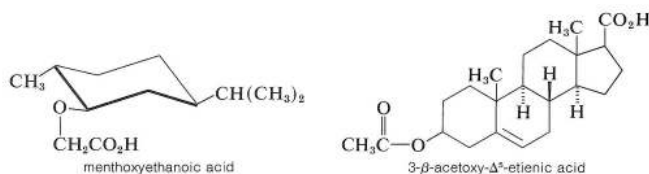


The principle is the same as for the resolution of a racemic acid with a chiral base, and the choice of acid will depend both on the ease of separation of the diastereomeric salts and, of course, on the availability of the acid for the scale of the resolution involved. Resolution methods of this kind 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

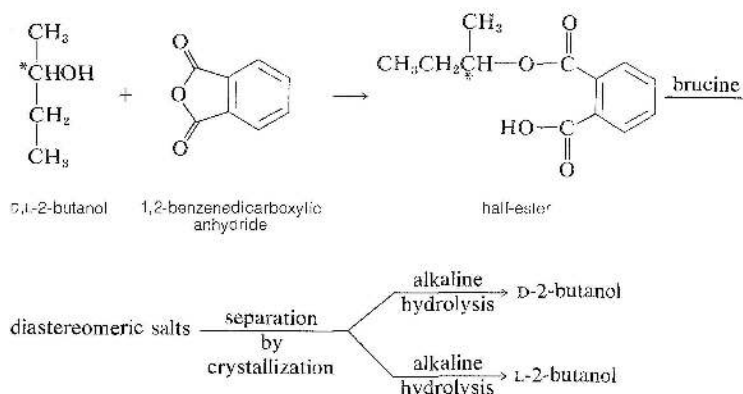
there is no further change in the measured optical rotation of the crystals. At this stage it is hoped that the crystalline salt is a pure diastereomer from which one pure enantiomer can be recovered. The optical rotation of this enantiomer will be a maximum value if it is "optically" pure because any 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:

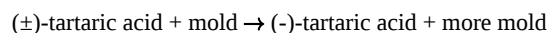


The most common method of resolving an alcohol is to convert it to a half-ester of a dicarboxylic acid, such as butanedioic (succinic) or 1,2-benzenedicarboxylic (phthalic) acid, with the corresponding anhydride. The resulting half-ester has a free carboxyl function and may then be resolvable with a chiral base, usually brucine:



OTHER METHODS OF RESOLUTION

One 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:



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 ($\pm$)-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.

Exercise

1. Indicate the reagents you would 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.

1. 1-phenyl-2-propanamine
2. 2,3-pentadienedioic acid
3. 1-phenylethanol

Solutions:

1.

a. React 1-phenyl-2-propanamine racemic mixture with a chiral acid such as (+)-tartaric acid (*R, R*).

Reaction will produce a mixture of diastereomeric salts (i.e. *R, R, R* and *S, R, R*).

Separate diastereomers through crystallization.

Treat salt with strong base (e.g. KOH) to recover the pure enantiomeric amine.

b. React 2,3-pentadienedioic acid mixture with a chiral base such as (*R*)-1-phenylethylamine.

Reaction will produce a mixture of diastereomeric salts.

Separate diastereomers through crystallization.

Treat salt with strong acid (e.g. HCl) to recover the pure enantiomer acid.

c. React 1-phenylethanol mixture with 1,2-benzenedicarboxylic anhydride.

Reaction will produce a mixture of diastereomeric salts.

Separate diastereomers through crystallization.

Then alkaline hydrolysis treatment to recover the pure enantiomeric alcohol.

CONTRIBUTORS AND ATTRIBUTIONS

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- 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."

5.9: Resolution (Separation) of Enantiomers is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

5.10: Biochemistry of Enantiomers

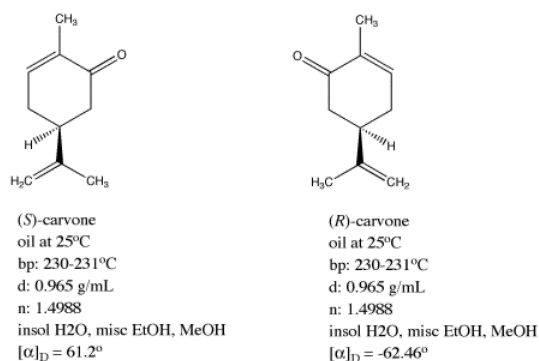
Learning Objective

- recognize and explain biochemical applications of chirality

Some Chiral Organic Biomolecules

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.



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.

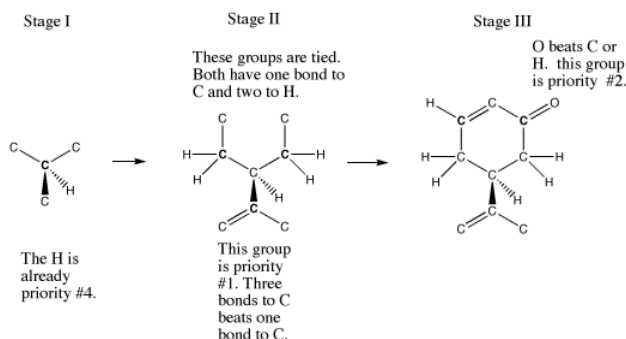
Note that (+)-carvone is the same thing as (S)-carvone. The (+) designation is based on its positive optical rotation value, which is experimentally measured. The (S) designation is determined by the Cahn-Ingold-Prelog rules for designating stereochemistry, which deal with looking at the groups attached 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.

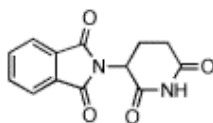


Comparing atoms step-by-step to assign configuration.

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 complementarity 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.



Thalidomide.

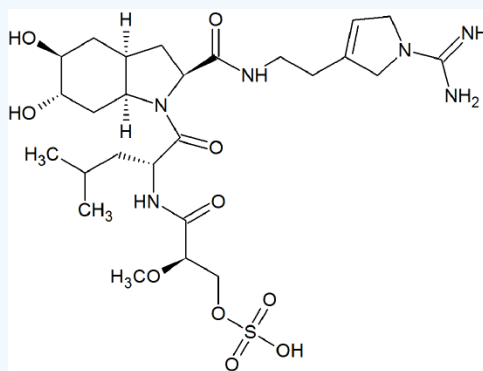
There are other reasons that we might concern ourselves with an understanding of enantiomers, apart from dietary and olfactory preferences. Perhaps the most dramatic example of the importance of enantiomers can be found in the case of thalidomide. Thalidomide was a drug commonly prescribed during the 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.

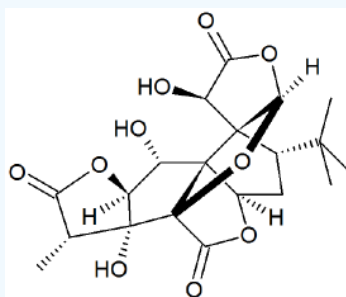
Exercises

1. Draw the two enantiomeric forms of 2-butanol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$. Label their configurations.
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.

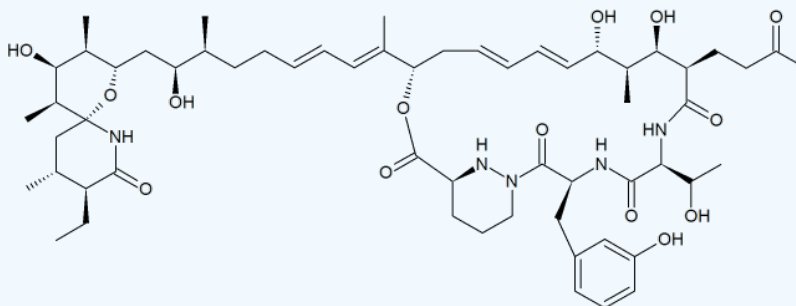
The following is the structure of dysynosin A, a potent thrombin inhibitor that consequently prevents blood clotting.



Ginkgolide B (below) is a secondary metabolite of the ginkgo tree, extracts of which are used in Chinese medicine.

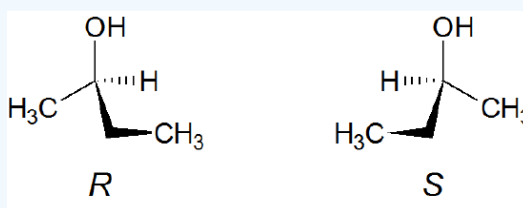


Sanglifehrin A, shown below, is produced by a bacteria that may be found in the soil of coffee plantations in Malawi. It is also a promising candidate for the treatment of organ transplant patients owing to its potent immuno-suppressant activity.

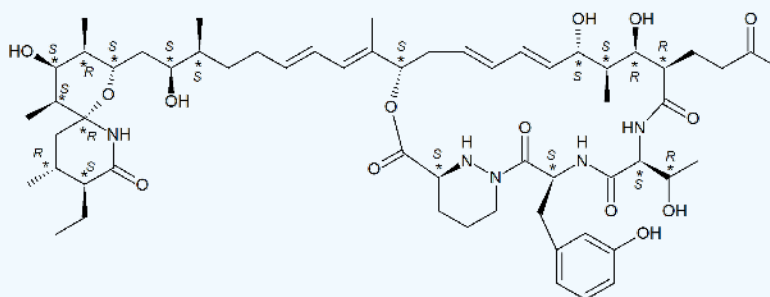
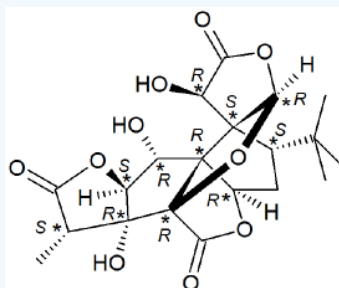
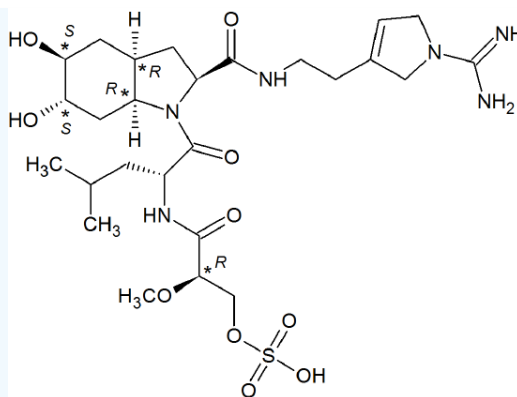


Solution

1.



2.



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."
- [Chris P Schaller, Ph.D.](#), ([College of Saint Benedict / Saint John's University](#))

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CHAPTER OVERVIEW

6: Alcohols, Phenols, Ethers, and Thiols

[6.1: Alcohols - Nomenclature and Classification](#)

[6.2: Physical Properties of Alcohols](#)

[6.3: Reactions of Alcohols](#)

[6.4: Oxidation and Reduction in Organic Chemistry](#)

[6.5: Glycols and Glycerol](#)

[6.6: Phenols](#)

[6.7: Ethers](#)

[6.8: Thiols \(Mercaptans\)](#)

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6.1: Alcohols - Nomenclature and Classification

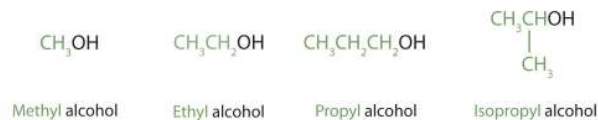
Learning Objectives

- Identify the general structure for an alcohol.
- Identify the structural feature that classifies alcohols as primary, secondary, or tertiary.
- Name alcohols with both common names and IUPAC names

An alcohol is an organic compound with a hydroxyl (OH) functional group on an aliphatic carbon atom. Because OH is the functional group of all alcohols, we often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH_3OH) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) are the first two members of the homologous series of alcohols.

Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol*:

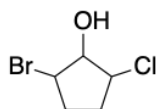
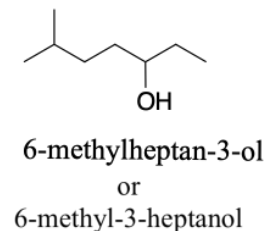
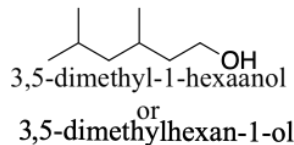
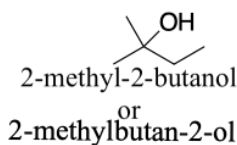


According to the International Union of Pure and Applied Chemistry (IUPAC), alcohols are named by changing the ending of the parent alkane name to *-ol*. Here are some basic IUPAC rules for naming alcohols:

1. The longest continuous chain (LCC) of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
2. The number that indicates the position of the OH group is prefixed to the name of the parent hydrocarbon, and the *-e* ending of the parent alkane is replaced by the suffix *-ol*. (In cyclic alcohols, the carbon atom bearing the OH group is designated C1, but the 1 is not used in the name.) Substituents are named and numbered as in alkanes.
3. If more than one OH group appears in the same molecule (polyhydroxy alcohols), suffixes such as *-diol* and *-triol* are used. In these cases, the *-e* ending of the parent alkane is retained.

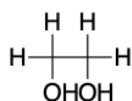
Figure 6.1.1 shows some examples of the application of these rules.

Rules 1 and 2

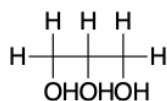


2-Bromo-5-chlorocyclopentanol

Rule 3



ethane-1,2-diol
1,2-ethanediol
(ethylene glycol)

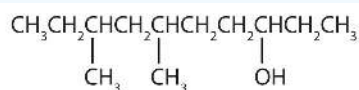


propane-1,2,3-triol
(glycerol)

Figure 6.1.1: IUPAC Rules for Alcohols. The names and structures of some alcohols demonstrate the use of IUPAC rules.

Example 6.1.1

Give the IUPAC name for each compound.

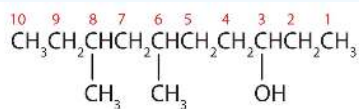


a.

b. HOCH₂CH₂CH₂CH₂CH₂OH

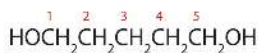
Solution

- a. Ten carbon atoms in the LCC makes the compound a derivative of decane (rule 1), and the OH on the third carbon atom makes it a 3-decanol (rule 2).



The carbon atoms are numbered from the end closest to the OH group. That fixes the two methyl (CH₃) groups at the sixth and eighth positions. The name is 6,8-dimethyl-3-decanol (not 3,5-dimethyl-8-decanol).

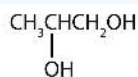
- b. Five carbon atoms in the LCC make the compound a derivative of pentane. Two OH groups on the first and fifth carbon atoms make the compound a diol and give the name 1,5-pentanediol (rule 3).



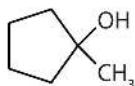
Exercise 6.1.1

Give the IUPAC name for each compound.

a.



b.



Example 6.1.2

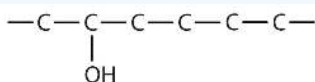
Draw the structure for each compound.

- 2-hexanol
- 3-methyl-2-pentanol

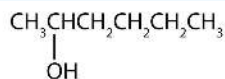
Solution

- The ending *-ol* indicates an alcohol (the OH functional group), and the *hex-* stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of six carbon atoms: —C—C—C—C—C—C— .

The 2 indicates that the OH group is attached to the second carbon atom.

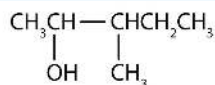


Finally, we add enough hydrogen atoms to give each carbon atom four bonds.



- The ending *-ol* indicates an OH functional group, and the *pent-* stem tells us that there are five carbon atoms in the LCC. We start by drawing a chain of five carbon atoms: —C—C—C—C—C—

The numbers indicate that there is a methyl (CH_3) group on the third carbon atom and an OH group on the second carbon atom.



Exercise 6.1.2

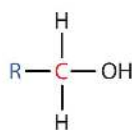
Draw the structure for each compound.

- 3-heptanol
- 2-methyl-3-hexanol

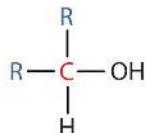
Classification of Alcohols

Some of the properties of alcohols depend on the number of carbon atoms attached to the specific carbon atom that is attached to the OH group. Alcohols can be grouped into three classes on this basis.

- A primary (1°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *one* other carbon atom (in blue). Its general formula is RCH_2OH .



- A secondary (2°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *two* other carbon atoms (in blue). Its general formula is R₂CHOH.



- A tertiary (3°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *three* other carbon atoms (in blue). Its general formula is R₃COH.



Table 6.1.1 names and classifies some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group (CH₃CH₂CH₂CH₂) discussed before, and three others:

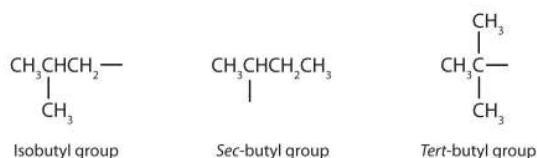
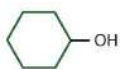


Table 6.1.1: Classification and Nomenclature of Some Alcohols

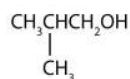
Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
CH ₃ OH	—	methyl alcohol	methanol
CH ₃ CH ₂ OH	primary	ethyl alcohol	ethanol
CH ₃ CH ₂ CH ₂ OH	primary	propyl alcohol	1-propanol
(CH ₃) ₂ CHOH	secondary	isopropyl alcohol	2-propanol
CH ₃ CH ₂ CH ₂ CH ₂ OH	primary	butyl alcohol	1-butanol
CH ₃ CH ₂ CHOHCH ₃	secondary	<i>sec</i> -butyl alcohol	2-butanol
(CH ₃) ₂ CHCH ₂ OH	primary	isobutyl alcohol	2-methyl-1-propanol
(CH ₃) ₃ COH	tertiary	<i>tert</i> -butyl alcohol	2-methyl-2-propanol
	secondary	cyclohexyl alcohol	cyclohexanol

Summary

In the IUPAC system, alcohols are named by changing the ending of the parent alkane name to *-ol*. Alcohols are classified according to the number of carbon atoms attached to the carbon atom that is attached to the OH group.

Concept Review Exercises

1. Is isobutyl alcohol primary, secondary, or tertiary? Explain.



2. What is the LCC in 2-ethyl-1-hexanol? What is taken as the LCC in naming the compound? Explain.

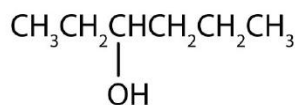
Answers

1. primary; the carbon atom bearing the OH group is attached to only one other carbon atom
2. 7 carbon atoms; the 6-atom chain includes the carbon atom bearing the OH group

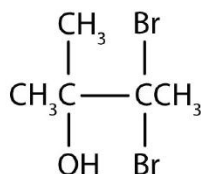
Exercises

1. Name each alcohol and classify it as primary, secondary, or tertiary.

- a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

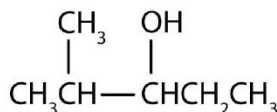


- b.

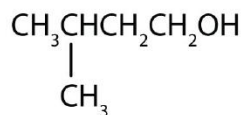


- c.

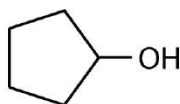
2. Name each alcohol and classify it as primary, secondary, or tertiary.



- a.



- b.



- c.

3. Draw the structure for each alcohol.

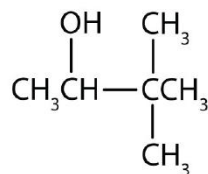
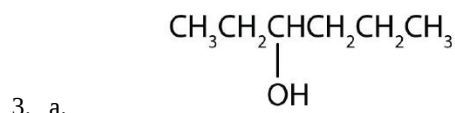
- a. 3-hexanol
- b. 3,3-dimethyl-2-butanol
- c. cyclobutanol

4. Draw the structure for each alcohol.

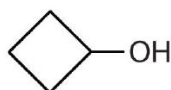
- a. cyclopentanol
- b. 4-methyl-2-hexanol
- c. 4,5-dimethyl-3-heptanol

Answers

1. a. 1-hexanol; primary
- b. 3-hexanol; secondary
- c. 3,3-dibromo-2-methyl-2-butanol; tertiary



b.



c.

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6.2: Physical Properties of Alcohols

Learning Objectives

- Explain why the boiling points of alcohols are higher than those of ethers and alkanes of similar molar masses.
- Explain why alcohols and ethers of four or fewer carbon atoms are soluble in water while comparable alkanes are not soluble.

Alcohols can be considered derivatives of water (H_2O ; also written as HOH).



Like the $\text{H}-\text{O}-\text{H}$ bond in water, the $\text{R}-\text{O}-\text{H}$ bond is bent, and alcohol molecules are polar. This relationship is particularly apparent in small molecules and reflected in the physical and chemical properties of alcohols with low molar mass. Replacing a hydrogen atom from an alkane with an OH group allows the molecules to associate through hydrogen bonding (Figure 6.2.1).

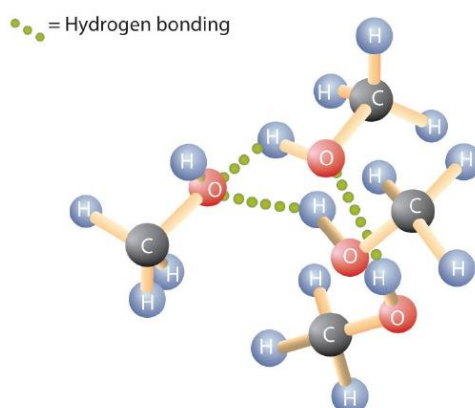


Figure 6.2.1: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table 6.2.1 lists the molar masses and the boiling points of some common compounds. The table shows that substances with similar molar masses can have quite different boiling points.

Table 6.2.1: Comparison of Boiling Points and Molar Masses

Formula	Name	Molar Mass	Boiling Point ($^{\circ}\text{C}$)
CH_4	methane	16	-164
HOH	water	18	100
C_2H_6	ethane	30	-89
CH_3OH	methanol	32	65
C_3H_8	propane	44	-42
$\text{CH}_3\text{CH}_2\text{OH}$	ethanol	46	78
C_4H_{10}	butane	58	-1
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	1-propanol	60	97

Alkanes are nonpolar and are thus associated only through relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with one carbon atom) is a liquid at room temperature. Hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. The boiling point is a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbors. If the molecules interact through hydrogen bonding, a relatively large quantity of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid into the gaseous state.

Alcohols can also engage in hydrogen bonding with water molecules (Figure 6.2.2). Thus, whereas the hydrocarbons are insoluble in water, alcohols with one to three carbon atoms are completely soluble. As the length of the chain increases, however, the solubility of alcohols in water decreases; the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) is essentially insoluble in water. We frequently find that the borderline of solubility in a family of organic compounds occurs at four or five carbon atoms.

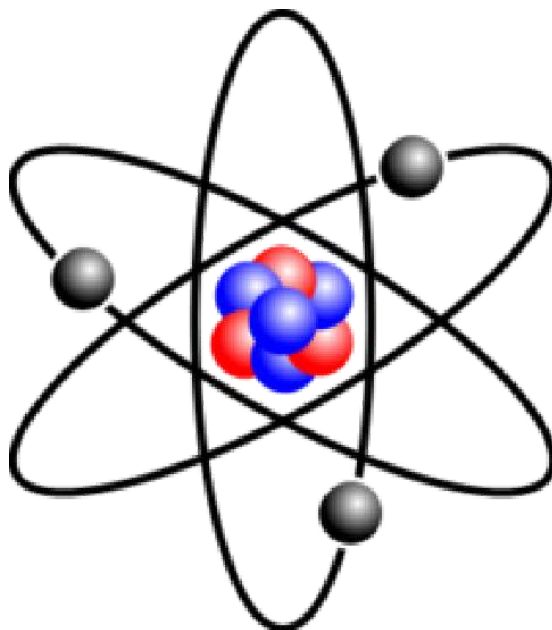


Figure 6.2.2: Hydrogen Bonding between Methanol Molecules and Water Molecules. Hydrogen bonding between the OH of methanol and water molecules accounts for the solubility of methanol in water.

Summary

Alcohols have higher boiling points than do ethers and alkanes of similar molar masses because the OH group allows alcohol molecules to engage in hydrogen bonding. Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen bonding with water molecules; comparable alkane molecules cannot engage in hydrogen bonding.

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6.3: Reactions of Alcohols

Learning Objectives

1. Give two major types of reactions of alcohols.
2. Describe the result of the oxidation of a primary alcohol.
3. Describe the result of the oxidation of a secondary alcohol.

Chemical reactions in alcohols occur mainly at the functional group, but some involve hydrogen atoms attached to the OH-bearing carbon atom or to an adjacent carbon atom. Of the three major kinds of alcohol reactions, which are summarized in Figure 6.3.1, two—dehydration and oxidation—are considered here. The third reaction type—esterification—is covered in CHE 202.

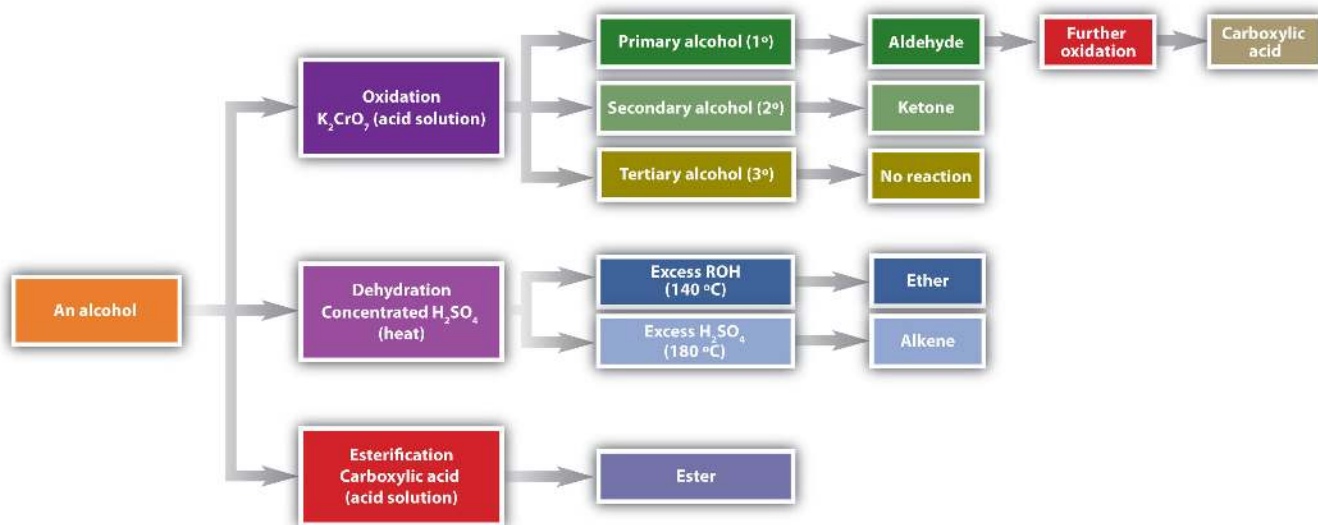
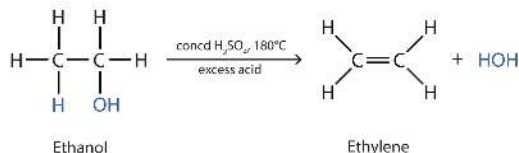


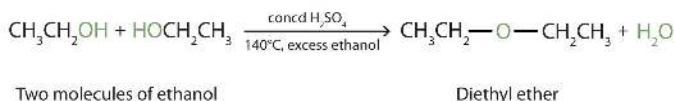
Figure 6.3.1: Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here.

Dehydration

As noted in Figure 6.3.1, an alcohol undergoes dehydration in the presence of a catalyst to form an alkene and water. The reaction removes the OH group from the alcohol carbon atom and a hydrogen atom from an adjacent carbon atom in the same molecule:



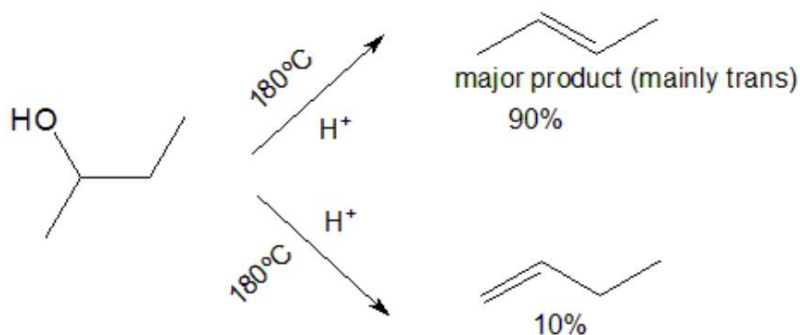
Under the proper conditions, it is possible for the dehydration to occur between two alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached to an oxygen atom form an ether molecule.



(Ethers are discussed in elsewhere) Thus, depending on conditions, one can prepare either alkenes or ethers by the dehydration of alcohols.

Dehydration at 180°C of asymmetric alcohols

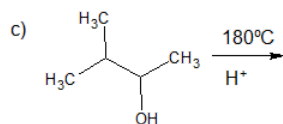
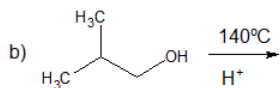
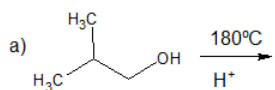
In cases where there are two adjacent carbon atoms to the one containing the OH group, two alkenes can be potentially be obtained by dehydration at 180°C (see figure below):



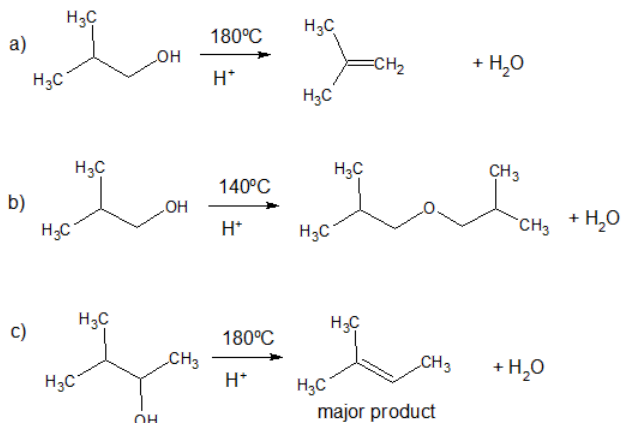
In such cases, the major product corresponds to the **most branched alkene possible**. This is because the reaction mechanism involves the formation of the most stable carbocation (secondary carbocation more stable than primary carbocation for the example above). This is in accordance with **Zaitsev's rule**. Additionally, when *cis* and *trans* geometric isomers are possible, ***trans* is also favored**.

Exercise

Show the major product of the following dehydration reactions

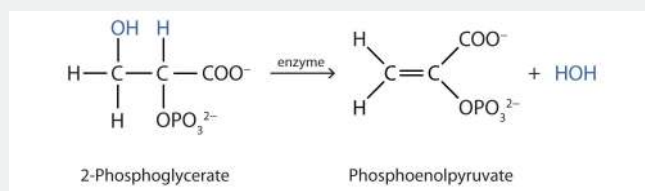


Answers



Alcohols reactions in biological systems

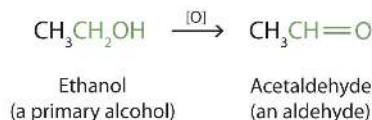
Both dehydration and hydration reactions occur continuously in cellular metabolism, with enzymes serving as catalysts and at a temperature of about 37°C. The following reaction occurs in the "Embden–Meyerhof" pathway



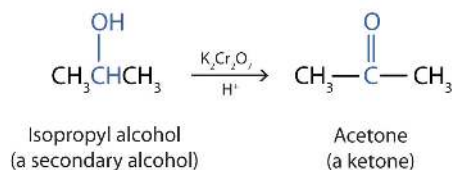
Although the participating compounds are complex, the reaction is the same: elimination of water from the starting material. The idea is that if you know the chemistry of a particular functional group, you know the chemistry of hundreds of different compounds.

Oxidation

Primary and secondary alcohols are readily oxidized. We saw earlier how methanol and ethanol are oxidized by liver enzymes to form aldehydes. Because a variety of oxidizing agents can bring about oxidation, we can indicate an oxidizing agent without specifying a particular one by writing an equation with the symbol [O] above the arrow. For example, we write the oxidation of ethanol—a primary alcohol—to form acetaldehyde—an aldehyde—as follows:



We shall see that **aldehydes** are even more easily oxidized than alcohols and yield carboxylic acids. Secondary alcohols are oxidized to **ketones**. The oxidation of isopropyl alcohol by potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) gives acetone, the simplest ketone:

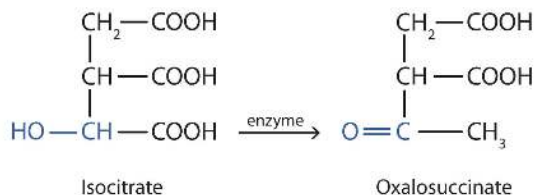


Unlike aldehydes, ketones are relatively resistant to further oxidation, so no special precautions are required to isolate them as they form. Note that in oxidation of both primary (RCH_2OH) and secondary (R_2CHOH) alcohols, two hydrogen atoms are removed from the alcohol molecule, one from the OH group and other from the carbon atom that bears the OH group.

These reactions can also be carried out in the laboratory with chemical oxidizing agents. One such oxidizing agent is potassium dichromate. The balanced equation (showing only the species involved in the reaction) in this case is as follows:



Alcohol oxidation is important in living organisms. Enzyme-controlled oxidation reactions provide the energy cells need to do useful work. One step in the metabolism of carbohydrates involves the oxidation of the secondary alcohol group in isocitric acid to a ketone group:



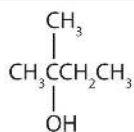
The overall type of reaction is the same as that in the conversion of isopropyl alcohol to acetone.

Tertiary alcohols (R_3COH) are resistant to oxidation because the carbon atom that carries the OH group does not have a hydrogen atom attached but is instead bonded to other carbon atoms. The oxidation reactions we have described involve the formation of a carbon-to-oxygen double bond. Thus, the carbon atom bearing the OH group must be able to release one of its attached atoms to form the double bond. The carbon-to-hydrogen bonding is easily broken under oxidative conditions, but carbon-to-carbon bonds are not. Therefore tertiary alcohols are not easily oxidized.

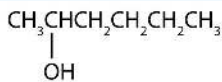
Example 6.3.1

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write “no reaction” after the arrow.

- a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$



- b.

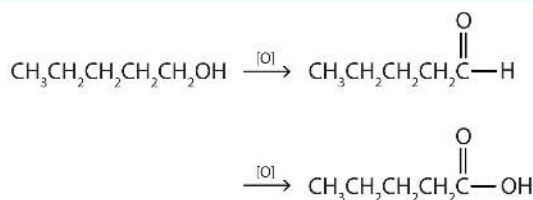


- c.

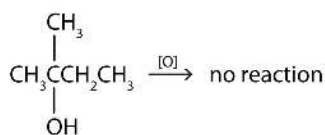
Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

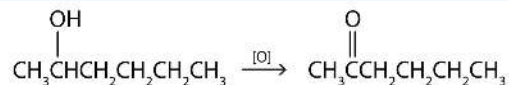
- a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.



- b. This alcohol has the OH group on a carbon atom that is attached to three other carbon atoms, so it is a tertiary alcohol. No reaction occurs.

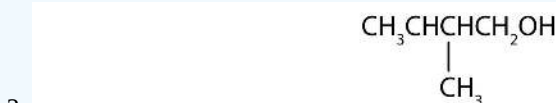


c. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol; oxidation gives a ketone.



Exercise 6.3.1

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.



Summary

Alcohols can be dehydrated to form either alkenes (higher temperature, excess acid) or ethers (lower temperature, excess alcohol). Primary alcohols are oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols are not readily oxidized.

Concept Review Exercises

Answers

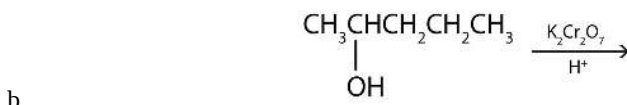
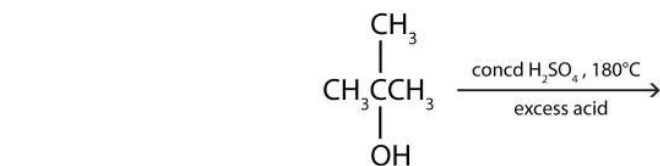
Exercises

Answers

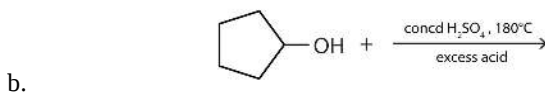
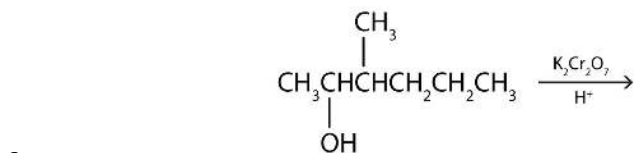
1. In a reaction, compound W with the molecular formula $\text{C}_4\text{H}_{10}\text{O}$ is converted to compound X with the formula $\text{C}_4\text{H}_8\text{O}$. Is W oxidized, reduced, dehydrated, or none of these? Explain.
2. In a reaction, 2 mol of compound Y with the molecular formula $\text{C}_4\text{H}_{10}\text{O}$ is converted to 1 mol of compound Z with the formula $\text{C}_8\text{H}_{18}\text{O}$. Is Y oxidized, reduced, or neither? Explain.
3. oxidized; H is removed
4. neither; water is removed
5. Name the three major types of chemical reactions of alcohols.

6. Why do tertiary alcohols not undergo oxidation? Can a tertiary alcohol undergo dehydration?

7. Draw the structure of the product for each reaction.



8. Draw the structure of the product for each reaction.



9. Write an equation for the dehydration of 2-propanol to yield each compound type.

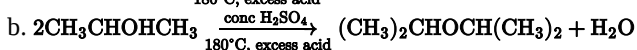
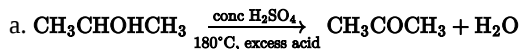
- an alkene
- an ether

10. Draw the structure of the alkene formed by the dehydration of cyclohexanol.

11. dehydration, oxidation, and esterification



13.



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6.4: Oxidation and Reduction in Organic Chemistry

Objectives

After completing this section, you should be able to

- identify organic reactions as being oxidations, reductions, or neither.
- rank given compounds in order of their oxidation level.

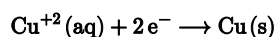
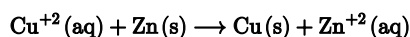
Key Terms

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

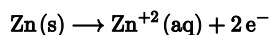
- oxidation
- reduction
- heteroatom

General Redox Reactions

General chemistry courses describe oxidation and reduction - when a compound or atom is oxidized it loses electrons, and when it is reduced it gains electrons. Also, oxidation and reduction half reactions occur in pairs: if one species is oxidized, another must be reduced at the same time. Thus, the combination of an oxidation and a reduction half reaction is termed a 'redox reaction.' Most of the redox reactions you have seen previously in general chemistry typically involved the flow of electrons from one metal to another, such as the reaction between copper ion in solution and metallic zinc:



Reduction



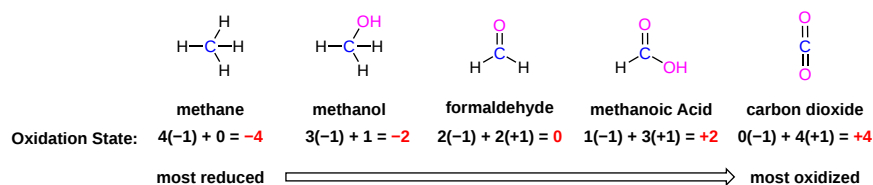
Oxidation

In order, to keep track of electrons in organic molecules an oxidation state formalism is used. Oxidation states do not represent the actual charge on an atom, but it will allow the number of electrons being gained or lost by a particular atom to be determined during a reaction.

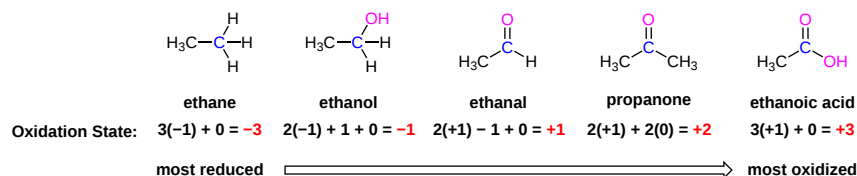
To calculate the oxidation state of a carbon atom the following rules are used:

1. A C-C bond does not affect the oxidation state of a carbon. So a carbon attached to 4 carbons has an oxidation state of zero.
2. Every C-H bond will **decrease** the oxidation state of the carbon by 1.
3. Each C-X bond will **increase** the oxidation state of the carbon by 1. Where X is an electronegative atom, such as nitrogen, oxygen, sulfur, or a halogen.

When looking at the oxidation states of carbon in the common functional groups shown below it can be said that carbon loses electron density as it becomes more oxidized. We'll take a series of single carbon compounds as an example. Methane (CH_4) is at the lowest oxidation level of carbon because it has the maximum possible number of bonds to hydrogen. Carbon dioxide (CO_2) is at the highest oxidation level because it has the maximum number of bonds to an electronegative atom.



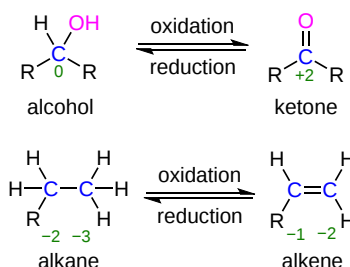
This pattern holds true for the relevant functional groups on organic molecules with two or more carbon atoms:



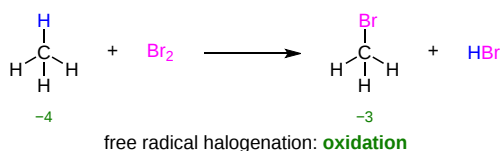
Organic Redox Reactions

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. If a reaction converts a compound to a higher oxidation level that is an oxidation. If it converts a compound to a lower oxidation level it is a reduction. If the oxidation level of the reactant does not change it is not a redox reaction.

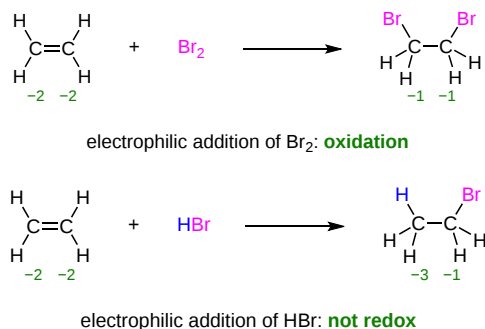
Two examples of organic redox reactions are shown below. The conversion of an alcohol to a ketone is considered an oxidation because the oxidation level of the carbon increases from 0 to +2. This implies that the reaction would require an oxidizing agent. Likewise, the conversion of a ketone to an alcohol is a reduction and would require a reducing agent. The conversion of an alkane to an alkene is an oxidation because the oxidation state on both carbons is increasing while the reverse reaction would be a reduction.



Now reaction previously discussed in this textbook can be considered to determine if they are in fact redox reaction. The free radical bromination of methane to bromomethane would be an oxidation because the oxidation level of carbon is raised from -4 to -3.

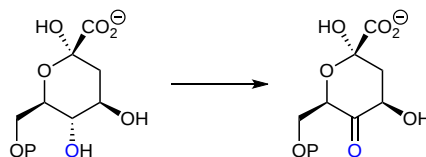


The electrophilic addition of Br_2 to an alkene to provide a 1,2-dibromide is an oxidation because both carbons increase their oxidation level from -2 to -1. However, the electrophilic addition of HBr to an alkene to provide an alkyl halide is not a redox reaction because the overall oxidation state of carbons involved are not changed. One carbon has its oxidation level decreased from -2 to -3 while the other carbon's oxidation level is increased from -2 to -1. Overall, the change in oxidation level cancels out to leave an overall change of oxidation level in the compound of 0.

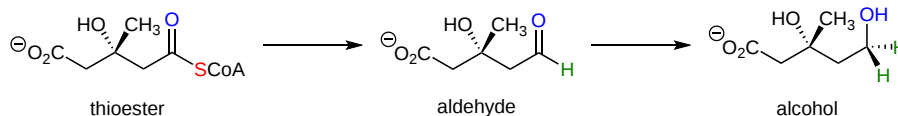


You should learn to recognize when a reaction involves a change in oxidation state in an organic reactant. Looking at the following transformation, for example, you should be able to quickly recognize that it is an oxidation: an alcohol functional group is

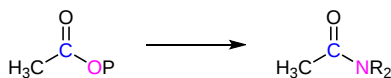
converted to a ketone, which is one step up on the oxidation ladder.



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).



carbon is in same oxidation state: **not redox**

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.

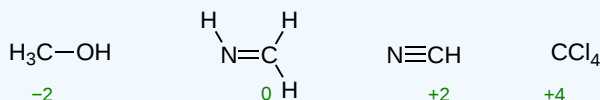
Worked Example 6.4.1

Rank the following compounds in order of increasing oxidation level:



Answer

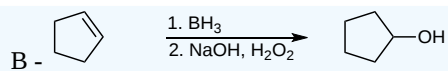
The easiest way to solve this problem is to calculate the oxidation level of the carbon in each compound. Remembering that hydrogens decrease the oxidation level by one, electronegative elements increase the oxidation level by one, and carbons do not change the oxidation level, the oxidation level of each carbon can be calculate. The carbon in CH_3OH has three bonds to hydrogens and one bond to oxygen so its oxidation level is $3(-1) + 1(+1) = -2$. The carbon in HCN has one bond to hydrogens and three bonds to nitrogen so its oxidation level is $1(-1) + 3(+1) = +2$. The carbon in CH_2NH has two bonds to hydrogens and two bond to nitrogen so its oxidation level is $2(-1) + 2(+1) = 0$. The carbon in CCl_4 has zero bonds to hydrogens and four bonds to chlorine so its oxidation level is $0(-1) + 4(+1) = +4$. The compounds now can be listing in the following order of increasing oxidation level.



? Exercise 6.4.2

In each case state whether the reaction is an oxidation or reduction of the organic compound.





Answer

A – Reduction

B – Oxidation

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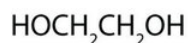
- [10.8: Oxidation and Reduction in Organic Chemistry](#) by Dietmar Kennepohl, Steven Farmer, Tim Soderberg is licensed [CC BY-SA 4.0](#).

6.5: Glycols and Glycerol

Learning Objectives

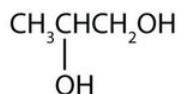
- To describe the structure and uses of some common polyhydric alcohols.

Alcohols with two OH groups on adjacent carbon atoms are commonly known as glycols. The most important of these is 1,2-ethanediol (the common name is ethylene glycol), a sweet, colorless, somewhat viscous liquid.



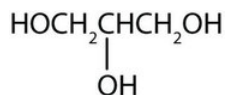
Ethylene glycol

Another common glycol, 1,2-propanediol, is commonly called propylene glycol. Its physical properties are quite similar to those of ethylene glycol.



Propylene glycol

Commonly called glycerol or glycerin, 1,2,3-propanetriol is the most important trihydroxy alcohol. Like the two glycols, it is a sweet, syrupy liquid. Glycerol is a product of the hydrolysis of fats and oils.

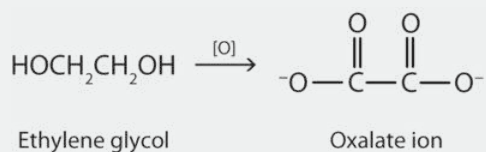


Glycerol

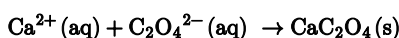
Ethylene glycol is the main ingredient in many antifreeze mixtures for automobile radiators. The two OH groups lead to extensive intermolecular hydrogen bonding. This results in a high boiling point—198°C; thus ethylene glycol does not boil away when it is used as an antifreeze. It is also completely miscible with water. A solution of 60% ethylene glycol in water freezes at −49°C (−56°F) and thus protects an automobile radiator down to that temperature. Ethylene glycol is also used in the manufacture of polyester fiber and magnetic film used in tapes for recorders and computers.

To Your Health: Glycols and Human Health

Ethylene glycol is quite toxic. Because it is sweet, pets often lap up spills of leaked antifreeze from a garage floor or driveway. Sometimes people, especially children, drink it. As with methanol, its toxicity is due to a metabolite. Liver enzymes oxidize ethylene glycol to oxalate ion.



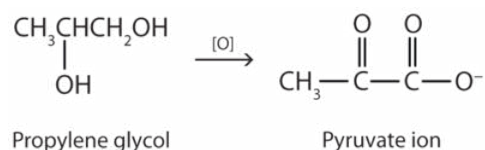
In the kidneys, the oxalate ion combines with the calcium (Ca^{2+}) ion, precipitating as calcium oxalate (CaC_2O_4).



These crystals cause renal damage and can lead to kidney failure and death.

Although propylene glycol has physical properties much like those of ethylene glycol, its physiological properties are quite different. Propylene glycol is essentially nontoxic, and it can be used as a solvent for drugs and as a moisturizing agent for foods.

Like other alcohols, propylene glycol is oxidized by liver enzymes.



In this case, however, the product is pyruvate ion, a normal intermediate in carbohydrate metabolism. Glycerol, a product of fat metabolism, is essentially nontoxic.

Summary

Glycols are alcohols with two OH groups on adjacent carbon atoms. Glycerol is the most important trihydroxy alcohol.

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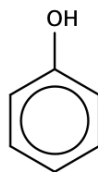
6.6: Phenols

Learning Objectives

- To describe the structure and uses of some phenols

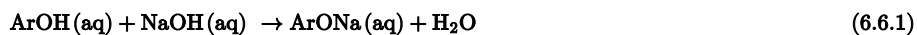
Structure of phenols and nomenclature

Compounds in which an OH group is attached directly to an aromatic ring are designated ArOH and called phenols.



Phenol, sometimes represented as ArOH

Phenols differ from alcohols in that they are slightly acidic in water. They react with aqueous sodium hydroxide (NaOH) to form salts.



The parent compound, C₆H₅OH, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive (“hospital smell”) odor.

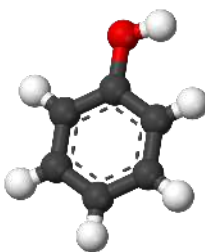
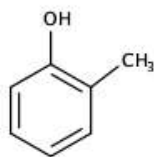
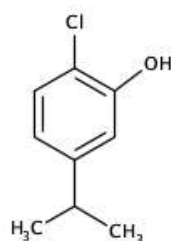


Figure 6.6.1: (Left) Structure of Phenol (right) Approximately two grams of phenol in glass vial. Image used with permission from Wikipedia

Other phenols are named as derivatives of the parent aromatic compound, for example:



2-methylphenol
or
o-methylphenol



2-chloro-5-isopropylphenol

Physical properties of phenols

Pure phenol is a white crystalline solid, smelling of disinfectant. It has to be handled with great care because it causes immediate white blistering to the skin. The crystals are often rather wet and discolored.

It is useful to compare phenol's melting and boiling points with those of methylbenzene (toluene). Both molecules contain the same number of electrons and are very similar shape. That means that the intermolecular attractions due to van der Waals dispersion forces are going to be very similar.

	melting point (°C)	boiling point (°C)
$\text{C}_6\text{H}_5\text{OH}$	40 - 43	182
$\text{C}_6\text{H}_5\text{CH}_3$	-95.0	111

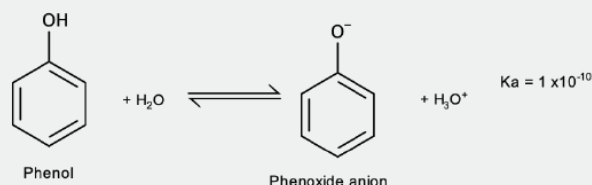
The reason for the higher values for phenol is in part due to permanent dipole-dipole attractions due to the electronegativity of the oxygen - but is mainly due to hydrogen bonding. Hydrogen bonds can form between a lone pair on an oxygen on one molecule and the hydrogen on the -OH group of one of its neighbors.

Phenol is moderately soluble in water - about 8 g of phenol will dissolve in 100 g of water. If you try to dissolve more than this, you get two layers of liquid. Phenol is somewhat soluble in water because of its ability to form hydrogen bonds with the water.

Chemical and biological properties of phenols

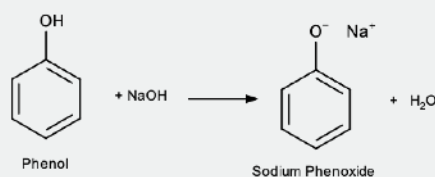
Acidity

Phenols differ from alcohols in that they are slightly acidic in water:



Salt formation

Also different from alcohols, phenols react with aqueous sodium hydroxide (NaOH) to form salts:



Phenol salts are ionic compounds, and therefore more soluble in water than phenol itself due to ion-dipole interactions.

Antiseptic properties

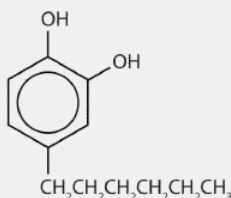
Phenols are widely used as antiseptics (substances that kill microorganisms on living tissue) and as disinfectants (substances intended to kill microorganisms on inanimate objects such as furniture or floors). The first widely used antiseptic was phenol. Joseph Lister used it for antiseptic surgery in 1867. Phenol is toxic to humans, however, and can cause severe burns when

applied to the skin. In the bloodstream, it is a systemic poison—that is, one that is carried to and affects all parts of the body. Its severe side effects led to searches for safer antiseptics, a number of which have been found.



An operation in 1753, painted by Gaspare Traversi, of a surgery before antiseptics were used.

One safer phenolic antiseptic is 4-hexylresorcinol (4-hexyl-1,3-dihydroxybenzene; resorcinol is the common name for 1,3-dihydroxybenzene, and 4-hexylresorcinol has a hexyl group on the fourth carbon atom of the resorcinol ring). It is much more powerful than phenol as a germicide and has fewer undesirable side effects. Indeed, it is safe enough to be used as the active ingredient in some mouthwashes and throat lozenges.



The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.

Antioxidant properties

Phenols act as **antioxidants** preventing oxidizing reactions on other compounds. Phenols such as BHA (butylated hydroxyanisole) and BHT (butylated hydroxytoluene) (2-*tert*-butyl-4-methylphenol) are widely used as antioxidants in foods, packing materials, cosmetic, and other chemical products.

 2-*tert*-Butyl-4-hydroxyanisole and 3-*tert*-butyl-4-hydroxyanisole 2D

Butylated hydroxyanisole (BHA) is an antioxidant consisting of a mixture of two isomeric organic compounds, 2-*tert*-butyl-4-hydroxyanisole and 3-*tert*-butyl-4-hydroxyanisole. Image by [Darkness3560](#), CC0, via Wikimedia Commons

 2,6-bis(1,1-dimethylethyl)-4-methylphenol

Butylated hydroxytoluene (BHT), also known as dibutylhydroxytoluene. Image by [User:Bryan Derksen](#), Public domain, via Wikimedia Commons

The ability of phenols to act as antioxidants is due to their ability to scavenge free radicals ($R\cdot$) generated in spoiled food:



Phenoxy radicals ($\text{PO}\cdot$) generated according to this reaction may be stabilized through resonance thus terminating the traditional chain reaction involving free radicals.

Summary

Phenols are compounds in which an OH group is attached directly to an aromatic ring. Many phenols are used as antiseptics.

Concept Review Exercises

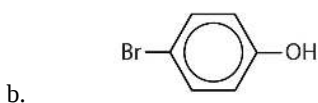
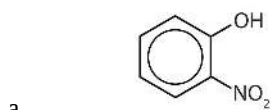
1. How do phenols differ from alcohols in terms of structure and properties?
2. How do phenols differ in properties from aromatic hydrocarbons?

Answers

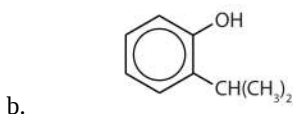
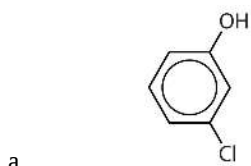
1. Phenols have an OH group attached directly to an aromatic ring. Phenols are weakly acidic.
2. Phenols have an OH group and are somewhat soluble in water.

Exercises

1. Name each compound.



2. Name each compound.



3. Draw the structure for each compound.

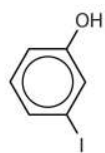
- a. *m*-iodophenol
- b. *p*-methylphenol (*p*-cresol)

4. Draw the structure for each compound.

- a. 2,4,6-trinitrophenol (picric acid)
- b. 3,5-diethylphenol

Answers

1. a. *o*-nitrophenol
b. *p*-bromophenol



3. a.



b.

Citations and attributions

1. "Phenols" by LibreTexts is licensed under CC BY-NC-SA .
2. "Physical Properties of Phenol" by Jim Clark. Retrieved May 20, 2021, from <https://chem.libretexts.org/@go/page/3986>
3. Wikipedia contributors. (2021, March 9). Butylated hydroxyanisole. In *Wikipedia, The Free Encyclopedia*. Retrieved 22:39, May 20, 2021, from https://en.wikipedia.org/w/index.php?title=Butylated_hydroxyanisole&oldid=1011151288
4. Wikipedia contributors. (2021, April 14). Butylated hydroxytoluene. In *Wikipedia, The Free Encyclopedia*. Retrieved 22:39, May 20, 2021, from https://en.wikipedia.org/w/index.php?title=Butylated_hydroxytoluene&oldid=1017824735
5. Wikipedia contributors. (2021, January 27). Antioxidant effect of polyphenols and natural phenols. In *Wikipedia, The Free Encyclopedia*. Retrieved 22:39, May 20, 2021, from https://en.wikipedia.org/w/index.php?title=Antioxidant_effect_of_polyphenols_and_natural_phenols&oldid=1003094201
6. Wikipedia contributors. (2021, May 2). Phenol. In *Wikipedia, The Free Encyclopedia*. Retrieved 22:40, May 20, 2021, from <https://en.wikipedia.org/w/index.php?title=Phenol&oldid=1021048584>

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6.7: Ethers

Learning Objectives

- Describe the structural difference between an alcohol and an ether that affects physical characteristics and reactivity of each.
- Name simple ethers.
- Describe the structure and uses of some ethers.

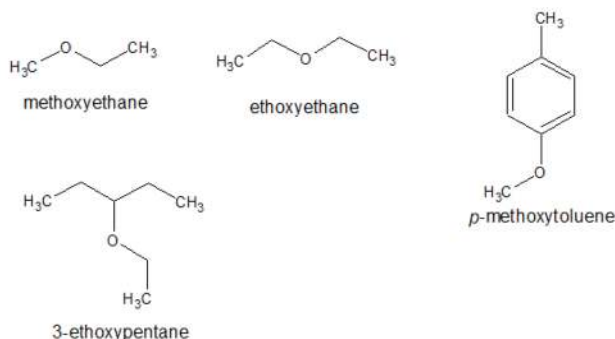
Structure and nomenclature of ethers

With the general formula ROR' , an ether may be considered a derivative of water in which both hydrogen atoms are replaced by alkyl or aryl groups. It may also be considered a derivative of an alcohol (ROH) in which the hydrogen atom of the OH group is been replaced by a second alkyl or aryl group:



Simple ethers have simple **common names**, formed from the names of the alkyl groups attached to oxygen atom listed alphabetically, followed by the generic name *ether*. For example, $CH_3-O-CH_2CH_2CH_3$ is methyl propyl ether. If both groups are the same, the group name should be preceded by the prefix *di-*, as in dimethyl ether (CH_3-O-CH_3) and diethyl ether $CH_3CH_2-O-CH_2CH_3$.

According to **IUPAC** rules, ethers are named as substituted alkanes bearing an $-O-R$ (alkoxy) substituent. The name of the $-O-R$ groups (which always contains the smaller $-R$) is obtained by replacing *-yl* ending of the R alkyl group by *-oxy*. For example, $-OCH_3$ is named as a methoxy substituent. When necessary, the position of the $-O-R$ group is indicated by numbers. Examples:



Physical properties

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table 6.7.1). Therefore, ethers are quite flammable.

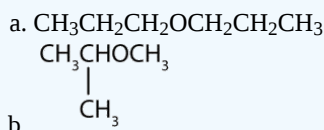
Table 6.7.1: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$\text{CH}_3\text{CH}_2\text{CH}_3$	propane	44	-42	no
CH_3OCH_3	dimethyl ether	46	-25	no
$\text{CH}_3\text{CH}_2\text{OH}$	ethyl alcohol	46	78	yes
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	pentane	72	36	no
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	diethyl ether	74	35	no
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	butyl alcohol	74	117	yes

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula $\text{C}_2\text{H}_6\text{O}$) are completely soluble in water, whereas diethyl ether and 1-butanol (both $\text{C}_4\text{H}_{10}\text{O}$) are barely soluble in water (8 g/100 mL of water). The solubility rapidly decreases with the number of atoms, and only ether up to three carbon atoms are soluble in water, that is, dimethyl ether and ethyl methyl ether

Example 6.7.1

What is the common name and IUPAC for each ether?



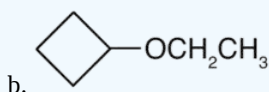
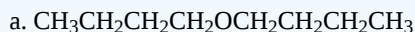
b.

Solution

- The carbon groups on either side of the oxygen atom are propyl ($\text{CH}_3\text{CH}_2\text{CH}_2$) groups, so the compound is dipropyl ether (common) or 1-propoxypropane (IUPAC)
- The three-carbon group is attached by the middle carbon atom, so it is an isopropyl group. The one-carbon group is a methyl group. The compound is isopropyl methyl ether (common) or 2-methoxypropane (IUPAC)

Exercise 6.7.1

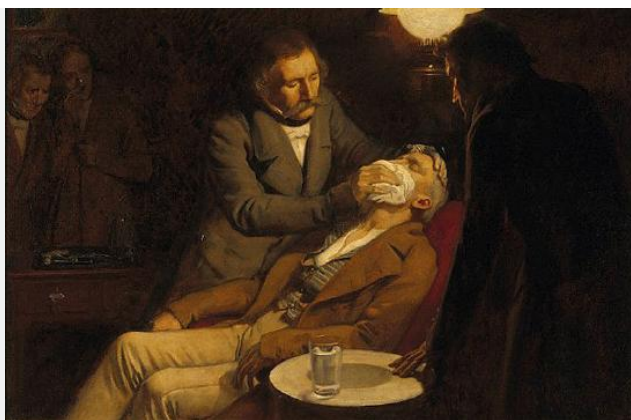
What is the common name for each ether?



Chemical and biological properties of ethers

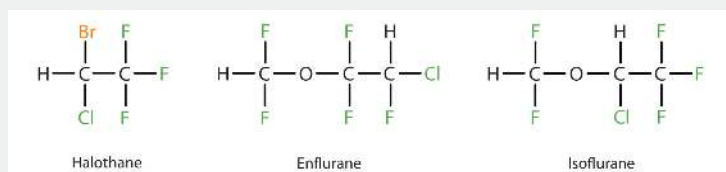
Besides being flammable, ethers are very stable and non-reactive, similarly to alkanes. For this reason, they are mainly used as solvents in the industry.

Ethers have *anesthetic properties*. A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) was the first general anesthetic to be used.



William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.



These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.

Summary

To give ethers common names, simply name the groups attached to the oxygen atom, followed by the generic name *ether*. If both groups are the same, the group name should be preceded by the prefix *di-*. In the IUPAC system, ethers are named as substituted alkanes bearing an alkoxy ($-O-R$) substituent. Ether molecules have no OH group and thus no intermolecular hydrogen bonding. Ethers therefore have quite low boiling points for a given molar mass. Ether molecules have an oxygen atom and can engage in hydrogen bonding with water molecules. An ether molecule has about the same solubility in water as the alcohol that is isomeric with it.

Concept Review Exercises

1. Why does diethyl ether ($CH_3CH_2OCH_2CH_3$) have a much lower boiling point than 1-butanol ($CH_3CH_2CH_2CH_2OH$)?
2. Which is more soluble in water—ethyl methyl ether ($CH_3CH_2OCH_3$) or 1-butanol ($CH_3CH_2CH_2CH_2OH$)? Explain.

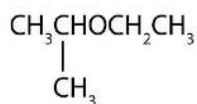
Answers

1. Diethyl ether has no intermolecular hydrogen bonding because there is no OH group; 1-butanol has an OH and engages in intermolecular hydrogen bonding.
2. Ethyl methyl ether (three carbon atoms, one oxygen atom) is more soluble in water than 1-butanol (four carbon atoms, one oxygen atom), even though both can engage in hydrogen bonding with water.

Exercises

1. How can ethanol give two different products when heated with sulfuric acid? Name these products.
2. Which of these ethers is isomeric with ethanol— $CH_3CH_2OCH_2CH_3$, $CH_3OCH_2CH_3$, or CH_3OCH_3 ?

3. Name each compound.



b.

4. Name each compound.



5. Draw the structure for each compound.

a. methyl ethyl ether

b. *tert*-butyl ethyl ether

6. Draw the structure for each compound.

a. diisopropyl ether

b. cyclopropyl propyl ether

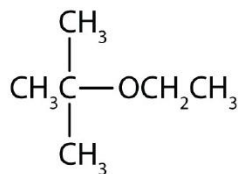
Answers

1. Intramolecular (both the H and the OH come from the same molecule) dehydration gives ethylene; intermolecular (the H comes from one molecule and the OH comes from another molecule) dehydration gives diethyl ether.

3. a. methyl propyl ether

b. ethyl isopropyl ether

5. a. $\text{CH}_3\text{OCH}_2\text{CH}_3$



b.

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6.8: Thiols (Mercaptans)

Objectives

After completing this section, you should be able to

1. Nomenclature and Reactivity
 - a. write the IUPAC name of a thiol, given its Kekulé, condensed or shorthand structure.
 - b. draw the structure of a thiol, given its IUPAC name.
 - c. write an equation to represent the formation of a thiol by the reaction of hydrosulfide anion with an alkyl halide.
 - d. write an equation to illustrate the preparation of a thiol by the reaction of thiourea with an alkyl halide.
2. write an equation to show the interconversion between thiols and disulfides.

Key Terms

- disulfide
- mercapto group
- thiol
-

Study Notes

The chemistry of sulfur-containing organic compounds is often omitted from introductory organic chemistry courses. However, we have included a short section on these compounds, not for the sake of increasing the amount of material to be digested, but because much of the chemistry of these substances can be predicted from a knowledge of their oxygen-containing analogues. A thiol is a compound which contains an SH functional group. The -SH group itself is called a mercapto group. A disulfide is a compound containing an -S-S- linkage. Table 18.1, below, provides a quick comparison of oxygen-containing and sulfur-containing organic compounds.

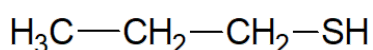
Oxygen-containing Compound	Sulphur Analogue
ether, R—O—R'	sulphide, R—S—R'
R—O—, alkoxy group	R—S—, alkylthio group
R—O ⁻ , alkoxy anion	R—S ⁻ , thiolate anion
alcohol, R—OH	thiol, R—SH
—OH, hydroxy group	—SH, mercapto group
R—O—O—R', peroxide	R—S—S—R', disulphide

Table 18.1 Comparison of compounds containing oxygen and sulphur

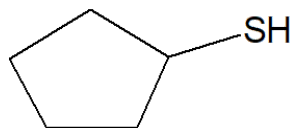
Note that when we name thiols, we include the "e" of the alkane name. Thus, CH₃CH₂SH is called "ethanethiol," not "ethanthiol."

Thiols

Thiols, which are also called mercaptans, are analogous to alcohols. They are named in a similar fashion as alcohols except the suffix *-thiol* is used in place of *-ol*. By itself the -SH group is called a mercapto group. The main physical characteristic of thiols is their pungent, disagreeable odor. According to IUPAC, thiols are named in a similar fashion as alcohols except the suffix *-thiol* is used instead of *-ol*. The root of the alkane name retains the final letter "e".



1-propanethiol



cyclopentanethiol

Physical properties of thiols

Since they are incapable of hydrogen bonding, thiols have lower boiling points and are less soluble in water and other polar solvents than alcohols of similar molecular weight.

Table 6.8.1. Physical properties of thiols and other compounds

Compound	Melting point	Boiling point	Solubility in water
ethanol	-114 °C	78 °C	Very soluble
ethanethiol	-148 °C	35 °C	0.7 g/ 100mL (20°C)
1-butanol	-90°C	118°C	7.3g/100 mL (25°C)
1-butanethiol	-116°C	98.2°C	0.06 g/100 mL (20°C)

The most recognizable property of thiols is their odors. **The odors of thiols, particularly those of low molecular weight, are often strong and repulsive.** The spray of skunks consists mainly of low-molecular-weight thiols and derivatives. These compounds are detectable by the human nose at concentrations of only 10 parts per billion. The negative. Since natural gas is odorless, natural gas distributors are required to add thiols, originally ethanethiol, to natural gas to detect leaking gas before a spark or match sets off an explosion.

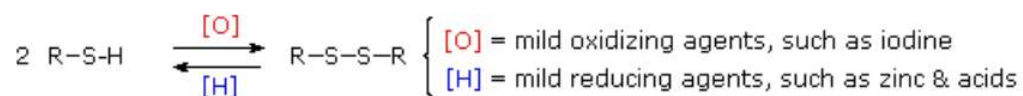


Chemical structure of some of the compounds in skunk musk. Image by [Karlhahn](#), Public domain, via Wikimedia Commons

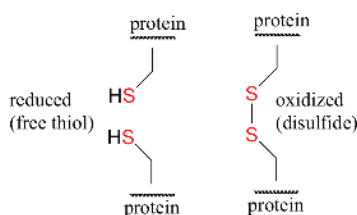
Chemical properties of thiols

Disulfides bond formation

Oxidation of thiols and other sulfur compounds changes the oxidation state of sulfur rather than carbon. We see some representative sulfur oxidations in the following examples. In the first case, mild oxidation converts thiols to disulfides. An equivalent oxidation of alcohols to peroxides is not normally observed. The reasons for this different behavior are not hard to identify. The S-S single bond is nearly twice as strong as the O-O bond in peroxides, and the O-H bond is more than 25 kcal/mole stronger than an S-H bond. Thus, thermodynamics favors disulfide formation over peroxide.

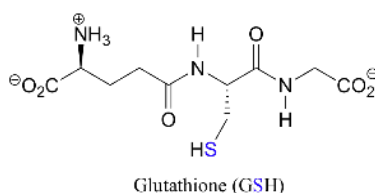


Disulfide (sulfur-sulfur) linkages between two cysteine residues are an integral component of the three-dimensional structure of many proteins. The interconversion between thiols and disulfide groups is a redox reaction: the thiol is the reduced state, and the disulfide is the oxidized state.



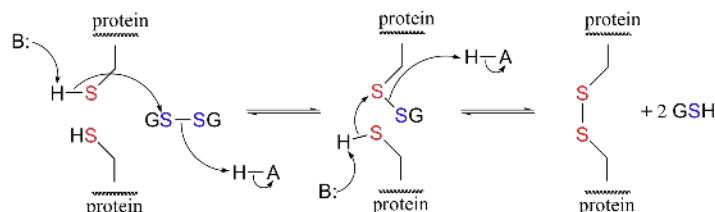
Notice that in the oxidized (disulfide) state, each sulfur atom has lost a bond to hydrogen and gained a bond to a sulfur - this is why the disulfide state is considered to be oxidized relative to the thiol state.

The redox agent that mediates the formation and degradation of disulfide bridges in most proteins is glutathione, a versatile coenzyme in biological systems:



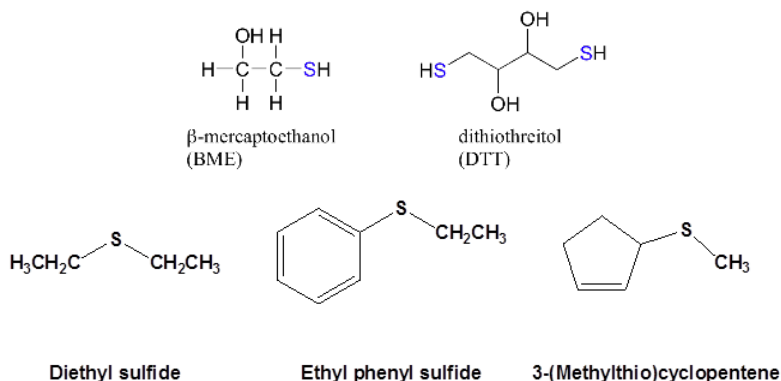
In its oxidized form, glutathione exists as a dimer of two molecules linked by a disulfide group, and is abbreviated 'GSSG'.

A new disulfide in a protein forms via a 'disulfide exchange' reaction with GSSH, a process that can be described as a combination of two S_N2 -like attacks. The end result is that a new cysteine-cysteine disulfide forms at the expense of the disulfide in GSSG.



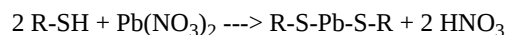
In its reduced (thiol) state, glutathione can reduce disulfides bridges in proteins through the reverse of the above reaction.

In the biochemistry lab, proteins are often maintained in their reduced (free thiol) state by incubation in buffer containing an excess concentration of β -mercaptoethanol (BME) or dithiothreitol (DTT). These reducing agents function in a manner similar to that of GSH, except that DTT, because it has two thiol groups, forms an intramolecular disulfide in its oxidized form.



Reaction with heavy metals

Thiols can also react with heavy metals (Pb^{2+} , Hg^{2+} , etc) forming insoluble compounds. This reaction is responsible for the biological toxicity of heavy metal salts, due to the inactivation of proteins containing -SH group as cysteine residues. Example:



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- 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)
- [Chris P Schaller, Ph.D., \(College of Saint Benedict / Saint John's University\)](#)
- Wikipedia contributors. (2021, May 14). Thiol. In *Wikipedia, The Free Encyclopedia*. Retrieved 23:23, May 20, 2021, from <https://en.wikipedia.org/w/index.php?title=Thiol&oldid=1023095689>

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