Semester Two

ORGANIC
CHEMISTRY

Hargeisa University

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Contents

Chapter one: Saturated Hydrocarbons

1.1 Organic and Inorganic Compounds

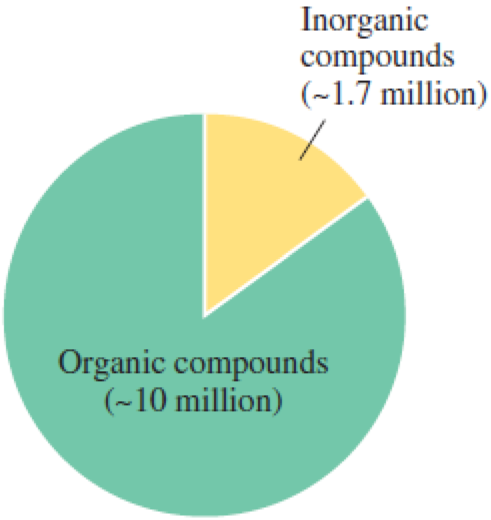
Organic chemistry is the study of hydrocarbons (compounds of carbon and hydrogen) and their derivatives.

Organic chemistry *is the study of carbon compounds with the exception of the simple carbon compounds:*

1. *Oxides*
2. *Carbonates*
3. *Hydrogen carbonates*
4. *Cyanides*
5. *carbides*

Inorganic chemistry *is the study of all substances other than hydrocarbons and their derivatives.*

There are approximately 10 million organic compounds and only an estimated 1.7 million inorganic compounds (Figure 1). This is an approximately 6:1 ratio between organic and inorganic compounds.



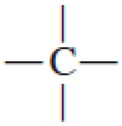
1.2 Bonding Characteristics of the Carbon Atom

Why does the element carbon form six times as many compounds as all the other elements combined? The answer is that carbon atoms have the unique ability to bond to each other in a wide variety of ways that involve long chains of carbon atoms or cyclic arrangements (rings) of carbon atoms. Sometimes both chains and rings of carbon atoms are present in the same molecule.

Bonding requirements for carbon atom

To obtain full outer shell (octet rule), carbon require to form four covalent bonds. Carbon can meet this four-bond requirement in three different ways:

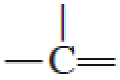
1. *By bonding to four other atoms.* This situation requires the presence of four single bonds.



$$-\overset{|}{\underset{|}{C}}-$$

Four single bonds

2. *By bonding to three other atoms.* This situation requires the presence of two single bonds and one double bond.



$$-\overset{|}{C}=$$

Two single bonds and
one double bond

3. *By bonding to two other atoms.* This situation requires the presence of either two double bonds or a triple bond and a single bond.

$=C=$

Two double bonds

$-C\equiv$

One triple bond and
one single bond

1.3 Hydrocarbons and Hydrocarbon Derivatives

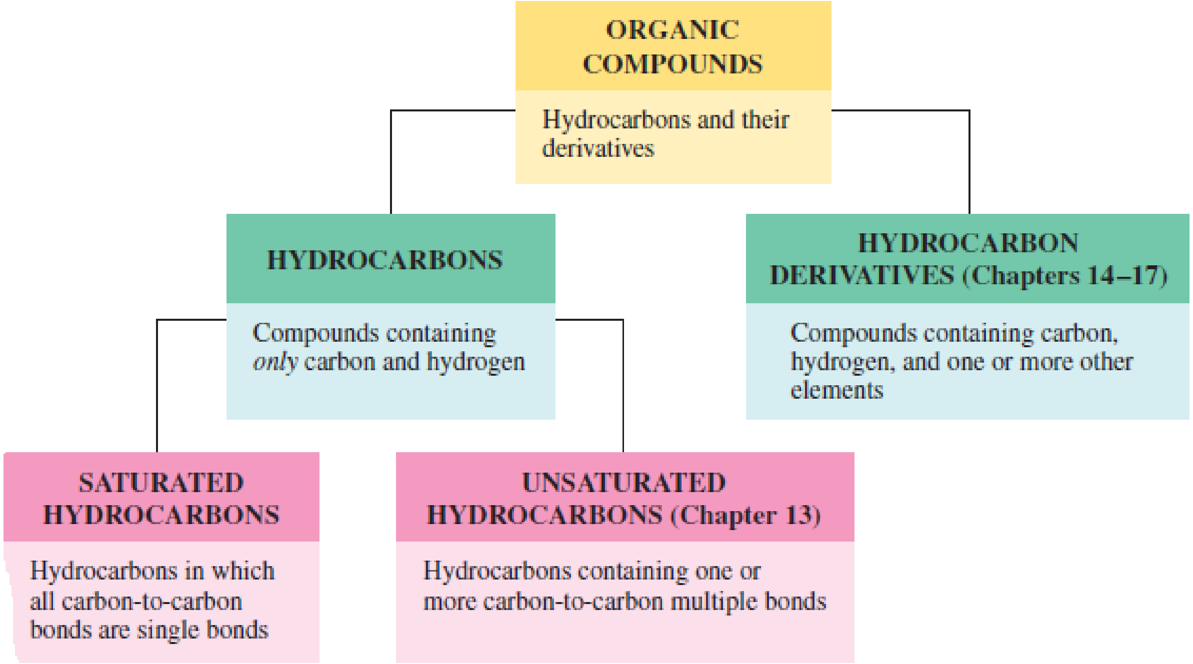
A **hydrocarbon** *is a compound that contains only carbon and hydrogen atoms.* Thousands of hydrocarbons are known.

A **hydrocarbon derivative** *is a compound that contains carbon and hydrogen and one or more additional elements.*

Additional elements commonly found in hydrocarbon derivatives include O, N, S, P, F, Cl, and Br. Millions of hydrocarbon derivatives are known.

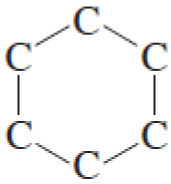
*Hydrocarbons may be divided into two large classes: saturated and unsaturated: A **saturated hydrocarbon** is a hydrocarbon in which all carbon–carbon bonds are single bonds. Saturated hydrocarbons are the simplest type of organic compound.*

*An **unsaturated hydrocarbon** is a hydrocarbon in which one or more carbon–carbon multiple bonds (double bonds, triple bonds, or both) are present. In general, saturated and unsaturated hydrocarbons undergo distinctly different chemical reactions.*



*Two categories of saturated hydrocarbons exist, those with **acyclic** carbon atom arrangements and those with **cyclic** carbon atom arrangements. The term **acyclic** means "**not cyclic**." The following notations contrast simple acyclic and cyclic arrangements of six-carbon atoms.*

Acyclic



Cyclic

1.4 Alkanes: Acyclic Saturated Hydrocarbons

An **alkane** *is a **saturated** hydrocarbon in which the carbon atom arrangement is **acyclic**.* Thus an alkane is a hydrocarbon that contains only carbon–carbon **single bonds** (saturated) and has no rings of carbon atoms (acyclic).

The molecular formulas of all alkanes fit the general formula $\mathrm{C}n\mathrm{H}2n+2$, where n is the number of carbon atoms present.

Note also that the geometrical arrangement of atoms about each carbon atom is tetrahedral, an arrangement consistent with the principles of VSEPR theory

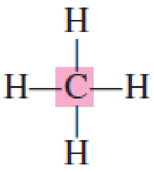
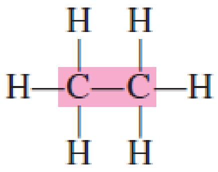
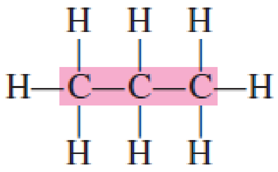
1.5 Structural Formulas

A **structural formula** *is a two-dimensional structural representation that shows how the various atoms in a molecule are bonded to each other.*

Structural formulas are of two types: expanded structural formulas and condensed structural formulas.

An **expanded structural formula** *is a structural formula that shows all atoms in a molecule and all bonds connecting the atoms.*

A **condensed structural formula** *is a structural formula that uses groupings of atoms, in which central atoms and the atoms connected to them are written as a group, to convey molecular structural information. The expanded and condensed structural formulas for methane, ethane, and propane follow.*

Expanded structural formula	 $\begin{array}{ccc} & H & \\ & \vert & \\ H- & C & -H \\ & \vert & \\ & H & \end{array}$	 $\begin{array}{cccc} & H & H & \\ & \vert & \vert & \\ H- & C- & C & -H \\ & \vert & \vert & \\ & H & H & \end{array}$	 $\begin{array}{ccccc} & H & H & H & \\ & \vert & \vert & \vert & \\ H- & C- & C- & C & -H \\ & \vert & \vert & \vert & \\ & H & H & H & \end{array}$
Condensed structural formula	CH_4	$CH_3—CH_3$	$CH_3—CH_2—CH_3$
	Methane	**Ethane**	**Propane**

The condensed structural formulas of hydrocarbons in which a long chain of carbon atoms is present are often condensed even more.

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$$

The formula can be further abbreviated as:

$$CH_3—(CH_2)_6—CH_3$$

Where parentheses and a subscript are used to denote the number of – CH_2--groups in the chain

Skeletal structural formula

A **skeletal structural formula** *is a structural formula that shows the arrangement and bonding of carbon atoms present in an organic molecule but does not show the hydrogen atoms attached to the carbon atoms.*

$$C—C—C—C—C$$

Skeletal structural formula

Line-Angle Structural Formulas

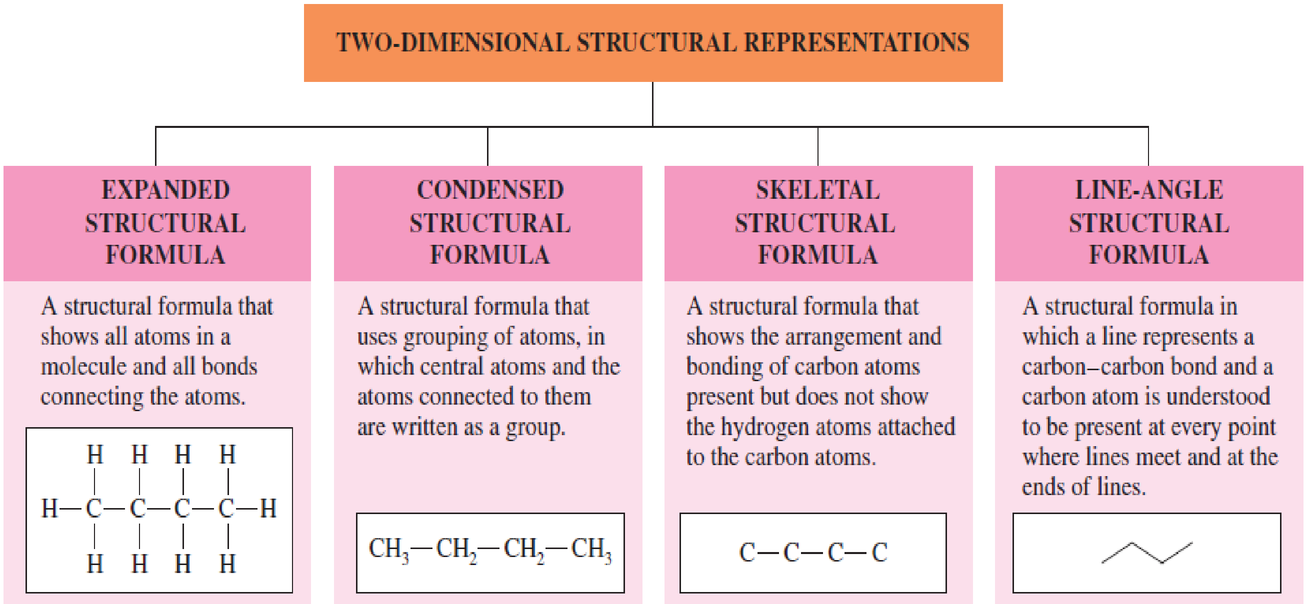
*A **line-angle structural formula** is a structural representation in which a line represents a carbon–carbon bond and a carbon atom is understood to be present at every point where two lines meet and at the ends of lines.*

Line-angle structural formulas for the alkanes propane, butane, and pentane are as follows:

Propane

Butane

Pentane



TWO-DIMENSIONAL STRUCTURAL REPRESENTATIONS

EXPANDED STRUCTURAL FORMULA

A structural formula that shows all atoms in a molecule and all bonds connecting the atoms.

CONDENSED STRUCTURAL FORMULA

A structural formula that uses grouping of atoms, in which central atoms and the atoms connected to them are written as a group.

$CH_3-CH_2-CH_2-CH_3$

SKELETAL STRUCTURAL FORMULA

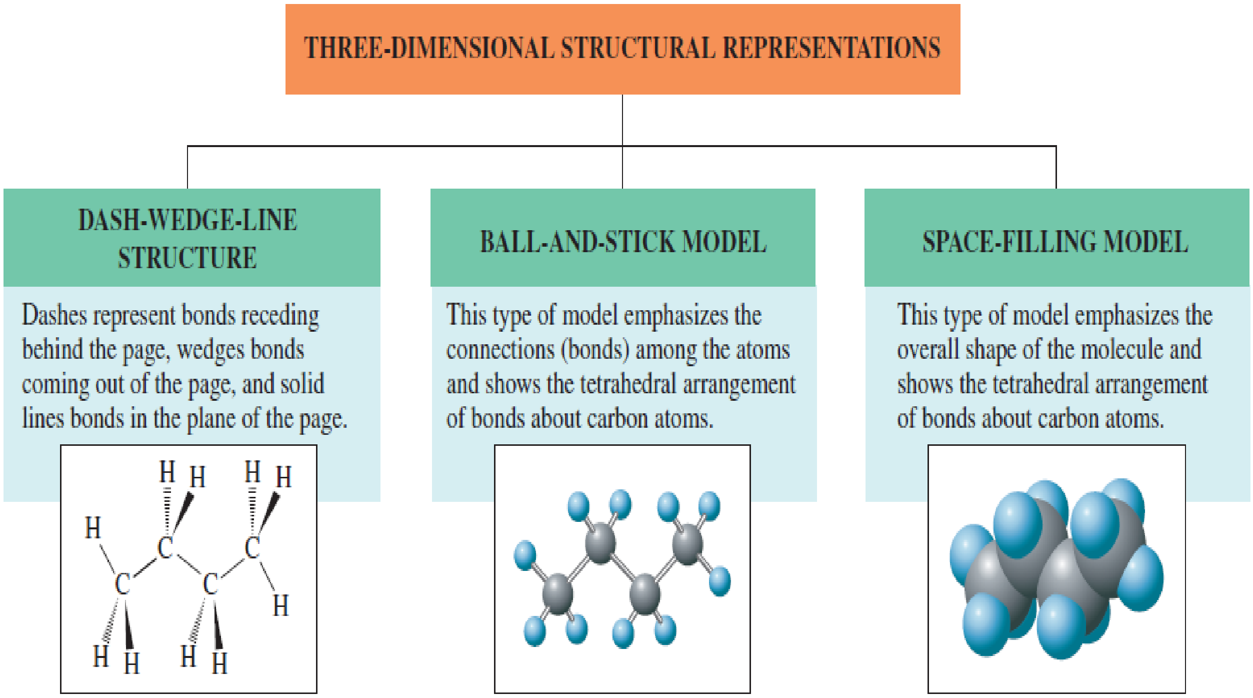
A structural formula that shows the arrangement and bonding of carbon atoms present but does not show the hydrogen atoms attached to the carbon atoms.

C—C—C—C

LINE-ANGLE STRUCTURAL FORMULA

A structural formula in which a line represents a carbon–carbon bond and a carbon atom is understood to be present at every point where lines meet and at the ends of lines.

Three dimensional Structural Representations



THREE-DIMENSIONAL STRUCTURAL REPRESENTATIONS

DASH-WEDGE-LINE STRUCTURE

Dashes represent bonds receding behind the page, wedges bonds coming out of the page, and solid lines bonds in the plane of the page.

BALL-AND-STICK MODEL

This type of model emphasizes the connections (bonds) among the atoms and shows the tetrahedral arrangement of bonds about carbon atoms.

SPACE-FILLING MODEL

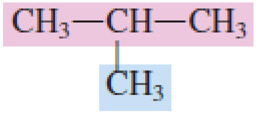
This type of model emphasizes the overall shape of the molecule and shows the tetrahedral arrangement of bonds about carbon atoms.

1.6 Alkane Isomerism

Isomers *are compounds that have the same molecular formula (that is, the same numbers and kinds of atoms) but that differ in the way the atoms are arranged.* Isomers, even though they have the same molecular formula, are always different compounds with different properties.

$CH_3-CH_2-CH_2-CH_3$

Butane



$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3$

Isobutane

Contrasting the two C_4H_{10} isomers structurally, note that butane has a chain of four carbon atoms. It is an example of a continuous-chain alkane.

A **continuous- chain alkane** *is an alkane in which all carbon atoms are connected in a continuous non-branching chain.*

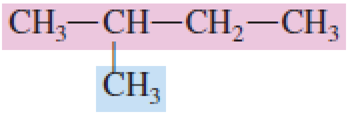
The other C_4H_{10} isomer, isobutane, has a chain of three carbon atoms with the fourth carbon attached as a branch on the middle carbon of the three-carbon chain. It is an example of a branched-chain alkane.

A **branched-chain alkane** *is an alkane in which one or more branches (of carbon atoms) are attached to a continuous chain of carbon atoms.*

There are three isomers for alkanes with five carbon atoms (C_5H_{12}):

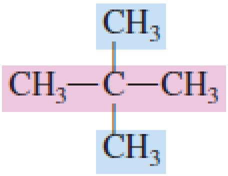
$CH_3-CH_2-CH_2-CH_2-CH_3$

Pentane



$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$

Isopentane



$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

Neopentane

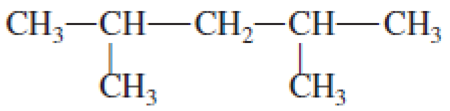
The number of possible alkane isomers increases dramatically with increasing numbers of carbon atoms in the alkane, as shown in Table

Molecular Formula	Possible Number of Isomers
CH_4	1
C_2H_6	1
C_3H_8	1
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	336,319
$C_{25}H_{52}$	36,797,588
$C_{30}H_{62}$	4,111,846,763

Several different types of isomerism exist. The alkane isomerism examples discussed in this section are examples of *constitutional isomerism.*

Constitutional isomers *are isomers that differ in the connectivity of atoms, that is, in the order in which atoms are attached to each other within molecules. Constitutional isomers are also frequently called* ***structural isomers.***

The condensed structural formulas for branched-chain alkanes can be further condensed to give linear (straight-line) condensed structural formulas. The linear condensed structural formula for the alkane is:



$$\begin{array}{ccccccccc} CH_3 & - & CH & - & CH_2 & - & CH & - & CH_3 \\ & & | & & & & | & & \\ & & CH_3 & & & & CH_3 & & \end{array}$$

$$CH_3{-}CH{-}(CH_3){-}CH_2{-}CH{-}(CH_3){-}CH_3$$

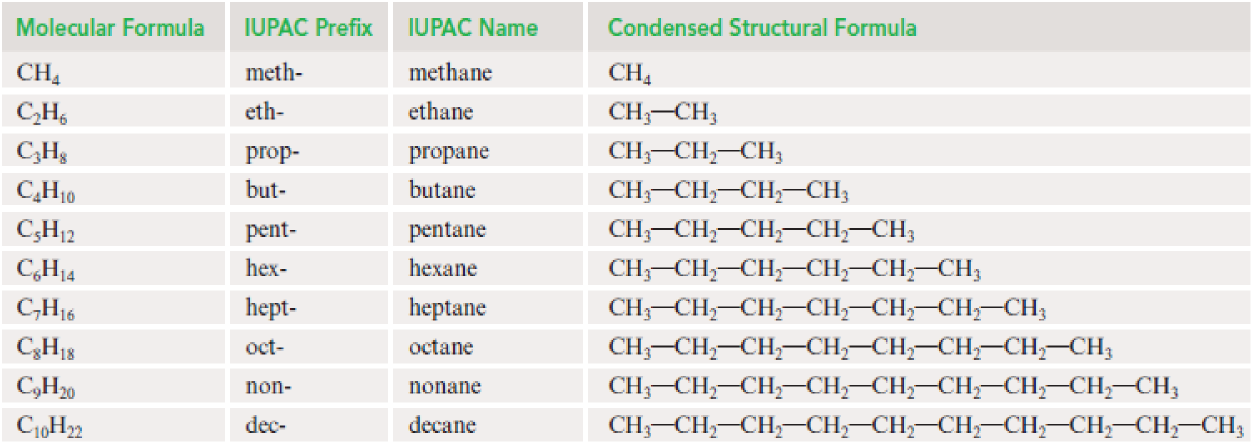
Groups in parentheses in such formulas are understood to be attached to the car- bon atom that *precedes* the group in the structural formula

1.7 IUPAC Nomenclature for Alkanes

Rules were formulated and are updated periodically by the International Union of Pure and Applied Chemistry (IUPAC), are known as *IUPAC rules.* The advantage of the IUPAC naming system is that it assigns each compound a name that not only identifies it but also enables its structural formula to be drawn.

Continuous and branched- chain alkanes

The existence of both continuous-chain alkanes and branched- chain alkanes was noted, IUPAC names for the first ten *continuous-chain* alkanes are given in Table 1.2



Molecular Formula	IUPAC Prefix	IUPAC Name	Condensed Structural Formula
CH_4	meth-	methane	CH_4
C_2H_6	eth-	ethane	$CH_3—CH_3$
C_3H_8	prop-	propane	$CH_3—CH_2—CH_3$
C_4H_{10}	but-	butane	$CH_3—CH_2—CH_2—CH_3$
C_5H_{12}	pent-	pentane	$CH_3—CH_2—CH_2—CH_2—CH_3$
C_6H_{14}	hex-	hexane	$CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$
C_7H_{16}	hept-	heptane	$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$
C_8H_{18}	oct-	octane	$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$
C_9H_{20}	non-	nonane	$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$
$C_{10}H_{22}$	dec-	decane	$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3$

Note that all of these names end in *-ane, Note also that beginning with the five-carbon alkane, Greek numerical prefixes are used to denote the actual number of carbon atoms in the continuous chain.*

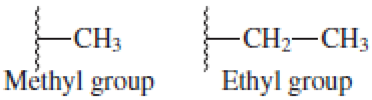
The key to name branched-chain alkanes is to know the name of the branch or branches that are attached to the main carbon chain. These branches are formally called substituents

A **substituent** *is an atom or group of atoms attached to a chain (or ring) of carbon atoms.* Note that *substituent* is a general term that applies to carbon-chain attachments in all organic molecules, not just alkanes.

Alkyl group (continuous)

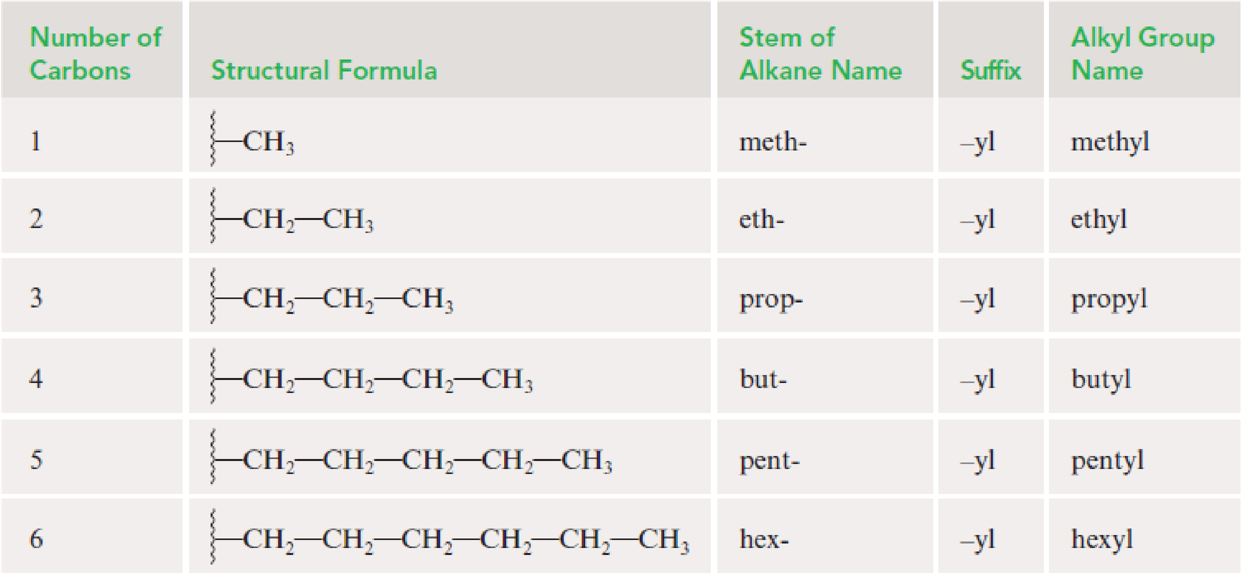
For branched-chain alkanes, the substituents are specifically called *alkyl groups.* An **alkyl group** *is the group of atoms that would be obtained by removing a hydrogen atom from an alkane.*

The two most commonly encountered alkyl groups are the two simplest: the one-carbon and two-carbon alkyl groups. Their formulas and names are



In these formulas the “squiggle” on the left denotes the point of attachment to the carbon chain. Note that alkyl groups do not lead a stable, independent existence; that is, they are not molecules. They are always found attached to another entity (usually a carbon chain).

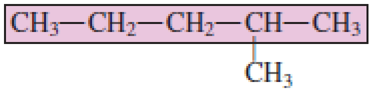
Table 1.3 Names for the First Six Continuous-Chain Alkyl Groups



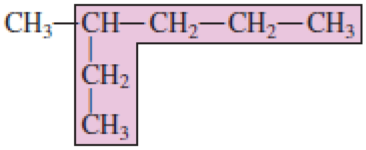
Number of Carbons	Structural Formula	Stem of Alkane Name	Suffix	Alkyl Group Name
1	$-\mathrm{CH_3}$	meth-	–yl	methyl
2	$-\mathrm{CH_2-CH_3}$	eth-	–yl	ethyl
3	$-\mathrm{CH_2-CH_2-CH_3}$	prop-	–yl	propyl
4	$-\mathrm{CH_2-CH_2-CH_2-CH_3}$	but-	–yl	butyl
5	$-\mathrm{CH_2-CH_2-CH_2-CH_2-CH_3}$	pent-	–yl	pentyl
6	$-\mathrm{CH_2-CH_2-CH_2-CH_2-CH_2-CH_3}$	hex-	–yl	hexyl

IUPAC rules for naming branched-chain alkanes are as follows:

Rule 1: Identify the longest continuous carbon chain (the parent chain), which may or may not be shown in a straight line, and name the chain.



The parent chain name is *pentane,* because it has five carbon atoms.

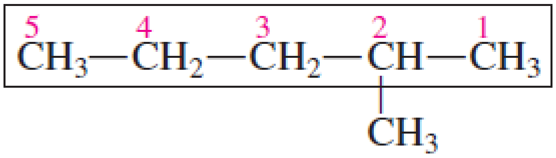


The parent chain name is *hexane,* because it has six carbon atoms.

$\mathrm{CH_3CH_2CH\ (CH_3)\ CH_2\ CH_2C\ H_3}$ condensed formula

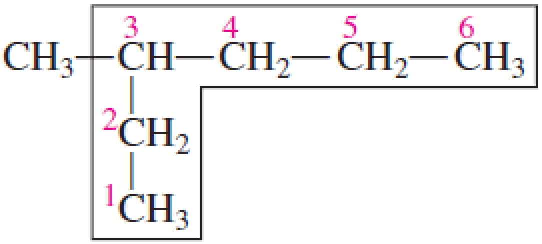
Rule 2: Number the carbon atoms in the parent chain from the end of the chain nearest a substituent (alkyl group).

There are always two ways to number the chain (either from left to right or from right to left). This rule gives the first-encountered alkyl group the lowest possible number.



$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H(CH_3)-\overset{1}{C}H_3$$

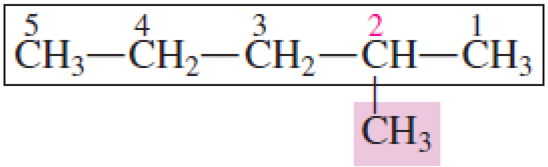
Right-to-left numbering system



$$CH_3-\overset{3}{C}H(\overset{2}{C}H_2\overset{1}{C}H_3)-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$$

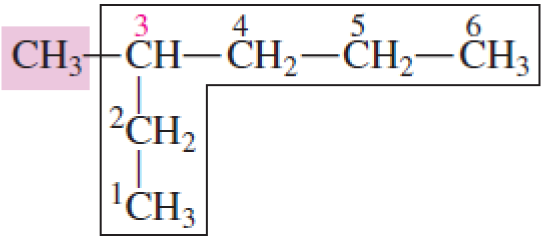
Left-to-right numbering system

Rule 3: If only one alkyl group is present, name and locate it (by number), and prefix the number and name to that of the parent carbon chain.



$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H(CH_3)-\overset{1}{C}H_3$$

2-Methylpentane

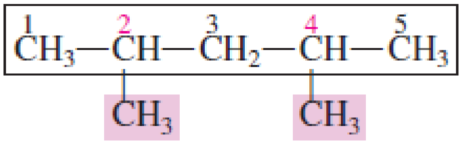


$$CH_3-\overset{3}{C}H(\overset{2}{C}H_2\overset{1}{C}H_3)-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$$

3-Methylhexane

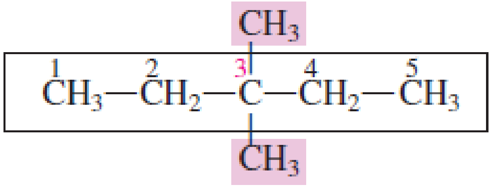
Note that the name is written as one word, with a hyphen between the number and the name of the alkyl group.

Rule 4: If two or more of the same kind *of alkyl group are present in a molecule, indicate the number with a Greek numerical prefix (di-, tri-, tetra-, penta-, and so forth). In addition, a number specifying the location of each identical group must be included. These position numbers, separated by commas, precede the numerical prefix. Numbers are separated from words by hyphens.*



$\overset{1}{CH_3}-\underset{CH_3}{\overset{2}{CH}}-\overset{3}{CH_2}-\underset{CH_3}{\overset{4}{CH}}-\overset{5}{CH_3}$

2,4-Dimethylpentane

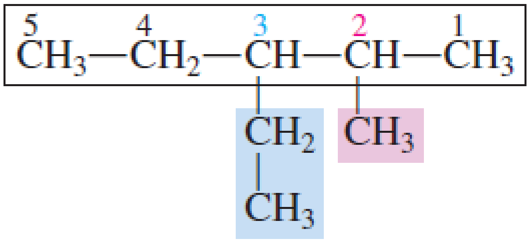


$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{CH_3}{\overset{CH_3}{\overset{3}{C}}}-\overset{4}{CH_2}-\overset{5}{CH_3}$

3,3-Dimethylpentane

Note that the numerical prefix *di-* must always be accompanied by two numbers, *tri-* by three, and so on, even if the same number is written twice, as in 3, 3-dimethylpentane.

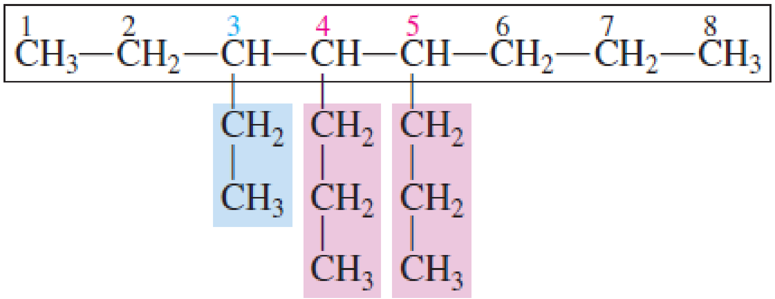
Rule 5: When two kinds of alkyl groups are present on the same carbon chain, number each group separately, and list the names of the alkyl groups in alphabetical order.



$\overset{5}{CH_3}-\overset{4}{CH_2}-\underset{\underset{CH_3}{CH_2}}{\overset{3}{CH}}-\underset{CH_3}{\overset{2}{CH}}-\overset{1}{CH_3}$

3-Ethyl-2-methylpentane

Note that ethyl is named first in accordance with the alphabetical rule.

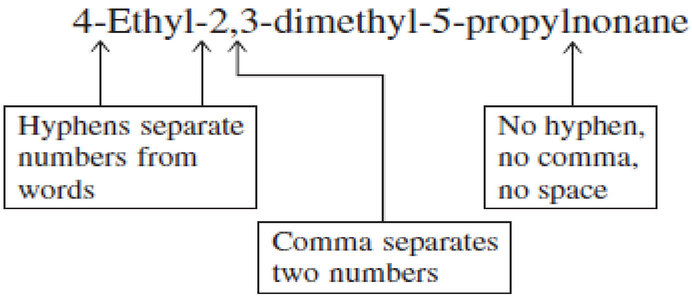


$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{\underset{CH_3}{CH_2}}{\overset{3}{CH}}-\underset{\underset{\underset{CH_3}{CH_2}}{CH_2}}{\overset{4}{CH}}-\underset{\underset{\underset{CH_3}{CH_2}}{CH_2}}{\overset{5}{CH}}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH_3}$

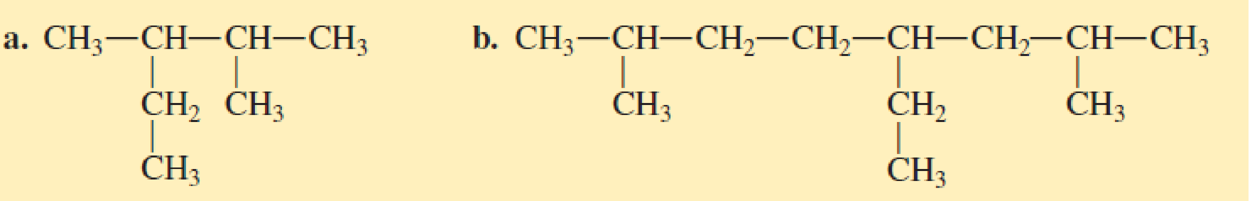
3-Ethyl-4,5-dipropyloctane

Note that the prefix *di-* does not affect the alphabetical order; *ethyl* precedes *propyl*

Rule 6: Follow IUPAC punctuation rules, which include the following: (1) Separate numbers from each other by commas. (2) Separate numbers from letters by hyphens. (3) Do not add a hyphen or a space between the last-named substituent and the name of the parent alkane that follows.



Give the IUPAC name for each of the following branched-chain alkanes



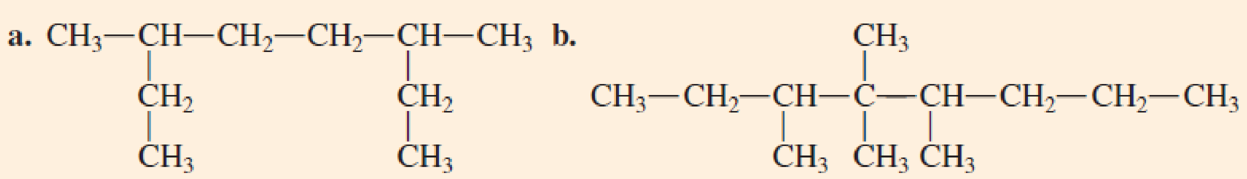
a. $CH_3-CH(CH_2-CH_3)-CH(CH_3)-CH_3$

b. $CH_3-CH(CH_3)-CH_2-CH_2-CH(CH_2-CH_3)-CH_2-CH(CH_3)-CH_3$

a. 2,3-dimethylpentane
b. 4-ethyl-2,7-dimethyloctane

Practice Exercise

Give the IUPAC name for each of the following alkanes



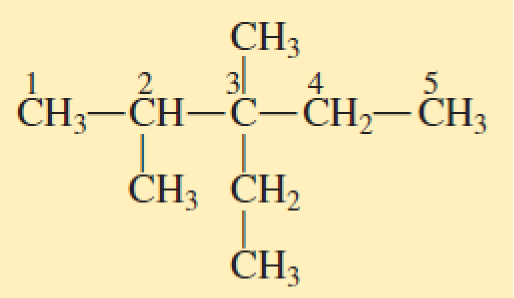
a. $CH_3-CH(CH_2-CH_3)-CH_2-CH_2-CH(CH_2-CH_3)-CH_3$

b. $CH_3-CH_2-CH(CH_3)-C(CH_3)_2-CH(CH_3)-CH_2-CH_2-CH_3$

Answers: **a.** 3,6-Dimethyloctane; **b.** 3,4,4,5-Tetramethyloctane

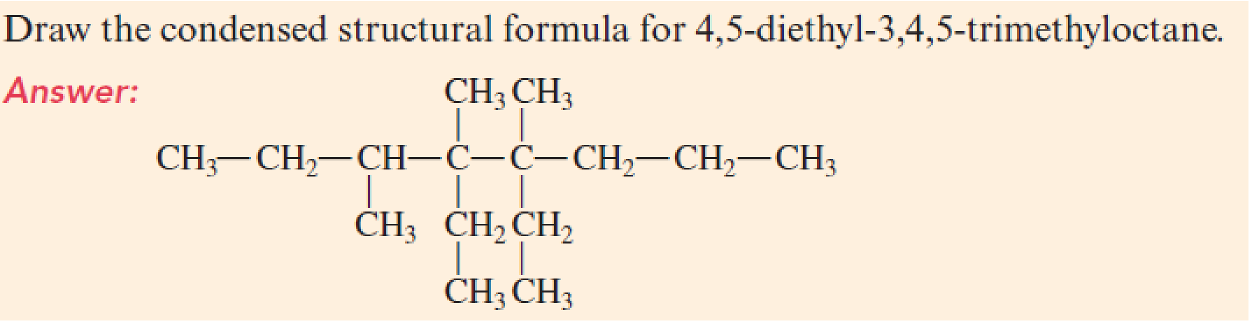
Generating the Structural Formula of an Alkane from Its IUPAC Name

Draw the condensed structural formula for 3-ethyl-2,3-dimethylpentane



$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}(CH_3)(CH_2-CH_3)-\overset{4}{C}H_2-\overset{5}{C}H_3$

Practice Exercise



Draw the condensed structural formula for 4,5-diethyl-3,4,5-trimethyloctane.

Answer:

$$\begin{array}{ccccccccccccccc} & & & & & & CH_3 & & CH_3 & & & & & & \\ & & & & & & | & & | & & & & & & \\ CH_3 & - & CH_2 & - & CH & - & C & - & C & - & CH_2 & - & CH_2 & - & CH_3 \\ & & & & | & & | & & | & & & & & & \\ & & & & CH_3 & & CH_2 & & CH_2 & & & & & & \\ & & & & & & | & & | & & & & & & \\ & & & & & & CH_3 & & CH_3 & & & & & & \end{array}$$

Determining Structural Formulas for and Naming Alkane Constitutional Isomers

Draw skeletal structural formulas for, and assign IUPAC names to, all C_6H_{14} alkane constitutional isomers.

Solution

Table 1.1 indicates that there are five constitutional isomers with the chemical formula C_6H_{14}. Part of the purpose of this example is to consider the "thinking pattern" needed to identify these five isomers. There are two concepts embedded in the thinking pattern

1) Carbon chains of varying length are examined for isomerism possibilities, starting with the chain of maximum length and then examining increasingly shorter chain lengths.
2) Substituents are added to the various carbon chains, with the number of added carbons determined by the chain length. Various location possibilities for the substituents are examined.

Step 1: A C_6 carbon chain is the longest chain possible; it contains all available carbon atoms.

$$C-C-C-C-C-C$$

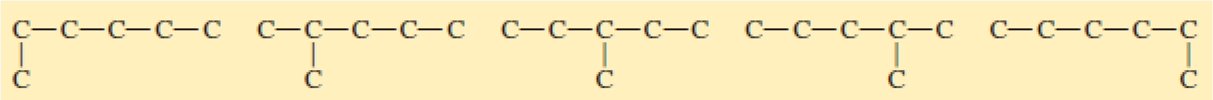
This is the molecule hexane, the first of the five constitutional isomers. No substituents are added to this chain, as that would increase the carbon count beyond six.

Step 2: Decreasing the carbon-chain length by one gives a C_5 chain.

$$C-C-C-C-C$$

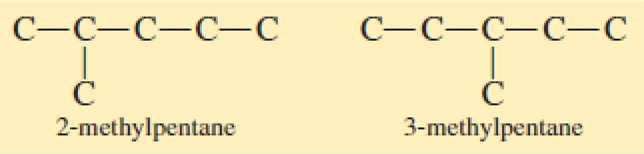
A methyl group must be added to the chain to bring the carbon count back up to six.

Theoretically, there are five possible positions for the methyl group:



These five structures do not represent five new isomers. The first and last structures represent two alternate ways of drawing the molecule hexane, the first isomer. A methyl group (or any alkyl group) added to the end carbons of a carbon chain will always increase the chain length.

The second and third structures do represent new isomers:



2-methylpentane

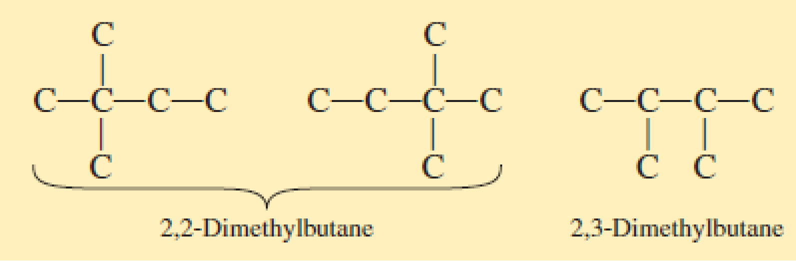
3-methylpentane

The fourth of the five structures is not a new isomer. Numbering its carbon chain from the right end shows that it is 2-methylpentane rather than 4-methylpentane. Thus the second and fourth structures are two representations of the same molecule.

Step 3: Decreasing the chain length to four carbon atoms is the next consideration.

Two carbon atoms must now be added as attachments. This can be done in two ways—dimethyl and ethyl.

Examining dimethyl possibilities first, eliminating structures that have methyl groups on terminal carbon atoms gives the following possibilities.



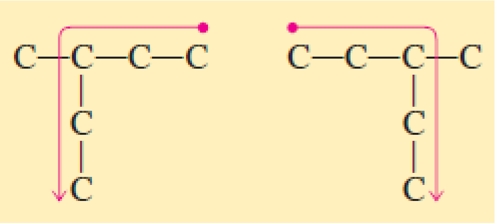
2,2-Dimethylbutane

2,3-Dimethylbutane

The first and second structures are the same; both represent the molecule 2,2-dimethylbutane, a fourth isomer.

The third structure, 2,3-dimethylbutane, is different from the other two. It is the fifth isomer.

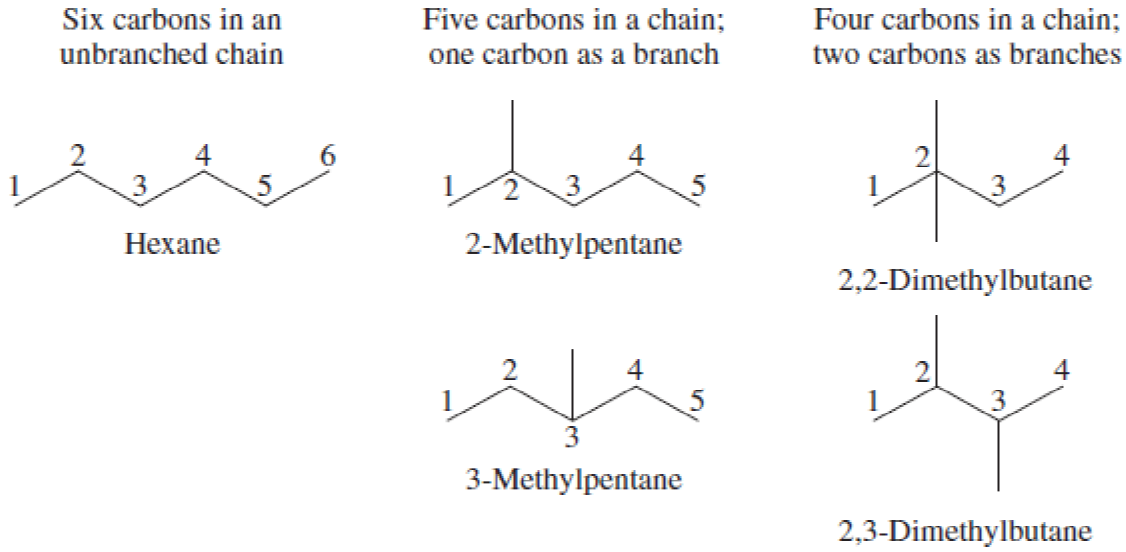
What about ethyl butanes?



Neither of these structures is a new isomer because both have a five-carbon chain. Both structures are actually depictions of 3-methylpentane, one of the isomers previously identified.

Step 4: A chain length of three does not generate any new isomers. A trimethyl structure is impossible, as the middle carbon atom, the only carbon to which substituents can be attached, would have five bonds. An ethyl methyl structure extends the carbon chain length, as does a single three-carbon attachment.

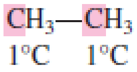
Thus, there are five constitutional isomers: *hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane.*



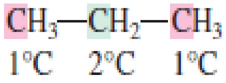
1.8 Classification of Carbon Atoms

Each of the carbon atoms within a hydrocarbon structure can be classified as a *primary* (**1°**), *secondary* (2°), *tertiary* (3°), or *quaternary* (4°) carbon atom.

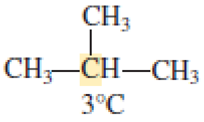
A **primary carbon atom** *is a carbon atom in an organic molecule that is directly bonded to one other carbon atom*. Both carbon atoms in ethane are primary carbon atoms.



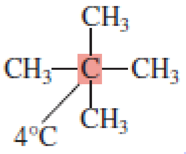
A **secondary carbon atom** *is a carbon atom in an organic molecule that is directly bonded to two other carbon atoms.* A propane molecule contains a secondary carbon atom as well as two primary carbon atoms.



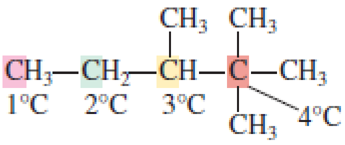
A **tertiary carbon atom** *is a carbon atom in an organic molecule that is directly bonded to three other carbon atoms.* The molecule 2-methylpropane contains a tertiary carbon atom.



A **quaternary carbon atom** *is a carbon atom in an organic molecule that is directly bonded to four other carbon atoms.* The molecule 2,2-dimethylpropane contains a quaternary carbon atom.



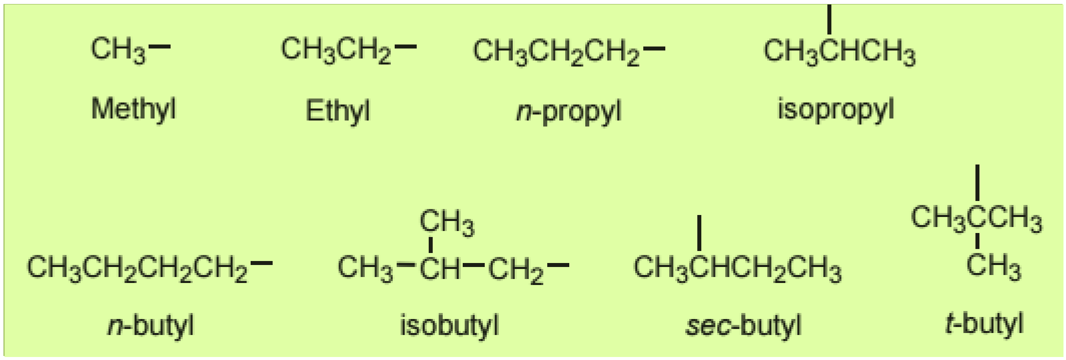
The alkane 2,2,3-trimethyl pentane is the simplest alkane in which all four types of carbon atoms (1°, 2°, 3°, and 4°) are present.



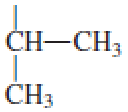
1.9 Branched-Chain Alkyl Groups

Methyl, ethyl, n-propyl and n-butyl are continuous chain alkyl groups

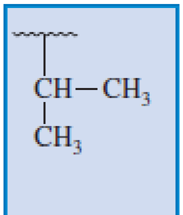
Isopropyl, isobutyl, s- butyl and t-butyl are branched -chain alkyl groups



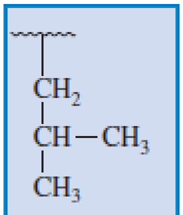
For the two groups whose names contain the prefix *iso-*, the common structural feature is an end-of-chain arrangement that contains two methyl groups.



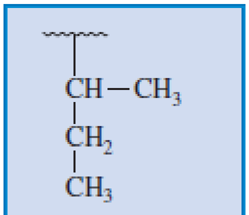
For the *secondary*-butyl group, the point of attachment of the group to the main carbon chain involves a *secondary* carbon atom. For the *tertiary*-butyl group, the point of attachment of the group to the main carbon chain involves a *tertiary* carbon atom. The name secondary-butyl is often shortened to sec-butyl or simply s-butyl. Similarly, tertiary-butyl is often written as tert-butyl or t-butyl.



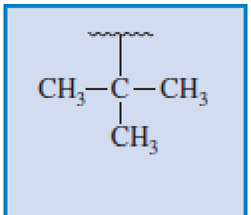
Isopropyl group



Isobutyl group



Secondary-butyl group

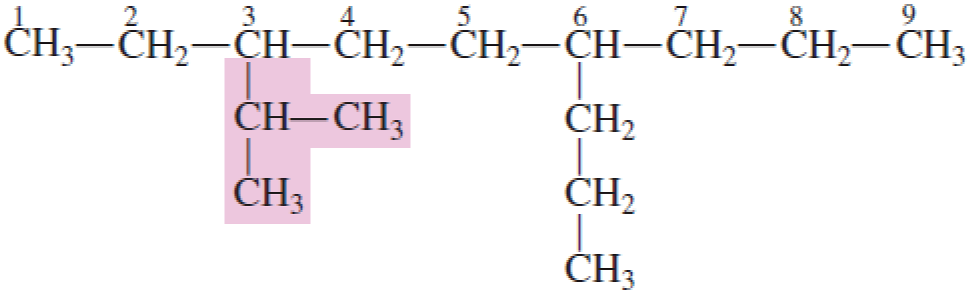


Tertiary-butyl group

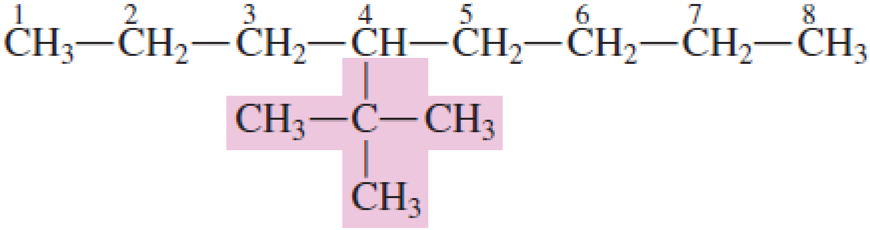
A single compound or group can have several acceptable names, but no two compounds or groups can have the same name

An alternate name for the sec-butyl group is the 1,1-dimethylethyl groups.

Two examples of alkanes containing branched-chain alkyl groups follow.



3-Isopropyl-6-propylnonane

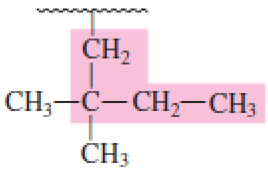


4-*tert*-Butyloctane

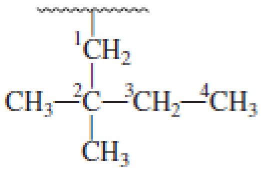
Complex Branched-Chain Alkyl Groups

"Simple" names, such as isobutyl and tert-butyl, do not exist for most branched-chain alkyl groups containing five or more carbon atoms. The IUPAC system provision for naming such larger groups involves naming them as if they were themselves compounds. The following rules are used

Rule 1:*The longest continuous carbon chain that begins at the point of attachment of the alkyl group becomes the base name.*

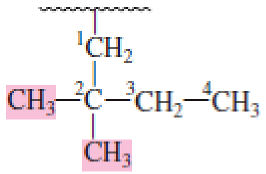


Rule 2: *The base chain is numbered beginning at the point of attachment.*



$\mathrm{{}^{1}CH_2{-}{}^{2}C(CH_3)_2{-}{}^{3}CH_2{-}{}^{4}CH_3}$

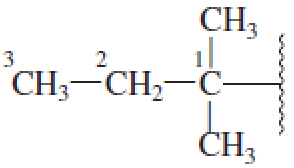
Rule 3: *Substituents on the base chain are listed in alphabetical order, using numerical prefixes when necessary, and substituent locations are designated using numbers.*



$\mathrm{{}^{1}CH_2{-}{}^{2}C(CH_3)_2{-}{}^{3}CH_2{-}{}^{4}CH_3}$

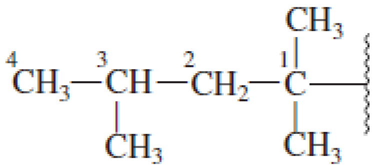
(2,2-dimethylbutyl) group

Two additional examples of IUPAC nomenclature for complex branched-chain alkyl groups are



$\mathrm{{}^{3}CH_3{-}{}^{2}CH_2{-}{}^{1}C(CH_3)_2{-}}$

(1,1-dimethylpropyl) group



$\mathrm{{}^{4}CH_3{-}{}^{3}CH(CH_3){-}{}^{2}CH_2{-}{}^{1}C(CH_3)_2{-}}$

(1,1, 3-trimethylbutyl) group

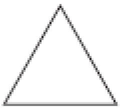
1.10 Cycloalkanes

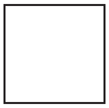
A **cycloalkane** *is a saturated hydrocarbon in which carbon atoms connected to one another in a cyclic (ring) arrangement are present.*

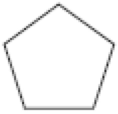
The simplest cycloalkane is cyclopropane, which contains a cyclic arrangement of three carbon atoms

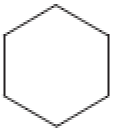
The general formula for Cycloalkanes is C_nH_{2n}. The general formula for Cycloalkanes is C_nH_{2n}. Thus a given cycloalkane contains two fewer hydrogen atoms than an alkane with the same number of hydrogen atoms

Line-angle structural formulas are generally used to represent cycloalkane structures. The line-angle structural formula for cyclopropane is a triangle, that for cyclobutane a square, that for cyclopentane a pentagon, and that for cyclohexane a hexagon.

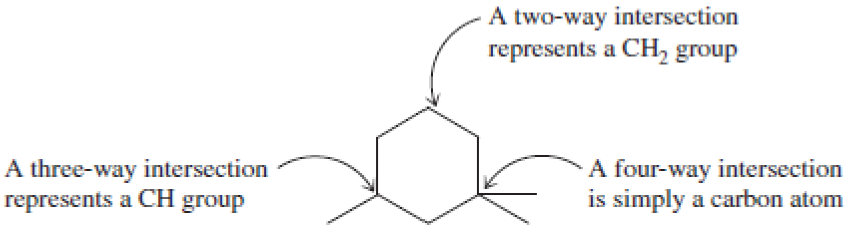

Cyclopropane


Cyclobutane


Cyclopentane


Cyclohexane

In such structures, the intersection of two lines represents a CH_2 group. Three- and four-way intersections of lines are possible when substituents are present on a ring. A three-way intersection represents a CH group, and a four-way intersection is simply a carbon atom.


A two-way intersection represents a CH_2 group

A three-way intersection represents a CH group

A four-way intersection is simply a carbon atom

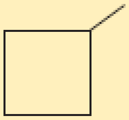
Cycloalkanes of ring sizes ranging from 3 to over 30 are found in nature, and, in principle, there is no limit to ring size. Five-membered rings (cyclopentane) and six- membered rings (cyclohexane) are especially abundant in nature

IUPAC Nomenclature for Cycloalkanes

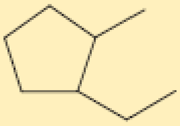
1. If there is just one ring substituent, it is not necessary to locate it by number.
2. When two ring substituents are present, the carbon atoms in the ring are numbered beginning with the substituent of higher alphabetical priority and preceding in the direction (clockwise or counterclockwise) that gives the other substituent the lower number.
3. When three or more ring substituents are present, ring numbering begins at the substituent that leads to the lowest set of location numbers. When two or more equivalent numbering sets exist, alphabetical priority among substituents determines the set used.

Assign IUPAC names to each of the following cycloalkanes.

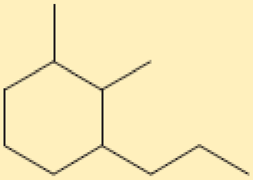
a.



b.



c.

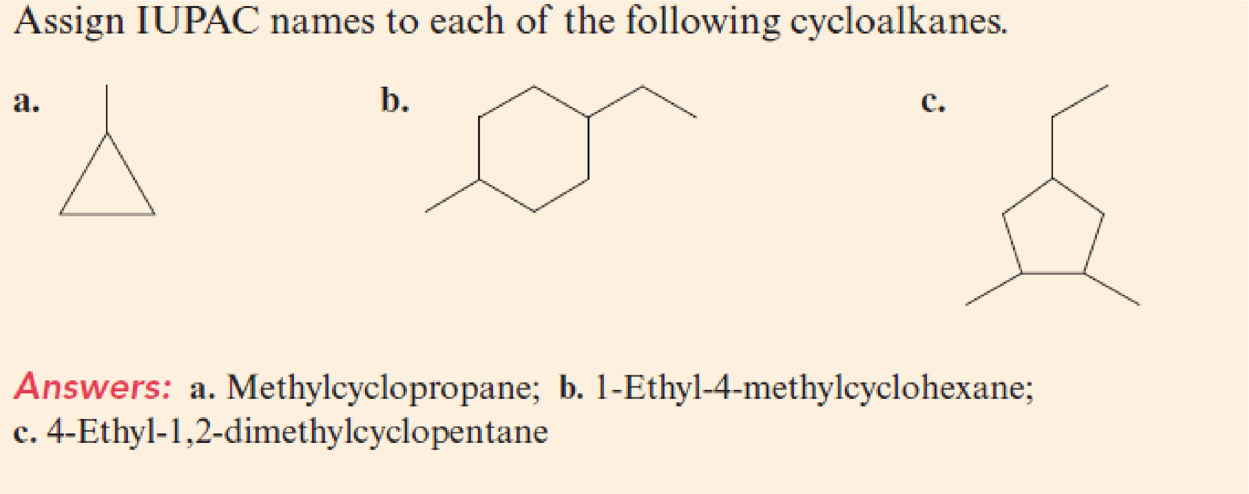


Solution

a. This molecule is a cyclobutane (four-carbon ring) with a methyl substituent. The IUPAC name is simply methylcyclobutane. No number is needed to locate the methyl group because all four ring positions are equivalent.

b. This molecule is a cyclopentane with ethyl and methyl substituents. The numbers for the carbon atoms that bear the substituents are 1 and 2. On the basis of alphabetical priority, the number 1 is assigned to the carbon atom that bears the ethyl group. The IUPAC name for the compound is 1-ethyl-2-methylcyclopentane.

c. This molecule is a dimethylpropylcyclohexane. Two different 1,2,3 numbering systems exist for locating the substituents. On the basis of alphabetical priority, the numbering system that has carbon 1 bearing a methyl group is used; methyl has alphabetical priority over propyl. Thus the compound name is 1,2-dimethyl-3-propylcyclohexane.

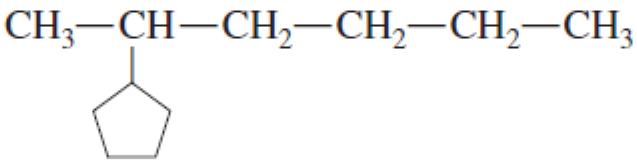


Assign IUPAC names to each of the following cycloalkanes.

a. **b.** **c.**

Answers: **a.** Methylcyclopropane; **b.** 1-Ethyl-4-methylcyclohexane; **c.** 4-Ethyl-1,2-dimethylcyclopentane

When a ring system contains fewer carbon atoms than an alkyl group attached to it, the compound is named as an alkane rather than as a cycloalkane; the ring is named as a cycloalkyl group.

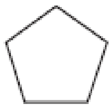


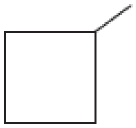
$CH_3-CH(C_5H_9)-CH_2-CH_2-CH_2-CH_3$

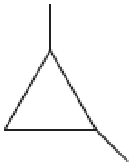
2-cyclopentylhexane

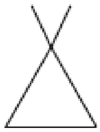
1.11 Isomerism in Cycloalkanes

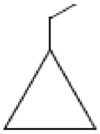
Constitutional isomers are possible for cycloalkanes that contain four or more carbon atoms. For example, there are five cycloalkane constitutional isomers that have the formula C_5H_{10}: one based on a five-membered ring, one based on a four membered ring, and three based on a three-membered ring. These isomers are


Cyclopentane


Methylcyclobutane


1,2-Dimethyl-
cyclopropane


1,1-Dimethyl-
cyclopropane

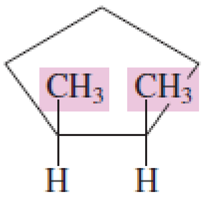

Ethylcyclopropane

A second type of isomerism, called *stereoisomerism,* is possible for some *substituted* cycloalkanes. Whereas constitutional isomerism results from differences in *connectivity,* stereoisomerism results from differences in *configuration*

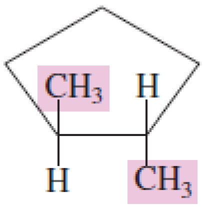
Stereoisomers *are isomers that have the same molecular and structural formulas but different orientations of atoms in space.* Several forms of stereoisomerism exist. The form associated with cycloalkanes is called *cis–trans isomerism.* ***Cis– trans* isomers** *are isomers that have the same molecular and structural formulas but different orientations of atoms in space because of restricted rotation about bonds.*

In alkanes, there is free rotation about all carbon–carbon bonds. In cycloalkanes, the ring structure restricts rotation for the carbon atoms in the ring. The consequence of this lack of rotation in a cycloalkane is the creation of “top” and “bottom” positions for the two attachments on each of the ring carbon atoms. This “top–bottom” situation leads to *cis–trans* isomerism in cycloalkanes in which each of two ring carbon atoms bears two different attachments.

Consider the following two structures for the molecule 1,2-dimethylcyclo- pentane.

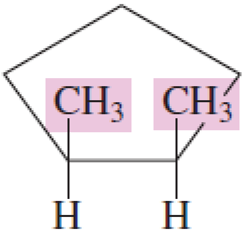


Structure A

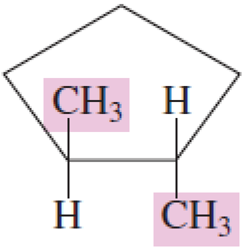


Structure B

In structure A, both methyl groups are above the plane of the ring (the “top” side). In structure B, one methyl group is above the plane of the ring (the “top” side) and the other below it (the "bottom" side). Structure A cannot be converted into structure B without breaking bonds. Hence structures A and B are isomers; there are two 1,2-dimethylcyclopentanes. The first isomer is called *cis*-1,2-dimethylcyclopentane and the second *trans*-1,2-dimethylcyclopentane.



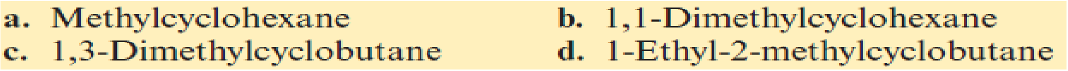
cis-1,2-Dimethylcyclopentane
Boiling point = 99°C



trans-1,2-Dimethylcyclopentane
Boiling point = 92°C

Cis- *is a prefix that means "on the same side."* In *cis*-1,2-dimethylcyclopentane, the two methyl groups are on the same side of the ring. ***Trans-*** *is a prefix that means "across from."* In *trans*-1,2-dimethylcyclopentane, the two methyl groups are on opposite sides of the ring.

Determine whether *cis–trans* isomerism is possible for each of the following cycloalkanes. If so, then draw structural formulas for the *cis* and *trans* isomers.



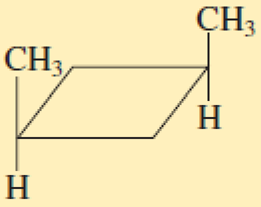
a. Methylcyclohexane
b. 1,1-Dimethylcyclohexane
c. 1,3-Dimethylcyclobutane
d. 1-Ethyl-2-methylcyclobutane

Solution

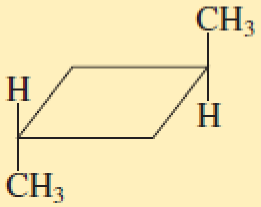
a. *Cis–trans* isomerism is not possible because there are not two substituents on the ring.

b. *Cis–trans* isomerism is not possible. There are two substituents on the ring, but they are on the same carbon atom. Each of two different carbons must bear substituents.

c. *Cis–trans* isomerism does exist.

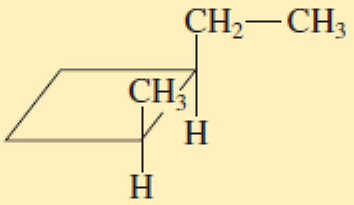


cis-1,3-Dimethylcyclobutane

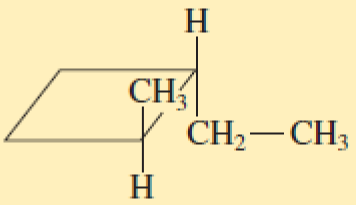


trans-1,3-Dimethylcyclobutane

d. *Cis–trans* isomerism does exist.



cis-1-Ethyl-2-methylcyclobutane

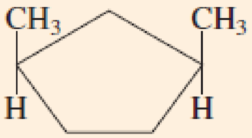


trans-1-Ethyl-2-methylcyclobutane

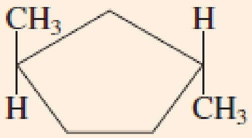
Determine whether *cis–trans* isomerism is possible for each of the following cycloalkanes. If so, then draw structural formulas for the *cis* and *trans* isomers.

a. 1-Ethyl-1-methylcyclopentane
b. Ethylcyclohexane
c. 1,3-Dimethylcyclopentane
d. 1,1-Dimethylcyclooctane

Answers: **a.** Not possible; **b.** Not possible; **c.**



cis isomer

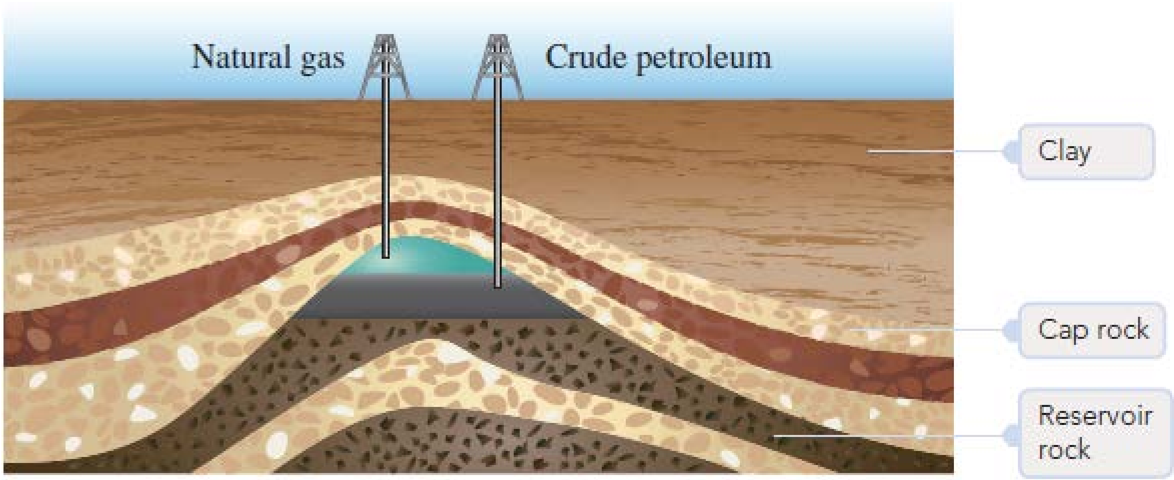


trans isomer

d. Not possible

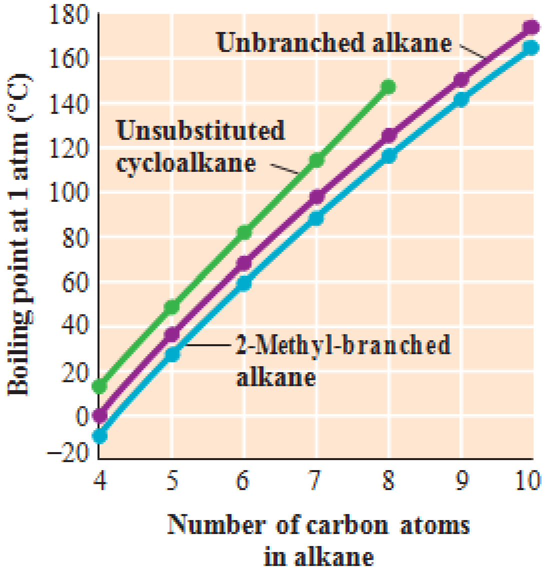
1.12 Sources of Alkanes and Cycloalkanes

Alkanes and cycloalkanes are not “laboratory curiosities” but, rather, two families of extremely important naturally occurring compounds. Natural gas and petroleum (crude oil) constitute their largest and most important natural source. Deposits of these resources are usually associated with underground dome-shaped rock formations. When a hole is drilled into such a rock formation, it is possible to recover some of the trapped hydrocarbons—that is, the natural gas and petroleum



1.13 Physical Properties of Alkanes and Cycloalkanes

1. *Alkanes and cycloalkanes are insoluble in water.* Water molecules are polar, and alkane and cycloalkane molecules are non-polar. Molecules of unlike polarity have limited solubility in one another
2. *Alkanes and cycloalkanes have densities lower than that of water.* Alkane and cycloalkane densities fall in the range 0.6 g/mL to 0.8 g/mL, compared with water's density of 1.0 g/ml. When alkanes and cycloalkanes are mixed with water, two layers form (because of insolubility), with the hydrocarbon layer on top (because of its lower density).
3. *The boiling points of continuous-chain alkanes and cycloalkanes increase with an increase in carbon-chain length or ring size.*



Trends in normal boiling points for continuous-chain alkanes, 2-methyl branched alkanes, and unsubstituted cycloalkanes as a function of the number of carbon atoms present. For a series of alkanes or cycloalkanes, melting point increases as carbon-chain length increases.

Branching on a carbon chain lowers the boiling point of an alkane. A comparison of the boiling points of unbranched alkanes and their 2-methyl-branched isomers is given in this Figure. Branched alkanes are more compact, with smaller surface areas than their straight-chain isomers.

Cycloalkanes have higher boiling points than their noncyclic counterparts with the same number of carbon atoms. These differences are due in large part to cyclic systems having more rigid and more symmetrical structures.

Cyclopropane and cyclobutane are gases at room temperature, and cyclopentane through cyclooctane are liquids at room temperature.

1.14 **Chemical Properties of Alkanes and Cycloalkanes**

Alkanes are the least reactive type of organic compound. They can be heated for long periods of time in strong acids and bases with no appreciable reaction. Strong oxidizing agents and reducing agents have little effect on alkanes.

Alkanes are not absolutely unreactive. Two important reactions that they undergo are combustion, which is reaction with oxygen, and halogenations, which is reaction with halogens.

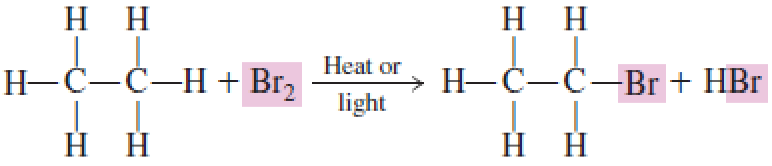
Combustion of alkanes

A **combustion reaction** *is a chemical reaction between a substance and oxygen (usually from air) that proceeds with the evolution of heat and light (usually as a flame).* Alkanes readily undergo combustion when ignited. When sufficient oxygen is present to support total combustion, carbon dioxide and water are the products.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{heat energy}$$
$$2C_6H_{14} + 19O_2 \longrightarrow 12CO_2 + 14H_2O + \text{heat energy}$$

Halogenation

A **halogenation reaction** *is a chemical reaction between a substance and a halogen in which one or more halogen atoms are incorporated into molecules of the substance.* Halogenation of an alkane produces a hydrocarbon derivative in which one or more halogen atoms have been substituted for hydrogen atoms. An example of an alkane halogenation reaction is

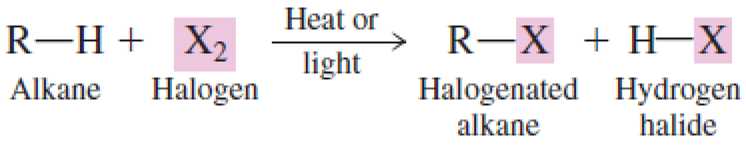


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H} + Br_2 \xrightarrow[\text{light}]{\text{Heat or}} \mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}Br} + HBr$$

Alkane halogenation is an example of a substitution reaction, a type of reaction that occurs often in organic chemistry.

A substitution reaction *is a chemical reaction in which part of a small reacting molecule replaces an atom or a group of atoms on a hydrocarbon or hydrocarbon derivative.*

A *general* equation for the substitution of a single halogen atom for one of the hydrogen atoms of an alkane is



$$\underset{\text{Alkane}}{R{-}H} + \underset{\text{Halogen}}{X_2} \xrightarrow[\text{light}]{\text{Heat or}} \underset{\text{Halogenated alkane}}{R{-}X} + \underset{\text{Hydrogen halide}}{H{-}X}$$

Note the following features of this general equation:

1. The notation R-H is a general formula for an alkane. R- in this case represents an alkyl group. Addition of a hydrogen atom to an alkyl group produces the parent hydrocarbon of the alkyl group.
2. The notation R-X on the product side is the general formula for a halogenated alkane. X is the general symbol for a halogen atom.
3. Reaction conditions are noted by placing these conditions on the equation arrow that separates reactants from products. Halogenation of an alkane requires the presence of heat or light.

The symbol R is used frequently in organic chemistry and will be encountered in numerous generalized formulas in subsequent chapters; it always represents a generalized organic group in a structural formula. An R group can be an alkyl group—methyl, ethyl, propyl, etc.—or any number of other organic groups.

In halogenation of an alkane, the alkane is said to undergo *fluorination, chlorination, bromination,* or *iodination,* depending on the identity of the halogen reactant. Chlorination and bromination are the two widely used alkane halogenation reactions. Fluorination reactions generally proceed too quickly, and iodination reactions go too slowly.

Methane and chlorine, when heated to a high temperature or in the presence of light, react as follows:

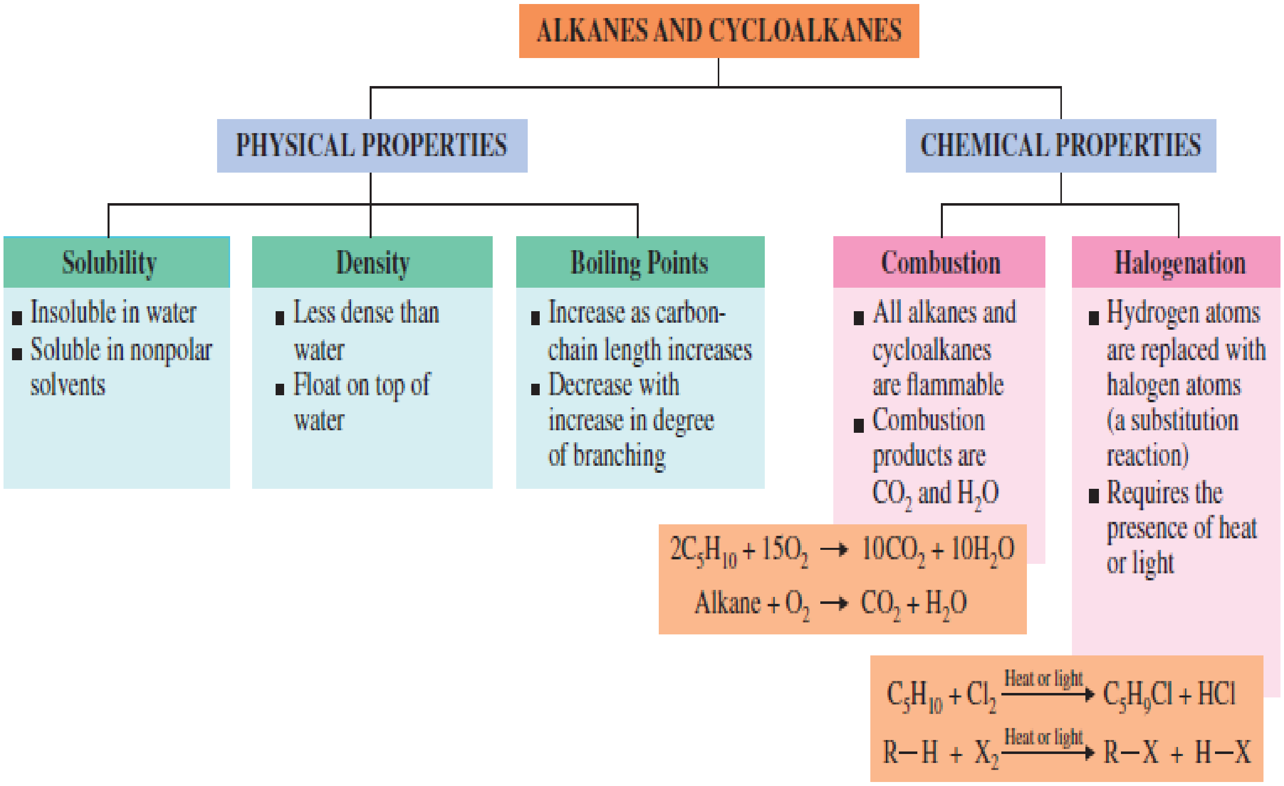
$$CH_4 + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CH_3Cl + HCl$$

The reaction does not stop at this stage, however, because the chlorinated methane product can react with additional chlorine to produce polychlorinated products.

$$CH_3Cl + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CCl_4 + HCl$$



- Insoluble in water
- Soluble in nonpolar solvents

- Less dense than water
- Float on top of water

- Increase as carbon-chain length increases
- Decrease with increase in degree of branching

- All alkanes and cycloalkanes are flammable
- Combustion products are CO_2 and H_2O

$$2C_5H_{10} + 15O_2 \rightarrow 10CO_2 + 10H_2O$$

$$\text{Alkane} + O_2 \rightarrow CO_2 + H_2O$$

- Hydrogen atoms are replaced with halogen atoms (a substitution reaction)
- Requires the presence of heat or light

$$C_5H_{10} + Cl_2 \xrightarrow{\text{Heat or light}} C_5H_9Cl + HCl$$

$$R{-}H + X_2 \xrightarrow{\text{Heat or light}} R{-}X + H{-}X$$

1.15 Halogenated Alkanes and Cycloalkanes

A **halogenated alkane** *is an alkane derivative in which one or more halogen atoms are present.* Similarly, a **halogenated cycloalkane** *is a cycloalkane derivative in which one or more halogen atoms are present.* Produced by halogenation reactions, these two types of compounds represent the first class of hydrocarbon derivatives formally considered in this text.

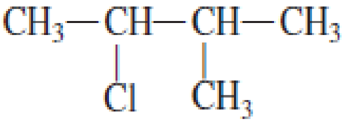
Alkanes have the general molecular formula $CnH2n+2$.Halogenated alkanes containing one halogen atom have the general molecular formula $C_nH_{2n+1}X$; a halogen atom has replaced a hydrogen atom. If two halogen atoms are present in a halogenated alkane, the general molecular formula is $C_nH_{2n}X_2$. Since cycloalkanes have the general molecular formula $CnH2n$ a halogenated cycloalkane with one halogen atom present will have a general molecular formula of $C_nH_{2n-1}X$.

Nomenclature of Halogenated Alkanes

The IUPAC rules for naming halogenated alkanes are similar to those for naming branched alkanes, with the following modifications:

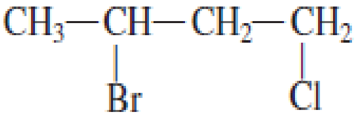
1. Halogen atoms, treated as substituents on a carbon chain, are called *fluoro*-, *chloro*-, *bromo*-, and *iodo*-.
2. When a carbon chain bears both a halogen and an alkyl substituent, the two substituents are considered of equal rank in determining the numbering system for the chain. The chain is numbered from the end closer to a substituent, whether it is a *halo*- or an alkyl group.
3. Alphabetical priority determines the order in which all substituents present are listed.

The following names are derived using these rule adjustments.



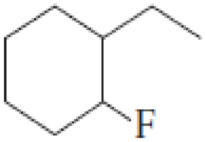
$CH_3-\underset{\underset{\textstyle Cl}{|}}{CH}-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_3$

2-Chloro-3-methylbutane



$CH_3-\underset{\underset{\textstyle Br}{|}}{CH}-CH_2-\underset{\underset{\textstyle Cl}{|}}{CH_2}$

3-Bromo-1-chlorobutane



1-Ethyl-2-fluorocyclohexane

Simple halogenated alkanes can also be named as *alkyl halides.* These common (non-IUPAC) names have two parts. The first part is the name of the hydrocarbon portion of the molecule (the alkyl group). The second part (as a separate word) identifies the halogen portion, which is named as if it were an ion (chloride, bromide, and so on), even though no ions are present (all bonds are covalent bonds). The following examples contrast the IUPAC names and the common names (in parentheses) of selected halogenated alkanes.

Physical Properties of Halogenated Alkanes

Halogenated alkane boiling points are generally higher than those of the corresponding alkane. An important factor contributing to this effect is the polarity of carbon–halogen bonds, which results in increased dipole–dipole interactions.

Two general trends relative to boiling points and melting points of halogenated hydrocarbons containing a single halogen atom are:

1. Boiling points and melting points increase as the size of the alkyl group present increases. This is due to increasing intermolecular forces associated with increased molecular surface area.
2. Boiling points and melting points increase as the size of the halogen atom increases from fluorine (F) to iodine (I).

Halogenated hydrocarbons do not have hydrogen-bonding capabilities since all hydrogen atoms are bonded to carbon atoms. Thus water solubility is very limited regardless of molecular size.

Some halogenated alkanes have densities that are greater than that of water, a situation not common for organic compounds. Chloroalkanes containing two or more chlorine atoms, bromoalkanes, and iodoalkanes are all denser than water.

Concepts to Remember

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Carbon atom bonding characteristics: Carbon atoms in organic compounds must have four bonds.

Types of hydrocarbons: Hydrocarbons, binary compounds of carbon and hydrogen, are of two types: saturated and unsaturated. In saturated hydrocarbons, all carbon–carbon bonds are single bonds. Unsaturated hydrocarbons have one or more carbon–carbon multiple bonds—double bonds, triple bonds, or both.

Alkanes: Alkanes are saturated hydrocarbons in which the car- bon atom arrangement is that of an unbranched or branched chain. The formulas of all alkanes can be represented by the general formula C*n*H2*n*+2, where *n* is the number of carbon atoms present

Structural formulas: Structural formulas are two-dimensional representations of the arrangement of the atoms in molecules. These formulas give complete information about the arrangement of the atoms in a molecule but not the spatial orientation of the atoms. Two types of structural formulas are commonly encountered: expanded and condensed.

Isomers: Isomers are compounds that have the same molecular formula (that is, the same numbers and kinds of atoms), but that differ in the way the atoms are arranged.

Constitutional isomers: Constitutional isomers are isomers that differ in the connectivity of atoms, that is, in the order in which atoms are attached to each other within molecules.

Conformations: Conformations are differing orientations of the same molecule made possible by free rotation about single bonds in the molecule.

Alkane nomenclature: The IUPAC name for an alkane is based on the longest continuous chain of carbon atoms in the molecule. A group of carbon atoms attached to the chain is an alkyl group. Both the position and the identity of the alkyl group are prefixed to the name of the longest carbon chain.

Line-angle structural formulas: A line-angle structural formula is a structural representation in which a line represents a carbon–carbon bond and a carbon atom is understood to be present at every point where two lines meet and at the ends of the line. Line-angle structural formulas are the most concise method for representing the structure of a hydrocarbon or hydrocarbon derivative.

Cycloalkanes: Cycloalkanes are saturated hydrocarbons in which at least one cyclic arrangement of carbon atoms is present. The formulas of all cycloalkanes can be represented by the general formula C*n*H2*n*, where *n* is the number of carbon atoms present

Cycloalkane nomenclature: The IUPAC name for a cycloalkane is obtained by placing the prefix *cyclo-* before the alkane name that corresponds to the number of carbon atoms in the ring. Alkyl groups attached to the ring are located by using a ring- numbering system.

***Cis–trans* isomerism:** For certain disubstituted cycloalkanes, *cis–trans* isomers exist. *Cis–trans* isomers are compounds that have the same molecular and structural formulas but different arrangements of atoms in space because of restricted rotation about bonds.

Natural sources of saturated hydrocarbons: Natural gas and petroleum are the largest and most important natural sources of both alkanes and cycloalkanes.

Physical properties of saturated hydrocarbons: Saturated hydro- carbons are not soluble in water and have lower densities than water. Melting and boiling points increase with increasing car- bon chain length or ring size.

Chemical properties of saturated hydrocarbons: Two important reactions that saturated hydrocarbons undergo are combustion and halogenation. In combustion, saturated hydrocarbons burn in air to produce CO_2 and H_2O. Halogenation is a substitution reaction in which one or more hydrogen atoms of the hydrocarbon are replaced by halogen atoms.

Halogenated alkanes: Halogenated alkanes are hydrocarbon derivatives in which one or more halogen atoms have replaced hydrogen atoms of the alkane

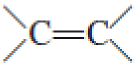
Halogenated alkane nomenclature: Halogenated alkanes are named by using the rules that apply to branched-chain alkanes, with halogen substituents being treated the same as alkyl groups

Chapter Two: Unsaturated Hydrocarbons

2.1 Unsaturated Hydrocarbons

An **unsaturated hydrocarbon** *is a hydrocarbon in which one or more carbon– carbon multiple bonds (double bonds, triple bonds, or both) are present*. Unsaturated hydrocarbons are chemically more reactive than their saturated counterparts. The increased reactivity of unsaturated hydrocarbons is related to the presence of the carbon– carbon multiple bond(s) in such compounds. These multiple bonds serve as locations where chemical reactions can occur.

A functional group *is the part of an organic molecule where most of its chemical reactions occur.* Carbon–carbon multiple bonds are the functional group for an unsaturated hydrocarbon.



Types of unsaturated hydrocarbons

Unsaturated hydrocarbons are subdivided into three groups on the basis of the type of multiple bond(s) present: (1) *alkenes,* which contain one or more carbon–carbon double bonds (2) *alkynes,* which contain one or more carbon– carbon triple bonds and (3) *aromatic hydrocarbons,* which exhibit a special type of “delocalized” bonding that involves a six-membered carbon ring.

2.2 Characteristics of Alkenes and Cycloalkenes

Alkenes

An **alkene** *is an acyclic unsaturated hydrocarbon that contains one or more carbon– carbon double bonds*. The alkene functional group is thus a C=C group. Note the close similarity between the family names *alkene* and *alkane*; they differ only in their endings: *-ene versus -ane.* The *-ene* ending means a double bond is present.

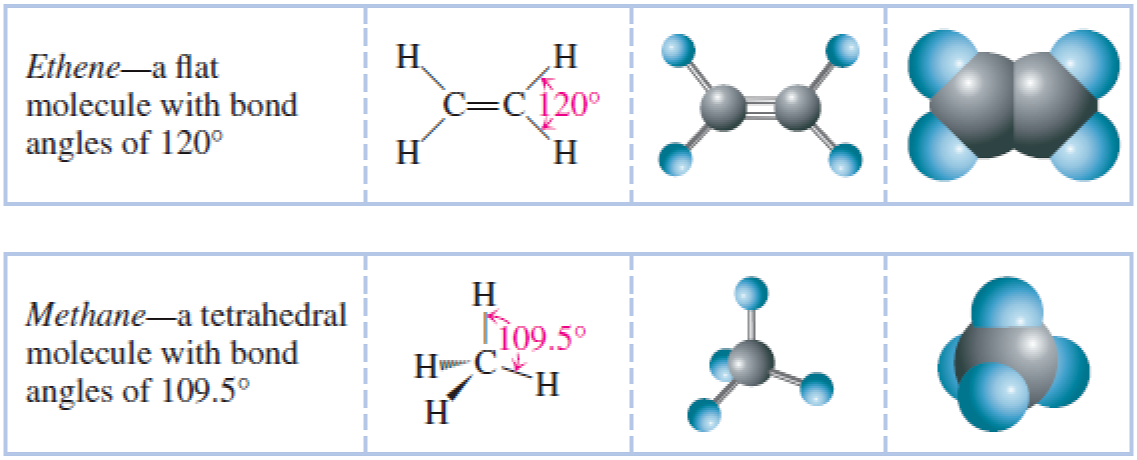
The simplest type of alkene contains only one carbon–carbon double bond. Such compounds have the general molecular formula C*n*H2*n*. Thus alkenes with one double bond have two fewer hydrogen atoms than do alkanes (CnH2n+2,).

The two simplest alkenes are ethene (C_2H_4) and propene (C_3H_6).

$$CH_2{=}CH_2 \qquad CH_2{=}CH{-}CH_3$$

Ethene Propene

Comparing the geometrical shape of ethene with that of methane (the simplest alkane) reveals a major difference. The arrangement of bonds about the carbon atom in methane is tetrahedral, whereas the carbon atoms in ethene have a trigonal planar arrangement of bonds; that is, they form a flat, triangle- shaped arrangement.



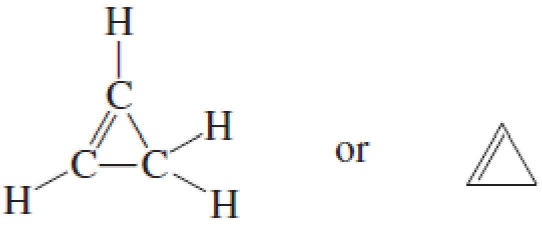
Three-dimensional representations of the structures of ethene and methane

In ethene, the atoms are in a flat (planar) rather than a tetrahedral arrangement. Bond angles are 120°

Cycloalkenes

A cycloalkene *is a cyclic unsaturated hydrocarbon that contains one or more carbon–carbon double bonds within the ring system.* Cycloalkenes in which there is only one double bond have the general molecular formula CnH2n-2

The simplest cycloalkene is the compound cyclopropene (C_3H_4), a three- membered carbon ring system containing one double bond.



Cyclopropene

Dienes and trienes

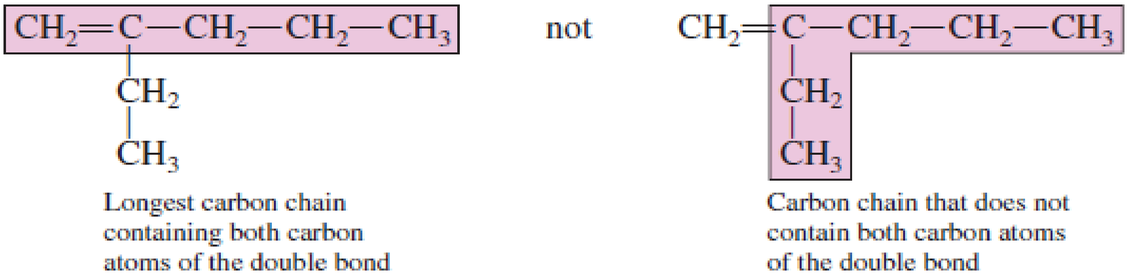
Alkenes with more than one carbon–carbon double bond are relatively common. When two double bonds are present, the compounds are often called *dienes;* for three double bonds the designation *trienes* is used. Cycloalkenes that contain more than one double bond are possible but are not common.

2.3 IUPAC Nomenclature for Alkenes and Cycloalkenes

The IUPAC rules previously presented for naming alkanes and cycloalkanes can be used, with some modification, to name alkenes and cycloalkenes.

Rule 1. *Replace the alkane suffix -ane with the suffix -ene, which is used to indicate the presence of a carbon–carbon double bond.*

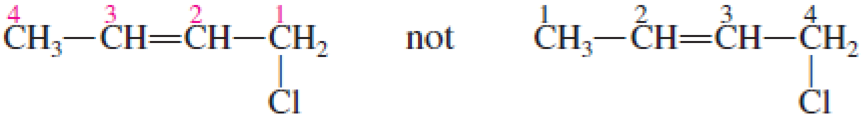
Rule 2. *Select as the parent carbon chain the longest continuous chain of carbon atoms that contains both carbon atoms of the double bond.* For example, select



Rule 3. *Number the parent carbon chain beginning at the end nearest the double bond.*

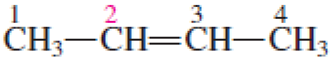
$$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-\overset{5}{C}H_3 \quad \text{not} \quad \overset{5}{C}H_3-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}H_2-\overset{1}{C}H_3$$

If the double bond is equidistant from both ends of the parent chain, begin numbering from the end closer to a substituent.



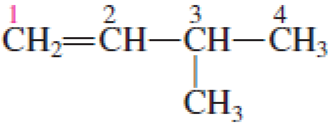
$$\overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}H-\underset{\displaystyle Cl}{\overset{1}{C}H_2} \quad \text{not} \quad \overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\underset{\displaystyle Cl}{\overset{4}{C}H_2}$$

Rule 4. *Give the position of the double bond in the chain as a single number, which is the lower-numbered carbon atom participating in the double bond.* This number is placed immediately before the name of the parent carbon chain



$$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$$

2-Butene



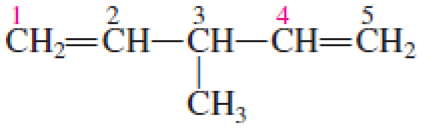
$$\overset{1}{C}H_2=\overset{2}{C}H-\underset{\displaystyle CH_3}{\overset{3}{C}H}-\overset{4}{C}H_3$$

3-Methyl-1-butene

Rule 5. *Use the suffixes -diene, -triene, -tetrene, and so on when more than one double bond is present in the molecule*. A separate number must be used to locate each double bond.

$\overset{1}{\mathrm{C}}\mathrm{H_2}{=}\overset{2}{\mathrm{C}}\mathrm{H}{-}\overset{3}{\mathrm{C}}\mathrm{H}{=}\overset{4}{\mathrm{C}}\mathrm{H_2}$

1,3-Butadiene

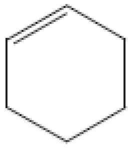


$\overset{1}{\mathrm{C}}\mathrm{H_2}{=}\overset{2}{\mathrm{C}}\mathrm{H}{-}\underset{\mathrm{CH_3}}{\overset{3}{\mathrm{C}}\mathrm{H}}{-}\overset{4}{\mathrm{C}}\mathrm{H}{=}\overset{5}{\mathrm{C}}\mathrm{H_2}$

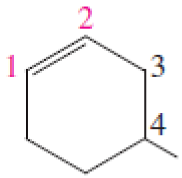
3-Methyl-1,4-pentadiene

Rule6. A number is not needed to locate the double bond in unsubstituted cycloalkenes with only one double bond because that bond is assumed to be between carbons 1 and 2.

Rule7. *In substituted cycloalkenes with only one double bond, the double-bonded carbon atoms are numbered 1 and 2 in the direction (clockwise or counter- clockwise) that gives the first-encountered substituent the lower number.* Again, no number is used in the name to locate the double bond

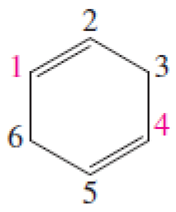


Cyclohexene

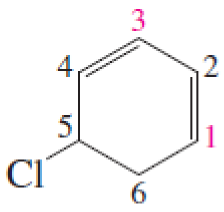


4-Methylcyclohexene

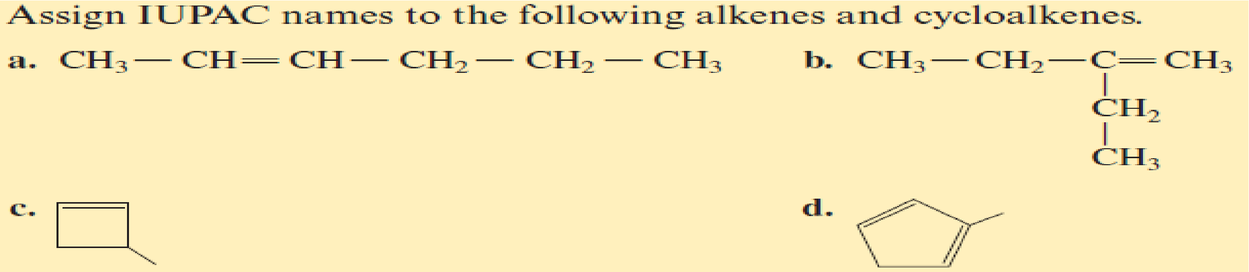
Rule8. In cycloalkenes with more than one double bond within the ring, assign one double bond the numbers 1 and 2 and the other double bonds the lowest numbers possible.



1,4-Cyclohexadiene



5-Chloro-1,3-cyclohexadiene



Assign IUPAC names to the following alkenes and cycloalkenes.

a. $CH_3-CH=CH-CH_2-CH_2-CH_3$

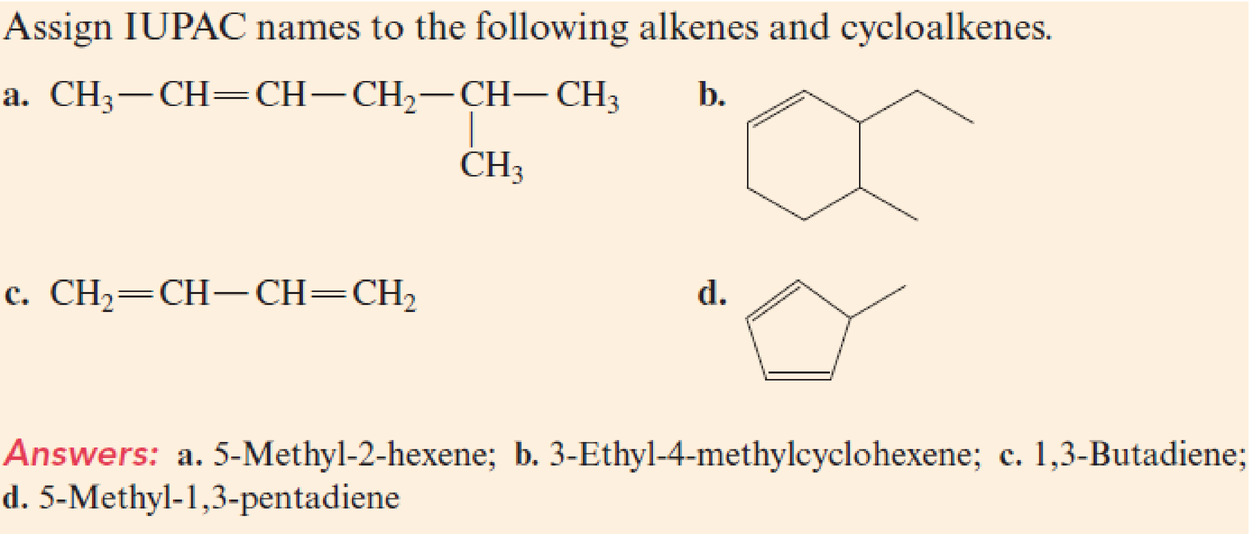
b. $CH_3-CH_2-\underset{\underset{CH_3}{|}}{\underset{CH_2}{\underset{|}{C}}}=CH_3$

c.

d.

a. 2-hexene
b. 2-ethyl-1-butene
c. Methylcyclobutane
d. 2-methyl-1,3-cyclopentadiene

Practical Exercise



Assign IUPAC names to the following alkenes and cycloalkenes.

a. $CH_3-CH=CH-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

b.

c. $CH_2=CH-CH=CH_2$

d.

Answers: **a.** 5-Methyl-2-hexene; **b.** 3-Ethyl-4-methylcyclohexene; **c.** 1,3-Butadiene; **d.** 5-Methyl-1,3-pentadiene

Common Names (Non-IUPAC Names)

The simpler members of most families of organic compounds, including alkenes, have common names in addition to IUPAC names.

The two simplest alkenes, ethene and propene, have common names, They are ethylene and propylene, respectively.

$CH_2=CH_2$
Ethylene

$CH_2=CH-CH_3$
Propylene

Alkenes as Substituents

Just as there are *alkanes* and *alkyl groups*, there are *alkenes* and *alkenyl groups.* An **alkenyl group** *is a noncyclic hydrocarbon substituent in which a carbon–carbon double bond is present.* The three most frequently encountered alkenyl groups are the one-, two-, and three-carbon entities, which may be named using IUPAC nomenclature (methylidene, ethenyl, and 2-propenyl) or common names (methylene, vinyl, and allyl).

$CH_2{=}$

Methylene group
(IUPAC name: methylidene group)

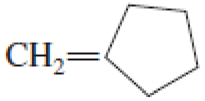
$CH_2{=}CH{—}$

Vinyl group
(IUPAC name: ethenyl group)

$CH_2{=}CH{—}CH_2{—}$

Allyl group
(IUPAC name: 2-propenyl group)

The use of these alkenyl group names in actual compound nomenclature is illustrated in the following examples.



Methylene cyclopentane
(IUPAC name: methylidenecyclopentane)

$CH_2{=}CH{—}Cl$

Vinyl chloride
(IUPAC name: chloroethene)

$CH_2{=}CH{—}CH_2{—}Br$

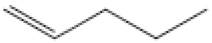
Allyl bromide
(IUPAC name: 3-bromopropene)

2.4 Line-Angle Structural Formulas for Alkenes

Line-angle formulas for the three- to six-carbon acyclic 1-alkenes are as follows.

Propene

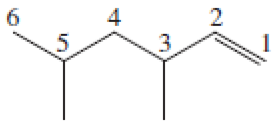
1-Butene



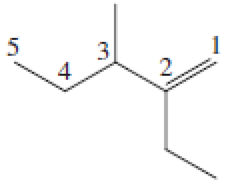
1-Pentene

1-Hexene

Representative line-angle structural formulas for substituent-bearing alkenes include



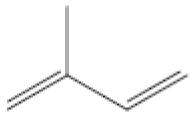
3,5-Dimethyl-1-hexene



2-Ethyl-3-methyl-1-pentene

Diene representations in terms of line-angle structural formulas include

1,4-Pentadiene

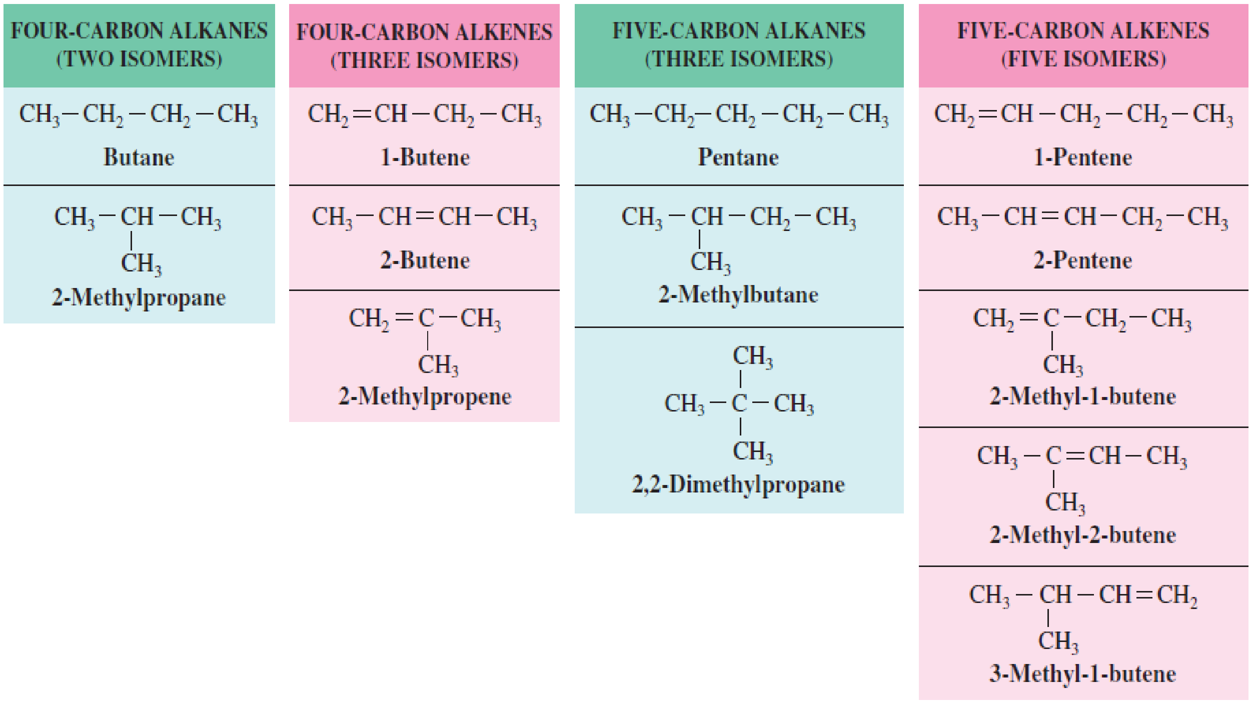


2-Methyl-1,3-butadiene

2.5 Constitutional Isomerism in Alkenes

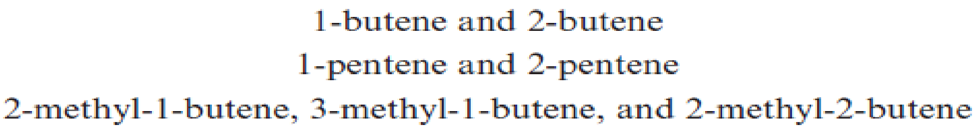
Constitutional isomerism is possible for alkenes, just as it was for alkanes. In general, there are more alkene isomers for a given number of carbon atoms than there are alkane isomers. This is because there is more than one location where a double bond can be placed in systems containing four or more carbon atoms.

A comparison of structural isomerism possibilities for four- and five-carbon alkane and alkene systems



FOUR-CARBON ALKANES (TWO ISOMERS)	FOUR-CARBON ALKENES (THREE ISOMERS)	FIVE-CARBON ALKANES (THREE ISOMERS)	FIVE-CARBON ALKENES (FIVE ISOMERS)
$CH_3-CH_2-CH_2-CH_3$ **Butane**	$CH_2=CH-CH_2-CH_3$ **1-Butene**	$CH_3-CH_2-CH_2-CH_2-CH_3$ **Pentane**	$CH_2=CH-CH_2-CH_2-CH_3$ **1-Pentene**
$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$ **2-Methylpropane**	$CH_3-CH=CH-CH_3$ **2-Butene**	$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-CH_3$ **2-Methylbutane**	$CH_3-CH=CH-CH_2-CH_3$ **2-Pentene**
	$CH_2=\underset{\underset{CH_3}{\vert}}{C}-CH_3$ **2-Methylpropene**	$CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_3$ **2,2-Dimethylpropane**	$CH_2=\underset{\underset{CH_3}{\vert}}{C}-CH_2-CH_3$ **2-Methyl-1-butene**
			$CH_3-\underset{\underset{CH_3}{\vert}}{C}=CH-CH_3$ **2-Methyl-2-butene**
			$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH=CH_2$ **3-Methyl-1-butene**

Positional isomers *are constitutional isomers with the same carbon-chain arrangement but different hydrogen atom arrangements as the result of differing location of the functional group present.*



1-butene and 2-butene
1-pentene and 2-pentene
2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene

Skeletal isomers *are constitutional isomers that have different carbon-chain arrangements as well as different hydrogen atom arrangements.* The C4 alkenes 1-butene and 2-methylpropene are skeletal isomers. All alkane isomers discussed in the previous chapter were skeletal isomers; positional isomerism is not possible for alkanes because they lack a functional group.

Determining Structural Formulas for Alkene Constitutional Isomers

Draw condensed structural formulas for all alkene constitutional isomers that have the molecular formula C5H10.

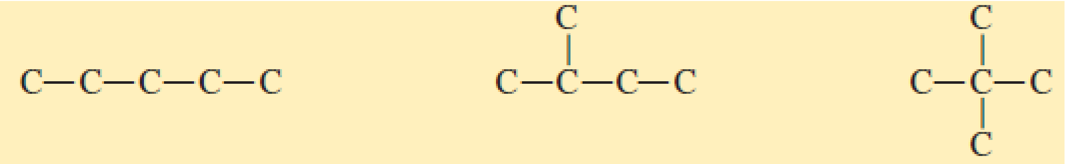
Solution

The answers for this problem have already been considered. The structures of the five C_5H_{10} alkene constitutional isomers are given in the above figure. The purpose of this example is to consider the “thinking pattern” used to obtain the given answers.

There are two concepts in the thinking pattern.

1. The different carbon skeletons (both unbranched and branched) that are possible using five carbon atoms are determined.
2. For each of the carbon skeletons determined, different positions for placement of the double bond are then considered.

Step 1: There are three possible arrangements for five carbon atoms:



$$\mathrm{C{-}C{-}C{-}C{-}C} \qquad \mathrm{C{-}\overset{\overset{C}{|}}{C}{-}C{-}C} \qquad \mathrm{C{-}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}{-}C}$$

These arrangements are the constitutional isomers for a 5-carbon alk*ane*

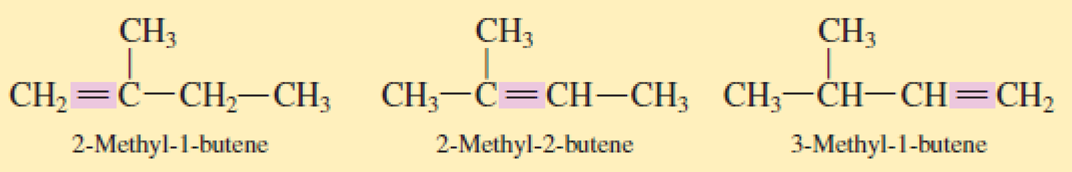
Step 2: For the first carbon skeleton (the unbranched chain), there are two possible locations for the double bond; that is, there are two positional isomers:

$$\mathrm{CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3} \qquad \mathrm{CH_3{-}CH{=}CH{-}CH_2{-}CH_3}$$

1-Pentene 2-Pentene

Moving the double bond farther to the right than in the second structure does not produce new isomers but, rather, duplicates of the two given structures. A double bond between carbons 3 and 4 (numbering from the left side) is the same as having the double bond between carbons 2 and 3 (numbering from the right side).

For the second carbon skeleton, there are three positional isomers—that is, three different positions for the double bond:



$CH_2{=}C(CH_3){-}CH_2{-}CH_3$

2-Methyl-1-butene

$CH_3{-}C(CH_3){=}CH{-}CH_3$

2-Methyl-2-butene

$CH_3{-}CH(CH_3){-}CH{=}CH_2$

3-Methyl-1-butene

For the third carbon skeleton, alkene structures are not possible. Placing a double bond at any location within the structure creates a situation where the central carbon atom has five bonds. Thus there are five alkene constitutional isomers with the molecular formula C_5H_{10}.

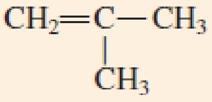
Practical exercise

Draw condensed structural formulas for all alkene constitutional isomers that have the molecular formula C_4H_8.

Answers: $CH_2{=}CH{-}CH_2{-}CH_3$; $CH_3{-}CH{=}CH{-}CH_3$;

1-Butene

2-Butene



$CH_2{=}C(CH_3){-}CH_3$

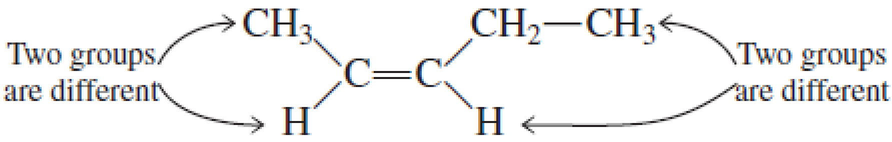
2-Methylpropene

2.6 Cis–Trans Isomerism in Alkenes

Cis–trans isomerism is possible for some alkenes. Such isomerism results from the structural rigidity associated with carbon–carbon double bonds: Unlike the situation in alkanes, where free rotation about carbon–carbon single bonds is possible, no rotation about carbon–carbon double bonds (or carbon–carbon triple bonds) can occur.

There are two requirements for cis-trans isomerism:

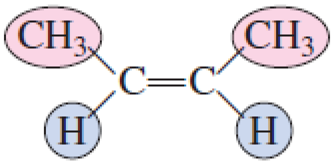
1. Rotation must be restricted in the molecule.
2. There must be **two different groups** on **each** doubly bonded carbon atom

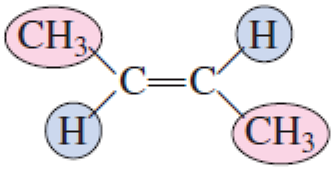


The simplest alkene for which *cis* and *trans* isomers exist is 2-butene.

$CH_3—CH=CH—CH_3$

2-butene


Structure A
(*cis*-2-butene)


Structure B
(*trans*-2-butene)

- Alkenes with a C=CH_2 unit do not exist as cis-trans isomers. (2-propene)
- 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 and *Trans* isomerism in substituted alkenes

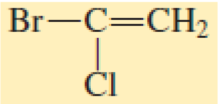
EXAMPLE **Determining Whether *Cis–Trans* Isomerism Is Possible in Substituted Alkenes**

Determine whether each of the following substituted alkenes can exist in *cis–trans* isomeric forms.

a. 1-Bromo-1-chloroethene
b. 2-Chloro-2-butene

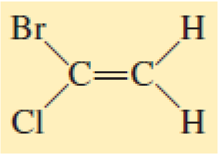
Solution

a. The condensed structural formula for this compound is



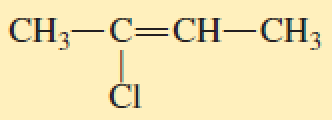
$$\underset{Cl}{Br—\overset{}{C}}=CH_2$$

Redrawing this formula to emphasize the four attachments to the double-bonded carbon atoms gives



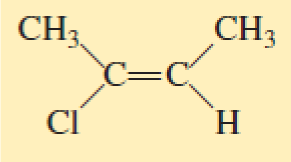
The carbon atom on the right has two identical attachments. Hence *cis–trans* isomerism is not possible.

b. The condensed structural formula for this compound is

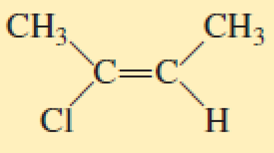


$$CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_3$$

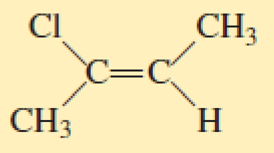
Redrawing this formula to emphasize the four attachments to the double-bonded carbon atoms gives



Because both carbon atoms of the double bond bear two different attachments, *cis–trans* isomers are possible.



cis-2-Chloro-2-butene



trans-2-Chloro-2-butene

Practice Exercise

Determine whether each of the following substituted alkenes can exist in *cis–trans* isomeric forms.

a. 1-Chloropropene
b. 2-Chloropropene

Answers: **a.** Yes; **b.** No

2.7 Physical Properties of Alkenes and Cycloalkenes

The general physical properties of alkenes and cycloalkenes include insolubility in water, solubility in non-polar solvents, and densities lower than that of water. Thus they have physical properties similar to those of alkanes. The melting point of an alkene is usually lower than that of the alkane with the same number of carbon atoms.

Alkenes with 2 to 4 carbon atoms are gases at room temperature. Unsubstituted alkenes with 5 to 17 carbon atoms and one double bond are liquids, and those with still more carbon atoms are solids.

2.8 Chemical Reactions of Alkenes

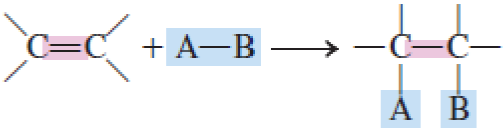
Alkenes, like alkanes, are very flammable. The combustion products, as with any hydrocarbon, are carbon dioxide and water.

$$\underset{\text{Ethene}}{C_2H_4} + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

Pure alkenes are, however, too expensive to be used as fuel.

Aside from combustion, nearly all other reactions of alkenes take place at the carbon–carbon double bond(s). These reactions are called *addition reactions* because a substance is *added* to the double bond. This behavior contrasts with that of alkanes, where the most common reaction type, aside from combustion, is ***substitution***.

An addition reaction *is a reaction in which atoms or groups of atoms are added to each carbon atom of a carbon–carbon multiple bonds in a hydrocarbon or hydrocarbon derivative.* A general equation for an alkene addition reaction is



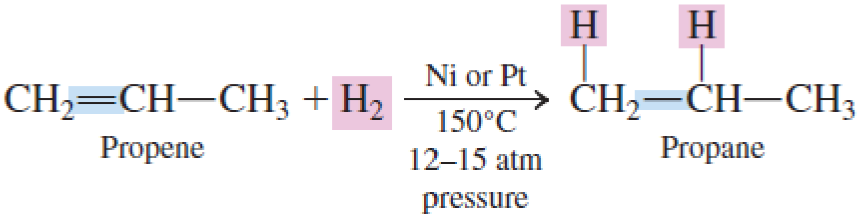
In this reaction, the (A) part of the reactant A-B becomes attached to one carbon atom of the double bond, and the B part to the other carbon atom (As this occurs, the carbon–carbon double bond simultaneously becomes a carbon– carbon single bond. Addition reactions can be classified as symmetrical or unsymmetrical *addition reaction*.

Symmetrical Addition Reactions

A **symmetrical addition reaction** *is an addition reaction in which identical atoms (or groups of atoms) are added to each carbon of a carbon–carbon multiple bond.*

The two most common examples of symmetrical addition reactions are hydrogenation and halogenation.

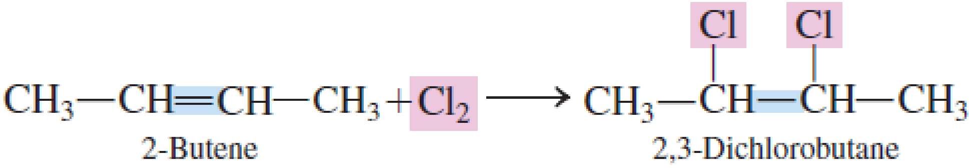
A ***hydrogenation reaction*** *is an addition reaction in which H_2 is incorporated into molecules of an organic compound. In alkene hydrogenation, a hydrogen atom is added to each carbon atom of a double bond. This is accomplished by heating the alkene and H_2 in the presence of a catalyst (usually Ni or Pt).*



$$\mathrm{CH_2{=}CH{-}CH_3 + H_2 \xrightarrow[\substack{150^\circ C\\ 12\text{–}15\ atm\\ pressure}]{Ni\ or\ Pt} \overset{\overset{\displaystyle H}{|}}{C}H_2{-}\overset{\overset{\displaystyle H}{|}}{C}H{-}CH_3}$$

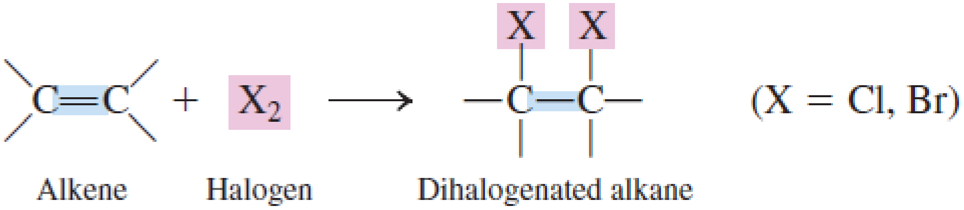
The hydrogenation of vegetable oils is a very important commercial process today. Vegetable oils from sources such as soybeans and cottonseeds are composed of long-chain organic molecules that contain several double bonds. When these oils are hydrogenated, they are converted to low-melting solids that are used in margarines and shortenings.

*A **halogenation reaction** is an addition reaction in which a halogen is incorporated into molecules of an organic compound. In alkene halogenation, a halogen atom is added to each carbon atom of a double bond. Chlorination (Cl_2) and bromination (Br_2) are the two halogenation processes most commonly encountered. No catalyst is needed.*



$$\mathrm{CH_3{-}CH{=}CH{-}CH_3 + Cl_2 \longrightarrow CH_3{-}\overset{\overset{\displaystyle Cl}{|}}{C}H{-}\overset{\overset{\displaystyle Cl}{|}}{C}H{-}CH_3}$$

In general terms, halogenation of an alkene can be written as



$$\mathrm{{>}C{=}C{<} + X_2 \longrightarrow {-}\underset{|}{\overset{\overset{\displaystyle X}{|}}{C}}{-}\underset{|}{\overset{\overset{\displaystyle X}{|}}{C}}{-} \qquad (X = Cl, Br)}$$

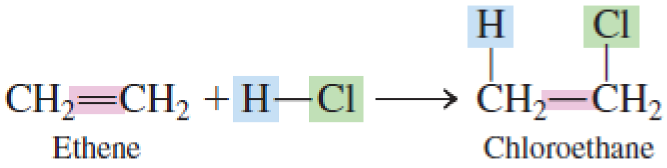
Bromination is often used to test for the presence of carbon–carbon double bonds in organic substances. Bromine in water or carbon tetrachloride is reddish-brown. The dibromo – compound(s) formed from the symmetrical addition of bromine to an organic compound is(are) colorless. Thus the decolorization of a Br_2 solution indicates the presence of carbon–carbon double bonds

Unsymmetrical Addition Reactions

An **unsymmetrical addition reaction** *is an addition reaction in which different atoms (or groups of atoms) are added to the carbon atoms of a carbon–carbon multiple bond.*

Two important types of unsymmetrical addition reactions are hydrohalogenation and hydration.

A ***hydrohalogenation reaction*** *is an addition reaction in which a hydrogen halide (HCl, HBr, or HI) is incorporated into molecules of an organic compound. In alkene hydrohalogenation, one carbon atom of a double bond receives a halogen atom and the other carbon atom receives a hydrogen atom. Hydrohalogenation reactions require no catalyst. For symmetrical alkenes, such as ethene, only one product results from hydrohalogenation.*



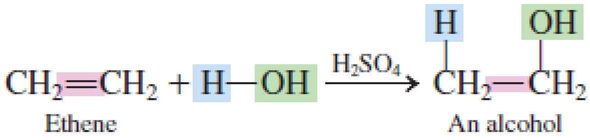
$$CH_2{=}CH_2 + H{-}Cl \longrightarrow \overset{H}{\overset{|}{C}}H_2{-}\overset{Cl}{\overset{|}{C}}H_2$$

Ethene

Chloroethane

A **hydration reaction** *is an addition reaction in which H_2O is incorporated into molecules of an organic compound.*

Alkene hydration requires a small amount of H_2SO_4 (sulfuric acid) as a catalyst. For *symmetrical* alkenes, only one product results from hydration



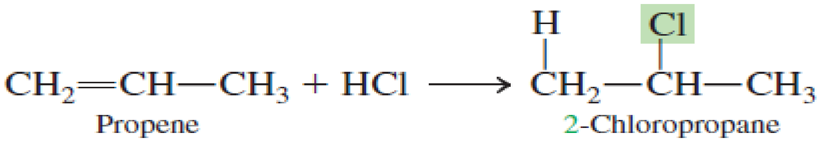
$$CH_2{=}CH_2 + H{-}OH \xrightarrow{H_2SO_4} \overset{H}{\overset{|}{C}}H_2{-}\overset{OH}{\overset{|}{C}}H_2$$

Ethene

An alcohol

Markovnikov's rule *states that when an unsymmetrical molecule of the form* HQ *adds to an unsymmetrical alkene, the hydrogen atom from the* HQ *becomes attached to the unsaturated carbon atom that already has the most hydrogen atoms.*

For example, the addition of HCl to propene (an unsymmetrical alkene) could produce either 1-chloropropane or 2-chloropropane. One product usually predominates. The dominant product can be predicted by using Markovnikov's rule. *Thus the major product in our example involving propene is 2-chloropropane.*



$$CH_2{=}CH{-}CH_3 + HCl \longrightarrow \overset{H}{\overset{|}{C}}H_2{-}\overset{Cl}{\overset{|}{C}}H{-}CH_3$$

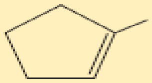
Propene

2-Chloropropane

Predicting Products in Alkene Addition Reactions Using Markovnikov's Rule

Using Markovnikov's rule, predict the predominant product in each of the following addition reactions.

a. $CH_3—CH_2—CH_2—CH=CH_2 + HBr \rightarrow$

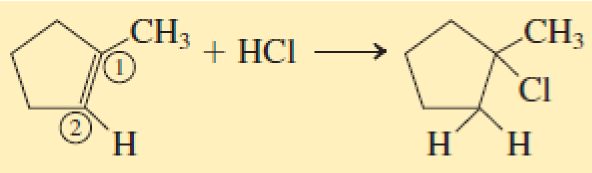
b.  $+ HCl \rightarrow$

c. $CH_3—CH=CH—CH_2—CH_3 + HBr \rightarrow$

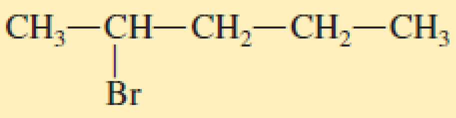
Solution

a. The predominant product of the addition will be 2-bromopentane

b. Carbon 1 of the double bond does not have any H atoms directly attached to it.
Carbon 2 of the double bond has one H atom (H atoms are not shown in the structure but are implied) attached to it. The H atom from the HCl will add to carbon 2, giving:
1-chloro-1-methylcyclopentane as the product

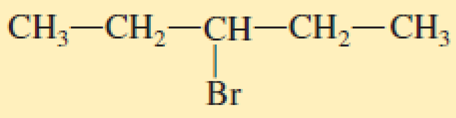


c. Each carbon atom of the double bond in this molecule has one hydrogen atom.
Thus Markovnikov's rule does not favor either carbon atom. The result is two isomeric products that are formed in almost equal quantities.


$CH_3—\underset{Br}{\underset{|}{CH}}—CH_2—CH_2—CH_3$

2-Bromopentane

and

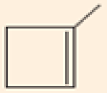

$CH_3—CH_2—\underset{Br}{\underset{|}{CH}}—CH_2—CH_3$

3-Bromopentane

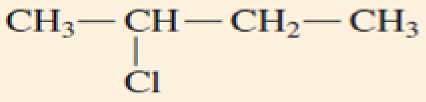
Practice Exercise

Using Markovnikov's rule, predict the predominant product in each of the following addition reaction.

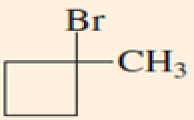
a. $CH_2=CH—CH_2—CH_3 + HCl \rightarrow$

b.  $+ HBr \rightarrow$

Answers: **a.**


$CH_3—\underset{Cl}{\underset{|}{CH}}—CH_2—CH_3$

b.



In compounds that contain more than one carbon–carbon double bond, such as dienes and trienes, addition can occur at each of the double bonds. In the complete hydrogenation of a diene and in that of a triene, the amounts of hydrogen needed are twice as much and three times as much, respectively, as that needed for the hydrogenation of an alkene with one double bond.

$$CH_2{=}CH-CH_2-CH_2-CH_2-CH_3 + H_2 \xrightarrow{Ni} CH_3-(CH_2)_4-CH_3$$

$$CH_2{=}CH-CH{=}CH-CH_2-CH_3 + 2H_2 \xrightarrow{Ni} CH_3-(CH_2)_4-CH_3$$

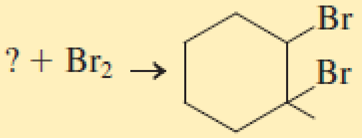
$$CH_2{=}CH-CH{=}CH-CH{=}CH_2 + 3H_2 \xrightarrow{Ni} CH_3-(CH_2)_4-CH_3$$

Predicting Reactants and Products in Alkene Addition Reactions

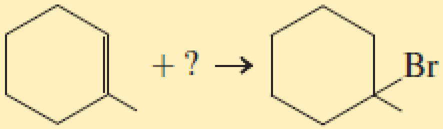
Supply the structural formula of the missing substance in each of the following addition reactions.

a. $CH_3-CH_2-CH{=}CH_2 + H_2O \xrightarrow{H_2SO_4} ?$

b.



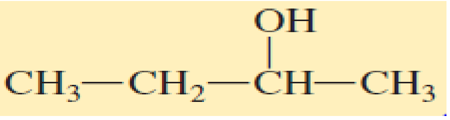
c.



d. $CH_3-CH{=}CH-CH{=}CH_2 + 2H_2 \xrightarrow{Ni} ?$

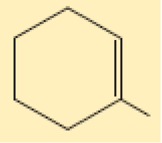
Solution

a. This is a hydration reaction. Based on Markovnikov's rule, the H will become attached to carbon 1, which has more hydrogen atoms than carbon 2, and the -OH group will be attached to carbon 2



$$CH_3-CH_2-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_3$$

b. The reactant alkene will have a double bond between the two carbon atoms that bromine atoms are attached to in the product.



c. HBr

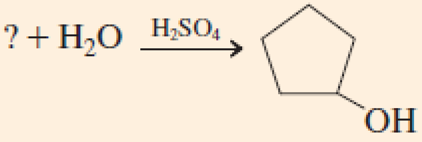
d. Pentane

Practice Exercise

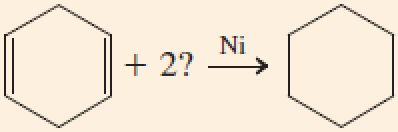
Supply the structural formula of the missing substance in each of the following addition reactions.

a. $CH_3-CH_2-CH=CH_2 + HBr \rightarrow ?$

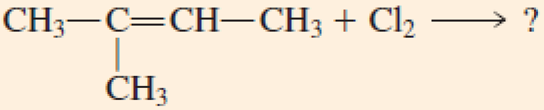
b.



c.

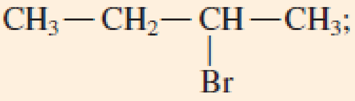


d.



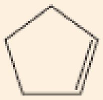
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3 + Cl_2 \longrightarrow ?$

Answers: **a.**

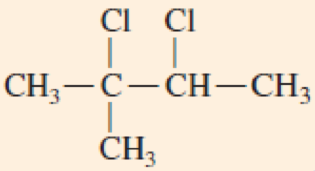


$CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$;

b.



c. H_2; **d.**



$CH_3-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\overset{\displaystyle Cl}{\overset{|}{CH}}-CH_3$

2.9 Polymerization of Alkenes: Addition Polymers

A **polymer** *is a large molecule formed by the repetitive bonding together of many smaller molecules.*

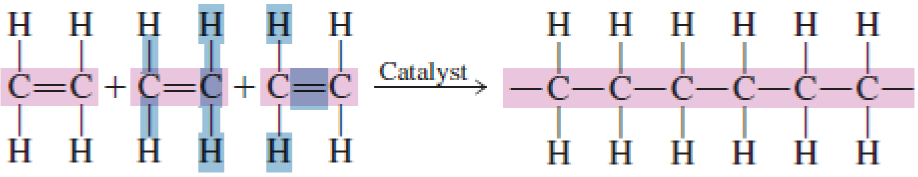
A **monomer** *is the small molecule that is the structural repeating unit in a polymer.*

A **polymerization reaction** *is a chemical reaction in which the repetitious combining of many small molecules (monomers) produces a very large molecule (the polymer)*

The type of polymer that alkenes and substituted alkenes form is an addition polymer

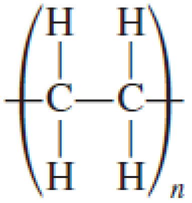
An **addition polymer** *is a polymer in which the monomers simply "add together" with no other products formed besides the polymer.*

The simplest alkene addition polymer has ethylene (ethene) as the monomer. With appropriate catalysts, ethylene readily adds to itself to produce polyethylene.



Polyethylene segment

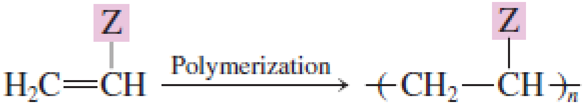
The formula of the simplest repeating unit (the monomer with the double bond changed to a single bond) is written in parentheses and then the subscript *n* is added after the parentheses, with *n* being understood to represent a very large number. Using this notation, the formula of polyethylene becomes



This notation clearly identifies the basic repeating unit found in the polymer

Substituted-Ethene Addition Polymers

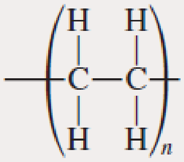
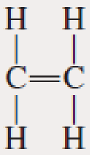
Many substituted alkenes undergo polymerization similar to that of ethene when they are treated with the proper catalyst. For a monosubstituted-ethene monomer, the general polymerization equation is

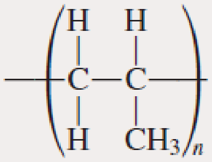
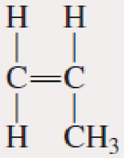
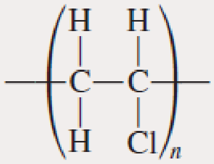
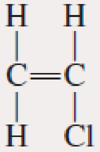
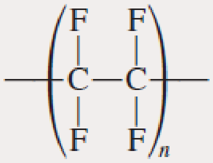
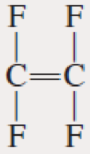
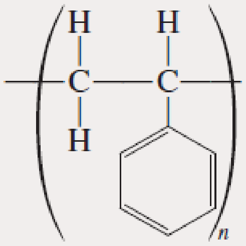
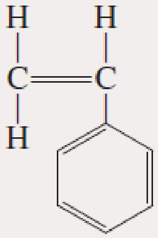


$$H_2C{=}CH(Z) \xrightarrow{\text{Polymerization}} \left(CH_2{-}CH(Z) \right)_n$$

Some Common Polymers Obtained from Ethene-Based Monomers

a. *polyethylene*
b. *polypropylene*
c. *poly(vinyl chloride) (PVC)*
d. *Teflon,* and
e. *Polystyrene*

Polymer Formula and Name	Monomer Formula and Name	Uses of Polymer
 polyethylene	 ethylene	bottles, plastic bags, toys, electrical insulation

 polypropylene	 propylene	indoor–outdoor carpeting, bottles, molded parts (including heart valves)
 poly(vinyl chloride) (PVC)	 vinyl chloride	plastic wrap, bags for intravenous drugs, garden hose, plastic pipe, simulated leather (Naugahyde)
 Teflon	 tetrafluoroethylene	cooking utensil coverings, electrical insulation, component of artificial joints in body parts replacement
 polystyrene	 styrene	toys, Styrofoam packaging, cups, simulated wood furniture

Butadiene-Based Addition Polymers

When dienes such as 1,3-butadiene are used as the monomers in addition polymerization reactions, the resulting polymers contain double bonds and are thus still unsaturated.

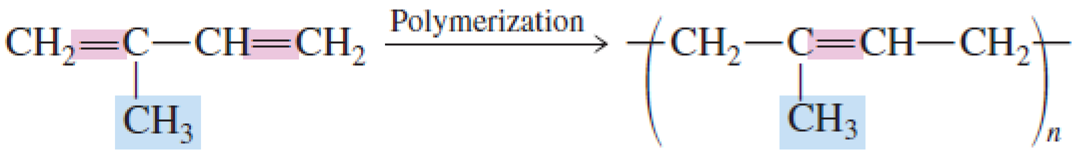
$$\underset{\text{1,3-Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow{\text{Polymerization}} \underset{\text{Polybutadiene}}{\left(CH_2{-}CH{=}CH{-}CH_2\right)_n}$$

In general, unsaturated polymers are much more flexible than the ethene-based saturated polymers. Natural rubber is a flexible addition polymer whose repeating unit is isoprene that is, 2-methyl-1,3-butadiene

Addition Copolymers

A **copolymer** *is a polymer in which two different monomers are present.*

Saran Wrap is a polymer in which two different monomers are present: chloroethene (vinyl chloride) and 1,1-dichloroethene.



$$CH_2{=}\underset{\substack{|\\CH_3}}{C}{-}CH{=}CH_2 \xrightarrow{\text{Polymerization}} \left(CH_2{-}\underset{\substack{|\\CH_3}}{C}{=}CH{-}CH_2\right)_n$$

Isoprene
(2-methyl-1,3-butadiene)

Polyisoprene
(natural rubber)

2.10 Alkynes

An **alkyne** *is an acyclic unsaturated hydrocarbon that contains one or more carbon–carbon triple bonds.* The alkyne functional group is, thus, a C≡C group. As the family name *alkyne* indicates, the characteristic “ending” associated with a triple bond is *-yne.*

$CH\equiv CH$
Ethyne

$CH\equiv C-CH_3$
Propyne

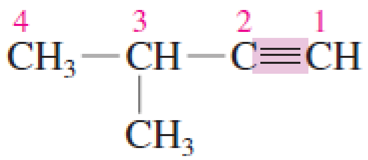
The general formula for an alkyne with one triple bond is C_nH_{2n-2} *Thus the simplest member of this type of alkyne has the formula* C_2H_2*, and the next member, with* $n = 3$*, has the formula* C_3H_4*.*

The presence of a carbon–carbon triple bond in a molecule always results in a linear arrangement for the two atoms attached to the carbons of the triple bond. Thus ethyne is a linear molecule

The simplest alkyne, ethyne (C_2H_2)*, is the most important alkyne from an industrial standpoint. A colorless gas, it goes by the common name acetylene and is used in oxyacetylene torches, high-temperature torches used for cutting and welding materials.*

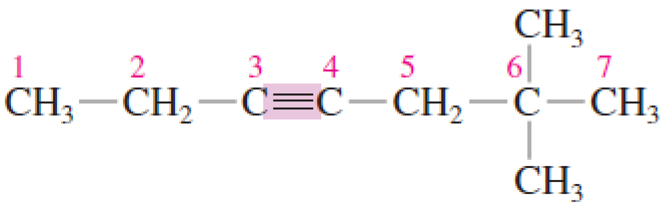
IUPAC Nomenclature for Alkynes

The rules for naming alkynes are identical to those used to name alkenes, except the ending -yne is used instead of -ene. Consider the following structures and their IUPAC names.



$$\overset{4}{CH_3}-\underset{\substack{|\\CH_3}}{\overset{3}{CH}}-\overset{2}{C}\equiv\overset{1}{CH}$$

3-Methyl-1-butyne



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{C}\equiv\overset{4}{C}-\overset{5}{CH_2}-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|\\6}}{C}}-\overset{7}{CH_3}$$

6,6-Dimethyl-3-heptyne

$$\overset{1}{CH}\equiv\overset{2}{C}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{C}\equiv\overset{7}{CH}$$

1,6-Heptadiyne

Common names for simple alkynes are based on the name *acetylene,* as shown in the following examples.

$CH \equiv CH$ — Acetylene

$CH_3 - C \equiv CH$ — Methylacetylene

$CH_3 - C \equiv C - CH_3$ — Dimethylacetylene

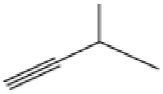
Isomerism and Alkynes

Because of the linearity (180 angles) about an alkyne's triple bond, *cis–trans* isomerism, such as that found in alkenes, is not possible for alkynes because there are no "up" and "down" positions. However, constitutional isomers are possible—both relative to the carbon chain (skeletal isomers) and to the position of the triple bond (positional isomers).

Skeletal isomers:

1-Pentyne

and

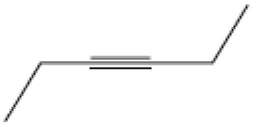


3-Methyl-1-butyne

Positional isomers:

1-Hexyne

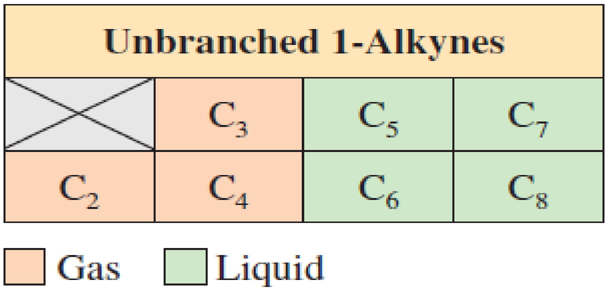
and



3-Hexyne

Physical and Chemical Properties of Alkynes

The physical properties of alkynes are similar to those of alkenes and alkanes. In general, alkynes are insoluble in water but soluble in organic solvents, have densities less than that of water, and have boiling points that increase with molecular mass. Low-molecular-mass alkynes are gases at room temperature

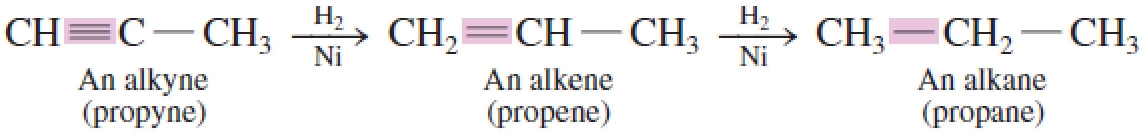


Unbranched 1-Alkynes

	🟧 C_3	🟩 C_5	🟩 C_7
🟧 C_2	🟧 C_4	🟩 C_6	🟩 C_8

🟧 Gas 🟩 Liquid

The triple-bond functional group of alkynes behaves chemically quite similarly to the double-bond functional group of alkenes. Thus there are many parallels between alkene chemistry and alkyne chemistry. The same substances that add to double bonds (H_2, HCl, Cl_2, and so on) also add to triple bonds. For example, propyne reacts with H_2 to form propene first and then to form propane.

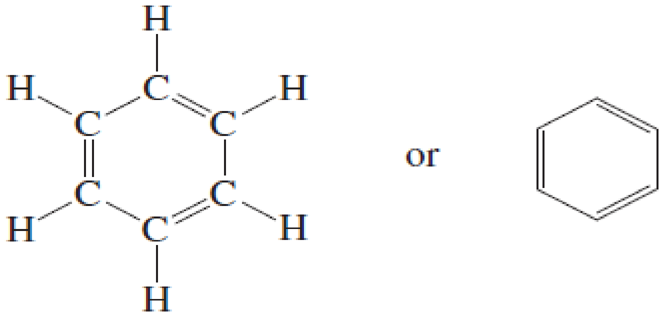


$$CH\equiv C-CH_3 \xrightarrow[Ni]{H_2} CH_2=CH-CH_3 \xrightarrow[Ni]{H_2} CH_3-CH_2-CH_3$$

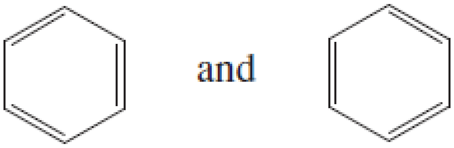
Alkynes, like alkenes and alkanes, are flammable; that is, they readily undergo combustion reactions.

2.11 Aromatic Hydrocarbons

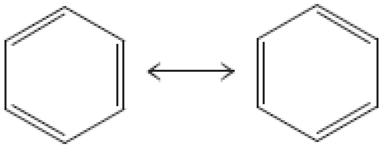
An **aromatic hydrocarbon** *is an unsaturated cyclic hydrocarbon that does not readily undergo addition reactions. The bonding present in this type of compound must differ significantly from that in alkenes and alkynes. Such is indeed the case. Benzene, the simplest aromatic hydrocarbon, is the key to understanding the "special type" of bonding that is characteristic of an aromatic hydrocarbon and to specifying the identity of the aromatic hydrocarbon functional group. Benzene, a flat, symmetrical molecule with a molecular formula of C_6H_6 , has a structural formula that involves a six-membered carbon ring in which three double bonds are present.*



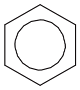
This structure is one of two equivalent structures that can be drawn for benzene that differ only in the locations of the double bonds (1,3,5 positions versus 2,4,6 positions):



Neither of these conventional structures, however, is totally correct. the correct bonding structure for benzene is an average of the two "triene" structures. Related to this "average"-structure situation is the concept that electrons associated with the ring double bonds are not held between specific carbon atoms; instead, they are free to move "around" the carbon ring. Thus the true structure for benzene, an intermediate between that represented by the two "triene" structures, is a situation in which all carbon–carbon bonds are equivalent; they are neither single nor double bonds but something in between. Placing a double-headed arrow between the conventional *structures that are averaged to obtain the true structure is one way to denote the average structure.*

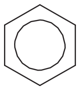


An alternative notation for denoting the bonding in benzene—a notation that involves a single structure—is



In this "circle-in-the-ring" structure for benzene, the circle denotes the electrons associated with the double bonds that move "around" the ring. Each carbon atom in the ring can be considered to participate in three conventional (localized) bonds (two C-C bonds and one C-H bond) and in one delocalized bond (the circle) that involves all six carbon atoms.

*A **delocalized bond** is a covalent bond in which electrons are shared among more than two atoms. This delocalized bond is what causes benzene and its derivatives to be resistant to addition reactions, a property normally associated with unsaturation in a molecule.*



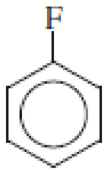
*The structure represented by the notation is called an aromatic ring system, and it is the functional group present in aromatic compounds. An **aromatic ring system** is a highly unsaturated carbon ring system in which both localized and delocalized bonds are present.*

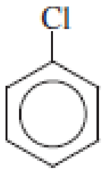
2.12 Names for Aromatic Hydrocarbons

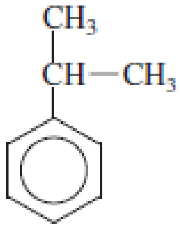
Replacement of one or more of the hydrogen atoms on benzene with other groups produces benzene derivatives. Compounds with alkyl groups or halogen atoms attached to the benzene ring are commonly encountered.

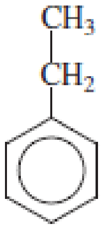
Benzene Derivatives with One Substituent

The IUPAC system of naming monosubstituted benzene derivatives uses the name of the substituent as a prefix to the name benzene. Examples of this type of nomenclature include

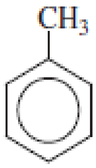

Fluorobenzene

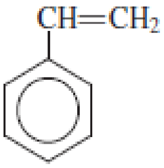

Chlorobenzene


Isopropylbenzene

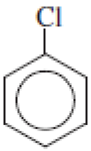

Ethylbenzene

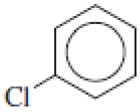
A few monosubstituted benzenes have names wherein the substituent and the benzene ring taken together constitute a new parent name. Two important examples of such nomenclature with hydrocarbon substituents are

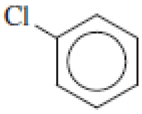

Toluene
(not methylbenzene)

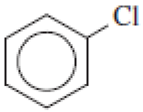

Styrene
(not vinylbenzene)

Both of these compounds are industrially important chemicals. Monosubstituted benzene structures are often drawn with the substituent at the "12 o'clock" position, as in the previous structures. However, because all the hydrogen atoms in benzene are equivalent, it does not matter at which carbon of the ring the substituted group is located. Each of the following formulas represents chlorobenzene.

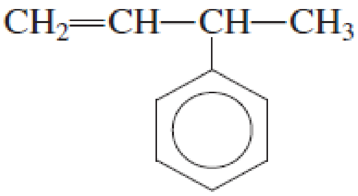








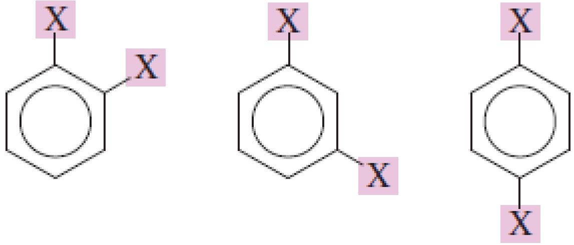
For monosubstituted benzene rings that have a group attached that is not easily named as a substituent, the benzene ring is often treated as a group attached to this substituent. In this reversed approach, the benzene ring attachment is called a phenyl group, and the compound is named according to the rules for naming alkanes, alkenes, and alkynes



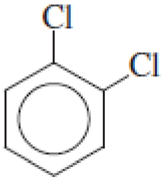
3-Phenyl-1-butene

Benzene Derivatives with Two Substituents

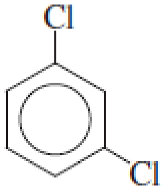
When two substituents, either the same or different, are attached to a benzene ring, three isomeric structures are possible.



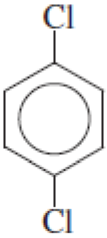
To distinguish among these three isomers, the positions of the substituents relative to one another must be specified. This can be done in either of two ways: by using numbers or by using nonnumerical prefixes.



1,2-Dichlorobenzene
(*ortho*-dichlorobenzene)



1,3-Dichlorobenzene
(*meta*-dichlorobenzene)



1,4-Dichlorobenzene
(*para*-dichlorobenzene)

The prefix system uses the prefixes ortho-, meta-, and para- (abbreviated o-, m-, and p-).

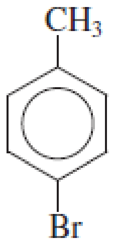
Ortho- means 1,2 disubstitution; the substituents are on adjacent carbon atoms.

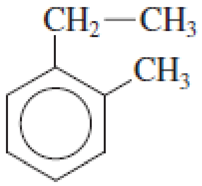
Meta- means 1,3 disubstitution; the substituents are one carbon removed from each other.

Para- means 1,4 disubstitution; the substituents are two carbons removed from each other (on opposite sides of the ring).

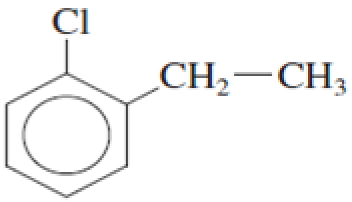
When prefixes are used, the three isomeric dichlorobenzene have the second-listed set of names above.

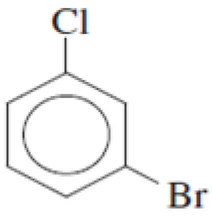
When one of the two substituents in a disubstituted benzene imparts a special name to the compound (as, for example, toluene), the compound is named as a derivative of that parent molecule. The special substituent is assumed to be at ring position 1


4-Bromotoluene
(not 1-bromo-4-methylbenzene)

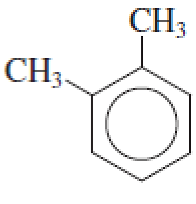

2-Ethyltoluene
(not 1-ethyl-2-methylbenzene)

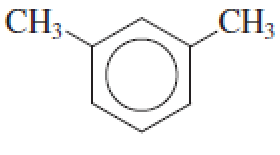
When neither substituent group imparts a special name, the substituents are cited in alphabetical order before the ending -benzene. The carbon of the benzene ring bearing the substituent with alphabetical priority becomes carbon

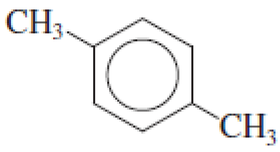

1-Chloro-2-ethylbenzene
(not 2-chloro-1-ethylbenzene)


1-Bromo-3-chlorobenzene
(not 3-bromo-1-chlorobenzene)

A benzene ring bearing two methyl groups is a situation that generates a new special base name. Such compounds (there are three isomers) are not named as dimethylbenzenes or as methyl toluenes. They are called xylenes.


o-Xylene

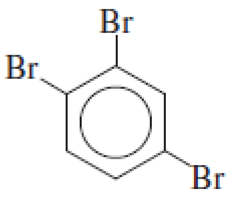

m-Xylene


p-Xylene

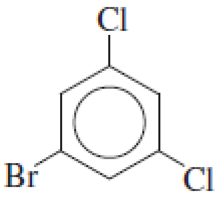
The xylenes are good solvents for grease and oil and are used for cleaning microscope slides and optical lenses and for removing wax from skis.

Benzene Derivatives with Three or More Substituents

When more than two groups are present on the benzene ring, their positions are indicated with numbers. The ring is numbered in such a way as to obtain the lowest possible numbers for the carbon atoms that have substituents. If there is a choice of numbering systems (two systems give the same lowest set), then the group that comes first alphabetically is given the lower number.



1,2,4-Tribromobenzene

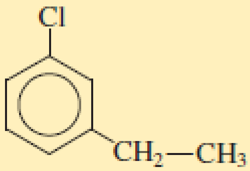


1-Bromo-3,5-dichlorobenzene

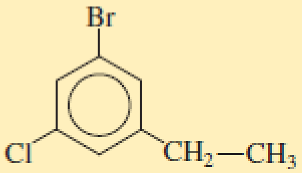
Assigning IUPAC Names to Benzene Derivatives

Assign IUPAC names to the following benzene derivatives.

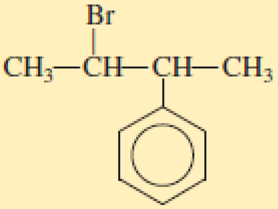
a.



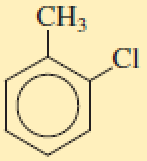
b.



c.



d.



a. *No substituents that will change the parent name from benzene are present on the ring. Alphabetical priority dictates that the chloro group is on carbon 1 and the ethyl group on carbon the compound is named 1-chloro-3-ethylbenzene (or m-chloroethylbenzene).*

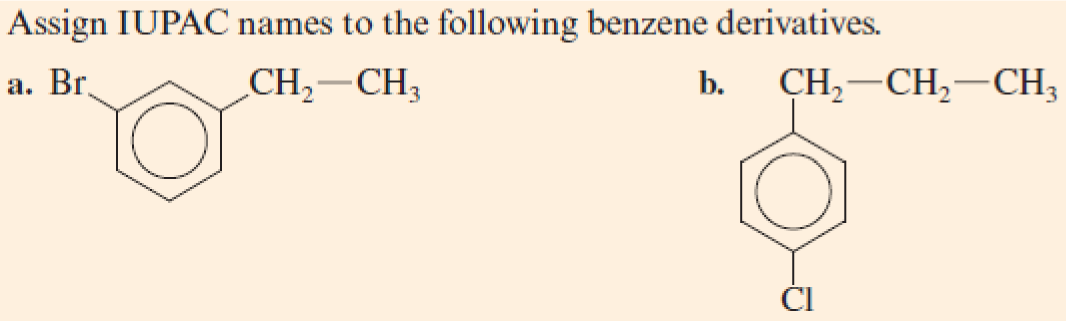
b. *Again, no substituents that will change the parent name from benzene are present on the ring. Alphabetical priority among substituents dictates that the bromo group is on carbon 1, the chloro group on carbon 3, and the ethyl group on carbon 5. The compound is named 1-bromo-3-chloro-5-ethylbenzene.*

c. *This compound is named with the benzene ring treated as a substituent—that is, as a phenyl group. The compound is named 2-bromo-3-phenylbutane. The methyl group present on the benzene ring changes the parent name from benzene to toluene.*

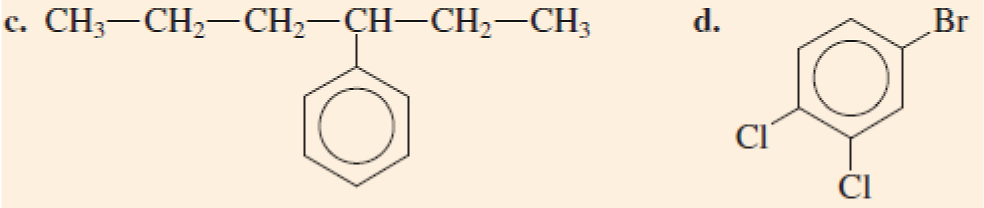
d. Carbon 1 bears the methyl group. Numbering clockwise, we obtain the name 2-chlorotoluene

Practice Exercise

Assign IUPAC names to the following benzene derivatives.



Assign IUPAC names to the following benzene derivatives.



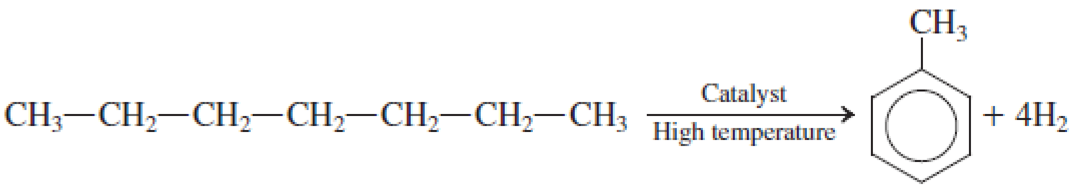
Answers: a. *1-Bromo-3-ethylbenzene or m-bromoethylbenzene;* ***b.*** *1-Chloro-4-propylbenzene or o-chloropropylbenzene;* ***c.*** *3-Phenylhexane;* ***d.*** *4-Bromo-1,2-dichlorobenzene*

Physical Properties and Sources of Aromatic Hydrocarbons

In general, aromatic hydrocarbons resemble other hydrocarbons in physical properties. They are insoluble in water, are good solvents for other nonpolar materials, and are less dense than water.

Benzene, monosubstituted benzenes, and many disubstituted benzenes are liquids at room temperature. Benzene itself is a colorless, flammable liquid that burns with a sooty flame because of incomplete combustion.

At one time, coal tar was the main source of aromatic hydrocarbons. Petroleum is now the primary source of such compounds. At high temperatures, with special catalysts, saturated hydrocarbons obtained from petroleum can be converted to aromatic hydrocarbons. The production of toluene from heptane is representative of such a conversion.



Benzene was once widely used as an organic solvent. Such use has been discontinued because benzene's short- and long-term toxic effects are now recognized. Benzene inhalation can cause nausea and respiratory problems.

Two common situations in which a person can be exposed to low-level benzene vapors are:

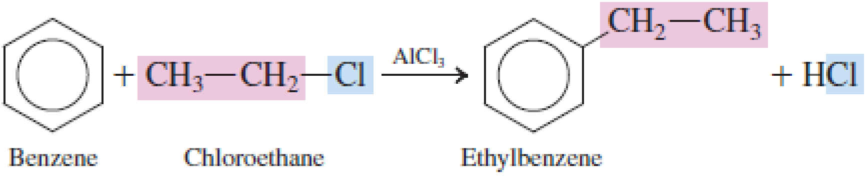
1. *Inhaling gasoline vapors while refueling an automobile. Gasoline contains about 2% (v/v) benzene.*
2. *Being around a cigarette smoker. Benzene is a combustion product present in cigarette smoke. For smokers themselves, inhaled cigarette smoke is a serious benzene exposure source.*

Chemical Reactions of Aromatic Hydrocarbons

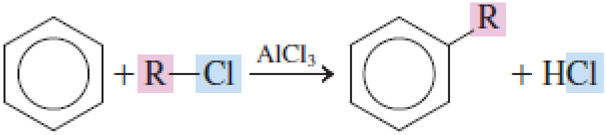
Aromatic hydrocarbons do not readily undergo the addition reactions. Benzene undergoes *substitution* reactions

Substitution reactions are characterized by different atoms or groups of atoms replacing hydrogen atoms in a hydrocarbon molecule. Two important types of substitution reactions for benzene and other aromatic hydrocarbons are alkylation and halogenation.

1. *Alkylation:* An alkyl group (R-) from an alkyl chloride (R-Cl) substitutes for a hydrogen atom on the benzene ring. A catalyst, $AlCl_3$, is needed for alkylation.

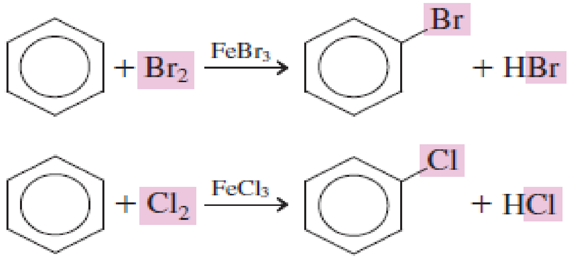


In general terms, the alkylation of benzene can be written as



Alkylation is the most important industrial reaction of benzene.

2. *Halogenation* (bromination or chlorination): A hydrogen atom on a benzene ring can be replaced by bromine or chlorine if benzene is treated with Br_2 or Cl_2 in the presence of a catalyst. The catalyst is usually $FeBr_3$ for bromination and $FeCl_3$ for chlorination.

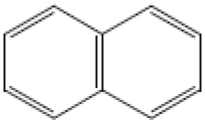


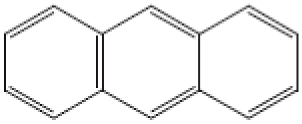
Aromatic halogenation differs from alkane halogenation (Section 12.17) in that light is not required to initiate aromatic halogenation

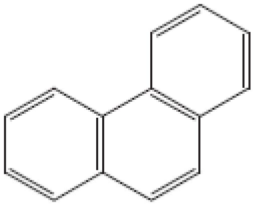
2.13 Fused-Ring Aromatic Hydrocarbons

Benzene and its substituted derivatives are not the only type of aromatic hydrocarbon that exists. Another large class of aromatic hydrocarbons is the fused-ring aromatic hydrocarbons. A ***fused-ring aromatic hydrocarbon*** *is an aromatic hydrocarbon whose structure contains two or more carbon rings fused together. Two carbon rings that share a pair of carbon atoms are said to be fused.*

The three simplest fused-ring aromatic compounds are naphthalene, anthracene, and phenanthrene. All three are solids at room temperature.


Naphthalene


Anthracene


Phenanthrene

Concepts to Remember

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Unsaturated hydrocarbons: An unsaturated hydrocarbon is a hydrocarbon that contains one or more carbon–carbon multiple bonds. Three main classes of unsaturated hydrocarbons exist: alkenes, alkynes, and aromatic hydrocarbons

Alkenes and cycloalkenes: An alkene is an acyclic unsaturated hydrocarbon in which one or more carbon–carbon double bonds are present. A cycloalkene is a cyclic unsaturated hydrocarbon that contains one or more carbon–carbon double bonds within the ring system

Alkene nomenclature: Alkenes and cycloalkenes are given IUPAC names using rules similar to those for alkanes and cycloalkanes, except that the ending *-ene* is used. Also, the double bond takes precedence both in selecting and in numbering the main chain or ring

Isomerism in alkenes: Two subtypes of constitutional isomers are possible for alkenes: skeletal isomers and positional isomers. Positional isomers differ in the location of the functional group (double bond) present

***Cis–trans* isomerism in alkenes:.** *Cis–trans* isomerism is possible for some alkenes because there is restricted rotation about a carbon–carbon double bond

Physical properties of alkenes: Alkenes and alkanes have similar physical properties. They are nonpolar, insoluble in water, less dense than water, and soluble in nonpolar solvents

Addition reactions of alkenes: Numerous substances, including H_2, Cl_2, Br_2, HCl, HBr, and H_2O, add to an alkene carbon–carbon double bond. When both the alkene and the substance to be added are unsymmetrical, the addition proceeds according to Markovnikov's rule: The carbon atom of the double bond that already has the greater number of H atoms gets one more

Addition polymers: Addition polymers are formed from alkene monomers that undergo repeated addition reactions with each other. Many familiar and widely used materials, such as fibers and plastics, are addition polymers

Alkynes and cycloalkynes: Alkynes and cycloalkynes are unsaturated hydrocarbons that contain one or more carbon–carbon triple bonds. They are named in the same way as alkenes and cycloalkenes, except that their parent names end in *-yne.* Like alkenes, alkynes undergo addition reactions. These occur in two steps, an alkene forming first and then an alkane.

Aromatic hydrocarbons: Benzene, the simplest aromatic hydro- carbon, and other members of this family of compounds contain a six-membered ring with a cyclic, delocalized bond. This aromatic ring is often drawn as a hexagon containing a circle, which represents six electrons that move freely around the ring

Nomenclature of aromatic hydrocarbons: Monosubstituted benzene compounds are named by adding the substituent name to the word *benzene.* Positions of substituents in disubstituted benzenes are indicated by using a numbering system or the *ortho*- (1,2), *meta*- (1,3), and *para*- (1,4) prefix system .

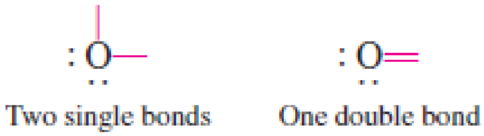
Chemical reactions of aromatic hydrocarbons: Aromatic hydrocarbons undergo substitution reactions rather than addition reactions. Important substitution reactions are alkylation and halogenation

Chapter 3: Alcohols, Phenols, and Ethers

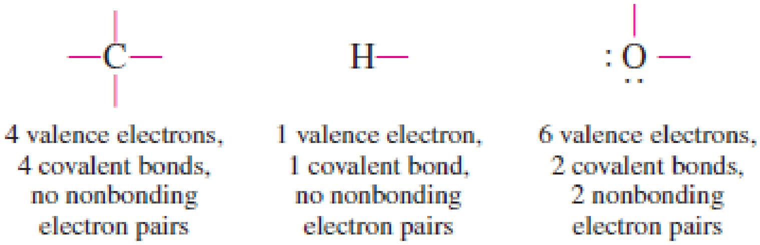
In this chapter, hydrocarbon derivatives whose functional groups contain one oxygen atom participating in two single bonds (alcohols, phenols, and ethers) are considered. Chapter 4 focuses on derivatives whose functional groups have one oxygen atom participating in a double bond (aldehydes and ketones), and Chapter 5 examines functional groups that contain two oxygen atoms, one participating in single bonds and the other in a double bond (carboxylic acids, esters, and other acid derivatives) are examined.

3.1 Bonding Characteristics of Oxygen Atoms in Organic Compounds

An understanding of the bonding characteristics of the oxygen atom is a prerequisite for the study of compounds with oxygen-containing functional groups. Normal bonding behavior for oxygen atoms in such functional groups is the formation of two covalent bonds. Oxygen is a member of Group VIA of the periodic table and thus possesses six valence electrons. To complete its octet by electron sharing, an oxygen atom can form either two single bonds or a double bond.



Thus, in organic chemistry, carbon forms four bonds, hydrogen forms one bond, and oxygen forms two bonds.

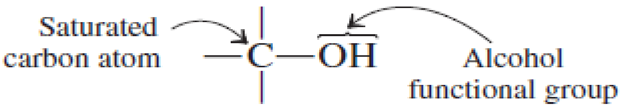


3.2 Structural Characteristics of Alcohols

Alcohols are the first type of hydrocarbon derivative containing a single oxygen atom to be considered. They have the generalized formula

$$\mathrm{R{-}OH}$$

An **alcohol** *is an organic compound in which an*−OH *group is bonded to a saturated carbon atom.* A *saturated* carbon atom is a carbon atom that is bonded to four other atoms



The −OH group, the functional group that is characteristic of an alcohol, is called a *hydroxyl group.* A **hydroxyl group** *is the* −OH *functional group.*

Examples of condensed structural formulas for alcohols include

$$\mathrm{CH_3{-}OH} \qquad \mathrm{CH_3{-}CH_2{-}OH} \qquad \mathrm{CH_3{-}CH_2{-}CH_2{-}OH}$$

Alcohols may be viewed structurally as being alkyl derivatives of water in which a hydrogen atom has been replaced by an alkyl group.

$$\mathrm{H{-}\ddot{\underset{..}{O}}{-}H} \qquad \mathrm{R{-}\ddot{\underset{..}{O}}{-}H}$$

Alcohols may also be viewed structurally as hydroxyl derivatives of alkanes in which a hydrogen atom has been replaced by a hydroxyl group.

$R-H$
An alkane

$R-OH$
An alcohol

3.3 Nomenclature for Alcohols

Common names exist for alcohols with simple (generally C1 through C4) alkyl groups. A common name is assigned using the following rules:

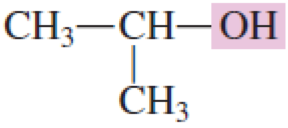
Rule 1: *Name all of the carbon atoms of the molecule as a single* alkyl group.

Rule 2: *Add the word* alcohol*, separating the words with a space.*

CH_3-OH
Methyl alcohol

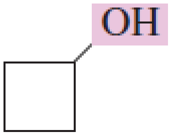
CH_3-CH_2-OH
Ethyl alcohol

$CH_3-CH_2-CH_2-OH$
Propyl alcohol



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$

Isopropyl alcohol



Cyclobutyl alcohol

IUPAC rules for naming alcohols that contain a single hydroxyl group follow.

Rule 1: *Name the longest carbon chain to which the hydroxyl group is attached.*

The chain name is obtained by dropping the final *-e* from the alkane name and adding the suffix *-ol.*

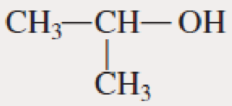
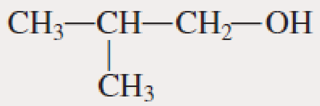
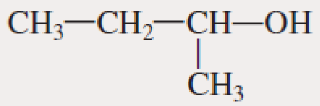
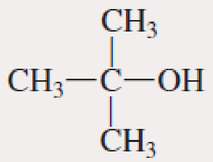
Rule 2: *Number the chain starting at the end nearest the hydroxyl group, and use the appropriate number to indicate the position of the* −OH *group.*

(In numbering of the longest carbon chain, the hydroxyl group has precedence over ("outranks") double and triple bonds, as well as over alkyl, cycloalkyl, and halogen substituents.)

Rule 3: Name and locate any other substituents present.

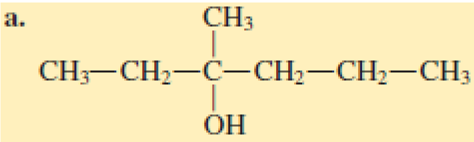
Rule 4: *In alcohols where the* −OH *group is attached to a carbon atom in a ring, the ring is numbered beginning with the* −OH *group.* Numbering then proceeds in a clockwise or counterclockwise direction to give the next substituent the lower number. The number "1" (for the hydroxyl group) is omitted from the name since by definition the hydroxyl-bearing carbon is carbon 1

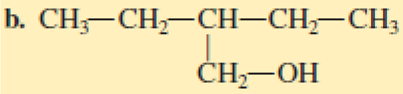
IUPAC and Common Names of Monohydroxy Alcohols That Contain Up to Four Carbon Atoms

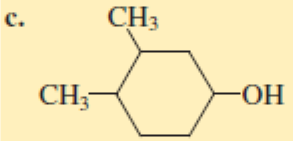
Formula	IUPAC Name	Common Name
One carbon atom (CH_3OH)		
CH_3-OH	methanol	methyl alcohol
Two carbon atoms (C_2H_5OH)		
CH_3-CH_2-OH	ethanol	ethyl alcohol
Three carbon atoms (C_3H_7OH); two constitutional isomers exist		
$CH_3-CH_2-CH_2-OH$	1-propanol	propyl alcohol
 $CH_3-\underset{CH_3}{CH}-OH$	2-propanol	isopropyl alcohol
Four carbon atoms (C_4H_9OH); four constitutional isomers exist		
$CH_3-CH_2-CH_2-CH_2-OH$	1-butanol	butyl alcohol
 $CH_3-\underset{CH_3}{CH}-CH_2-OH$	2-methyl-1-propanol	isobutyl alcohol
 $CH_3-CH_2-\underset{CH_3}{CH}-OH$	2-butanol	*sec*-butyl alcohol
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$	2-methyl-2-propanol	*tert*-butyl alcohol

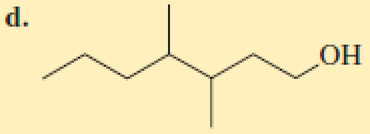
EXAMPLE 1 Determining IUPAC Names for Alcohols

Name the following alcohols, utilizing IUPAC nomenclature rules.


$CH_3-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_2-CH_2-CH_3$


$CH_3-CH_2-\underset{CH_2-OH}{CH}-CH_2-CH_3$





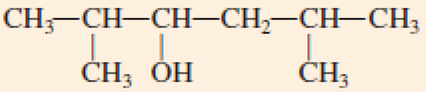
Solution

a. 3-methyl-3-hexanol
b. 2-ethyl-1-butanol
c. 3,4-dimethylcyclo-hexanol
d. 3,4-dimethyl-1-heptanol

Practice Exercise

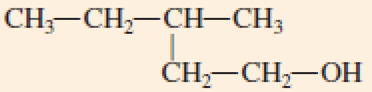
Name the following alcohols utilizing IUPAC nomenclature rules.

a.



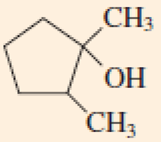
$$CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-CH_2-\underset{CH_3}{CH}-CH_3$$

b.

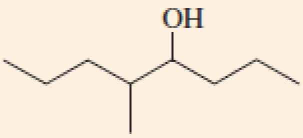


$$CH_3-CH_2-\underset{CH_2-CH_2-OH}{CH}-CH_3$$

c.



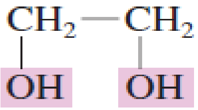
d.



Answers: **a.** 2,5-Dimethyl-3-hexanol; **b.** 3-Methyl-1-pentanol; **c.** 1,2-Dimethylcyclopentanol; **d.** 5-Methyl-4-octanol

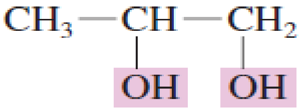
Polyhydroxy alcohols

Polyhydroxy alcohols—alcohols that possess more than one hydroxyl group— can be named with only a slight modification of the preceding IUPAC rules. An alcohol in which two hydroxyl groups are present is named as a *diol;* one containing three hydroxyl groups is named as a *triol,* and so on. In these names for diols, triols, and so forth, the final -*e* of the parent alkane name is retained for pronunciation reasons.



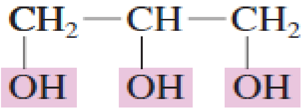
$$\underset{OH}{CH_2}-\underset{OH}{CH_2}$$

1,2-Ethanediol



$$CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}$$

1,2-Propanediol



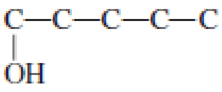
$$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$$

1,2,3-Propanetriol

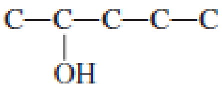
The first two of the preceding compounds have the common names *ethylene glycol* and *propylene glycol.* These two alcohols are synthesized, respectively, from the alkenes ethylene and propylene. The other alcohol has common name glycerol.

Isomerism for Alcohols

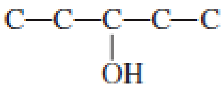
Constitutional isomerism is possible for alcohols containing three or more carbon atoms. As with alkenes both *skeletal* isomers and *positional* isomers are possible. For Monohydroxy saturated alcohols, there are two C_3 isomers, four C_4 isomers, and eight C_5 isomers. Structures for the C_3 and C_4 isomers are found in The C5 isomers are



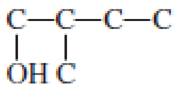
1-Pentanol



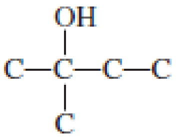
2-Pentanol



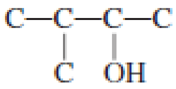
3-Pentanol



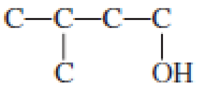
2-Methyl-1-butanol



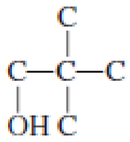
2-Methyl-2-butanol



3-Methyl-2-butanol



3-Methyl-1-butanol



2,2-Dimethyl-1-propanol

The three pentanols are positional isomers as are the four methylbutanols.

Methyl Alcohol (Methanol)

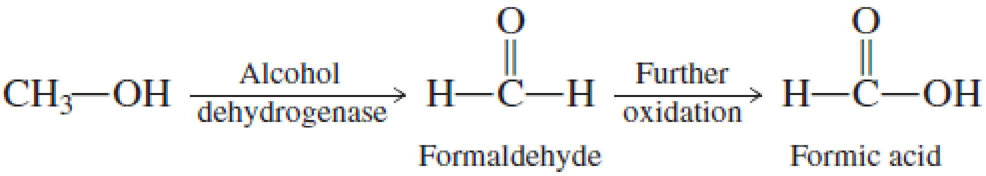
Methyl alcohol, with one carbon atom and one −OH group, is the simplest alcohol. It is a colorless liquid that has excellent solvent properties, and it is the solvent of choice for many shellacs and varnishes. Racing cars at the Indianapolis Speedway were fueled with methyl alcohol from 1965 to 2005.

Preparation of methanol

Methyl alcohol is sometimes called *wood alcohol,* terminology that draws attention to an early method for its preparation—the heating of wood to a high temperature in the absence of air. Today, nearly all methyl alcohol is produced via the reaction between H_2 and CO.

$$CO + 2H_2 \xrightarrow[300°C - 400°C,\ 200\ atm]{ZnO—Cr_2O_3} CH_3—OH$$

Drinking methyl alcohol is very dangerous. Within the human body, methyl alcohol is oxidized by the liver enzyme *alcohol dehydrogenase* to the toxic metabolites formaldehyde and formic acid.

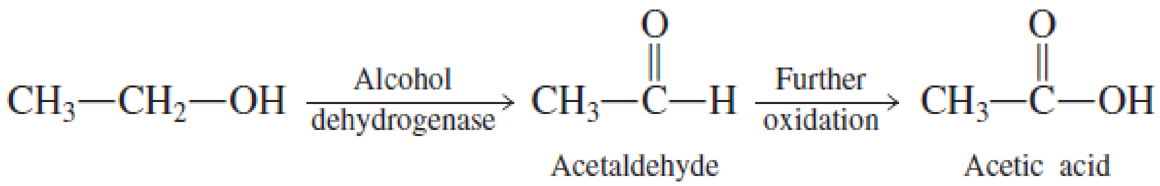


$$CH_3—OH \xrightarrow[dehydrogenase]{Alcohol} \underset{Formaldehyde}{H—\overset{\overset{O}{\|}}{C}—H} \xrightarrow[oxidation]{Further} \underset{Formic\ acid}{H—\overset{\overset{O}{\|}}{C}—OH}$$

Formaldehyde can cause blindness (temporary or permanent). Formic acid causes acidosis. Ingesting as little as 1 oz (30 mL) of methyl alcohol can cause optic nerve damage.

Ethyl Alcohol (Ethanol)

Ethyl alcohol, the two-carbon Monohydroxy alcohol, is the alcohol present in alcoholic beverages and is commonly referred to simply as alcohol or *drinking alcohol.* Like methyl alcohol, ethyl alcohol is oxidized in the human body by the liver enzyme *alcohol dehydrogenase.*



$$CH_3-CH_2-OH \xrightarrow[\text{dehydrogenase}]{\text{Alcohol}} \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\Large O}{\|}}{C}-H} \xrightarrow[\text{oxidation}]{\text{Further}} \underset{\text{Acetic acid}}{CH_3-\overset{\overset{\Large O}{\|}}{C}-OH}$$

Acetaldehyde, the first oxidation product, is largely responsible for the symptoms of hangover. The odors of both acetaldehyde and acetic acid are detected on the breath of someone who has consumed a large amount of alcohol. Ethyl alcohol oxidation products are less toxic than those of methyl alcohol.

Long-term excessive use of ethyl alcohol may cause undesirable effects such as cirrhosis of the liver, loss of memory, and strong physiological addiction.

Preparation of ethanol

Ethyl alcohol can be produced by yeast fermentation of sugars found in plant extracts. The synthesis of ethyl alcohol in this manner, from grains such as corn, rice, and barley, is the reason why ethyl alcohol is often called *grain alcohol.*

$$\underset{\substack{\text{Sugar}\\ \text{(glucose)}}}{C_6H_{12}O_6} \xrightarrow[\text{Fermentation}]{\text{Yeast}} \underset{\text{Ethyl alcohol}}{2CH_3-CH_2-OH} + 2CO_2$$

Fermentation is the process by which ethyl alcohol for alcoholic beverages is produced. The maximum concentration of ethyl alcohol obtainable by fermentation is about 18% (v/v) because yeast enzymes cannot function in stronger alcohol solutions. Alcoholic beverages with a higher concentration of alcohol than this are prepared by either distillation or fortification with alcohol obtained by the distillation of another fermentation product.

Denatured alcohol

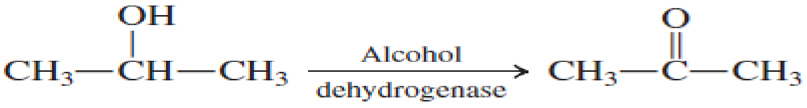
Denatured alcohol is ethyl alcohol that has been rendered unfit to drink by the addition of small amounts of toxic substances (denaturing agents). Almost all of the ethyl alcohol used for industrial purposes is denatured alcohol.

Most ethyl alcohol used in industry is prepared from ethene via a hydration reaction

The reaction produces a product that is 95% alcohol and 5% water. In applications where water does interfere with its use, the mixture is treated with a dehydrating agent to produce 100% ethyl alcohol. Such alcohol, with all traces of water removed, is called ***absolute alcohol***.

Isopropyl Alcohol (2-Propanol)

Isopropyl alcohol is one of two three-carbon monohydroxy alcohols; the other is propyl alcohol. A 70% isopropyl alcohol–30% water solution is marketed as *rubbing alcohol.* Isopropyl alcohol's rapid evaporation rate creates a dramatic cooling effect when it is applied to the skin; hence its use for alcohol rubs to combat high body temperature. It also finds use in cosmetics formulations such as after-shave lotion and hand lotions. Isopropyl alcohol has a bitter taste. Its toxicity is twice that of ethyl alcohol, but it causes few fatalities because it often induces vomiting and thus doesn't stay down long enough to be fatal. In the body, it is oxidized to acetone

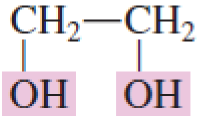


$$\mathrm{CH_3{-}\overset{\displaystyle OH}{\overset{|}{C}}H{-}CH_3 \xrightarrow[\text{dehydrogenase}]{\text{Alcohol}} CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3}$$

Isopropyl alcohol Acetone

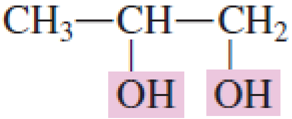
Ethylene Glycol (1,2-Ethanediol) and Propylene Glycol (1,2-Propanediol)

Ethylene glycol and propylene glycol are the two simplest alcohols possessing two −OH groups. Besides being diols, they are also classified as glycols. A **glycol** *is a diol in which the two* −OH *groups are on adjacent carbon atoms.*



$$\mathrm{\underset{\displaystyle OH}{\underset{|}{CH_2}}{-}\underset{\displaystyle OH}{\underset{|}{CH_2}}}$$

Ethylene glycol

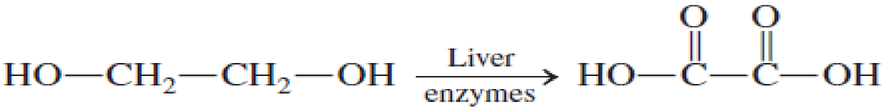


$$\mathrm{CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}\underset{\displaystyle OH}{\underset{|}{CH_2}}}$$

Propylene glycol

Both of these glycols are colorless, odorless, high-boiling liquids that are completely miscible with water. Their major uses are as the main ingredient in automobile "year-round" antifreeze and airplane "deicers" and as a starting material for the manufacture of polyester fibers.

Ethylene glycol is extremely toxic when ingested. In the body, liver enzymes oxidize it to oxalic acid.

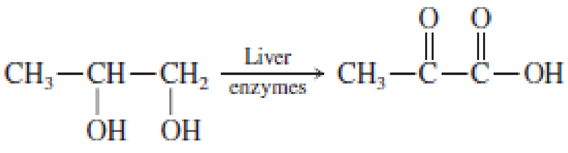


$$\mathrm{HO{-}CH_2{-}CH_2{-}OH \xrightarrow[\text{enzymes}]{\text{Liver}} HO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH}$$

Ethylene glycol Oxalic acid

Oxalic acid, as a calcium salt, crystallizes in the kidneys, which leads to renal problems.

Propylene glycol, on the other hand, is essentially nontoxic and has been used as a solvent for drugs. Like ethylene glycol, it is oxidized by liver enzymes; however, pyruvic acid, its oxidation product, is a compound normally found in the human body, being an intermediate in carbohydrate metabolism.



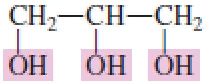
$$\underset{\displaystyle\text{OH}}{\underset{|}{\text{CH}_3-\text{CH}}}-\underset{\displaystyle\text{OH}}{\underset{|}{\text{CH}_2}}\xrightarrow[\text{enzymes}]{\text{Liver}}\text{CH}_3-\overset{\displaystyle\text{O}}{\overset{\|}{\text{C}}}-\overset{\displaystyle\text{O}}{\overset{\|}{\text{C}}}-\text{OH}$$

Propylene glycol Pyruvic acid

Propylene glycol use as an antifreeze is increasing.

Glycerol (1, 2, 3-Propanetriol)

Glycerol, which is often also called glycerin, is a clear, thick liquid that has the consistency of honey. Its molecular structure involves three −OH groups on three different carbon atoms.

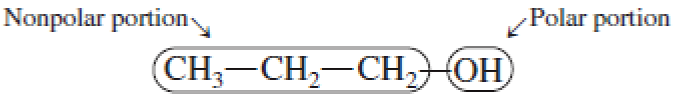


$$\underset{\displaystyle\text{OH}}{\underset{|}{\text{CH}_2}}-\underset{\displaystyle\text{OH}}{\underset{|}{\text{CH}}}-\underset{\displaystyle\text{OH}}{\underset{|}{\text{CH}_2}}$$

Glycerol is normally present in the human body because it is a product of fat metabolism. It is present, in combined form, in all animal fats and vegetable oils.

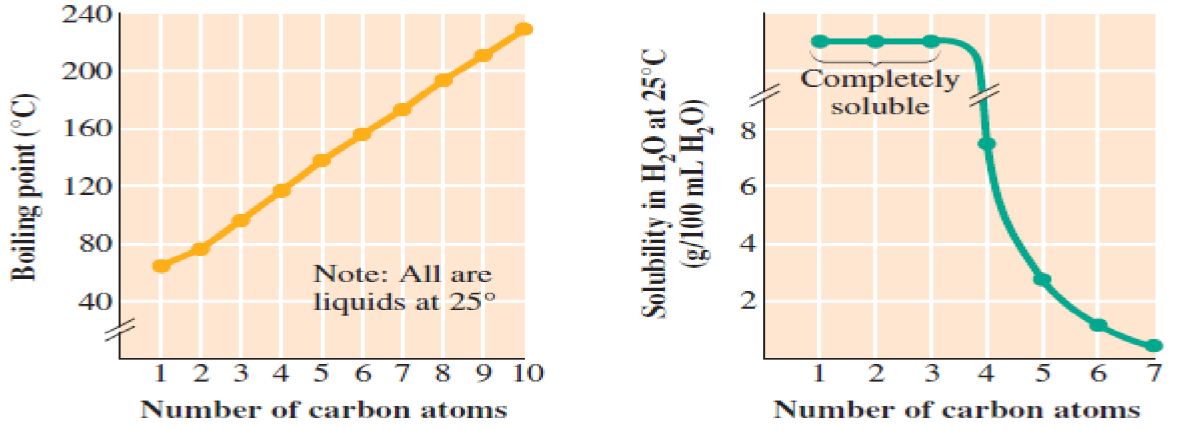
3.6 Physical Properties of Alcohols

Alcohol molecules have both polar and nonpolar character. The hydroxyl groups present are polar, and the alkyl (R) group present is nonpolar.



The physical properties of an alcohol depend on whether the polar or the nonpolar portion of its structure "dominates." Factors that determine this include the *length* of the nonpolar carbon chain present and the *number* of polar hydroxyl groups present

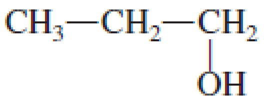
Boiling Points and Water Solubilities



a Boiling points.

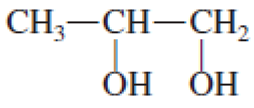
b Solubilities in water of selected 1-alcohols.

The above figure shows that the boiling point for 1-alcohols, unbranched-chain alcohols with an −OH group on an end carbon, increases as the length of the carbon chain increases. This trend results from increasing London forces with increasing carbon-chain length. Alcohols with more than one hydroxyl group present have significantly higher boiling points (bp) than their monohydroxy counterparts.



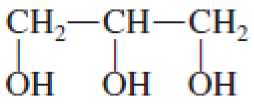
$CH_3—CH_2—CH_2(OH)$

bp = 97°C



$CH_3—CH(OH)—CH_2(OH)$

bp = 188°C

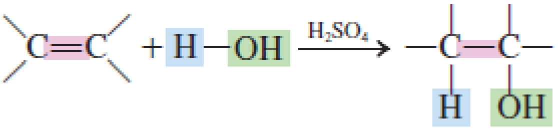


$CH_2(OH)—CH(OH)—CH_2(OH)$

bp = 290°C

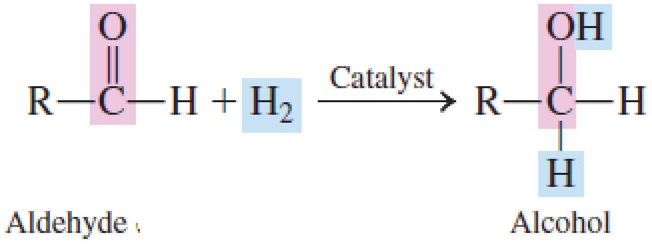
3.7 Preparation of Alcohols

A general method for preparing alcohols—the hydration of alkenes—was discussed in the previous chapter. Alkenes react with water (an unsymmetrical addition agent) in the presence of sulfuric acid (the catalyst) to form an alcohol. Markovnikov's rule is used to determine the predominant alcohol product.

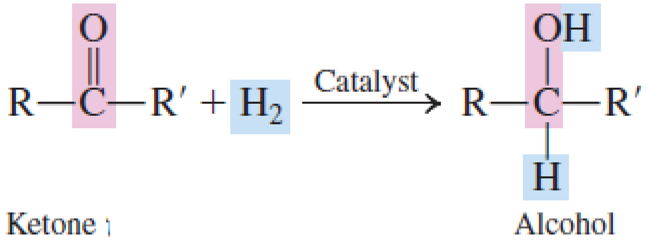


$$>C=C< + H—OH \xrightarrow{H_2SO_4} —\underset{H}{\overset{|}{C}}—\underset{OH}{\overset{|}{C}}—$$

Another method of synthesizing alcohols involves the addition of H_2 to a carbon–oxygen double bond (a carbonyl group, GCP). (The carbonyl group is a functional group that will be discussed in detail in Chapter 4.) A carbonyl group behaves very much like a carbon–carbon double bond when it reacts with H2 under the proper conditions. As a result of H2 addition, the oxygen of the carbonyl group is converted to an −OH group.



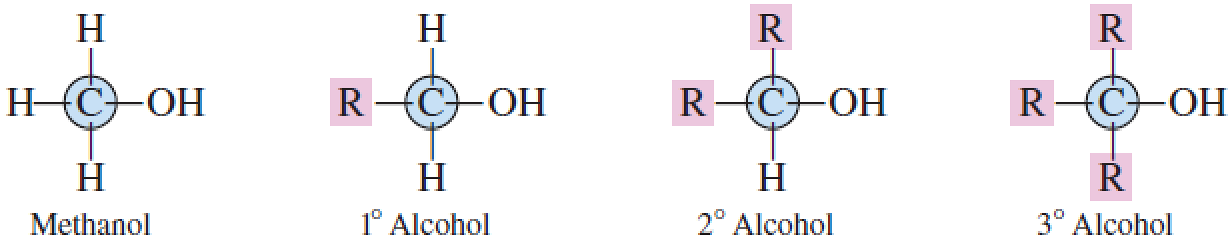
$$R-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow{\text{Catalyst}} R-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H$$



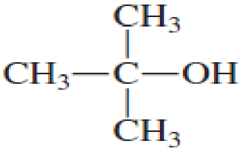
$$R-\overset{O}{\overset{\|}{C}}-R' + H_2 \xrightarrow{\text{Catalyst}} R-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R'$$

3.8 Classification of Alcohols

Alcohols are classified as primary (**1°**), secondary (**2°**) or tertiary (**3°**), depending on the number of carbon atoms bonded to the carbon atom that bears the hydroxyl group. A **primary alcohol** *is an alcohol in which the hydroxyl-bearing carbon atom is bonded to only one other carbon atom.* A **secondary alcohol** *is an alcohol in which the hydroxyl-bearing carbon atom is bonded to two other carbon atoms.* A **tertiary alcohol** *is an alcohol in which the hydroxyl-bearing carbon atom is bonded to three other carbon atoms.* Chemical reactions of alcohols often depend on alcohol class

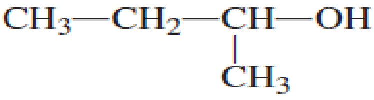


Although all alcohols are able to participate in hydrogen bonding, increasing the number of R groups around the carbon atom bearing the OH group decreases the extent of hydrogen bonding. This effect, called stearic hindrance, becomes particularly important when the R groups are large. Thus, **1°** alcohols are best able to hydrogen-bond and **3°** alcohols are least able to hydrogen-bond. For alcohols of similar molecular mass, **1°** alcohols have higher boiling points than 2° alcohols, which in turn have higher boiling points than 3° alcohols, because of how stearic hindrance affects hydrogen bonding. The following data for three C4 alcohols illustrates this situation



$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$

3° alcohol
b.p. = 83°C



$CH_3-CH_2-\underset{CH_3}{CH}-OH$

2° alcohol
b.p. = 98°C

$CH_3-CH_2-CH_2-CH_2-OH$

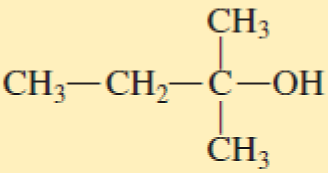
1° alcohol
b.p. = 118°C

Example

Classify each of the following alcohols as a primary, secondary, or tertiary alcohol.

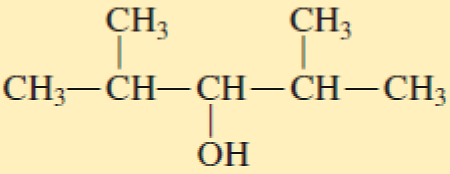
a. $CH_3-CH_2-CH_2-OH$

b.



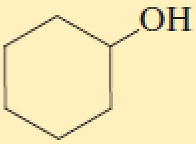
$CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH$

c.



$CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}-\overset{CH_3}{CH}-CH_3$

d.



Solution

a. This is a primary alcohol. The carbon atom to which the OH group is attached is bonded to only one other carbon atom.

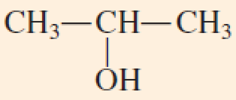
b. This is a tertiary alcohol. The carbon atom bearing the OH group is bonded to three other carbon atoms.

c. This is a secondary alcohol. The hydroxyl-bearing carbon atom is bonded to two other carbon atoms.

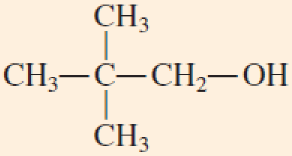
d. This is a secondary alcohol. The ring carbon atom to which the OH group is attached is bonded to two other ring carbon atoms.

Practice Exercise

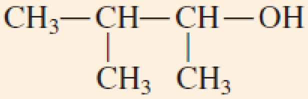
Classify each of the following alcohols as a primary, secondary, or tertiary alcohol.

a. 

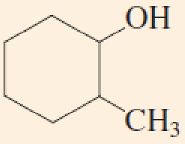
$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$

b. 

$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-OH$

c. 

$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-OH$

d. 

Answers: **a.** Secondary; **b.** Primary; **c.** Secondary; **d.** Secondary

3.9 Chemical Reactions of Alcohols

Of the many chemical reactions that alcohols undergo, four will be considered in this section: (1) combustion (2) dehydration (3) oxidation and (4) halogenation.

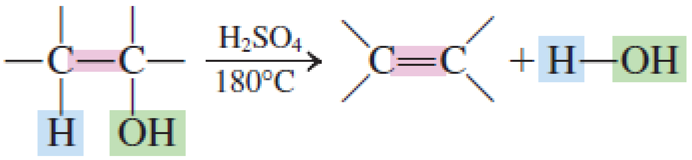
Combustion

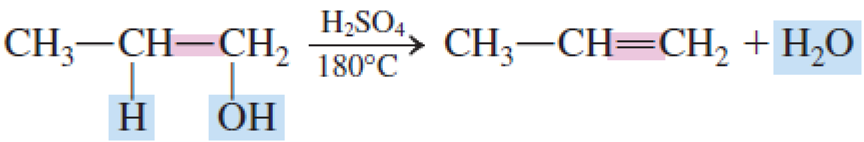
As has been seen in the previous two chapters, hydrocarbons of all types undergo combustion in air to produce carbon dioxide and water.

Intramolecular Alcohol Dehydration

A **dehydration reaction** *is a chemical reaction in which the components of water (H and OH) are removed from a single reactant or from two reactants (H from one and OH from the other).* In *intramolecular* dehydration, both water components are removed from the same molecule.

Reaction conditions for the intramolecular dehydration of an alcohol are a temperature of 180°C and the presence of sulfuric acid (H_2SO_4) as a catalyst. The dehydration product is an alkene



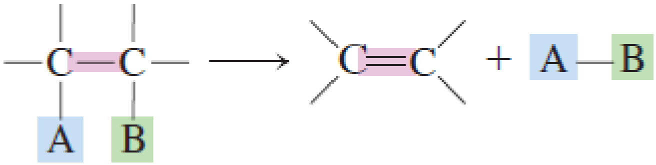


$$CH_3-\underset{\underset{\displaystyle H}{|}}{CH}-\underset{\underset{\displaystyle OH}{|}}{CH_2}\xrightarrow[180^\circ C]{H_2SO_4}CH_3-CH=CH_2+H_2O$$

Intramolecular alcohol dehydration is an example of an ***elimination reaction,*** as contrasted to a substitution reaction and an addition reaction.

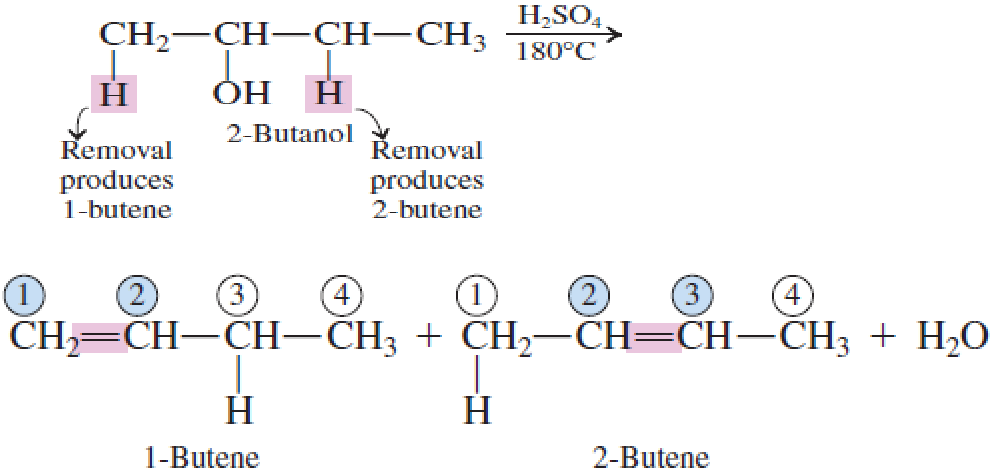
Elimination reaction

An **elimination reaction** *is a reaction in which two groups or two atoms on neighboring carbon atoms are removed, or eliminated, from a molecule, leaving a multiple bond between the carbon atoms.*



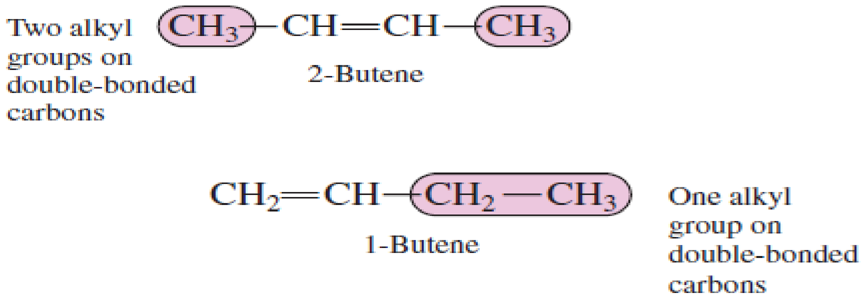
What occurs in an elimination reaction is the reverse of what occurs in an addition reaction.

Dehydration of an alcohol can result in the production of more than one alkene product. This happens when there is more than one neighboring carbon atom from which hydrogen loss can occur. Dehydration of 2-butanol produces two alkenes



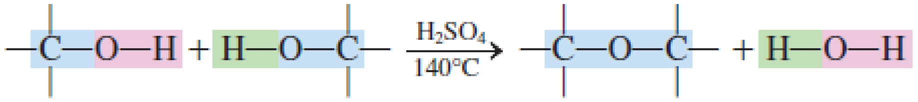
Although both products are formed, a large amount of one product is formed whereas only a small amount of the other product is formed. Prediction of which product is the major product and which is the minor product can be made using Zaitsev's (pronounced "*zait-zeff*") rule

Zaitsev's rule states that *the major product in an intramolecular alcohol dehydration reaction is the alkene that has the greatest number of alkyl groups attached to the carbon atoms of the double bond.* In the preceding reaction, 2-butene (with two alkyl groups) is favored over 1-butene (with one alkyl group).



Intermolecular Alcohol Dehydration

At a lower temperature (140°C) than that required for alkene formation (180°C), an *inter*molecular rather than an *intra*molecular alcohol dehydration process can occur to produce an ether—a compound with the general structure R-O-R. In such ether formation, two alcohol molecules interact, an H atom being lost from one and an OH group from the other. The resulting "leftover" portions of the two alcohol molecules join to form the ether. This reaction, which gives useful yields only for primary alcohol reactants (2° and 3° alcohols yield predominantly alkenes), can be written as



$$-\overset{|}{\underset{|}{C}}-O-H + H-O-\overset{|}{\underset{|}{C}}- \xrightarrow[140°C]{H_2SO_4} -\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}- + H-O-H$$

$$\underset{\text{Ethanol}}{CH_3-CH_2-O-H} + \underset{\text{Ethanol}}{H-O-CH_2-CH_3} \xrightarrow[140°C]{H_2SO_4}$$

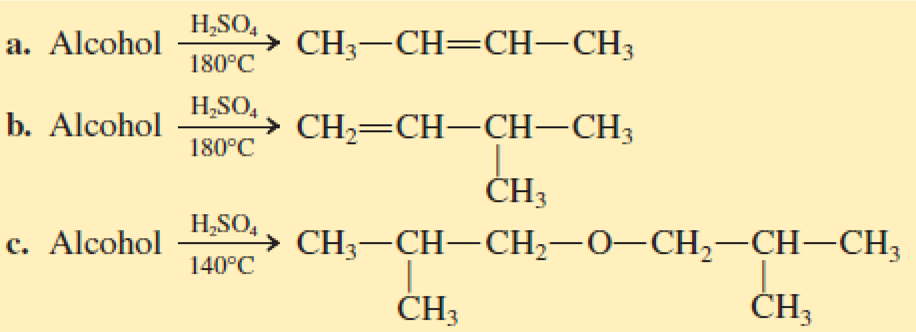
$$CH_3-CH_2-O-CH_2-CH_3 + H_2O$$

The preceding reaction is an example of ***condensation.***

Condensation reaction

A **condensation reaction** *is a chemical reaction in which two molecules combine to form a larger one while liberating a small molecule, usually water.* In this case, two alcohol molecules combine to give an ether and water

Example: Predicting the Reactant in an Alcohol Dehydration Reaction When Given the Product



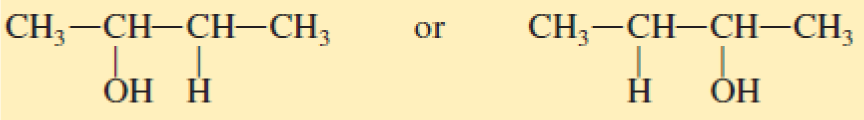
$$\textbf{a.}\ \text{Alcohol} \xrightarrow[180^\circ C]{H_2SO_4} CH_3{-}CH{=}CH{-}CH_3$$

$$\textbf{b.}\ \text{Alcohol} \xrightarrow[180^\circ C]{H_2SO_4} CH_2{=}CH{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_3$$

$$\textbf{c.}\ \text{Alcohol} \xrightarrow[140^\circ C]{H_2SO_4} CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}O{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_3$$

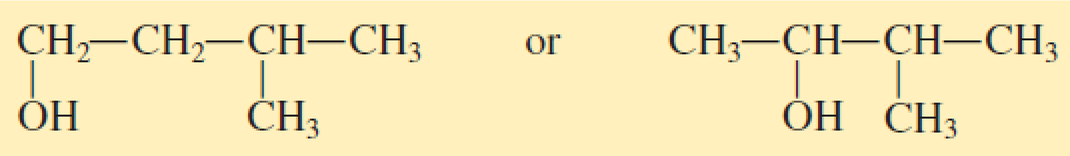
Solution

a. **Both** carbon atoms of the double bond are equivalent to each other. Add an H atom to one carbon atom of the double bond and an OH group to the other carbon atom of the double bond. It does not matter which goes where; you get the same molecule either way.



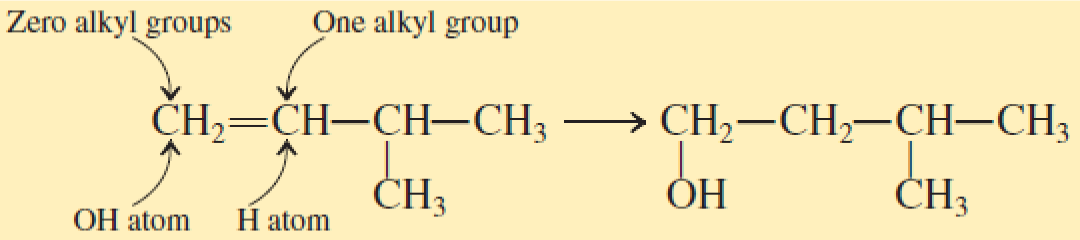
$$CH_3{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}\underset{\underset{\displaystyle H}{|}}{CH}{-}CH_3 \quad \text{or} \quad CH_3{-}\underset{\underset{\displaystyle H}{|}}{CH}{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}CH_3$$

b. There are two possible parent alcohols: one with an OH group on carbon 1 and the other with an OH group on carbon 2.



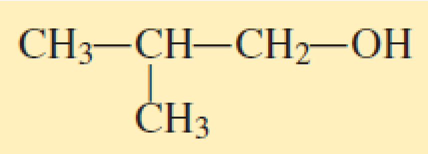
$$\underset{\underset{\displaystyle OH}{|}}{CH_2}{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_3 \quad \text{or} \quad CH_3{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_3$$

Based on the reverse of Zaitsev's rule, the hydrogen atom will go back on the double-bonded carbon that bears the most alkyl groups.



$$CH_2{=}CH{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_3 \longrightarrow \underset{\underset{\displaystyle OH}{|}}{CH_2}{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_3$$

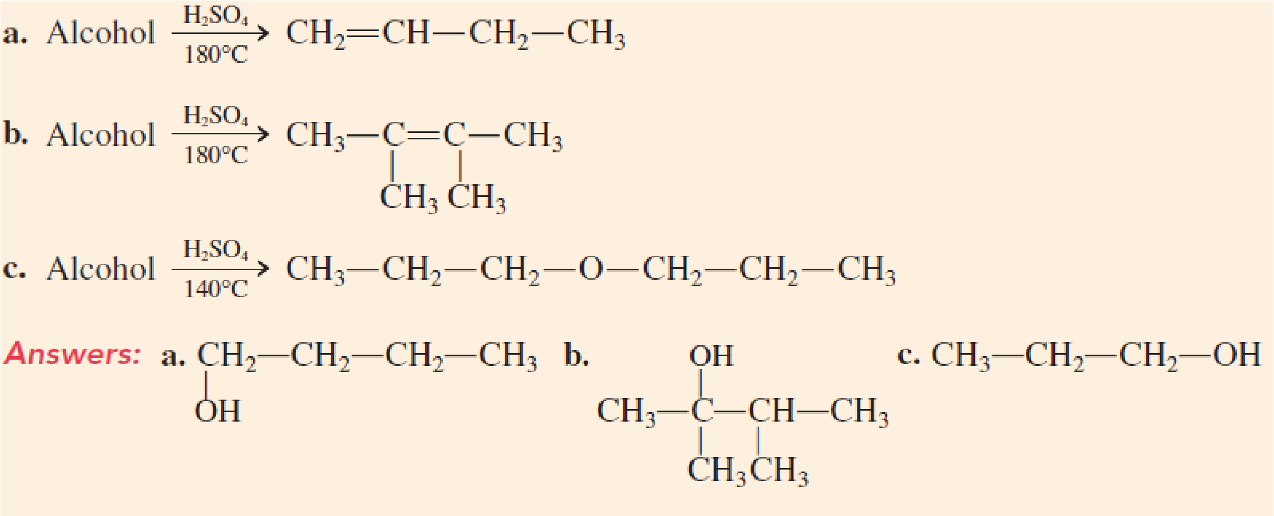
c. This is ether. The primary alcohol from which the ether was formed will have the same alkyl group present as is in the ether. Thus the alcohol is



$$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}OH$$

Practice Exercise

Identify the starting alcohol from which each of the following products was obtained by an alcohol dehydration reaction.



a. $\text{Alcohol} \xrightarrow[180°C]{H_2SO_4} CH_2{=}CH-CH_2-CH_3$

b. $\text{Alcohol} \xrightarrow[180°C]{H_2SO_4} CH_3-\underset{\substack{|\\CH_3}}{C}=\underset{\substack{|\\CH_3}}{C}-CH_3$

c. $\text{Alcohol} \xrightarrow[140°C]{H_2SO_4} CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$

Answers: **a.** $\underset{\substack{|\\OH}}{CH_2}-CH_2-CH_2-CH_3$ **b.** $CH_3-\overset{\substack{OH\\|}}{\underset{\substack{|\\CH_3}}{C}}-\underset{\substack{|\\CH_3}}{CH}-CH_3$ **c.** $CH_3-CH_2-CH_2-OH$

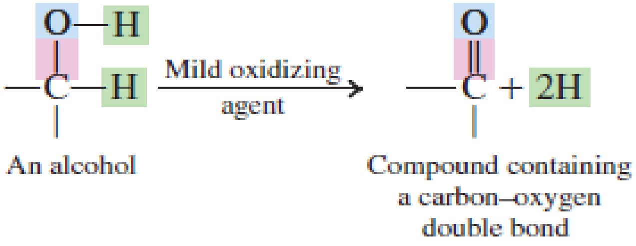
Oxidation

1. An *organic oxidation* is an oxidation that increases the number of C-O bonds and/or decreases the number of C-H bonds.
2. An *organic reduction* is a reduction that decreases the number of C-O bonds and/or increases the number of C-H bonds.

Note that these operational definitions for oxidation and reduction are “opposites.” This is just as it should be; oxidation and reduction are “opposite” processes.

Some alcohols readily undergo oxidation with mild oxidizing agents; others are resistant to oxidation with these same oxidizing agents. Primary and secondary alcohols, but not tertiary alcohols, readily undergo oxidation in the presence of mild oxidizing agents to produce compounds that contain a carbon–oxygen double bond (aldehydes, ketones, and carboxylic acids). A number of different oxidizing agents can be used for the oxidation, including potassium permanganate (KMnO4), potassium dichromate ($K_2Cr_2O_7$), and chromic acid (H_2CrO_4).

The net effect of the action of a mild oxidizing agent on a primary or secondary alcohol is the removal of two hydrogen atoms from the alcohol. One hydrogen atom comes from the OH group, the other from the carbon atom to which the OH group is attached. This H removal generates a carbon–oxygen double bond.



The two “removed” hydrogen atoms combine with oxygen supplied by the oxidizing agent to give H_2O.

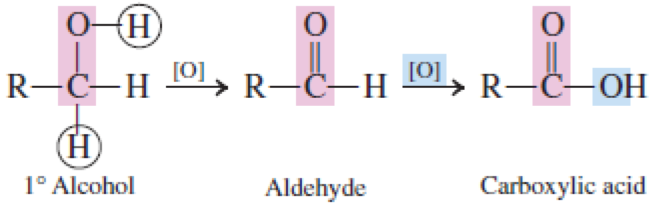
Primary and secondary alcohols, the two types of oxidizable alcohols, yield different products upon oxidation. A 1° alcohol produces an *aldehyde* that is often then further oxidized to a *carboxylic acid,* and a 2° alcohol produces a *ketone.*

$$\text{Primary alcohol} \xrightarrow[\text{ox. agent}]{\text{Mild}} \text{aldehyde} \xrightarrow[\text{ox. agent}]{\text{Mild}} \text{carboxylic acid}$$

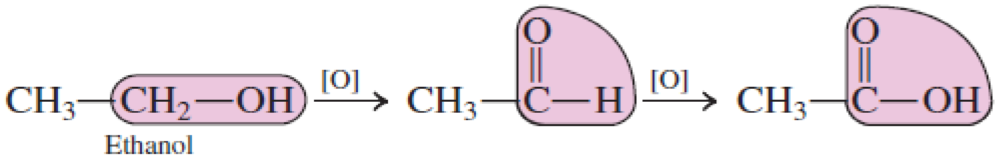
$$\text{Secondary alcohol} \xrightarrow[\text{ox. agent}]{\text{Mild}} \text{ketone}$$

$$\text{Tertiary alcohol} \xrightarrow[\text{ox. agent}]{\text{Mild}} \text{no reaction}$$

The general reaction for the oxidation of a primary alcohol is

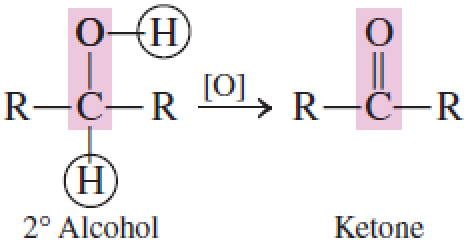


In this equation, the symbol [O] represents the mild oxidizing agent. The immediate product of the oxidation of a primary alcohol is an aldehyde. Because aldehydes themselves are readily oxidized by the same oxidizing agents that oxidize alcohols, aldehydes are further converted to carboxylic acids. A specific example of a primary alcohol oxidation reaction is

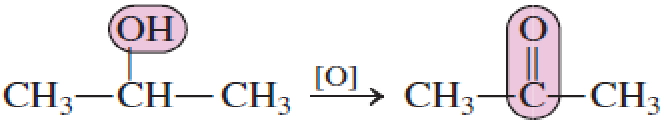


This specific oxidation reaction—that of ethanol—is the basis for the "breathalyzer test" used by law enforcement officers to determine whether an automobile driver is "drunk"

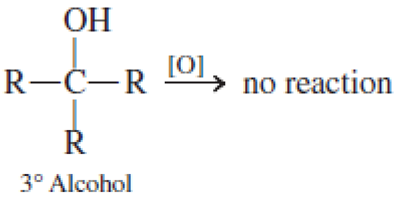
The general reaction for the oxidation of a secondary alcohol is



As with primary alcohols, oxidation involves the removal of two hydrogen atoms. Unlike aldehydes, ketones are resistant to further oxidation. A specific example of the oxidation of a secondary alcohol is

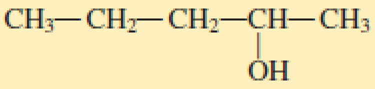


Tertiary alcohols do not undergo oxidation with mild oxidizing agents. This is because they do not have hydrogen on the -OH-bearing carbon atom

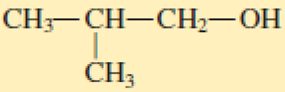


Example: Predicting Products in Alcohol Oxidation Reactions

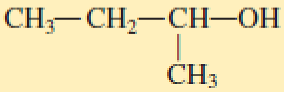
Draw the structural formula(s) for the product(s) formed by oxidation of the following alcohols with a mild oxidizing agent. If no reaction occurs, write "no reaction

a. 

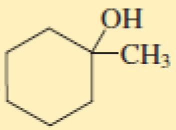
$$\mathrm{CH_3{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}CH_3}$$

b. 

$$\mathrm{CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}OH}$$

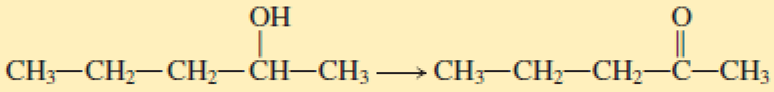
c. 

$$\mathrm{CH_3{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}OH}$$

d. 

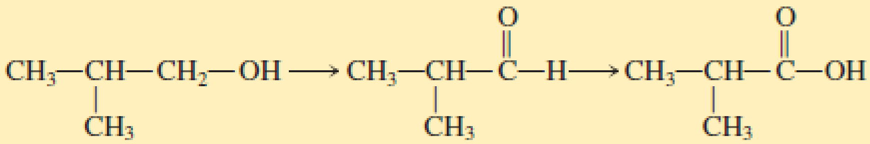
Solution

a. The oxidation product will be a ketone, as this is a 2° alcohol.



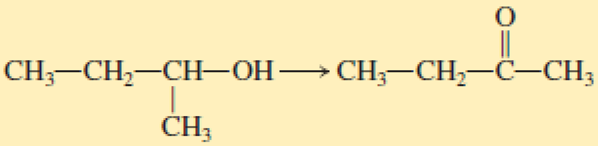
$$\mathrm{CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}CH_3 \longrightarrow CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3}$$

b. A 1° alcohol undergoes oxidation first to an aldehyde and then to a carboxylic acid.



$$\mathrm{CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}OH \longrightarrow CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H \longrightarrow CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH}$$

c. A ketone is the product from the oxidation of a 2° alcohol.



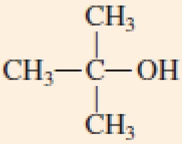
$$\mathrm{CH_3{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}OH \longrightarrow CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3}$$

d. This cyclic alcohol is a tertiary alcohol. The hydroxyl-bearing carbon atom is attached to two ring carbon atoms and a methyl group. Tertiary alcohols do not undergo oxidation with mild oxidizing agents. Therefore, "no reaction."

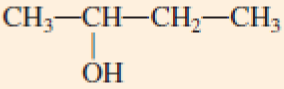
Practice Exercise

Draw the structural formula(s) for the product(s) formed by oxidation of the following alcohols with a mild oxidizing agent. If no reaction occurs, write "no reaction

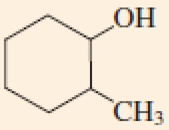
a. $\mathrm{CH_3{-}CH_2{-}CH_2{-}OH}$

b. 

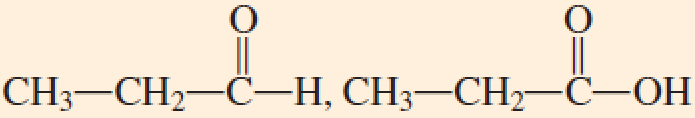
$$\mathrm{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}OH}$$

c. 

$CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2—CH_3$

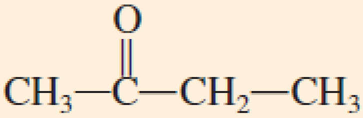
d. 

Answers:

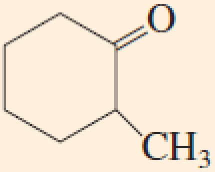
a. 

$CH_3—CH_2—\overset{\displaystyle O}{\overset{\|}{C}}—H, CH_3—CH_2—\overset{\displaystyle O}{\overset{\|}{C}}—OH$

b. No reaction

c. 

$CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—CH_2—CH_3$

d. 

Halogenation

Alcohols undergo halogenation reactions in which a halogen atom is substituted for the hydroxyl group, producing an alkyl halide.

Several different halogen-containing reactants, including phosphorus tri- halides (PX3; X is Cl or Br), are useful in producing alkyl halides from alcohols.

$$3R—OH + PX_3 \xrightarrow{heat} 3R—X + H_3PO_3$$

Note that heating of the reactants is required.

3.10 Phenols

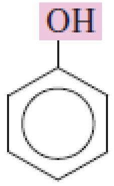
A **phenol** *is an organic compound in which an -OH group is attached to a carbon atom that is part of an aromatic carbon ring system*

The general formula for phenols is Ar–OH, where Ar represents an *aryl group.* An **aryl group** *is an aromatic carbon ring system from which one hydrogen atom has been removed.*

A hydroxyl group is thus the functional group for both phenols and alcohols.

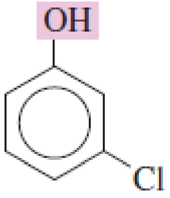
Nomenclature for Phenols

Besides being the name for a family of compounds, *phenol* is also the IUPAC- approved name for the simplest member of the phenol family of compounds.

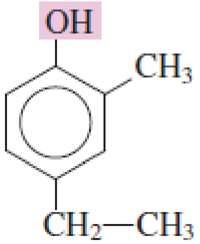


Phenol

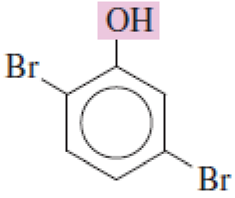
The IUPAC rules for naming phenols are simply extensions of the rules used to name benzene derivatives with hydrocarbon or halogen substituents. The parent name is phenol. Ring numbering always begins with the hydroxyl group and proceeds in the direction that gives the lower number to the next carbon atom bearing a substituent. The numerical position of the hydroxyl group is not specified in the name because it is 1 by definition.



3-Chlorophenol
(or *meta*-Chlorophenol)



4-Ethyl-2-methylphenol



2,5-Dibromophenol

Physical and Chemical Properties of Phenols

Phenols are generally low-melting solids or oily liquids at room temperature. Most of them are only slightly soluble in water. Many phenols have antiseptic and disinfectant properties. The simplest phenol, phenol itself, is a colorless solid with a medicinal odor. Its melting point is 41°C, and it is more soluble in water than are most other phenols.

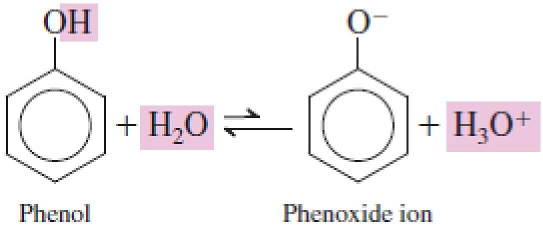
Chemical Properties

The similarities and differences between alcohols and phenols

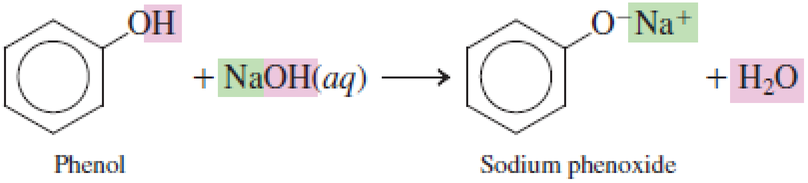
1. Both alcohols and phenols are flammable.
2. Dehydration is a reaction of alcohols but not of phenols; phenols cannot be dehydrated.
3. Both 1° and 2° alcohols are oxidized by mild oxidizing agents. Tertiary (38) alcohols and phenols do not react with the oxidizing agents that cause 1° and 2°alcohol oxidation. Phenols can be oxidized by stronger oxidizing agents.
4. Both alcohols and phenols undergo halogenation in which the hydroxyl group is replaced by a halogen atom in a substitution reaction.

Acidity of Phenols

One of the most important properties of phenols is their acidity. Unlike alcohols, phenols are weak acids in solution. As acids, phenols have *Ka* values of about 10^{-10}. Such *Ka* values are lower than those of most weak inorganic acids (10^{-5} to 10^{-10}). The acid ionization reaction for phenol itself is

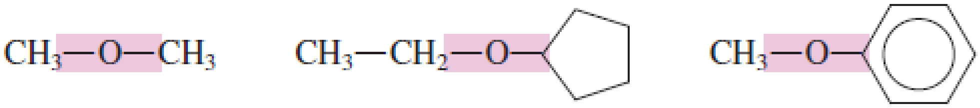


Note that the negative ion produced from the ionization is called the phenoxide ion. When phenol itself is reacted with sodium hydroxide (a base), the salt sodium phenoxide is produced.



Ethers

Ether *is an organic compound in which an oxygen atom is bonded to two carbon atoms by single bonds.* In ether, the carbon atoms that are attached to the oxygen atom can be part of alkyl, cycloalkyl, or aryl groups. Examples of ethers include



All ethers contain a C—O—C unit, which is the ether functional group.

$$\text{---}\overbrace{\text{C—O—C}}^{\text{Ether functional group}}\text{---}$$

Generalized formulas for ethers, which depend on the types of groups attached to the oxygen atom (alkyl or aryl), include R—O—R, R—O—R′ (where R′ is an alkyl group different from R), R—O—Ar, and Ar—O—Ar.

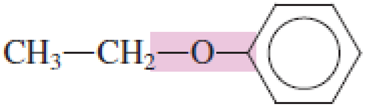
3.16 Nomenclature for Ethers.

Common names are almost always used for ethers whose alkyl groups contain four or fewer carbon atoms. There are two rules, one for unsymmetrical ethers (two different alkyl/aryl groups) and one for symmetrical ethers (two identical alkyl/aryl groups).

Rule 1: *For unsymmetrical ethers, name both hydrocarbon groups bonded to the oxygen atom in alphabetical order and add the word* ether, *separating the words with a space. Such ether names have three separate words within them.*

$$CH_3{-}O{-}CH_2{-}CH_3$$

Ethyl methyl ether



Ethyl phenyl ether

Rule 2: *For symmetrical ethers, name the alkyl group, add the prefix* di-, *and then add the word* ether, *separating the words with a space. Such ether names have two separate words within them.*

$$CH_3{-}O{-}CH_3$$

Dimethyl ether

$$CH_3{-}CH_2{-}O{-}CH_2{-}CH_3$$

Diethyl ether

Ethers with more complex alkyl/aryl groups are named using the IUPAC system. In this system, ethers are named as substituted hydrocarbons. The smaller hydrocarbon attachment and the oxygen atom are called an *alkoxy group,* and this group is considered a substituent on the larger hydrocarbon group.

An **alkoxy group** *is an -OR group, an alkyl (or aryl) group attached to an oxygen atom.* Simple alkoxy groups include the following:

$$CH_3{-}O{-}$$

Methoxy group

$$CH_3{-}CH_2{-}O{-}$$

Ethoxy group

$$CH_3{-}CH_2{-}CH_2{-}O{-}$$

Propoxy group

The general symbol for an alkoxy group is R-O- (or RO-).

The rules for naming an ether using the IUPAC system are

Rule 1: *Select the longest carbon chain and use its name as the base name.*

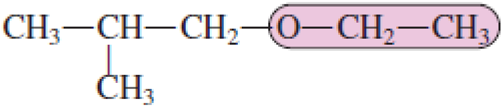
Rule 2: *Change the* -yl *ending of the other hydrocarbon group to* -oxy *to obtain the alkoxy group name;* methyl *becomes* methoxy, ethyl *becomes* ethoxy, *etc.*

Rule 3: *Place the alkoxy name, with a locator number, in front of the base chain name.*

Two examples of IUPAC ether nomenclature, with the alkoxy groups present highlighted in each structure are:

$CH_3{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

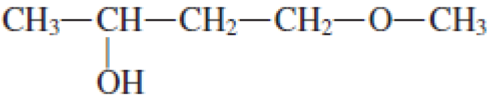
1-Methoxybutane



$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}O{-}CH_2{-}CH_3$$

1-Ethoxy-2-methylpropane

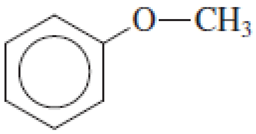
It is possible to have compounds that contain both ether and alcohol functional groups such as



$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}O{-}CH_3$$

4-Methoxy-2-butanol

The simplest aromatic ether involves a methoxy group attached to a benzene ring. This ether goes by the common name anisole.



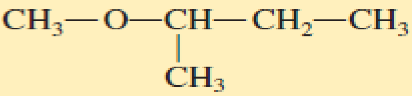
Anisole

Example: Determining IUPAC Names for Ethers

Name the following ethers utilizing IUPAC nomenclature rules.

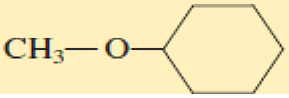
a. $CH_3{-}CH_2{-}O{-}CH_2{-}CH_2{-}CH_3$

b.



$$CH_3{-}O{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_3$$

c.



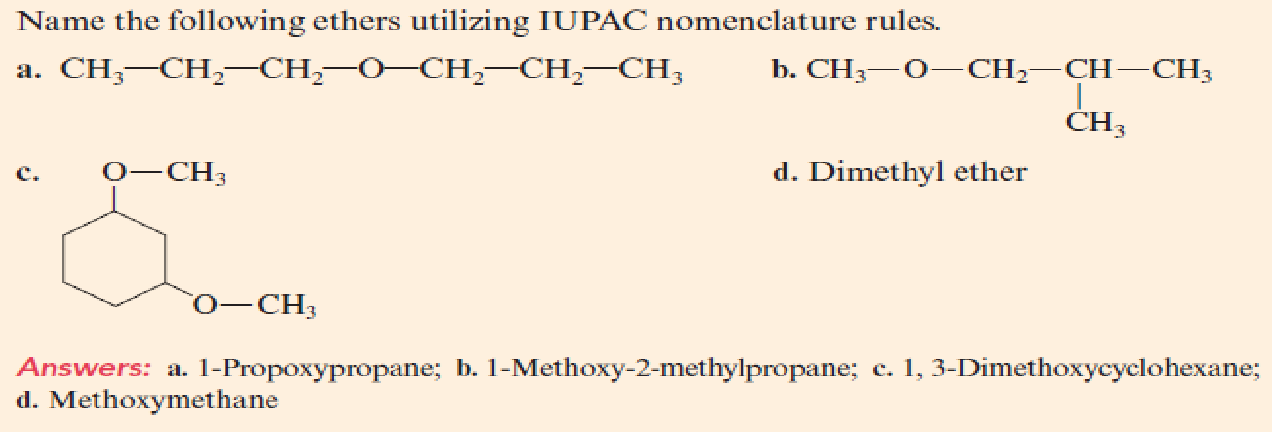
d. Ethyl methyl ether

Solution

a. 1-ethoxypropane
b. 2-methoxybutane
c. methoxycyclohexane
d. methoxyethane

Practice Exercise

Name the following ethers utilizing IUPAC nomenclature rules



Name the following ethers utilizing IUPAC nomenclature rules.

a. $CH_3—CH_2—CH_2—O—CH_2—CH_2—CH_3$

b. $CH_3—O—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

c.

d. Dimethyl ether

Answers: **a.** 1-Propoxypropane; **b.** 1-Methoxy-2-methylpropane; **c.** 1, 3-Dimethoxycyclohexane; **d.** Methoxymethane

3.15 Isomerism for Ethers

Ethers contain two carbon chains (two alkyl groups), unlike the one carbon chain found in alcohols. Constitutional isomerism possibilities in ethers depend on

1. the partitioning of carbon atoms between the two alkyl groups
2. Isomerism possibilities for the individual alkyl groups present.

Isomerism is not possible for a C_2 ether (two methyl groups) or a C_3 ether (a methyl and an ethyl group). For C_4 ethers, isomerism arises not only from carbon-atom partitioning between the alkyl groups (C_1-C_3 and C_2-C_2) but also from isomerism within a C_3 group (propyl and isopropyl). There are three C_4 ether constitutional isomers.

$CH_3—CH_2—O—CH_2—CH_3$

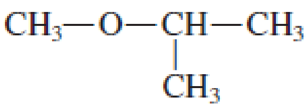
Diethyl ether

$(C_2—C_2)$

$CH_3—O—CH_2—CH_2—CH_3$

Methyl propyl ether

$(C_1—C_3)$



$CH_3—O—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

Isopropyl methyl ether

$(C_1—C_3)$

Functional Group Isomerism

Ethers and alcohols with the same number of carbon atoms and the same degree of saturation have the same molecular formula

$CH_3—O—CH_3$

Dimethyl ether

$CH_3—CH_2—OH$

Ethyl alcohol

Functional group isomers *are constitutional isomers that contain different functional groups*

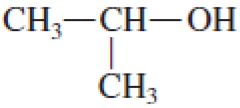
When three carbon atoms are present, the ether–alcohol functional group isomerism possibilities are

$CH_3—CH_2—O—CH_3$

Ethyl methyl ether

$CH_3—CH_2—CH_2—OH$

Propyl alcohol



$CH_3—CH(CH_3)—OH$

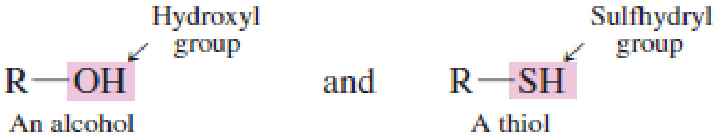
Isopropyl alcohol

All three compounds have the molecular formula C_3H_8O.

Thiols

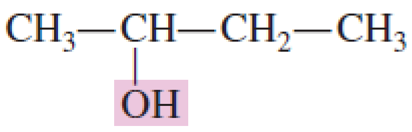
Thiols, the sulfur analogs of alcohols, contain -SH functional groups instead of -OH functional groups. The thiol functional group is called a sulfhydryl group

*A **thiol** is an organic compound in which a sulfhydryl group is bonded to a saturated carbon atom. An older term used for thiols is mercaptans.*



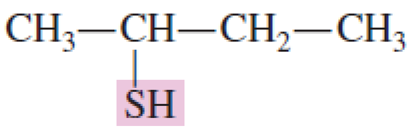
Nomenclature for Thiols

Thiols are named in the same way as alcohols in the IUPAC system, except that the-ol becomes -thiol. The suffix -thiol indicates the substitution of a sulfur atom for an oxygen atom in a compound.



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3$$

2-Butanol



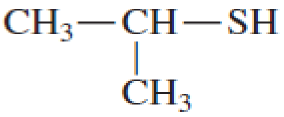
$$CH_3-\underset{\displaystyle SH}{\underset{|}{CH}}-CH_2-CH_3$$

2-Butanethiol

Common names for thiols are based on use of the term mercaptan, the older name for thiols. The name of the alkyl group present (as a separate word) precedes the word mercaptan.

CH_3-CH_2-SH

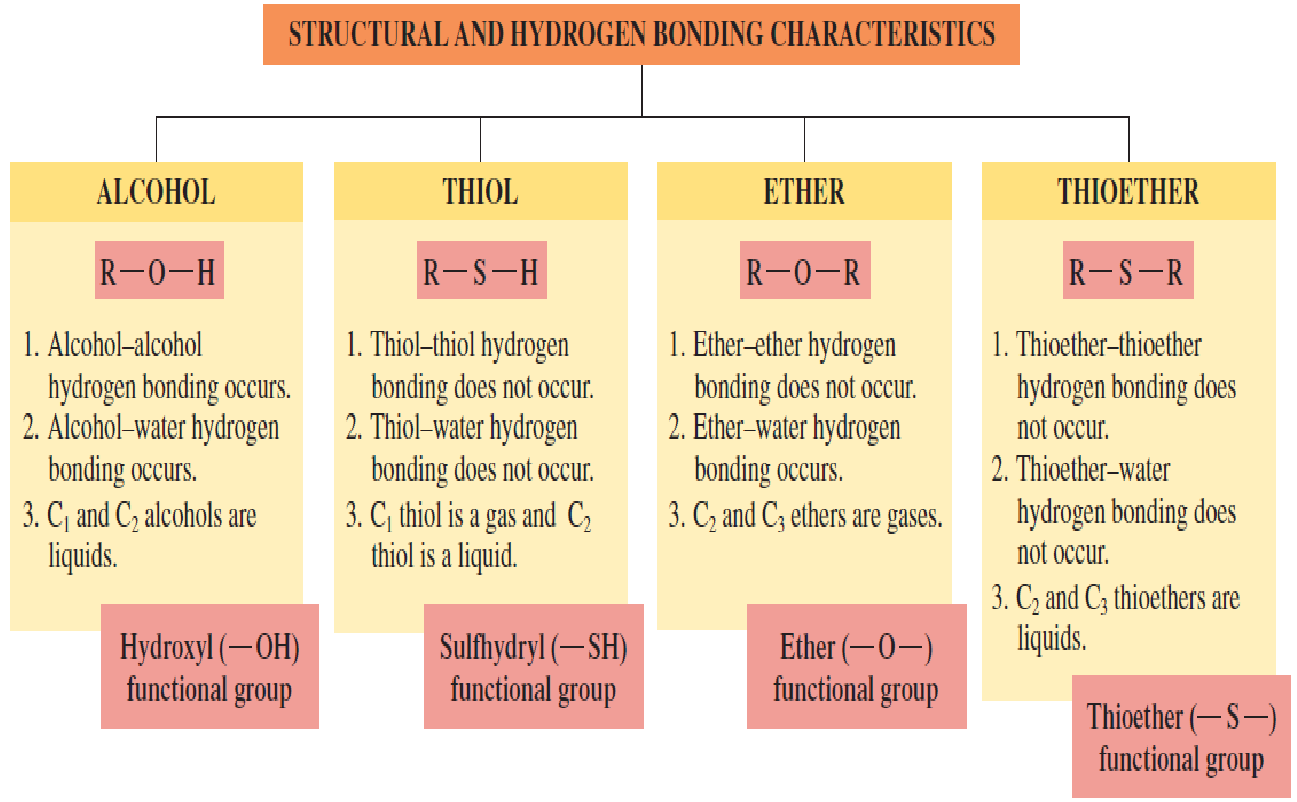
Ethyl mercaptan



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-SH$$

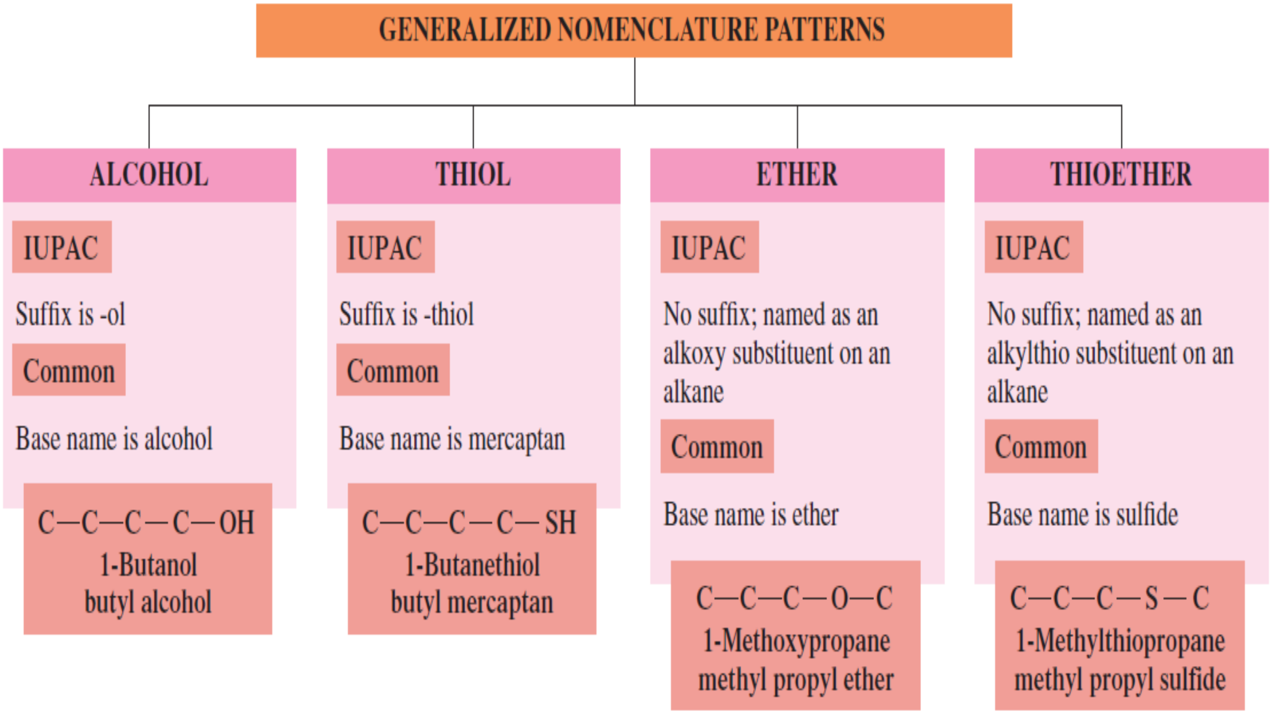
Isopropyl mercaptan

AT A GLANCE Alcohols, Thiols, Ethers, and Thioethers



STRUCTURAL AND HYDROGEN BONDING CHARACTERISTICS

ALCOHOL	THIOL	ETHER	THIOETHER
$R-O-H$	$R-S-H$	$R-O-R$	$R-S-R$
1. Alcohol–alcohol hydrogen bonding occurs. 2. Alcohol–water hydrogen bonding occurs. 3. C_1 and C_2 alcohols are liquids.	1. Thiol–thiol hydrogen bonding does not occur. 2. Thiol–water hydrogen bonding does not occur. 3. C_1 thiol is a gas and C_2 thiol is a liquid.	1. Ether–ether hydrogen bonding does not occur. 2. Ether–water hydrogen bonding occurs. 3. C_2 and C_3 ethers are gases.	1. Thioether–thioether hydrogen bonding does not occur. 2. Thioether–water hydrogen bonding does not occur. 3. C_2 and C_3 thioethers are liquids.
Hydroxyl (—OH) functional group	Sulfhydryl (—SH) functional group	Ether (—O—) functional group	Thioether (—S—) functional group



GENERALIZED NOMENCLATURE PATTERNS

ALCOHOL

IUPAC

Suffix is -ol

Common

Base name is alcohol

C—C—C—C—OH
1-Butanol
butyl alcohol

THIOL

IUPAC

Suffix is -thiol

Common

Base name is mercaptan

C—C—C—C—SH
1-Butanethiol
butyl mercaptan

ETHER

IUPAC

No suffix; named as an alkoxy substituent on an alkane

Common

Base name is ether

C—C—C—O—C
1-Methoxypropane
methyl propyl ether

THIOETHER

IUPAC

No suffix; named as an alkylthio substituent on an alkane

Common

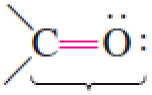
Base name is sulfide

C—C—C—S—C
1-Methylthiopropane
methyl propyl sulfide

Chapter 4: Aldehydes and Ketones

4.1 The Carbonyl Group

Both aldehydes and ketones contain a carbonyl functional group. A **carbonyl group** *is a carbon atom double-bonded to an oxygen atom.* The structural representation for a carbonyl group is



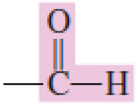
Carbonyl group

Compounds containing a carbonyl functional group:

1. Aldehydes
2. Ketones
3. Carboxylic acids
4. Esters
5. Amides

4.2 The Aldehyde and Ketone Functional Groups

An **aldehyde** *is a carbonyl-containing organic compound in which the carbonyl carbon atom has at least one hydrogen atom directly attached to it.* The remaining group attached to the carbonyl carbon atom can be hydrogen, an alkyl group (R), a cycloalkyl group, or an aryl group (Ar). The aldehyde functional group is



$$-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

Linear notations for an aldehyde functional group and for an aldehyde itself are

—CHO and RCHO

Nomenclature for Aldehydes

The IUPAC rules for naming aldehydes are as follows:

Rule 1: *Select as the parent carbon chain the longest chain that* includes *the carbon atom of the carbonyl group.*

Rule 2: *Name the parent chain by changing the* -e *ending of the corresponding alkane name to* -al*.*

Rule 3: *Number the parent chain by assigning the number 1 to the carbonyl carbon atom of the aldehyde group. The number 1, however, does not become part of the name.*

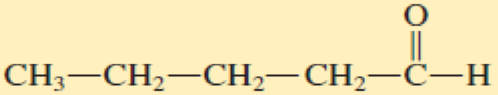
Rule 4: *Determine the identity and location of any substituents, and append this information to the front of the parent chain name.*

Rule 5: *When an aldehyde functional group is attached to a carbon ring, name the ring and add the suffix* –carbaldehyde

Example

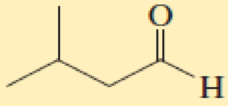
Assign IUPAC names to the following aldehydes.

a.

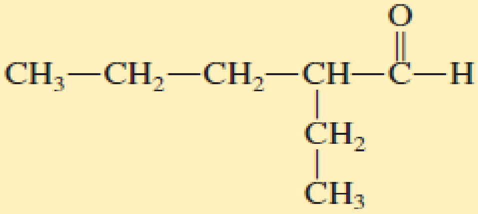


$$CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$$

b.

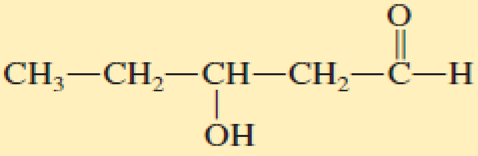


c.



$$CH_3-CH_2-CH_2-\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{CH}-\overset{O}{\overset{\|}{C}}-H$$

d.



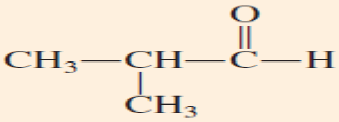
$$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

a. *Pentanal*
b. *3-methylbutanal*
c. *2-ethylpentanal*
d. *3-hydroxypentanal.*

Practical exercise

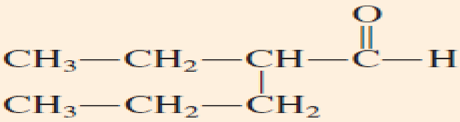
Assign IUPAC names to the following aldehydes.

a.



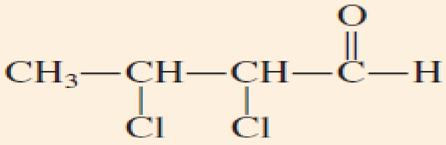
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{O}{\overset{\|}{C}}-H$$

b.



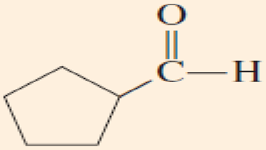
$$\begin{array}{l} CH_3-CH_2-CH-\overset{O}{\overset{\|}{C}}-H \\ \qquad\qquad\qquad | \\ CH_3-CH_2-CH_2 \end{array}$$

c.



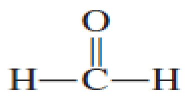
$$CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-\overset{O}{\overset{\|}{C}}-H$$

d.



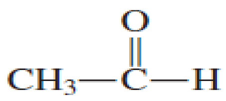
Answers: **a.** 2-Methylpropanal; **b.** 2-Ethylpentanal; **c.** 2,3-Dichlorobutanal; **d.** Cyclopentanecarbaldehyde

Small unbranched aldehydes have common names:



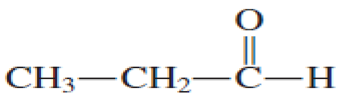
$H-\overset{O}{\overset{\|}{C}}-H$

Formaldehyde



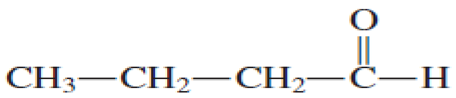
$CH_3-\overset{O}{\overset{\|}{C}}-H$

Acetaldehyde



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

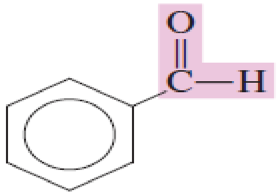
Propionaldehyde



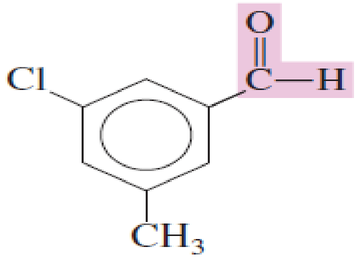
$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$

Butyraldehyde

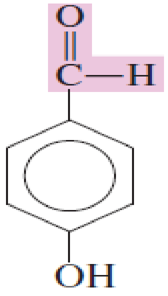
In the IUPAC system, aromatic aldehydes—compounds in which an aldehyde group is attached to a benzene ring—are named as derivatives of benzaldehyde, the parent compound



Benzaldehyde



3-Chloro-5-methylbenzaldehyde



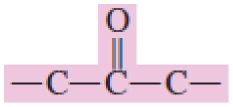
4-Hydroxybenzaldehyde

The last of these compounds is named as a benzaldehyde rather than as a phenol because the aldehyde group has priority over the hydroxyl group in the IUPAC naming system.

4.3 Ketones

A **ketone** *is a carbonyl-containing organic compound in which the carbonyl carbon atom has two other carbon atoms directly attached to it.* The groups containing these bonded carbon atoms may be alkyl, cycloalkyl, or aryl.

The ketone functional group is



$-C-\overset{O}{\overset{\|}{C}}-C-$

The general condensed formula for a ketone is RCOR

4.4 Nomenclature for Ketones

Assigning IUPAC names to ketones is similar to naming aldehydes except that the ending -*one* is used instead of -*al.* The rules for IUPAC ketone nomenclature follow:

Rule 1: *Select as the parent carbon chain the longest carbon chain that* includes *the carbon atom of the carbonyl group.*

Rule 2: *Name the parent chain by changing the* -e *ending of the corresponding alkane name to* -one*. This ending, -one, is pronounced "own."*

Rule 3: *Number the carbon chain such that the carbonyl carbon atom receives the lowest possible number. The position of the carbonyl carbon atom is noted by placing a number immediately before the name of the parent chain.*

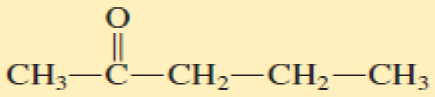
Rule 4: *Determine the identity and location of any substituents, and append this information to the front of the parent chain name.*

Rule 5: *Cyclic ketones are named by assigning the number 1 to the carbon atom of the carbonyl group. Numbering then proceeds in a clockwise or counterclockwise direction to give the next encountered substituent the lower number. The "1," designating the carbonyl carbon atom location, is omitted from the name.*

Example: Determining IUPAC Names for Ketones

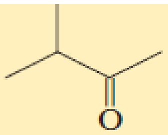
Assign IUPAC names to the following ketones.

a.

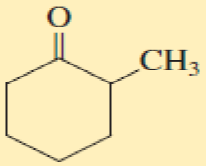


$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$

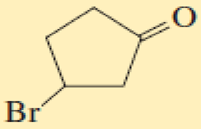
b.



c.



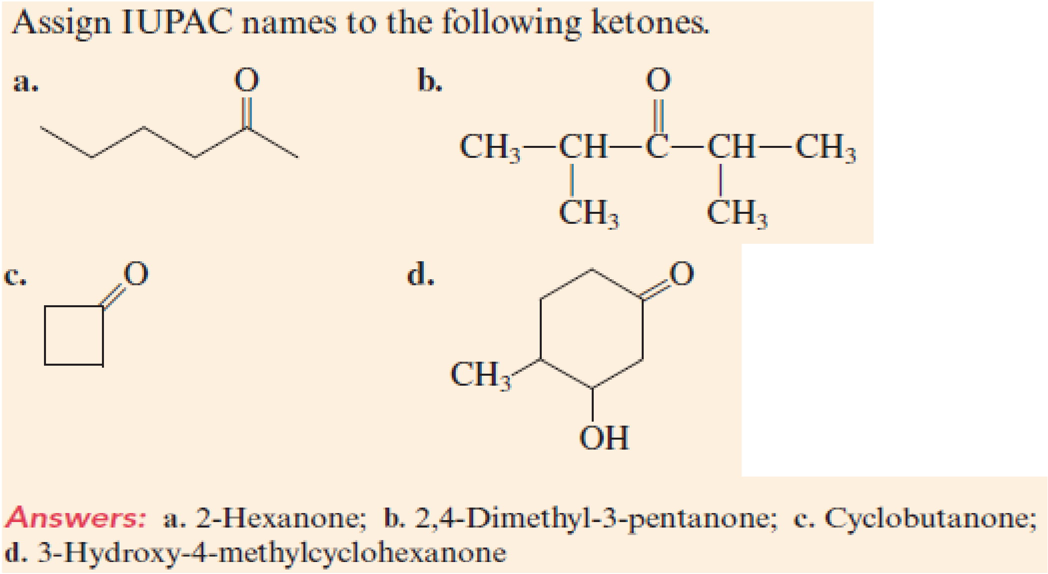
d.



Solution

a. *2-pentanone*
b. *3-methyl-2-butanone*
c. *2-methylcyclohexanone*
d. *3-bromocyclopentanone*

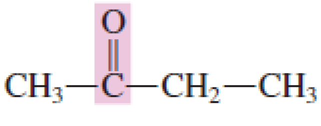
Practice Exercise



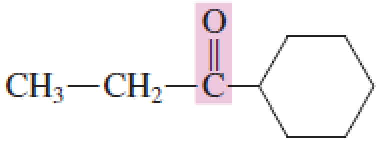
Assign IUPAC names to the following ketones.

Answers: **a.** 2-Hexanone; **b.** 2,4-Dimethyl-3-pentanone; **c.** Cyclobutanone; **d.** 3-Hydroxy-4-methylcyclohexanone

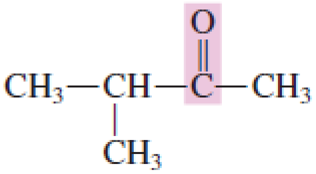
The procedure for coining common names for ketones is the same as that used for ether common names .They are constructed by giving, in alphabetical order, the names of the alkyl or aryl groups attached to the carbonyl functional group and then adding the word ketone. Unlike aldehyde common names, which are one word, those for ketones are two or three words



Ethyl methyl ketone

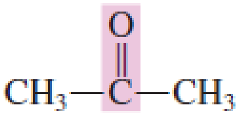


Cyclohexyl ethyl ketone

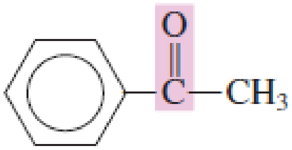


Isopropyl methyl ketone

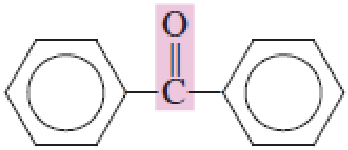
Three ketones have additional common names besides those obtained with the preceding procedures. These three ketones are



Acetone
(dimethyl ketone)



Acetophenone
(methyl phenyl ketone)

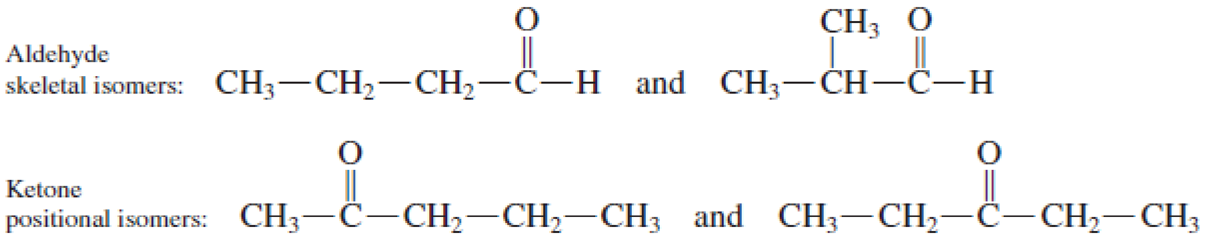


Benzophenone
(diphenyl ketone)

Acetophenone is the simplest aromatic ketone

Isomerism for Aldehydes and Ketones

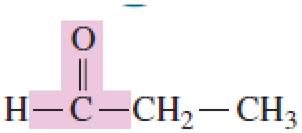
Like the classes of organic compounds previously discussed (alkanes, alkenes, alkynes, alcohols, ethers, etc.), constitutional isomers exist for aldehydes and for ketones, and *between* aldehydes and ketones (functional group isomerism). The compounds butanal and 2-methylpropanal are examples of skeletal aldehyde isomers; the compounds 2-pentanone and 3-pentanone are examples of positional ketone isomers.



$$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H \quad \text{and} \quad CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

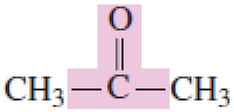
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_3 \quad \text{and} \quad CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

Aldehydes and ketones with the same number of carbon atoms and the same degree of saturation are functional group isomers. Molecular models for the isomeric C_3 compounds propanal and propanone, which both have the molecular formula C_3H_6O, are shown here



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$$

C_3 aldehyde

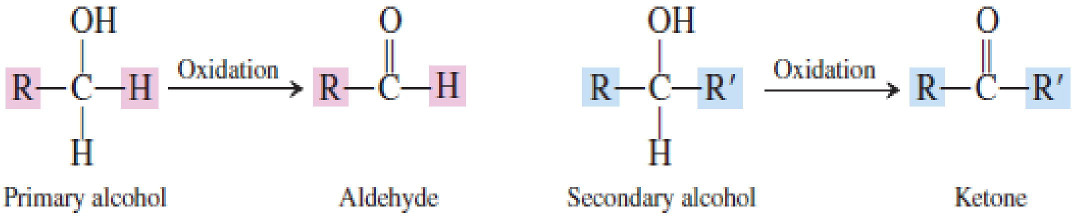


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

C_3 ketone

4.5 Preparation of Aldehydes and Ketones

Aldehydes and ketones can be produced by the oxidation of primary and secondary alcohols, respectively, using mild oxidizing agents such as KMnO4 or $K_2Cr_2O_7$



$$R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H \xrightarrow{\text{Oxidation}} R-\overset{\overset{\displaystyle O}{\|}}{C}-H \qquad R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-R' \xrightarrow{\text{Oxidation}} R-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$

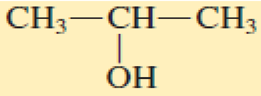
When this type of reaction is used for aldehyde preparation, reaction conditions must be sufficiently mild to avoid further oxidation of the aldehyde to a carboxylic acid. Ketones do not undergo the further oxidation that aldehydes do

Example Predicting Products in Alcohol Oxidation Reactions

Draw the structure of the aldehyde or ketone formed from the oxidation of each of the following alcohols. Assume that reaction conditions are sufficiently mild that any aldehydes produced are not oxidized further.

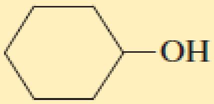
a. $CH_3-CH_2-CH_2-OH$

b.

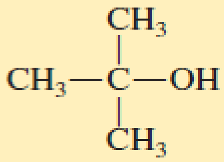


$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

c.



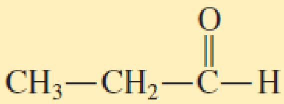
d.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

Solution

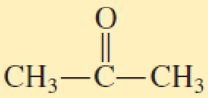
a. This is a primary alcohol that will give the aldehyde *propanal* as the oxidation product.



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$$

Propanal

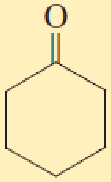
b. This is a secondary alcohol. Upon oxidation, secondary alcohols are converted to ketones.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Propanone

c. This cyclic alcohol is a secondary alcohol; hence a ketone is the oxidation product.



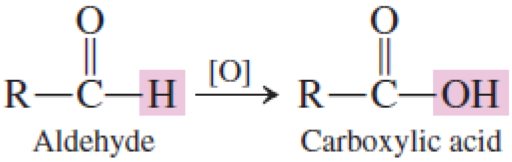
Cyclohexanone

d. This is a tertiary alcohol. Tertiary alcohols do not undergo oxidation

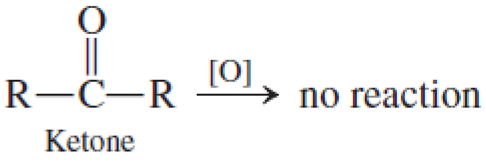
4.6 Oxidation and Reduction of Aldehydes and Ketones

Oxidation of Aldehydes and Ketones

Aldehydes readily undergo oxidation to carboxylic acids, and ketones are resistant to oxidation.



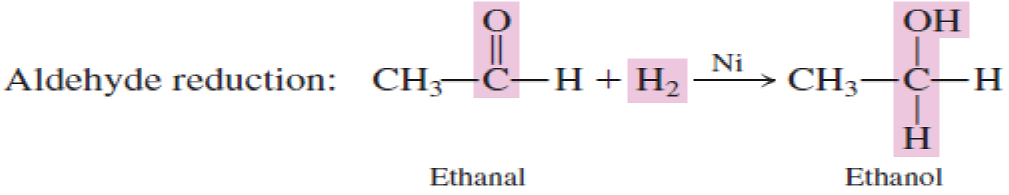
$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-OH$$



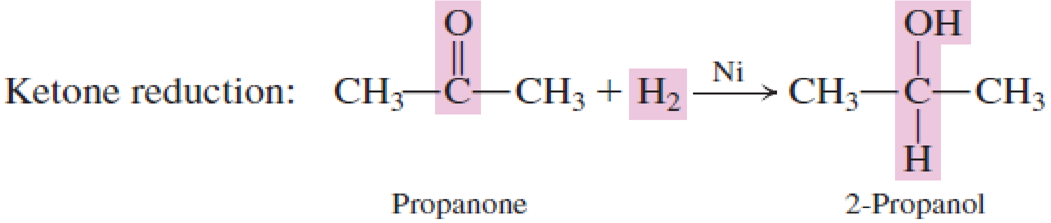
$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{[O]} \text{no reaction}$$

Reduction of Aldehydes and Ketones

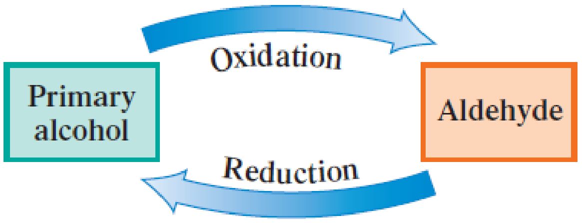
Aldehydes and ketones are easily reduced by hydrogen gas (H2), in the presence of a catalyst (Ni, Pt, or Cu), to form alcohols. The reduction of aldehydes produces primary alcohols, and the reduction of ketones yields secondary alcohols.

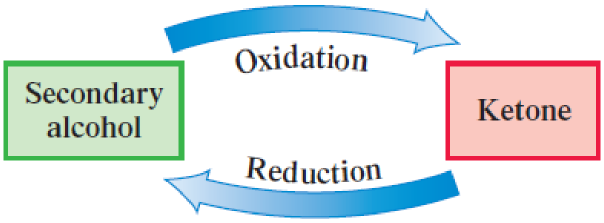


$$CH_3-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow{Ni} CH_3-\overset{OH}{\underset{H}{C}}-H$$



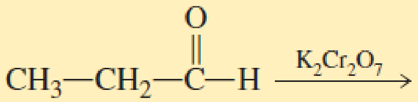
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2 \xrightarrow{Ni} CH_3-\overset{OH}{\underset{H}{C}}-CH_3$$



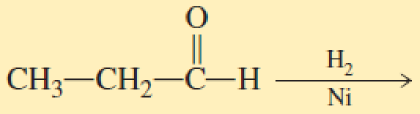


Example: Predicting Product Identity in Aldehyde/Ketone Oxidation/ Reduction Reactions

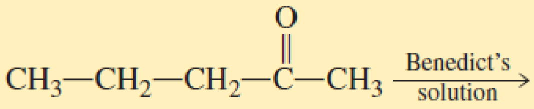
Draw the structure of the organic product formed when each of the following aldehydes and ketones are subjected to oxidation or reduction. If no reaction occurs, state that such is the case.

a. 

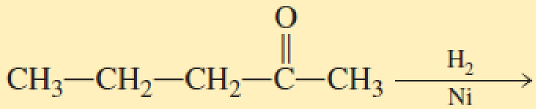
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{K_2Cr_2O_7}$$

b. 

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[Ni]{H_2}$$

c. 

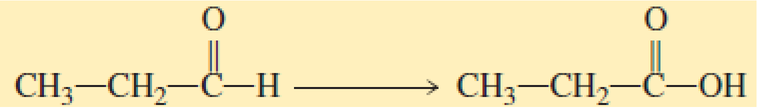
$$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{solution}]{\text{Benedict's}}$$

d. 

$$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[Ni]{H_2}$$

Solution

a. Aldehyde oxidation produces a carboxylic acid.



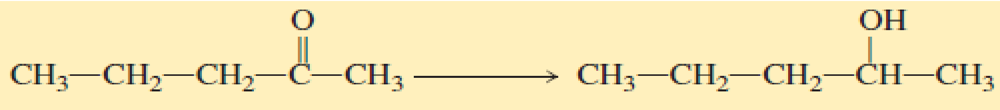
$$\mathrm{CH_3{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}H \longrightarrow CH_3{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}OH}$$

b. Aldehyde reduction produces a primary alcohol.

$$\mathrm{CH_3{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}H \longrightarrow CH_3{-}CH_2{-}\overset{\overset{OH}{|}}{CH_2}}$$

c. Ketones cannot be oxidized by mild oxidizing agents; therefore, no reaction occurs.

d. Ketone reduction produces a secondary alcohol.

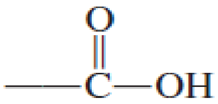


$$\mathrm{CH_3{-}CH_2{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \longrightarrow CH_3{-}CH_2{-}CH_2{-}\overset{\overset{OH}{|}}{CH}{-}CH_3}$$

Chapter 5: Carboxylic Acids, Esters and other Acid Derivatives

5.1 carboxylic acids

A **carboxylic acid** *is an organic compound whose functional group is the carboxyl group.* What is a carboxyl group? A **carboxyl group** *is a carbonyl group (C=O) that has a hydroxyl group (-OH) bonded to the carbonyl carbon atom.* A general structural representation for a carboxyl group is

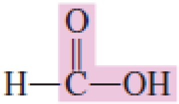


$$-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}$$

Abbreviated linear designations for the carboxyl group are

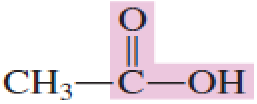
$$-\mathrm{COOH} \quad \text{and} \quad -\mathrm{CO_2H}$$

The simplest carboxylic acid has a hydrogen atom attached to the carboxyl group carbon atom.

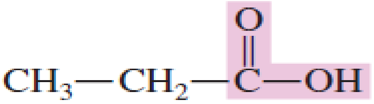


$$\mathrm{H}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}$$

Structures for the next two simplest carboxylic acids,

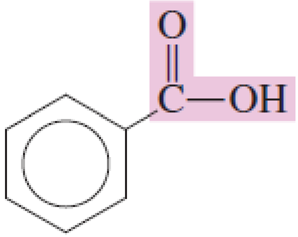


$$\mathrm{CH_3}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}$$



$$\mathrm{CH_3}-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}$$

The structure of the simplest aromatic carboxylic acid involves a benzene ring to which a carboxyl group is attached.



5.2 IUPAC Nomenclature for Carboxylic Acids

IUPAC rules for naming carboxylic acids resemble those for naming aldehydes

A **monocarboxylic acid** *is a carboxylic acid in which one carboxyl group is present.*

IUPAC rules for naming such compounds are:

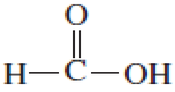
Rule 1: Select as the parent carbon chain the longest carbon chain that includes *the carbon atom of the carboxyl group.*

Rule 2: Name the parent chain by changing the -e ending of the corresponding alkane to -oic acid.

Rule 3: Number the parent chain by assigning the number 1 to the carboxyl carbon atom, but omit this number from the name.

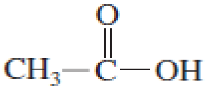
Rule 4: Determine the identity and location of any substituents in the usual manner, and append this information to the front of the parent chain name.

Rule 5: If the carbonyl group is bonded to a carbon ring, name the ring and add the words carboxylic acid. The carbon bearing the carboxyl group is always carbon 1. Locate any other ring substituents in the usual manner.



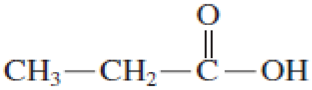
$H-\overset{\overset{O}{\|}}{C}-OH$

Methanoic acid



$CH_3-\overset{\overset{O}{\|}}{C}-OH$

Ethanoic acid



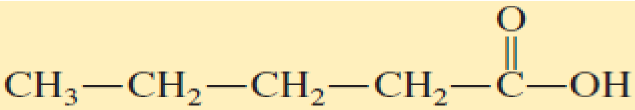
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$

Propanoic acid

Example: Determining IUPAC Names for Carboxylic Acids

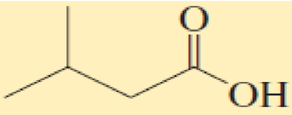
Assign IUPAC names to the following carboxylic acids.

a.

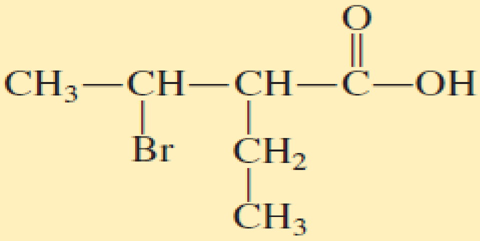


$CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$

b.

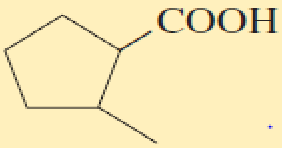


c.



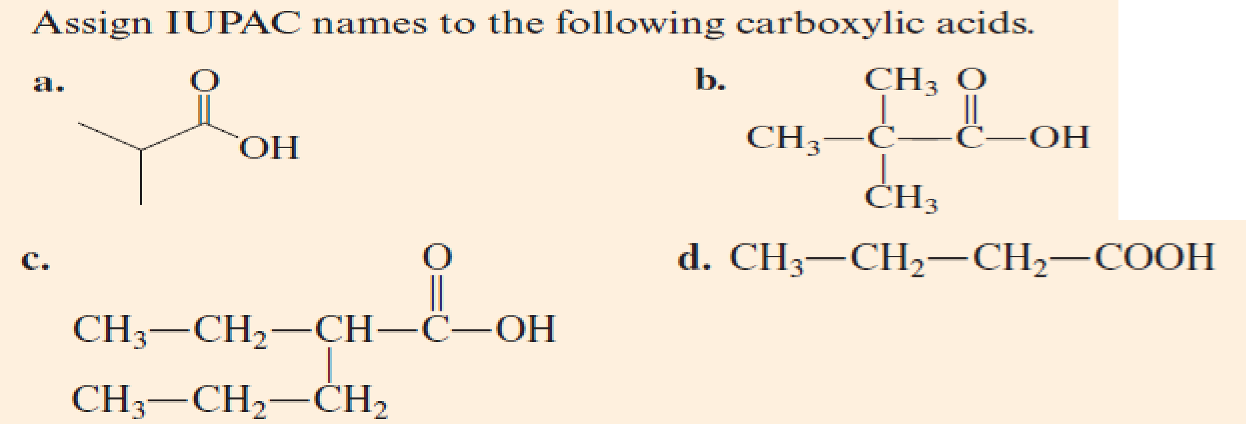
$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{\underset{CH_3}{|}}{CH_2}}{\underset{|}{CH}}-\overset{\overset{O}{\|}}{C}-OH$

d.



- a. *Pentanoic acid*
- b. *3-methylbutanoic acid*
- c. *3-bromo-2-ethylbutanoic acid*
- d. *2-methylcyclopentanecarboxylic acid*

Assign IUPAC names to the following carboxylic acids



Assign IUPAC names to the following carboxylic acids.

a.

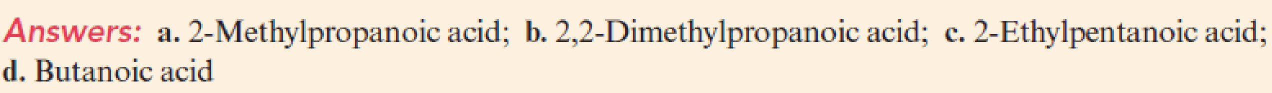
b.

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

c.

$$CH_3-CH_2-\underset{\displaystyle CH_3-CH_2-CH_2}{CH}-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

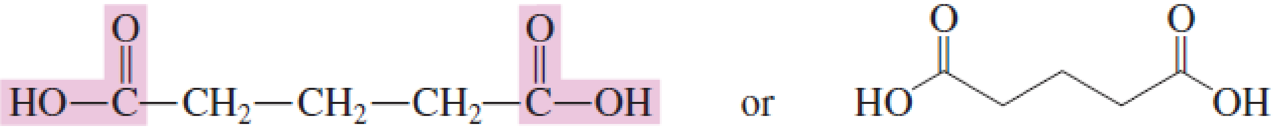
d. $CH_3-CH_2-CH_2-COOH$



Answers: **a.** 2-Methylpropanoic acid; **b.** 2,2-Dimethylpropanoic acid; **c.** 2-Ethylpentanoic acid; **d.** Butanoic acid

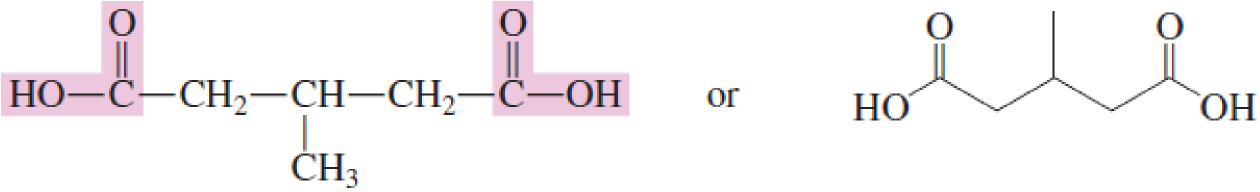
Dicarboxylic Acids

A ***dicarboxylic acid*** *is a carboxylic acid that contains two carboxyl groups, one at each end of a carbon chain. Saturated acids of this type are named by appending the suffix -dioic acid to the corresponding alkane name (the -e is retained to facilitate pronunciation). Both carboxyl carbon atoms must be part of the parent car- bon chain, and the carboxyl locations need not be specified with numbers because they will always be at the two ends of the chain.*



$$HO-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

Pentanedioic acid

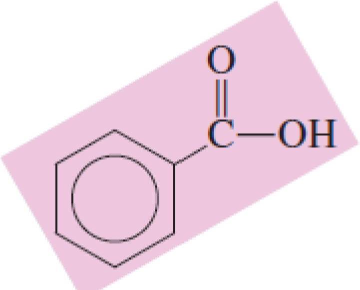


$$HO-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-\underset{\displaystyle CH_3}{CH}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

3-Methylpentanoic acid

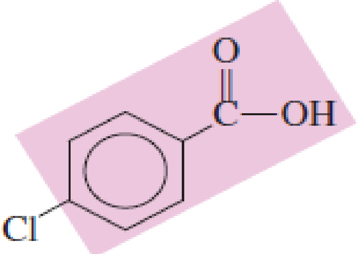
Aromatic Carboxylic Acids

The simplest aromatic carboxylic acid is called benzoic acid

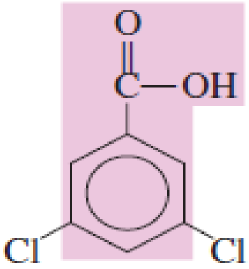


Benzoic acid

Other simple aromatic acids are named as derivatives of benzoic acid.



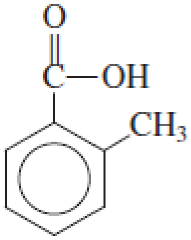
4-Chlorobenzoic acid
(*p*-chlorobenzoic acid)



3,5-Dichlorobenzoic acid

In substituted benzoic acids, the ring carbon atom bearing the carboxyl group is always carbon 1.

Methyl benzoic acids go by the name toluic acid. (This situation parallels methyl benzene being called toluene.)



o-Toluic acid

5.3 Common Names for Carboxylic Acids

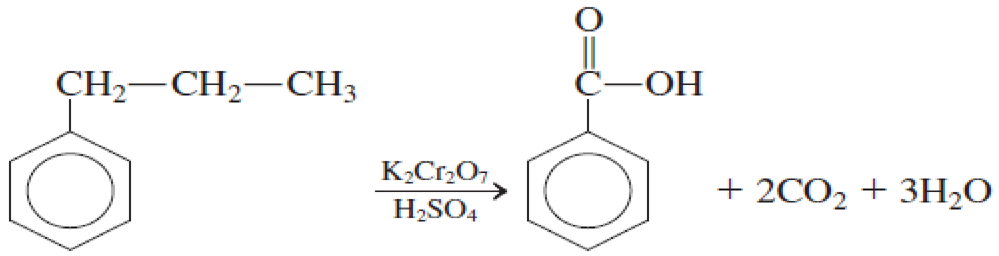
Length of Carbon Chain	Structural Formula	Latin or Greek Root	Common Name*
C_1 monoacid	H—COOH	form-	formic acid
C_2 monoacid	CH_3—COOH	acet-	acetic acid
C_3 monoacid	CH_3—CH_2—COOH	propion-	propionic acid
C_4 monoacid	CH_3—$(CH_2)_2$—COOH	butyr-	butyric acid
C_5 monoacid	CH_3—$(CH_2)_3$—COOH	valer-	valeric acid
C_6 monoacid	CH_3—$(CH_2)_4$—COOH	capro-	caproic acid

Preparation of Carboxylic Acids

Oxidation of primary alcohols or aldehydes, using an oxidizing agent such as CrO_3 or $K_2Cr_2O_7$, produces carboxylic acids

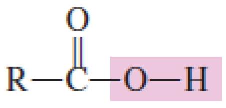
$$\text{Primary alcohol} \xrightarrow{[O]} \text{aldehyde} \xrightarrow{[O]} \text{carboxylic acid}$$

Aromatic acids can be prepared by oxidizing a carbon side chain (alkyl group) on a benzene derivative. In this process, all the carbon atoms of the alkyl group except the one attached to the ring are lost. The remaining carbon becomes part of a carboxyl group



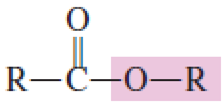
5.4 Structure of Esters

An **ester** *is a carboxylic acid derivative in which the -OH portion of the carboxyl group has been replaced with an -OR group.*



$$R-\overset{O}{\overset{\|}{C}}-O-H$$

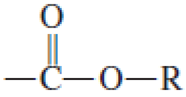
Carboxylic acid



$$R-\overset{O}{\overset{\|}{C}}-O-R$$

Ester

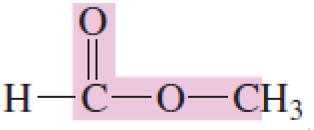
The ester functional group is thus



$-\overset{O}{\overset{\|}{C}}-O-R$

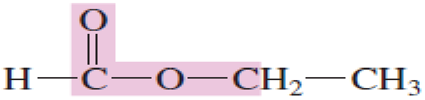
In linear form, the ester functional group can be represented as —COOR or —CO_2R.

The simplest ester, which has two carbon atoms, has a hydrogen atom attached to the ester functional group.



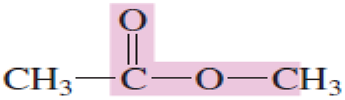
$H-\overset{O}{\overset{\|}{C}}-O-CH_3$

There are two three-carbon esters.



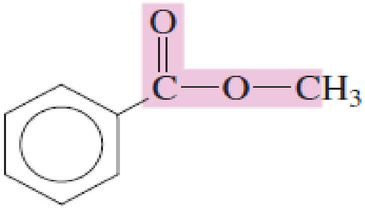
$H-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$

and

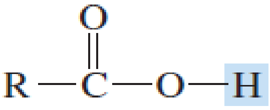


$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$

The structure of the simplest aromatic ester is derived from the structure of benzoic acid, the simplest aromatic carboxylic acid.



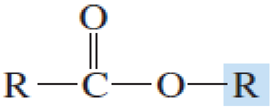
Note that the difference between a carboxylic acid and an ester is a "H versus R" relationship.



$R-\overset{O}{\overset{\|}{C}}-O-H$

Acid

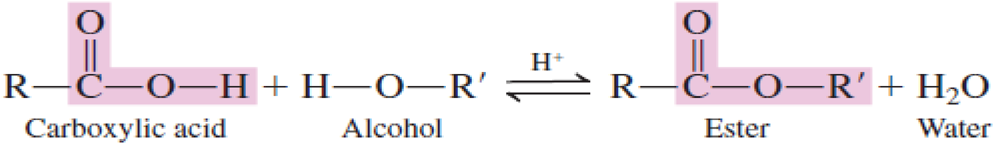
and



$R-\overset{O}{\overset{\|}{C}}-O-R$

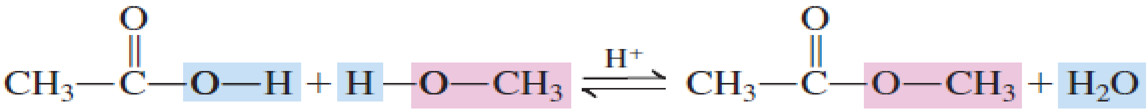
Ester

5.5 Preparation of Esters



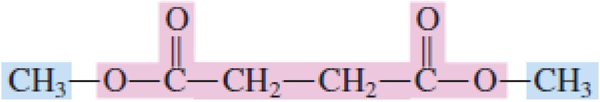
$$R-\overset{O}{\overset{\|}{C}}-O-H + H-O-R' \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-O-R' + H_2O$$

In the esterification process, a -OH group is lost from the carboxylic acid, a -H atom is lost from the alcohol, and water is formed as a by-product. The net effect of this reaction is substitution of the -OR group of the alcohol for the -OH group of the acid.



$$CH_3-\overset{\overset{O}{\|}}{C}-O-H + H-O-CH_3 \overset{H^+}{\rightleftharpoons} CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3 + H_2O$$

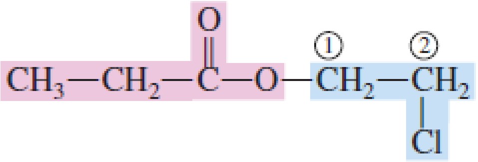
Dicarboxylic acids can form diesters, with each of the carboxyl groups undergoing esterification. An example of such a molecule and how it is named is



$$CH_3-O-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3$$

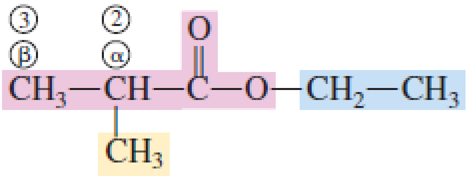
IUPAC: Dimethyl butanedioate
Common: Dimethyl succinate

Further examples of ester nomenclature, for compounds in which substituents are present



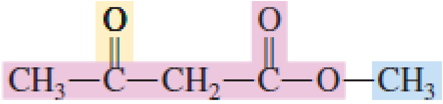
$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{Cl}{|}}{CH_2}$$

IUPAC: 2-Chloroethyl propanoate
Common: 2-Chloroethyl propionate



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$$

Ethyl 2-methylpropanoate
Ethyl α-methylpropionate



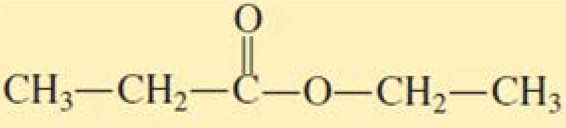
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3$$

IUPAC: Methyl 3-oxobutanoate
Common: Methyl β-oxobutyrate

Example: Determining IUPAC and Common Names for Esters

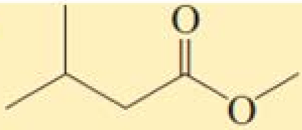
Assign both IUPAC and common names to the following esters.

a.

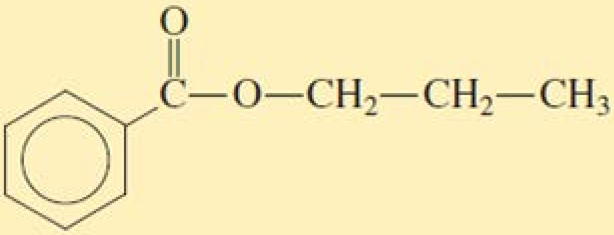


$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$$

b.



c.



$C_6H_5-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$

a. *ethyl propanoate (IUPAC) or ethyl propionate (common)*

b. *methyl 3-methylbutanoate* (IUPAC) or *methyl* β*-methylbutyrate* (common)

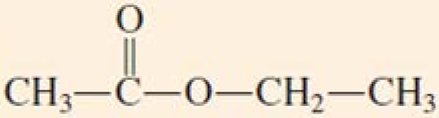
c. *propyl benzoate*

The name propyl characterizes the alkyl part of the molecule. The name of the acyl part of the molecule is derived from benzoic acid (both IUPAC and common name). Hence the ester name in both systems is propyl benzoate

Practical Exercise

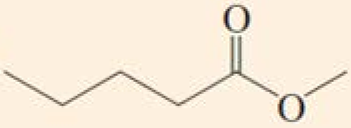
Assign both IUPAC and common names to the following esters.

a.

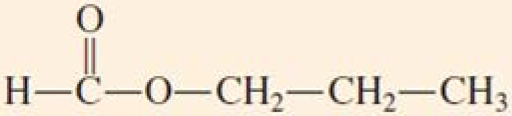


$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$

b.



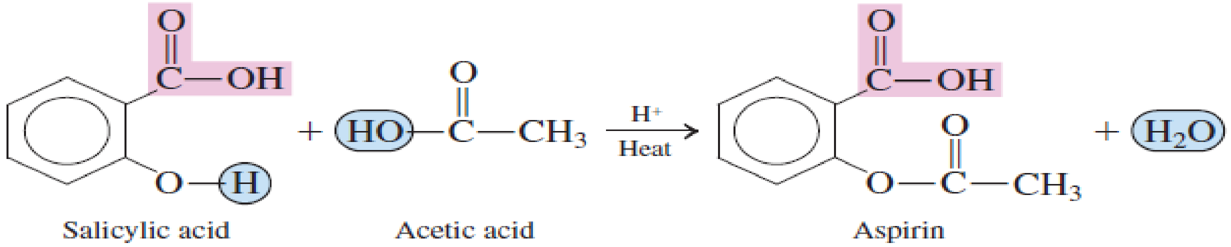
c.



$H-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3$

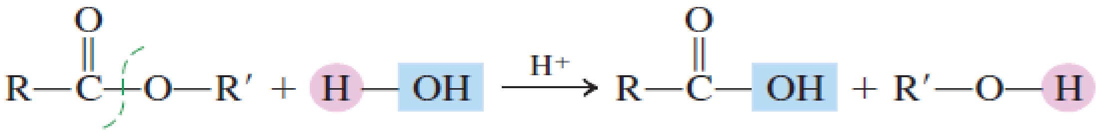
Answers: **a.** Ethyl ethanoate, ethyl acetate; **b.** Methyl pentanoate, methyl valerate; **c.** Propyl methanoate, propyl formate

Reaction of acetic acid with the alcohol group of salicylic acid produces aspirin

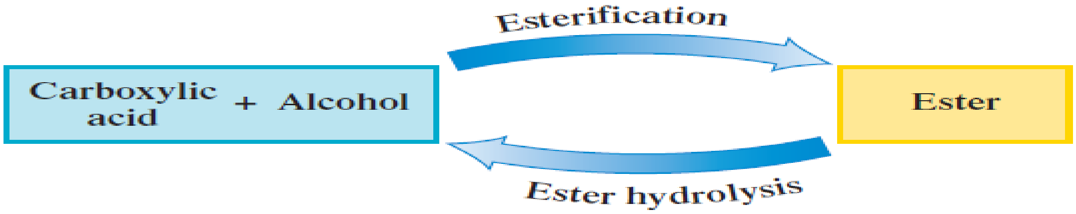


Ester Hydrolysis

In ester hydrolysis, an ester reacts with water, producing the carboxylic acid and alcohol from which the ester was formed.



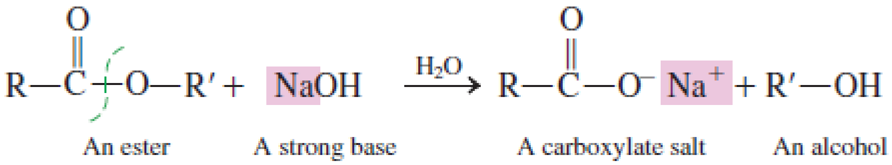
This reaction process is called either ester hydrolysis or ester saponification, depending on reaction conditions.



Ester Saponification

*A **saponification reaction** is the hydrolysis of an organic compound, under basic conditions, in which a carboxylic acid salt is one of the products.*

In ester saponification, either NaOH or KOH is used as the base and the saponification products are an alcohol and a carboxylic acid salt. (Any carboxylic acid product formed is converted to its salt because of the basic reaction conditions.)



Chapter 6: Amines and Amides

6.1 Structure and Classification of Amines

An **amine** *is an organic derivative of ammonia (NH_3) in which one or more alkyl, cyclo- alkyl, or aryl groups have replaced ammonia hydrogen atoms.* Amines are classified as primary (1°), secondary (2°), or tertiary (3°) on the basis of how many hydrocarbon groups have replaced ammonia hydrogen atoms.

A **primary amine** *is an amine in which the nitrogen atom is bonded to one hydrocarbon group and two hydrogen atoms.* The generalized formula for a primary amine is RNH_2; one carbon–nitrogen bond is present.

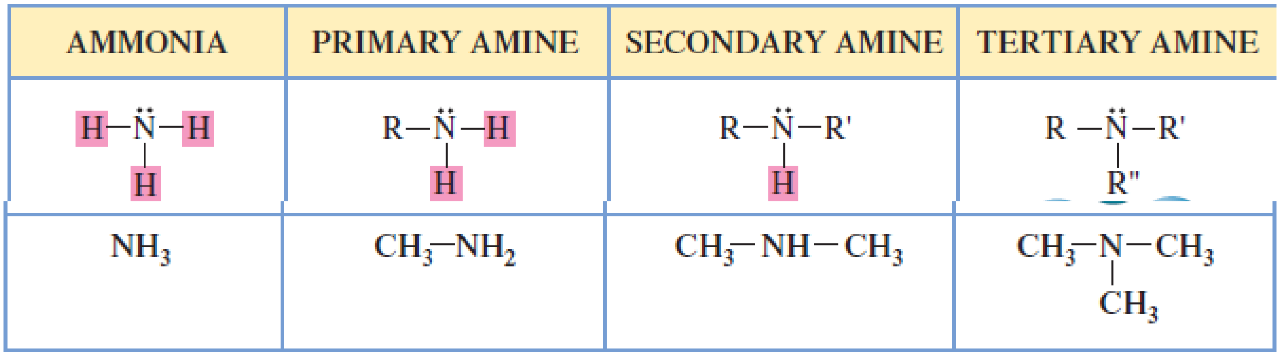
A **secondary amine** *is an amine in which the nitrogen atom is bonded to two hydrocarbon groups and one hydrogen atom.* The generalized formula for a secondary amine is R_2NH; two carbon–nitrogen bonds are present.

A **tertiary amine** *is an amine in which the nitrogen atom is bonded to three hydrocarbon groups and no hydrogen atoms.* The generalized formula for a tertiary amine is R_3N; three carbon–nitrogen bonds are present.

The basis for the amine primary-secondary-tertiary classification system differs from that for alcohols

1. For alcohols how many R groups are on a *carbon* atom, the hydroxyl-bearing carbon atom is the determining factor.
2. For amines how many R groups are on the *nitrogen* atom is the determining factor.

Tert-butyl alcohol is a *tertiary* alcohol, whereas *tert*-butylamine is a *primary* amine

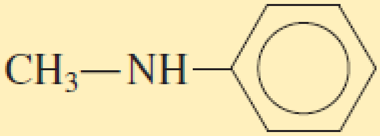


AMMONIA	PRIMARY AMINE	SECONDARY AMINE	TERTIARY AMINE
$\begin{array}{c} \mathrm{H-\ddot{N}-H} \\ \mid \\ \mathrm{H} \end{array}$	$\begin{array}{c} \mathrm{R-\ddot{N}-H} \\ \mid \\ \mathrm{H} \end{array}$	$\begin{array}{c} \mathrm{R-\ddot{N}-R'} \\ \mid \\ \mathrm{H} \end{array}$	$\begin{array}{c} \mathrm{R-\ddot{N}-R'} \\ \mid \\ \mathrm{R''} \end{array}$
NH_3	CH_3-NH_2	$CH_3-NH-CH_3$	$\begin{array}{c} \mathrm{CH_3-N-CH_3} \\ \mid \\ \mathrm{CH_3} \end{array}$

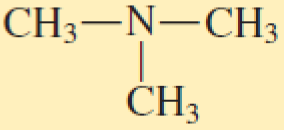
Example: Classifying Amines as Primary, Secondary, or Tertiary

Classify each of the following amines as a primary, secondary, or tertiary amine

a.

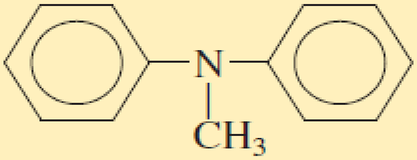


b.

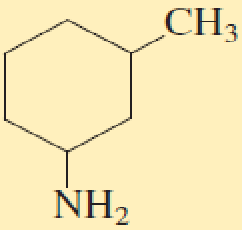


$$\begin{array}{c} \mathrm{CH_3-N-CH_3} \\ \mid \\ \mathrm{CH_3} \end{array}$$

c.



d.

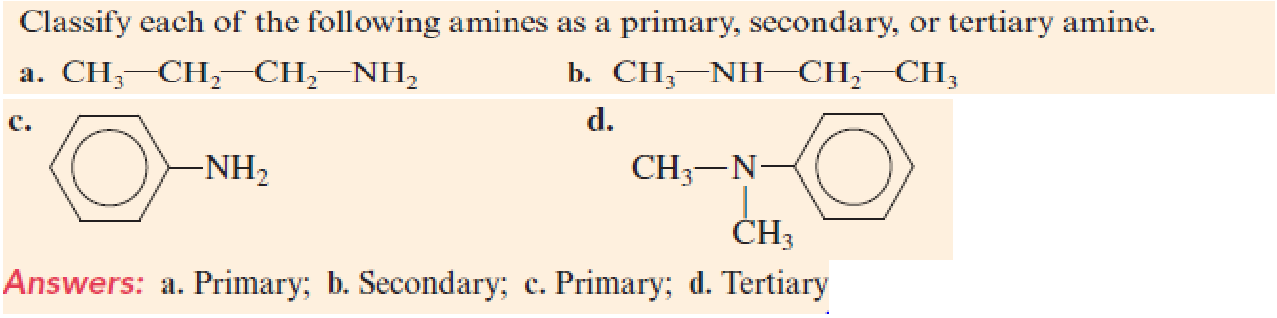


Solution

The number of carbon atoms directly bonded to the nitrogen atom determines the amine classification.

- *a.* *This is a secondary amine because the nitrogen is bonded to both a methyl group and a phenyl group.*
- *b.* *This is a tertiary amine because the nitrogen atom is bonded to three methyl groups.*
- *c.* *This is also a tertiary amine; the nitrogen atom is bonded to two phenyl groups and a methyl group.*
- *d.* *This is a primary amine. The nitrogen atom is bonded to only one carbon atom, a carbon atom in the ring structure.*

Practical Exercise



Classify each of the following amines as a primary, secondary, or tertiary amine.

a. $CH_3—CH_2—CH_2—NH_2$ **b.** $CH_3—NH—CH_2—CH_3$

c. **d.**

Answers: **a.** Primary; **b.** Secondary; **c.** Primary; **d.** Tertiary

6.2 Nomenclature for Amines

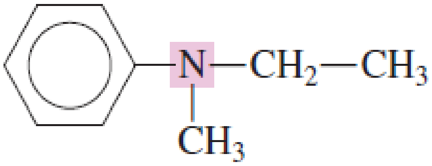
Both common and IUPAC names are extensively used for amines. In the common system of nomenclature, amines are named by listing the alkyl group or groups attached to the nitrogen atom in alphabetical order and adding the suffix -amine; all of this appears as one word. Prefixes such as di- and tri- are added when identical groups are bonded to the nitrogen atom.

$CH_3—CH_2—NH_2$

Ethylamine

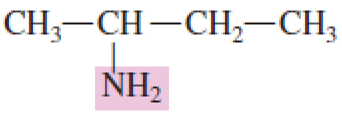
$CH_3—NH—CH_3$

Dimethylamine



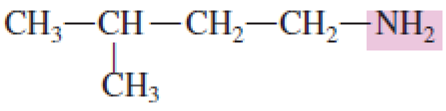
Ethylmethylphenylamine

The IUPAC rules for naming amines are similar to those for alcohols. Alcohols are named as alkanols and amines are named as alkanamines. IUPAC rules for naming primary amines are as follows:



$$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_2-CH_3$$

2-Butanamine



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-NH_2$$

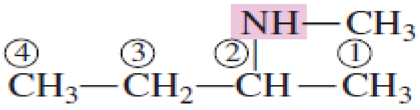
3-Methyl-1-butanamine

In diamines, the final *-e* of the carbon chain name is retained for ease of pronunciation. Thus the base name for a four-carbon chain bearing two amino groups is butan*e*diamine.

$$H_2N-CH_2-CH_2-CH_2-CH_2-NH_2$$

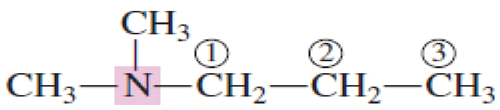
1,4-Butanediamine

Secondary and tertiary amines are named as *N*-substituted primary amines. The largest carbon group bonded to the nitrogen is used as the parent amine name. The names of the other groups attached to the nitrogen are appended to the front of the base name, and *N*- or *N; N*- prefixes are used to indicate that these groups are attached to the nitrogen atom rather than to the base carbon chain.



$$\overset{④}{CH_3}-\overset{③}{CH_2}-\overset{\displaystyle NH-CH_3}{\overset{|}{\overset{②}{CH}}}-\overset{①}{CH_3}$$

N-Methyl-2-butanamine

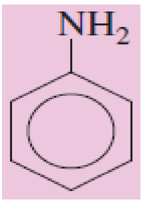


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{N}}-\overset{①}{CH_2}-\overset{②}{CH_2}-\overset{③}{CH_3}$$

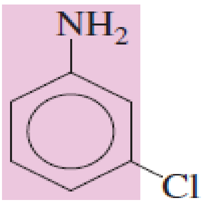
N,N-Dimethyl-1-propanamine

In amines where additional functional groups are present, the amine group is treated as a substituent. As a substituent, an -NH_2 group is called an *amino* group.

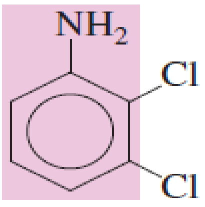
The simplest aromatic amine, a benzene ring bearing an amino group, is called *aniline*. Other simple aromatic amines are named as derivatives of aniline.



Aniline



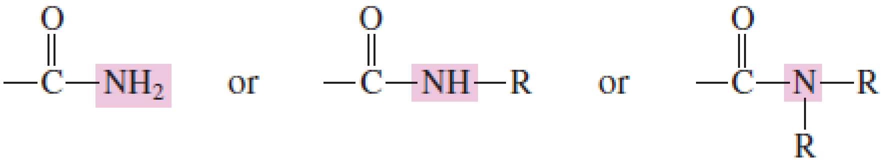
m-Chloroaniline



2,3-Dichloroaniline

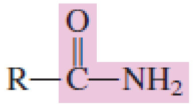
6.3 Structure and Classification of Amides

An **amide** *is a carboxylic acid derivative in which the carboxyl -OH group has been replaced with an amino or a substituted amino group.* The amide functional group is thus depending on the degree of substitution



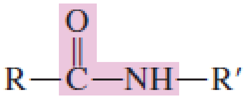
$$-\overset{O}{\overset{\|}{C}}-NH_2 \quad \text{or} \quad -\overset{O}{\overset{\|}{C}}-NH-R \quad \text{or} \quad -\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{N}}-R$$

Amides, like amines, can be classified as primary (1°), secondary (2°), or tertiary (3°), depending on how many hydrogen atoms are attached to the nitrogen atom.



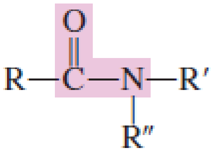
$R-\overset{O}{\overset{\|}{C}}-NH_2$

Primary amide



$R-\overset{O}{\overset{\|}{C}}-NH-R'$

Secondary amide



$R-\overset{O}{\overset{\|}{C}}-\underset{R''}{\underset{|}{N}}-R'$

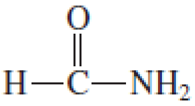
Tertiary amide

A **primary amide** *is an amide in which two hydrogen atoms are bonded to the amide nitrogen atom.* Such amides are also called *unsubstituted* amides.

A **secondary amide** *is an amide in which an alkyl (or aryl) group and a hydrogen atom are bonded to the amide nitrogen atom. Monosubstituted* amide is another name for this type of amide.

A **tertiary amide** *is an amide in which two alkyl (or aryl) groups and no hydrogen atoms are bonded to the amide nitrogen atom.* Such amides are *disubstituted* amides.

The simplest amide has a hydrogen atom attached to an unsubstituted amide functional group



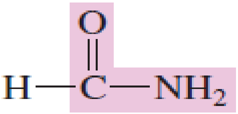
$$H-\overset{O}{\overset{\|}{C}}-NH_2$$

6.4 Nomenclature for Amides

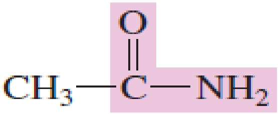
For nomenclature purposes (both IUPAC and common), amides are considered to be derivatives of carboxylic acids. Hence their names are based on the name of the parent carboxylic acid. (A similar procedure was used for naming esters. The rules are as follows:

Rule 1: *The ending of the name of the carboxylic acid is changed from* -ic acid *(common) or* -oic acid *(IUPAC) to* -amide. *For example,* benzoic acid *becomes* benzamide.

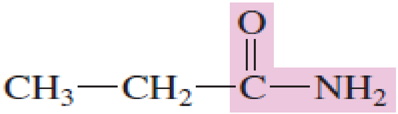
Rule 2: *The names of groups attached to the nitrogen (2° and 3° amides) are appended to the front of the base name, using an* N- *prefix as a locator.* Selected primary amide IUPAC names (with the common name in parentheses) are


$H-\overset{O}{\overset{\|}{C}}-NH_2$

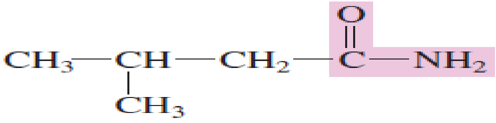
Methanamide
(formamide)


$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$

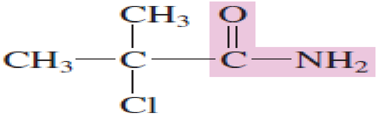
Ethanamide
(acetamide)


$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH_2$

Propanamide
(propionamide)

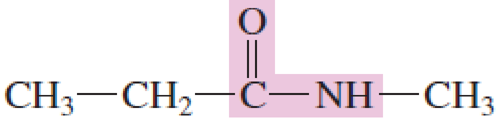

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-NH_2$

3-Methylbutanamide
(β-methylbutyramide)

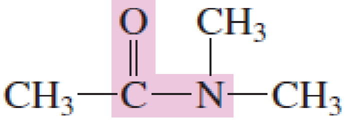

$CH_3-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-NH_2$

2-Chloro-2-methylpropanamide
(α-chloro-α-methylpropionamide)

Nomenclature for secondary and tertiary amides, amides with substituted amino groups, involves use of the prefix N-, a practice that was previously encountered with amine nomenclature.

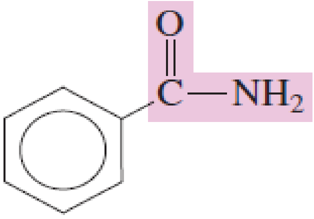

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-NH-CH_3$

N-Methylpropanamide
(*N*-methylpropionamide)

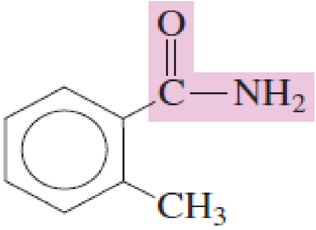

$CH_3-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{N}}-CH_3$

N,*N*-Dimethylethanamide
(*N*,*N*-dimethylacetamide)

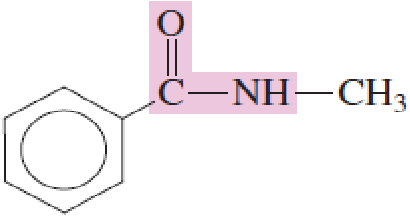
The simplest aromatic amide, a benzene ring bearing an unsubstituted amide group, is called benzamide. Other aromatic amides are named as benzamide derivatives.



Benzamide



2-Methylbenzamide

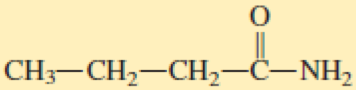


N-Methylbenzamide

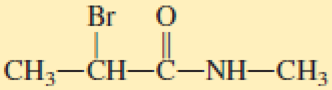
When an amide functional group is attached to a nonaromatic ring, the suffixcarboxamide is used in the name.

Assign both common and IUPAC names to each of the following amides.

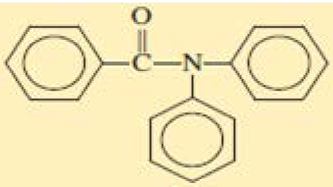
a.


$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH_2$

b.


$CH_3-\overset{Br}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-NH-CH_3$

c.



d.

Solution

a. The parent acid for this amide is butyric acid (common) or butanoic acid (IUPAC). The common name for this amide is *butyramide,* and the IUPAC name is *butanamide.*

b. The common and IUPAC names of the acid are very similar; they are propionic acid and propanoic acid, respectively. The common name for this amide is *α-bromo-N-methylpropionamide,* and the IUPAC name is *2-bromo-N-methylpropanamide.* The prefix *N-* must be used with the methyl group to indicate that it is attached to the nitrogen atom.

c. In both the common and IUPAC systems of nomenclature, the name of the parent acid is the same: benzoic acid. The name of the amide is *N,N-diphenylbenzamide.*

d. The amide is derived from valeric acid (common name) or pentanoic acid (IUPAC name). The complete name must take into account the presence of the methyl group on the carbon chain. The amide's common name is *β-methylvaleramide* and its IUPAC name is *3-methylpentanamide.*

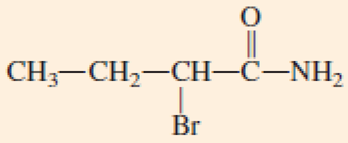
c. In both the common and IUPAC systems of nomenclature, the name of the parent acid is the same: benzoic acid. The name of the amide is *N,N-diphenylbenzamide.*

d. The amide is derived from valeric acid (common name) or pentanoic acid (IUPAC name). The complete name must take into account the presence of the methyl group on the carbon chain. The amide's common name is *β-methylvaleramide* and its IUPAC name is *3-methylpentanamide.*

Practical Exercise

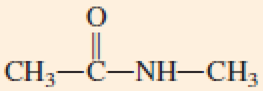
Assign both common and IUPAC names to each of the following amides.

a.



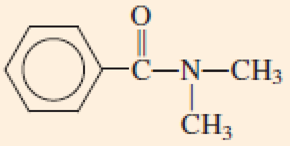
$CH_3-CH_2-\underset{\substack{|\\ Br}}{CH}-\overset{\substack{O\\ \|}}{C}-NH_2$

b.

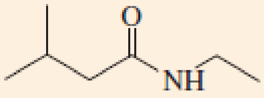


$CH_3-\overset{\substack{O\\ \|}}{C}-NH-CH_3$

c.



d.



Answers: **a.** α-bromobutyramide, 2-bromobutanamide; **b.** *N*-methylacetamide, *N*-methylethanamide; **c.** *N,N*-dimethylbenzamide (both common and IUPAC name); **d.** *N*-ethyl-β-methylbutyramide, *N*-ethyl-3-methylbutanamide

6.5 Preparation of Amides

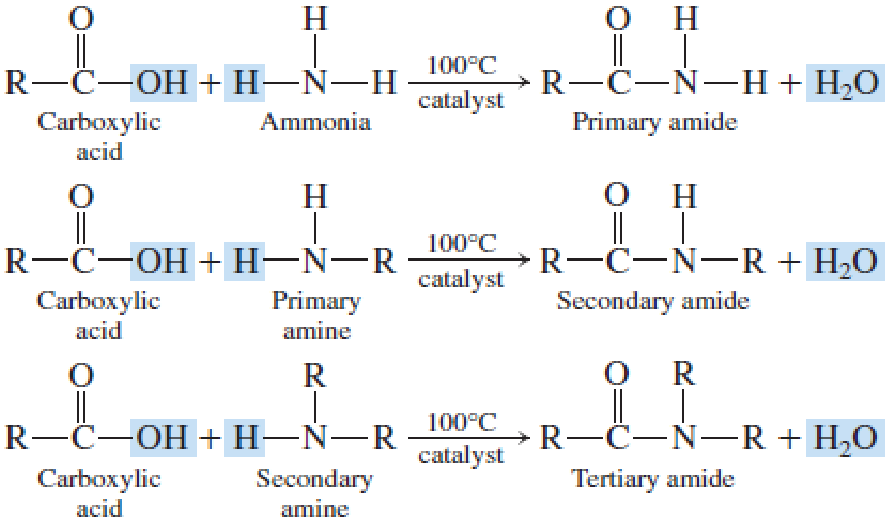
The reaction of a carboxylic acid with ammonia or a 1° or 2°amine produces an amide, provided that the reaction is carried out at an elevated temperature (greater than 100°C) and a dehydrating agent is present.

$$\text{Ammonia} + \text{carboxylic acid} \xrightarrow[\text{Catalyst}]{100^\circ\text{C}} 1^\circ \text{ amide}$$

$$1^\circ \text{ Amine} + \text{carboxylic acid} \xrightarrow[\text{Catalyst}]{100^\circ\text{C}} 2^\circ \text{ amide}$$

$$2^\circ \text{ Amine} + \text{carboxylic acid} \xrightarrow[\text{Catalyst}]{100^\circ\text{C}} 3^\circ \text{ amide}$$

General structural equations for 1°, 2°, and 3° amide production from carboxylic acids are



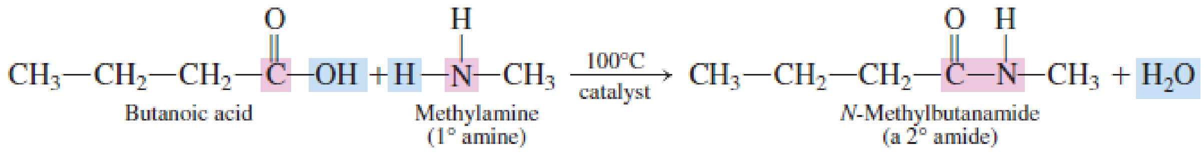
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-\overset{\overset{\displaystyle H}{|}}{N}-H \xrightarrow[\text{catalyst}]{100^\circ\text{C}} R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-H + H_2O$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-\overset{\overset{\displaystyle H}{|}}{N}-R \xrightarrow[\text{catalyst}]{100^\circ\text{C}} R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-R + H_2O$$

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-\overset{\overset{\displaystyle R}{|}}{N}-R \xrightarrow[\text{catalyst}]{100^\circ\text{C}} R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R}{|}}{N}-R + H_2O$$

Amidification reaction

These reactions are called amidification reactions. An ***amidification reaction*** *is the reaction of a carboxylic acid with an amine (or ammonia) to produce an amide. In amidification, an -OH group is lost from the carboxylic acid, a -H atom is lost from the ammonia or amine, and water is formed as a by-product. Amidification reactions are thus condensation reactions. Two specific amidification reactions, in which a 2° amide and a 3° amide are produced, respectively, are*



$$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-\overset{\overset{\displaystyle H}{|}}{N}-CH_3 \xrightarrow[\text{catalyst}]{100^\circ\text{C}} CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-CH_3 + H_2O$$