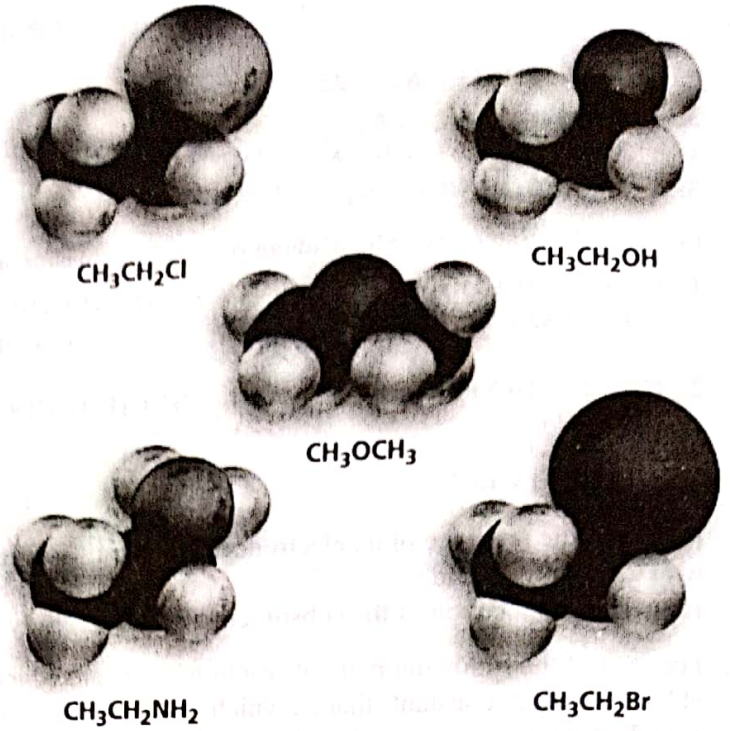
CHAPTER 2

An Introduction to Organic Compounds:

Nomenclature, Physical Properties, and Representation of Structure



This book organizes organic chemistry according to how organic compounds react. However, we must not forget that whenever an organic compound undergoes a reaction, a new organic compound is synthesized. In other words, while we are learning how organic compounds react, we will also be learning how to synthesize new compounds.

$$\underset{\text{Y is reacting}}{Y} \longrightarrow \underset{\text{Z is being synthesized}}{Z}$$

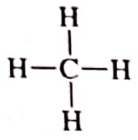
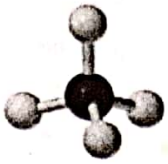
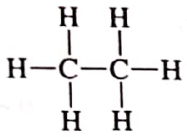
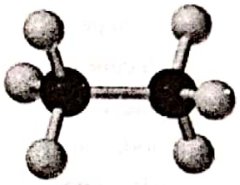
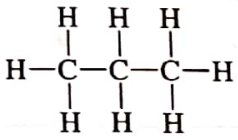
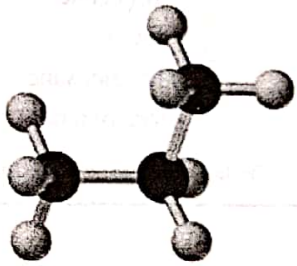
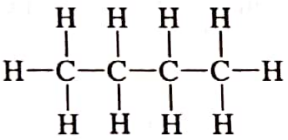
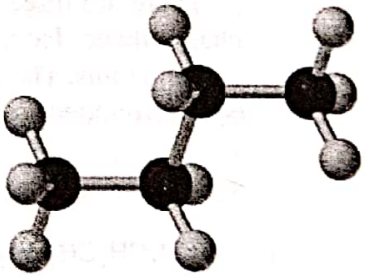
The main classes of compounds that are synthesized by the reactions we will study in Chapters 3–11 are alkanes, alkyl halides, ethers, alcohols, and amines. As we learn how to synthesize compounds, we will need to be able to refer to them by name. So we will begin our study of organic chemistry by learning how to name these five classes of compounds.

First we will learn how to name alkanes because they form the basis for the names of almost all organic compounds. **Alkanes** are composed of only carbon atoms and hydrogen atoms and contain only single bonds. (A **hydrocarbon** is a compound that is composed of only carbon and hydrogen, so an alkane is a hydrocarbon that has only single bonds.) Alkanes in which the carbons form a continuous chain with no branches are called **straight-chain alkanes.** The names of several straight-chain alkanes are given in Table 2.1. It is important that you learn the names of at least the first 10.

The family of alkanes shown in Table 2.1 is an example of a homologous series. A **homologous series** (*homos* is Greek for "the same as") is a family of compounds in which each member differs from the next by one **methylene (CH_2) group.** The members of a homologous series are called **homologs.** Propane ($CH_3CH_2CH_3$) and butane ($CH_3CH_2CH_2CH_3$) are homologs.

By looking at the relative numbers of carbon and hydrogen atoms in the alkanes listed in Table 2.1, you can conclude that the general molecular formula for an alkane is C_nH_{2n+2}, where n is any integer. So, if an alkane has one carbon atom, it must

have four hydrogen atoms; if it has two carbon atoms, it must have six hydrogens. We have seen that carbon forms four covalent bonds and hydrogen forms only one covalent bond (Section 1.4). This means that there is only one possible structure for an alkane with molecular formula CH_4 (methane), and only one structure for an alkane with molecular formula C_2H_6 (ethane). We have examined the structures of these compounds in Section 1.7. There is also only one structure for an alkane with molecular formula C_3H_8 (propane).

name	Kekulé structure	condensed structure	ball-and-stick model
methane		CH_4	
ethane		CH_3CH_3	
propane		$CH_3CH_2CH_3$	
butane		$CH_3CH_2CH_2CH_3$	


3-D Molecules: Propane; Butane

As the number of carbons in the alkane increases, the number of possible structures also increases. There are two possible structures for an alkane with molecular formula C_4H_{10}. In addition to butane—a straight-chain alkane—there is a branched butane called isobutane. Both of these structures fulfill the requirement that each carbon bonds to four atoms and each hydrogen forms only one bond.

Compounds such as butane and isobutane that have the same molecular formula but differ in the order in which the atoms are connected are called **constitutional isomers** (their molecules have different constitutions). In fact, isobutane got its name because it is an "iso"mer of butane. The structural unit with two methyl groups and a hydrogen bonded to a carbon that occurs in isobutane has come to be called "iso." Thus, the name isobutane tells you that it is a four-carbon alkane with an iso structural unit.

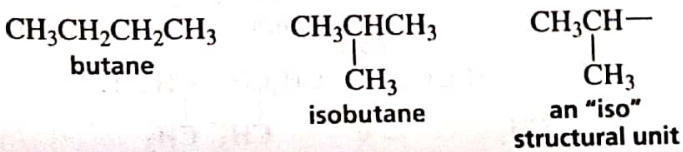
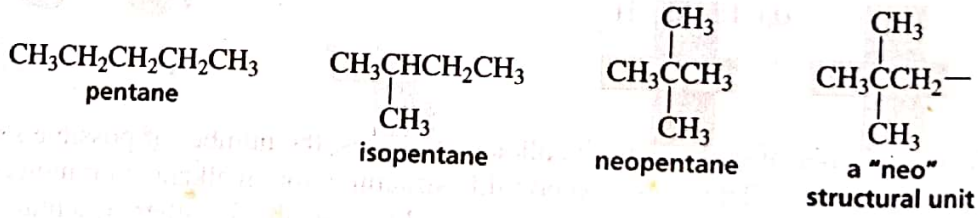


TABLE 2.1 Nomenclature and Physical Properties of Straight-Chain Alkanes

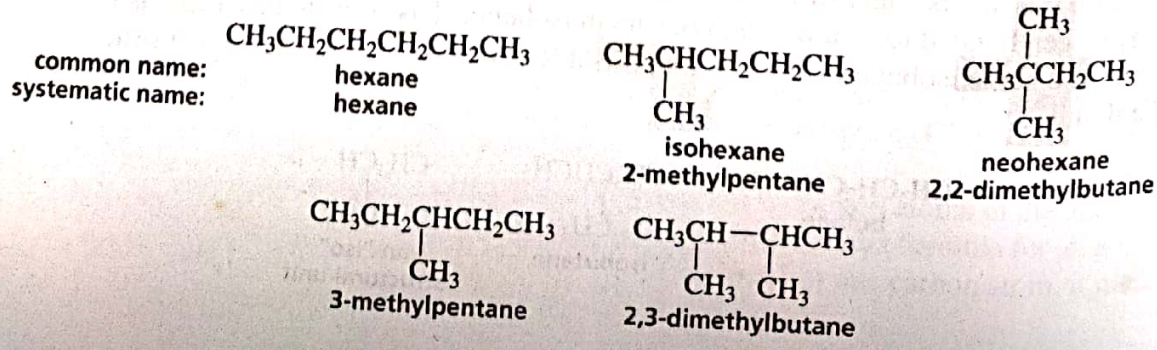
Number of carbons	Molecular formula	Name	Condensed structure	Boiling point (°C)	Melting point (°C)	Density[a] (g/mL)
1	CH_4	methane	CH_4	−167.7	−182.5	
2	C_2H_6	ethane	CH_3CH_3	−88.6	−183.3	
3	C_3H_8	propane	$CH_3CH_2CH_3$	−42.1	−187.7	
4	C_4H_{10}	butane	$CH_3CH_2CH_2CH_3$	−0.5	−138.3	
5	C_5H_{12}	pentane	$CH_3(CH_2)_3CH_3$	36.1	−129.8	0.5572
6	C_6H_{14}	hexane	$CH_3(CH_2)_4CH_3$	68.7	−95.3	0.6603
7	C_7H_{16}	heptane	$CH_3(CH_2)_5CH_3$	98.4	−90.6	0.6837
8	C_8H_{18}	octane	$CH_3(CH_2)_6CH_3$	127.7	−56.8	0.7026
9	C_9H_{20}	nonane	$CH_3(CH_2)_7CH_3$	150.8	−53.5	0.7177
10	$C_{10}H_{22}$	decane	$CH_3(CH_2)_8CH_3$	174.0	−29.7	0.7299
11	$C_{11}H_{24}$	undecane	$CH_3(CH_2)_9CH_3$	195.8	−25.6	0.7402
12	$C_{12}H_{26}$	dodecane	$CH_3(CH_2)_{10}CH_3$	216.3	−9.6	0.7487
13	$C_{13}H_{28}$	tridecane	$CH_3(CH_2)_{11}CH_3$	235.4	−5.5	0.7546
20	$C_{20}H_{42}$	eicosane	$CH_3(CH_2)_{18}CH_3$	343.0	36.8	0.7886
21	$C_{21}H_{44}$	heneicosane	$CH_3(CH_2)_{19}CH_3$	356.5	40.5	0.7917
30	$C_{30}H_{62}$	triacontane	$CH_3(CH_2)_{28}CH_3$	449.7	65.8	0.8097

[a]Density is temperature-dependent. The densities given are those determined at 20 °C ($d^{20°}$).

There are three alkanes with molecular formula C_5H_{12}. Pentane is the straight-chain alkane. Isopentane, as its name indicates, has an iso structural unit and five carbon atoms. The third isomer is called neopentane. The structural unit with a carbon surrounded by four other carbons is called "neo."

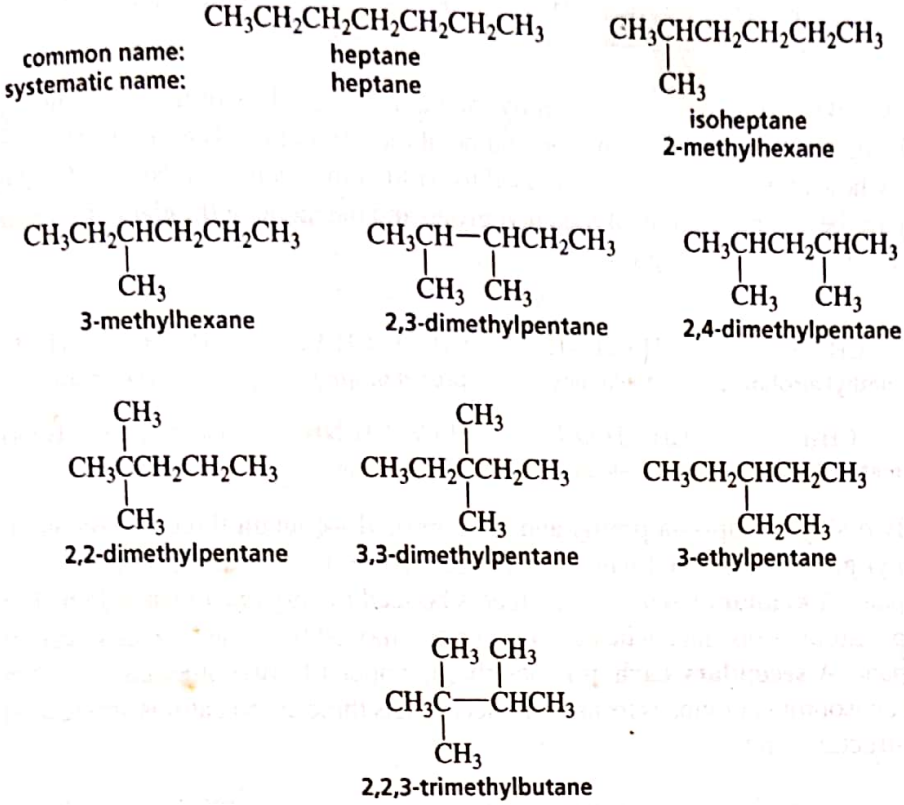


There are five isomers with molecular formula C_6H_{14}. We are now able to name three of them (hexane, isohexane, and neohexane), but we cannot name the other two without defining names for new structural units. (At this point, ignore the names written in blue.)



There are nine isomers with molecular formula C_7H_{16}. We can name only two of them (heptane and isoheptane) without defining new structural units. Notice that neoheptane cannot be used as a name because three different heptanes have a carbon that is bonded to four other carbons and *a name must be specific to only one compound.*

A compound can have more than one name, but a name must specify only one compound.

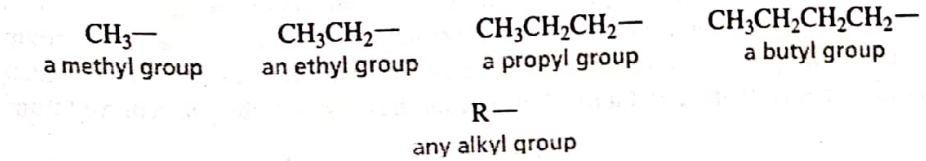


The number of different structural units increases rapidly as the number of carbons in an alkane increases. For example, there are 75 alkanes with molecular formula $C_{10}H_{22}$ and 4347 alkanes with molecular formula $C_{15}H_{32}$. To avoid having to memorize the names of many different structural units, chemists have devised rules that name compounds on the basis of their structures. This way, only the rules have to be learned. Because the name is based on the structure, these rules make it possilbe to deduce the structure of a compound from its name.

This method of nomenclature is called **systematic nomenclature.** It is also called **IUPAC nomenclature** because it was designed by a commission of the International Union of Pure and Applied Chemistry (abbreviated IUPAC and pronounced "Eye-You-Pack") at a meeting in Geneva, Switzerland, in 1892. The IUPAC rules have been continually revised by the commission since then. Names such as isobutane and neopentane—nonsystematic names—are called **common names** and are shown in red in this text. The systematic or IUPAC names are shown in blue for all of the alkanes with six and seven carbon atoms. Before we can understand how an IUPAC name for an alkane is constructed, we must learn how to name alkyl substituents.

2.1 NOMENCLATURE OF ALKYL SUBSTITUENTS

Removal of a hydrogen from an alkane results in an **alkyl substituent** (or an alkyl group). Alkyl substituents are named by replacing the "ane" ending of the alkane with "yl." The letter "R" is used to indicate any alkyl group.



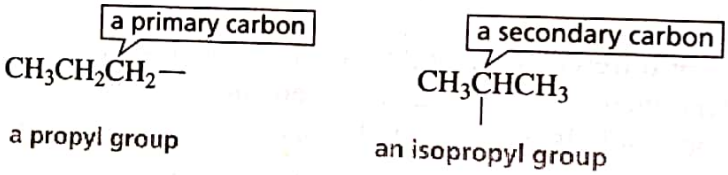
If a hydrogen of an alkane is replaced by an OH, the compound becomes an **alcohol;** if it is replaced by an NH_2, the compound becomes an **amine;** and if it is replaced by a halogen, the compound becomes an **alkyl halide.**

R—OH	R—NH_2	R—X	X = F, Cl, Br, or I
an alcohol	an amine	an alkyl halide	

An alkyl group name followed by the name of the class of the compound (alcohol, amine, etc.) yields the common name of the compound. The following examples show how alkyl group names are used to build common names. Notice that there is a space between the name of the alkyl group and the name of the class of compound, except in the case of amines.

CH_3OH	$CH_3CH_2NH_2$	$CH_3CH_2CH_2Br$	$CH_3CH_2CH_2CH_2Cl$
methyl alcohol	**ethylamine**	**propyl bromide**	**butyl chloride**
CH_3I	CH_3CH_2OH	$CH_3CH_2CH_2NH_2$	$CH_3CH_2CH_2CH_2OH$
methyl iodide	**ethyl alcohol**	**propylamine**	**butyl alcohol**

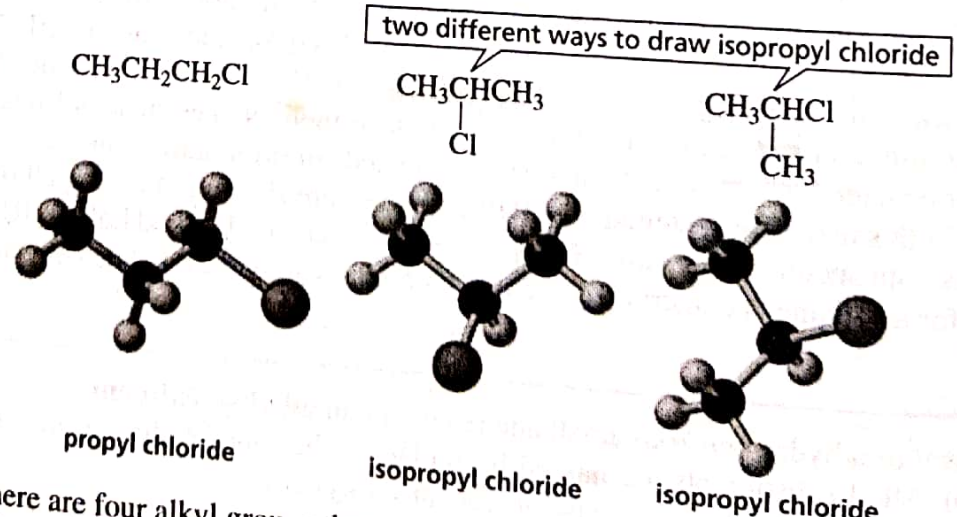
Two alkyl groups—a propyl and an isopropyl—contain three carbon atoms. A propyl group is obtained when a hydrogen is removed from a primary carbon of propane. A **primary carbon** is one that is bonded to only one other carbon. An isopropyl group is obtained when a hydrogen is removed from the secondary carbon of propane. A **secondary carbon** is one that is bonded to two other carbons. Notice that an isopropyl group, as its name indicates, has three carbon atoms arranged as an iso structural unit.



uild models of the two representations of isopropyl loride and convince yourself that they represent the ame compound.

Molecular structures can be drawn in different ways. Isopropyl chloride, for example, is drawn here in two ways. Both represent the same compound because the central carbon in each is bonded to a hydrogen, a chlorine, and two methyl groups.

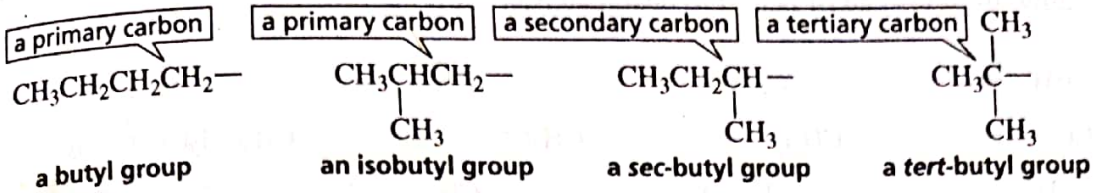
3-D Molecules: Propyl chloride; Isopropyl choride



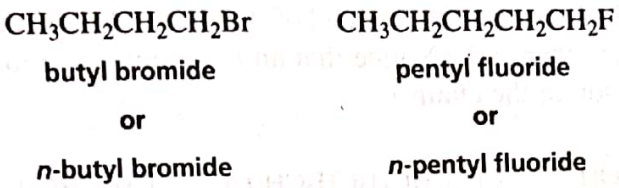
There are four alkyl groups that contain four carbons. Butyl and isobutyl groups have both had a hydrogen removed from a primary (1°) carbon. A *sec*-butyl group has had a hydrogen removed from a secondary (2°) carbon (*sec*-, often abbreviated *s*-, stands for secondary); and a *tert*-butyl group has had a hydrogen removed from

a tertiary (3°) carbon (*tert*-, sometimes abbreviated *t*-, stands for tertiary). A **tertiary carbon** is one that is bonded to three other carbons.

A primary carbon is bonded to one carbon, a secondary carbon is bonded to two carbons, and a tertiary carbon is bonded to three carbons.

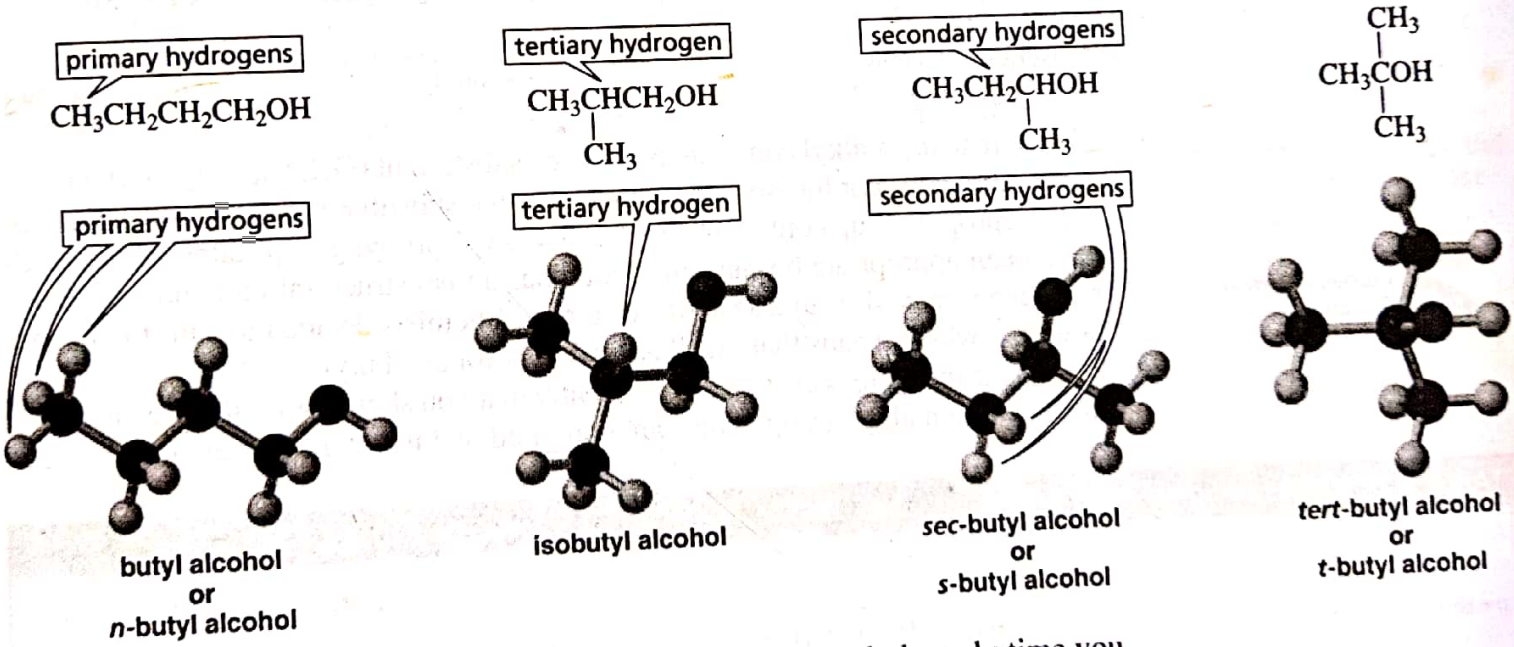


A straight-chain alkyl group is sometimes called *n*-butyl (*n* for normal) to emphasize that its four carbon atoms are in an unbranched chain. However, if the name does not have a prefix such as "*n*" or "iso," it is assumed that the carbons are in an unbranched chain.

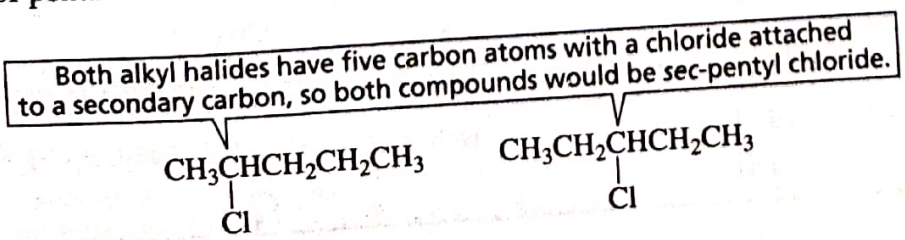


3-D Molecules: *n*-Butyl alcohol; *sec*-Butyl alcohol; *tert*-Butyl alcohol

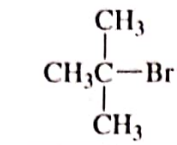
The hydrogens in a molecule are also referred to as primary, secondary, and tertiary. **Primary hydrogens** are attached to primary carbons, **secondary hydrogens** are attached to secondary carbons, and **tertiary hydrogens** are attached to tertiary carbons.

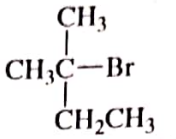


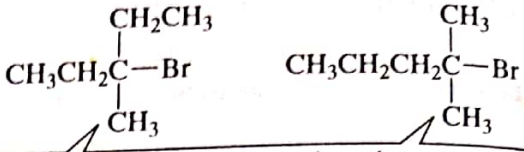
Because a chemical name must apply to only one compound, the only time you will see the prefix "*sec*" is in *sec*-butyl. The name "*sec*-pentyl" cannot be used because pentane has two different secondary carbon atoms. Therefore, there are two different alkyl groups that result from the removal of a hydrogen from a secondary carbon of pentane.



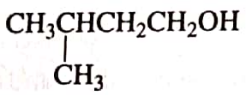
The prefix "*tert*" is found in *tert*-butyl and *tert*-pentyl because each of these substituent names describes only one alkyl group. The name "*tert*-hexyl" cannot be used because it describes two different alkyl groups. (In older literature, you might find amyl used instead of pentyl to designate five carbons.)

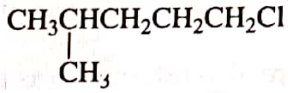

tert-butyl bromide

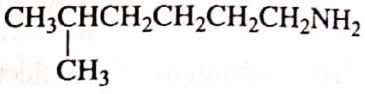

tert-pentyl bromide

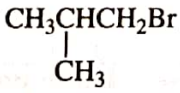

Both alkyl bromides have six carbon atoms with a bromine attached to a tertiary carbon, so both compounds would be *tert*-hexyl bromide.

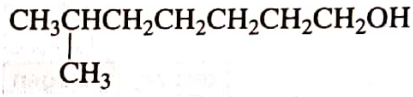
The prefix "iso" can be used regardless of the number of carbons in the alkyl group. This prefix means that there is an iso structural unit (a carbon bonded to two methyl groups and a hydrogen) at one end of the molecule, and any group replacing a hydrogen is at the other end. (Notice that an iso group has a methyl group on the next to the last carbon in the chain.)

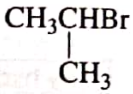

isopentyl alcohol or isoamyl alcohol


isohexyl chloride


isoheptylamine


isobutyl bromide


isooctyl alcohol


isopropyl bromide

Notice that *all* isoalkyl compounds have the substituent (OH, Cl, NH_2, etc.) on a primary carbon except for isopropyl, which has the substituent on a secondary carbon. The isopropyl group could have been called a *sec*-propyl group. Either name would have been appropriate because the group has an iso structural unit and a hydrogen has been removed from a secondary carbon. Chemists decided to call it isopropyl, however, which means that "*sec*" is used only for *sec*-butyl.


Tutorial: Common alkyl groups

Alkyl group names are used so frequently that you should learn them. Some of the most common alkyl group names are compiled in Table 2.2 for your convenience.

TABLE 2.2 Names of Some Alkyl Groups

methyl	CH_3-	*sec*-butyl	$CH_3CH_2CH(CH_3)-$	neopentyl	$CH_3C(CH_3)_2CH_2-$
ethyl	CH_3CH_2-				
propyl	$CH_3CH_2CH_2-$			hexyl	$CH_3CH_2CH_2CH_2CH_2CH_2-$
isopropyl	$CH_3CH(CH_3)-$	*tert*-butyl	$CH_3C(CH_3)_2-$	isohexyl	$CH_3CH(CH_3)CH_2CH_2CH_2-$
butyl	$CH_3CH_2CH_2CH_2-$	pentyl	$CH_3CH_2CH_2CH_2CH_2-$	heptyl	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2-$
isobutyl	$CH_3CH(CH_3)CH_2-$	isopentyl	$CH_3CH(CH_3)CH_2CH_2-$	isoheptyl	$CH_3CH(CH_3)CH_2CH_2CH_2CH_2-$

PROBLEM 1◆

Write a structure for each of the following compounds:

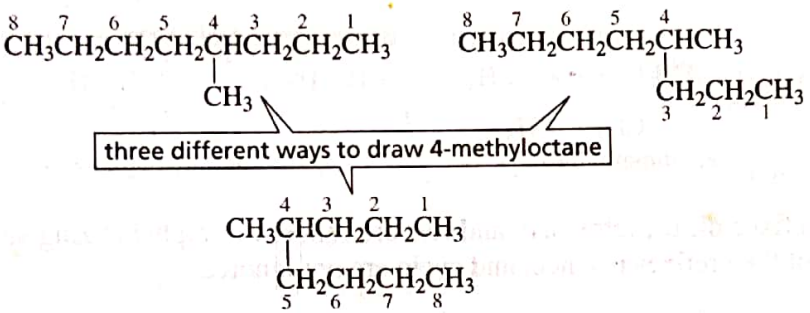
a. isopropyl alcohol
b. isopentyl fluoride
c. *sec*-butyl iodide
d. neopentyl chloride
e. *tert*-butylamine
f. isooctyl bromide

2.2 NOMENCLATURE OF ALKANES

The systematic name of an alkane is obtained using the following rules:

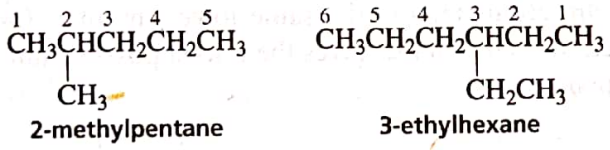
Determine the number of carbons in the longest continuous chain.

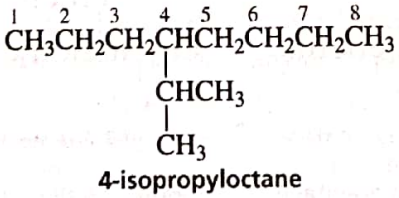
1. Determine the number of carbons in the longest continuous carbon chain. This chain is called the **parent hydrocarbon.** The alkane name indicating the number of carbons in the parent hydrocarbon becomes the alkane's "last name." Notice that the longest continuous chain is chosen regardless of how the molecule is written. Sometimes you have to "turn a corner" to obtain the longest continuous chain.



Number the chain so that the substituent gets the lowest possible number.

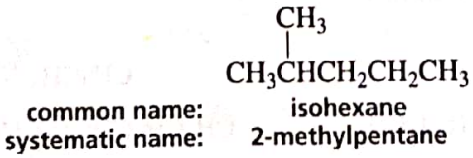
2. The name of the alkyl substituent that hangs off the parent hydrocarbon is cited before the name of the parent hydrocarbon with a number to designate the carbon to which it is attached. The chain is numbered in the direction that gives the substituent as low a number as possible. The substituent name and the name of the parent hydrocarbon are joined in one word, and there is a hyphen between the number and the substituent name.





Numbers are used only for systematic names and never for common names.

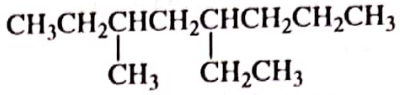
Notice that only systematic names have numbers; common names never contain numbers.



3. If more than one substituent is attached to the parent hydrocarbon, the chain is numbered in the direction that will result in the lowest possible number in the name

of the compound. The substituents are listed in alphabetical order (not numerical order), with each substituent getting the appropriate number. In the following example, the correct name (5-ethyl-3-methyloctane) contains a 3 as its lowest number, while the incorrect name (4-ethyl-6-methyloctane) contains a 4 as its lowest number.

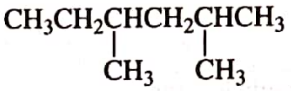
List substituents in alphabetical order.



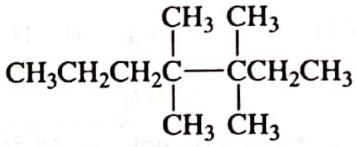
5-ethyl-3-methyloctane
not
4-ethyl-6-methyloctane
because 3 < 4

A number and a word are separated by a hyphen; numbers are separated by a comma.

If two or more substituents are the same, the prefixes di, tri, and tetra are used with the substituent names. The numbers indicating the locations of the identical substituents are cited together, separated by commas. Notice that there must be as many numbers in a name as there are substituents.



2,4-dimethylhexane

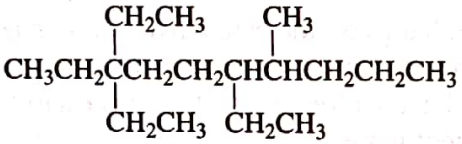


3,3,4,4-tetramethylheptane

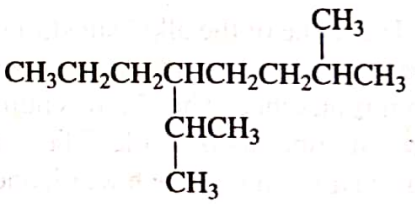
di, tri, tetra, *sec*, and *tert* are ignored in alphabetizing.

iso, neo, and cyclo are not ignored in alphabetizing.

The prefixes di, tri, tetra, *sec*, and *tert* are ignored in alphabetizing substituent groups, but the prefixes iso, neo, and cyclo are not ignored.

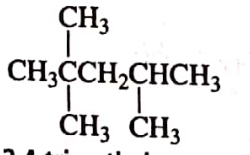


3,3,6-triethyl-7-methyldecane

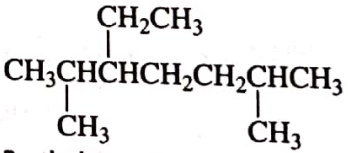


5-isopropyl-2-methyloctane

4. When both directions lead to the same lowest number for one of the substituents, the direction is chosen that gives the lowest possible number to one of the remaining substituents.



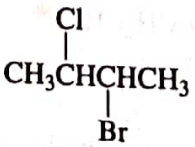
2,2,4-trimethylpentane
not
2,4,4-trimethylpentane
because 2 < 4



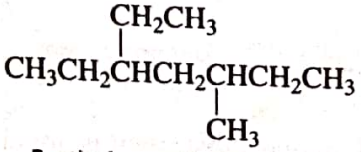
3-ethyl-2,6-dimethylheptane
not
5-ethyl-2,6-dimethylheptane
because 3 < 5

Only if the same set of numbers is obtained in both directions does the first cited group get the lower number.

5. If the same substituent numbers are obtained in both directions, the first cited group receives the lower number.



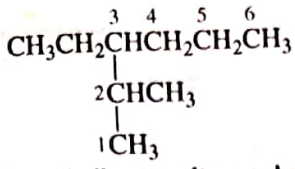
2-bromo-3-chlorobutane
not
3-bromo-2-chlorobutane



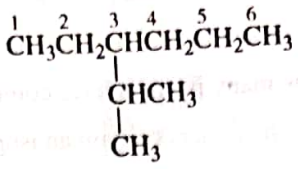
3-ethyl-5-methylheptane
not
5-ethyl-3-methylheptane

6. If a compound has two or more chains of the same length, the parent hydrocarbon is the chain with the greatest number of substituents.

In the case of two hydrocarbon chains with the same number of carbons, choose the one with the most substituents.



3-ethyl-2-methylhexane (two substituents)

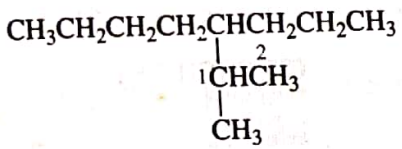


not

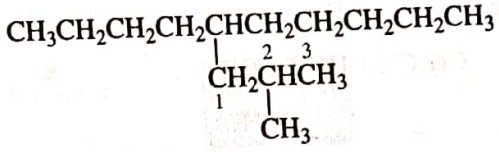
3-isopropylhexane (one substituent)

Rule 6 is why 3-ethyl-2,6-dimethylheptane (one of the examples shown for Rule 4) cannot be named 5-isopropyl-2-methylheptane.

7. Names such as isopropyl, *sec*-butyl, and *tert*-butyl are acceptable substituent names in the IUPAC system of nomenclature, but systematic substituent names are preferable. Systematic substituent names are obtained by numbering the substituent starting at the carbon that is attached to the parent hydrocarbon. This means that the carbon that is attached to the parent hydrocarbon is always the number 1 carbon of the substituent. In a compound such as 4-(1-methylethyl)octane, the substituent name is in parentheses; the number inside the parentheses indicates a position on the substituent, whereas the number outside the parentheses indicates a position on the parent hydrocarbon.

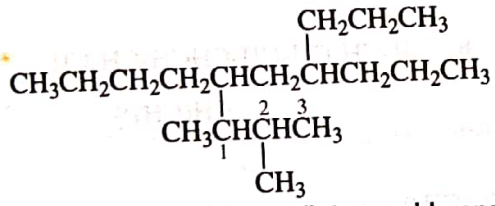


4-isopropyloctane
or
4-(1-methylethyl)octane

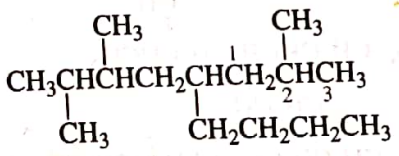


5-isobutyldecane
or
5-(2-methylpropyl)decane

Some substituents have only a systematic name.



6-(1,2-dimethylpropyl)-4-propyldecane



2,3-dimethyl-5-(2-methylpropyl)nonane
or
5-isobutyl-2, 3-dimethylnonane

These rules will allow you to name thousands of alkanes, and eventually you will learn the additional rules necessary to name many other kinds of compounds. These rules are also important if you want to look up a compound in scientific literature because it ususally will be listed by its systematic name. Nevertheless, you must still learn common names because they have been in existence for so long and are so entrenched in chemists' vocabulary that they are widely used in scientific conversation and are often found in the literature.

Tutorial: Nomenclature of alkanes

Look at the systematic names shown for the isomeric hexanes and isomeric heptanes at the beginning of this chapter to make sure you understand how they were constructed.

PROBLEM 2 ◆

Write the structure for each of the following compounds:

a. 2,3-dimethylhexane

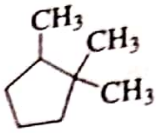
b. 4-isopropyl-2,4,5-trimethylheptane

c. 4,4-diethyldecane

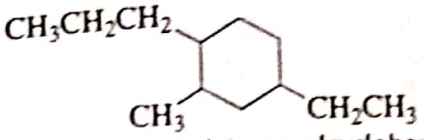
d. 2,2-dimethyl-4-propyloctane

e. 4-isobutyl-2,5-dimethyloctane

f. 4-(1,1-dimethylethyl)octane



1,1,2-trimethylcyclopentane
not
1,2,2-trimethylcyclopentane
because 1 < 2
not
1,1,5-trimethylcyclopentane
because 2 < 5



4-ethyl-2-methyl-1-propylcyclohexane
not
1-ethyl-3-methyl-4-propylcyclohexane
because 2 < 3
not
5-ethyl-1-methyl-2-propylcyclohexane
because 4 < 5

PROBLEM 5◆

Convert the following condensed structures into skeletal structures. (Remember that condensed structures show atoms but few, if any, bonds; skeletal structures show bonds but few, if any, atoms.

a. $CH_3CH_2CH_2CH_2CH_2CH_2OH$

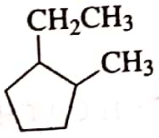
b. $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$

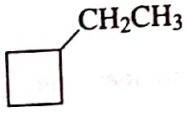
c. $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

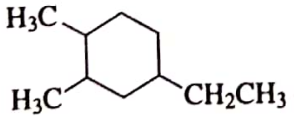
d. $CH_3CH_2CH_2CH_2OCH_3$

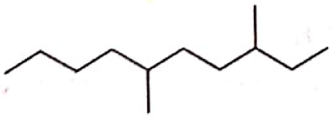
PROBLEM 6◆

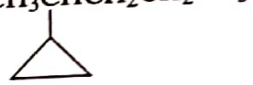
Give the systematic name for each of the following compounds:

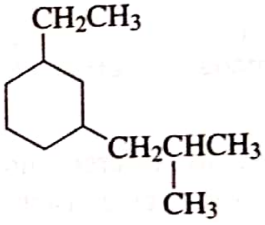
a. 

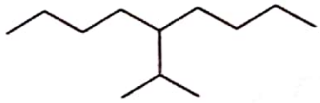
b. 

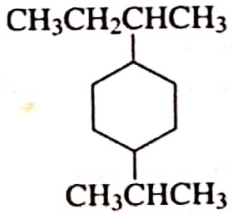
c. 

d. 

e. 

f. 

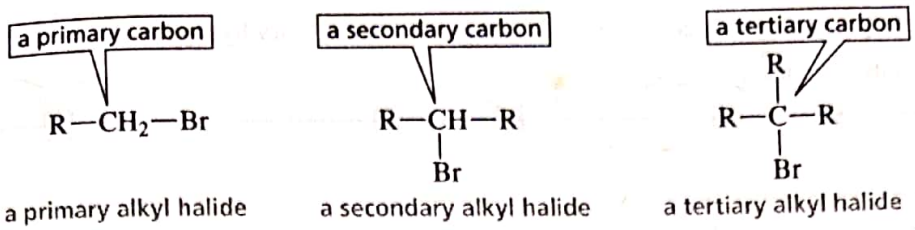
g. 

h. 

2.4 NOMENCLATURE OF ALKYL HALIDES

Alkyl halides are compounds in which a hydrogen of an alkane has been replaced by a halogen. Alkyl halides are classified as primary, secondary, or tertiary depending on the carbon to which the halogen is attached. The halogen is bonded to a primary carbon (a carbon bonded to one other carbon) in a **primary alkyl halide,** to a secondary carbon (a carbon bonded to two other carbons) in a **secondary alkyl**

halide, and to a tertiary carbon (a carbon bonded to three other carbons) in a **tertiary alkyl halide.** The nonbonding electrons on the halogens are generally not shown unless they are needed to draw your attention to some chemical property of the atom.



a primary alkyl halide — a secondary alkyl halide — a tertiary alkyl halide

The common names of alkyl halides are obtained by citing the name of the alkyl group followed by the name of the halogen.

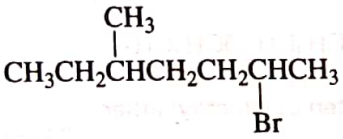
CH_3Cl — methyl chloride

CH_3CH_2F — ethyl fluoride

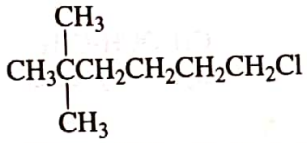
CH_3CHICH_3 — isopropyl iodide

$CH_3CH_2CHBrCH_3$ — *sec*-butyl bromide

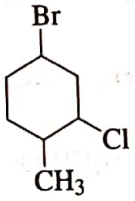
In the IUPAC system, alkyl halides are named as substituted alkanes. The substituent prefix names for the halogens replace the "ine" ending in the name of the element with "o" (i.e., fluoro, chloro, bromo, iodo). Therefore, alkyl halides are often called haloalkanes.



2-bromo-5-methylheptane



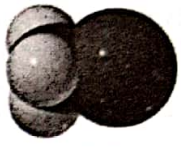
1-chloro-5,5-dimethylhexane



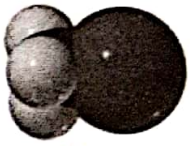
4-bromo-2-chloro-1-methylcyclohexane

CH_3F
methyl fluoride

CH_3Cl
methyl chloride



CH_3Br
methyl bromide

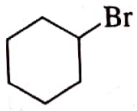


CH_3I
methyl iodide

PROBLEM 7◆

Give two names for each of the following compounds and tell whether each alkyl halide is primary, secondary, or tertiary.

a. $CH_3CH_2CHCH_3$ (Cl)

c. 

b. $CH_3CHCH_2CH_2CH_2CH_2Cl$ (CH_3)

d. CH_3CHCH_3 (F)

PROBLEM 8◆

Draw **a–c** by substituting a chlorine for a hydrogen of methylcyclohexane. Name each of the alkyl halides.

a. primary alkyl halide

b. three different secondary alkyl halides

c. a tertiary alkyl halide

3-D Molecules: Methyl fluoride; Methyl choloride; Methyl bromide; Methyl iodide

PROBLEM 10◆

a. What is the systematic (IUPAC) name for each of the following ethers?

1. $CH_3OCH_2CH_3$

2. $CH_3CH_2OCH_2CH_3$

3. $CH_3CH_2CH_2CH_2CH(OCH_3)CH_2CH_2CH_3$

4. $CH_3CH_2CH_2OCH_2CH_2CH_2CH_3$

5. $CH_3CH(CH_3)OCHCH_2CH_2CH_3$ (CH_3)

6. $CH_3CH(CH_3)OCH_2CH_2CH(CH_3)CH_3$

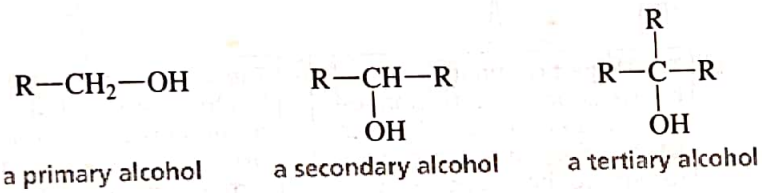
b. Do all of these ethers have common names?

c. What are their common names?

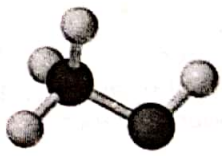
Tutorial: Nomenclature of ethers

2.6 NOMENCLATURE OF ALCOHOLS

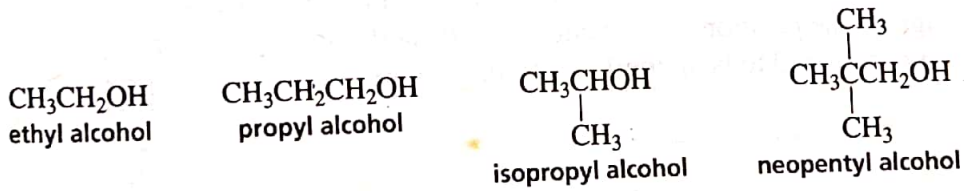
Alcohols are compounds in which a hydrogen of an alkane has been replaced by an OH group. Alcohols are classified as **primary alcohols, secondary alcohols,** or **tertiary alcohols** depending on whether the OH group is bonded to a primary, secondary, or tertiary carbon. This is similar to the way alkyl halides are classified.



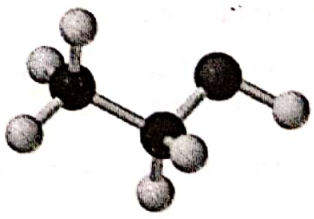
The common name of an alcohol is obtained by citing the name of the alkyl group to which the OH group is attached, followed by the word "alcohol."



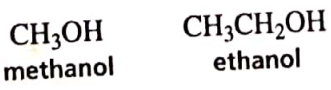
methyl alcohol



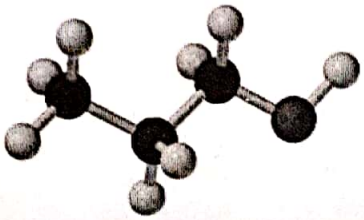
The **functional group** is the center of reactivity in a molecule. In an alcohol molecule, the OH is the functional group. The IUPAC system uses a suffix to denote certain functional groups. The systematic name of an alcohol, for example, is obtained by replacing the "e" at the end of the name of the parent hydrocarbon with the suffix "ol."



ethyl alcohol

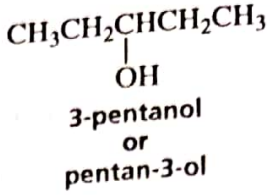


When necessary, the position of the functional group is indicated by a number immediately preceding the name of the alcohol, or immediately preceding the suffix. The most recently approved IUPAC names are those with the number immediately preceeding the suffix. However, names with the number preceding the name of the alcohol have been in use for a long time, so those are the ones most likely to



propyl alcohol

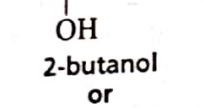
appear in the literature, on reagent bottles, and on standardized tests. Those will also appear most often in this book.



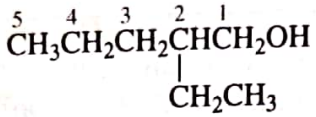
3-pentanol
or
pentan-3-ol

Use the following rules when naming a compound that has a functional group suffix:

1. The parent hydrocarbon is the longest continuous chain *containing the functional group.*
2. The parent hydrocarbon is numbered in the direction that gives the *functional group suffix the lowest possible number.*

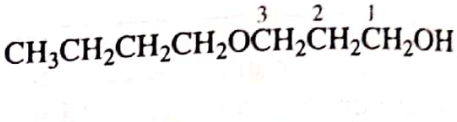


2-butanol
or
butan-2-ol



2-ethyl-1-pentanol
or
2-ethylpentan-1-ol

The longest continuous chain has six carbons, but the longest continuous chain containing the OH functional group has five carbons so the compound is named as a pentanol.



3-butoxy-1-propanol
or
3-butoxypropan-1-ol

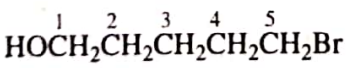
The longest continuous chain has four carbons, but the longest continuous chain containing the OH functional group has three carbons, so the compound is named as a propanol.

When there is only a substituent, the substituent gets the lowest number.

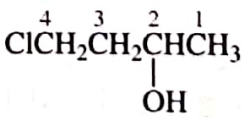
When there is only a functional group suffix, the functional group suffix gets the lowest number.

When there is a functional group suffix and a substituent, the functional group suffix gets the lowest number.

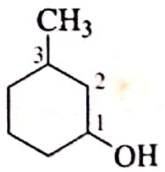
3. If there is a functional group suffix and a substituent, the functional group suffix gets the lowest possible number. Notice that a number is not needed to designate the position of a functional group suffix in a cyclic compound because it is assumed to be at the 1-position.



5-bromo-1-pentanol

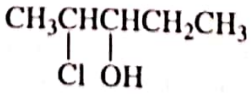


4-chloro-2-butanol

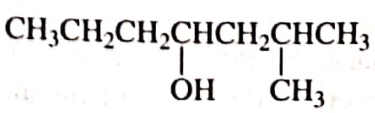


3-methylcyclohexanol

4. If the same number for the functional group suffix is obtained in both directions, the chain is numbered in the direction that gives a substituent the lowest possible number.



2-chloro-3-pentanol
not
4-chloro-3-pentanol



2-methyl-4-heptanol
not
6-methyl-4-heptanol

c. a ten-carbon compound with one π bond and two rings

d. an eight-carbon compound with three π bonds and one ring

SOLUTION TO 1a For a five-carbon hydrocarbon with no π bonds and no rings, $C_nH_{2n+2} = C_5H_{12}$; a five-carbon hydrocarbon with $(\pi + r) = 2$, has four fewer hydrogens because two hydrogens are subtracted for every π bond or ring present in the compound. Therefore, its molecular formula is C_5H_8.

PROBLEM 2 / SOLVED ◆

Determine $(\pi + r)$ for the hydrocarbons with the following molecular formulas:

a. $C_{10}H_{16}$ b. $C_{20}H_{34}$ c. C_8H_{16} d. $C_{12}H_{20}$

SOLUTION TO 2a For a ten-carbon hydrocarbon with no π bonds and no rings, $C_nH_{2n+2} = C_{10}H_{22}$. Thus, a ten-carbon compound with molecular formula $C_{10}H_{16}$ has six fewer hydrogens. Therefore, $(\pi + r) = 3$.

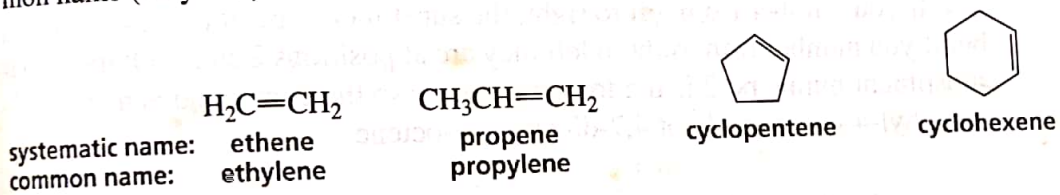
PROBLEM 3

Draw possible structures for compounds with the following molecular formulas:

a. C_3H_6 b. C_3H_4 c. C_4H_6

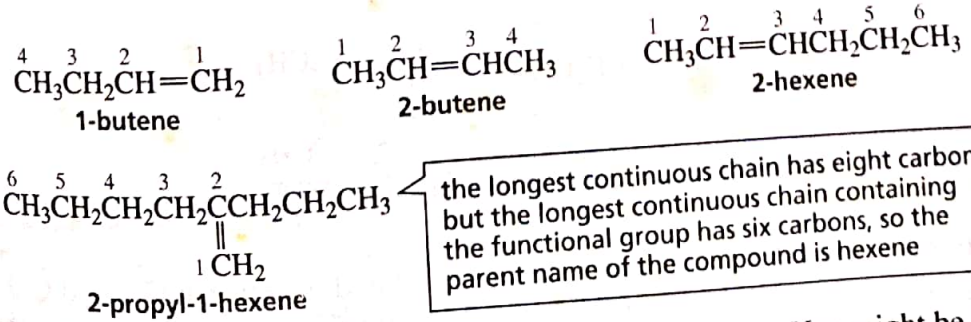
3.2 NOMENCLATURE OF ALKENES

The systematic (IUPAC) name of an alkene is obtained by replacing the "ane" ending of the alkane with "ene." For example, a two-carbon alkene is called ethene and a three-carbon alkene is called propene. Ethene is frequently referred to by its common name (ethylene).



Most alkene names need a number to indicate the position of the double bond. (The previous names do not because there is no ambiguity.) The same IUPAC rules we learned in Chapter 2 are followed in naming alkenes.

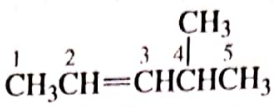
1. The longest continuous chain containing the functional group (in this case, the carbon–carbon double bond) is numbered in a direction that gives the functional group suffix the lowest possible number. For example, 1-butene signifies that the double bond is between the first and second carbons of butene; 2-hexene signifies that the double bond is between the second and third carbons of hexene.



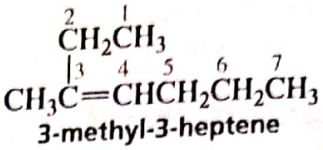
Notice that 1-butene does not have a common name. You might be tempted to call it "butylene," which is analogous to "propylene" for propene, but

butylene is not an appropriate name. A name must be unambiguous and "butylene" could signify either 1-butene or 2-butene.

2. If the chain has substituents, it is still numbered in the direction that gives the functional group suffix the lowest possible number.



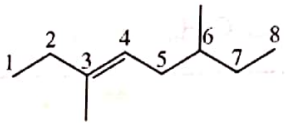
4-methyl-2-pentene



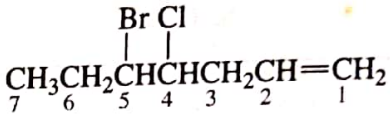
3-methyl-3-heptene

4-pentoxy-1-butene

3. If a chain has more than one substituent, the substituents are cited in alphabetical (not numerical) order, using the same rules for alphabetizing that you learned in Section 2.2 (the prefixes di, tri, *sec*, and *tert* are ignored in alphabetizing, but iso, neo, and cyclo are not ignored).

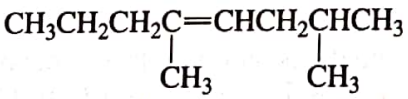


3,6-dimethyl-3-octene

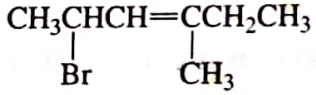


5-bromo-4-chloro-1-heptene

4. If the same number for the alkene functional group suffix is obtained in both directions, the correct name is the one that contains the lowest substituent number. For example, in 2,5-dimethyl-4-octene, the compound is a 4-octene whether the longest continuous chain is numbered from left to right or from right to left. If you number from left to right, the substituents are at positions 4 and 7, but if you number from right to left they are at positions 2 and 5. Of those four substituent numbers, 2 is the lowest number, so the compound is named 2,5-dimethyl-4-octene and not 4,7-dimethyl-4-octene.



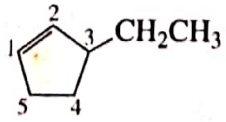
2,5-dimethyl-4-octene
not
4,7-dimethyl-4-octene
because 2 < 4



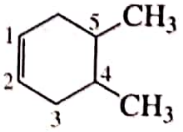
2-bromo-4-methyl-3-hexene
not
5-bromo-3-methyl-3-hexene
because 2 < 3

5. In cyclic compounds, a number is not needed to denote the position of the functional group because the ring is always numbered so that the double bond is between carbons 1 and 2.


Tutorial: Alkene nomenclature



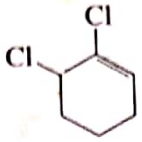
3-ethylcyclopentene



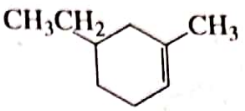
4,5-dimethylcyclohexene

In the following cyclohexenes, the double bond is between C-1 and C-2 regardless of whether you move around the ring clockwise or counterclockwise. Therefore, you move around the ring in the direction that puts the lowest substituent number into the name, *not* in the direction that gives the lowest

sum of the substituent numbers. For example, 1,6-dichlorocyclohexene is not called 2,3-dichlorocyclohexene even though the latter has the lowest sum of the substituent numbers (1 + 6 = 7 *versus* 2 + 3 = 5); 1,6-dichlorocyclohexene is the correct name because it has the lowest substituent number (1).

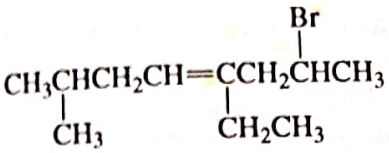


1,6-dichlorocyclohexene
not
2,3-dichlorocyclohexene
because 1 < 2

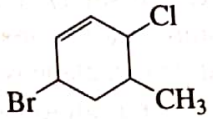


5-ethyl-1-methylcyclohexene
not
4-ethyl-2-methylcyclohexene
because 1 < 2

6. If both directions lead to the same number for the alkene functional group suffix and the same low number(s) for one or more of the substituents, then those substituents are ignored and the direction is chosen that gives the lowest number to one of the remaining substituents.

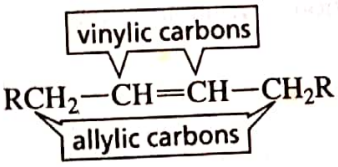


2-bromo-4-ethyl-7-methyl-4-octene
not
7-bromo-5-ethyl-2-methyl-4-octene
because 4 < 5



6-bromo-3-chloro-4-methylcyclohexene
not
3-bromo-6-chloro-5-methylcyclohexene
because 4 < 5

The sp^2 carbons of an alkene are called **vinylic carbons.** An sp^3 carbon that is adjacent to a vinylic carbon is called an **allylic carbon.**



There are two groups that contain a carbon–carbon double bond that are used as substituent groups in common names—the **vinyl group** and the **allyl group.** The vinyl group is the smallest possible group that contains a vinylic carbon, and the allyl group is the smallest possible group that contains an allylic carbon. When allyl is used in nomenclature, the substituent must be attached to the allylic carbon.

Tutorial: Common names of alkyl groups

	$H_2C{=}CH-$	$H_2C{=}CHCH_2-$
	the vinyl group	**the allyl group**
	$H_2C{=}CHCl$	$H_2C{=}CHCH_2Br$
systematic name:	**chloroethene**	**3-bromopropene**
common name:	**vinyl chloride**	**allyl bromide**

PROBLEM 4 ◆

Draw the structure for each of the following compounds.

a. 3,3-dimethylcyclopentene

b. 6-bromo-2,3-dimethyl-2-hexene

c. ethyl vinyl ether

d. allyl alcohol

Acetylene (HC≡CH), the common name for the smallest alkyne, may be a familiar word to you because of the oxyacetylene torch used in welding. Acetylene is supplied to the torch from one high-pressure gas tank and oxygen is supplied from another. Burning acetylene produces a high-temperature flame capable of melting and vaporizing iron and steel.

PROBLEM 1 ◆

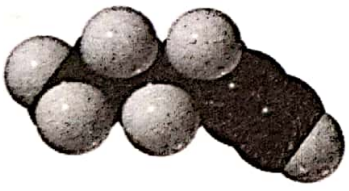
What is the molecular formula for a cyclic alkyne with 14 carbons and 2 triple bonds?

5.1 NOMENCLATURE OF ALKYNES

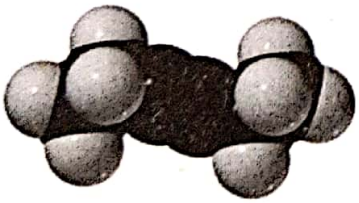
The systematic name of an alkyne is obtained by replacing the "ane" ending of the alkane name with "yne." Analogous to naming compounds with other functional groups, the longest continuous chain containing the carbon–carbon triple bond is numbered in a direction that gives the alkyne functional group suffix as low a number as possible. If the triple bond is at the end of the chain, the alkyne is classified as a **terminal alkyne.** Alkynes with triple bonds located elsewhere along the chain are called **internal alkynes.** For example, 1-butyne is a terminal alkyne whereas 2-pentyne is an internal alkyne.

3-D Molecules: 1-Hexyne; 3-Hexyne

	$HC{\equiv}CH$	$CH_3CH_2C{\equiv}CH$	$CH_3C{\equiv}CCH_2CH_3$	$CH_3CHC{\equiv}CCH_3$ with CH_2CH_3
Systematic:	ethyne	1-butyne	2-pentyne	4-methyl-2-hexyne
Common:	acetylene	ethylacetylene	ethylmethylacetylene	*sec*-butylmethylacetylene
		a terminal alkyne	an internal alkyne	



1-hexyne



3-hexyne

In common nomenclature, alkynes are named as substituted acetylenes. The common name is obtained by naming the alkyl groups, in alphabetical order, that have replaced the hydrogens of acetylene. Acetylene is an unfortunate common name for the smallest alkyne because its "ene" ending is characteristic of a double bond rather than a triple bond.

If the same number for the alkyne functional group suffix is obtained in both directions along the carbon chain, the correct systematic name is the one that contains the lowest substituent number. If the compound contains more than one substituent, the substituents are listed in alphabetical order.

$CH_3CH(Cl)CH(Br)C{\equiv}CCH_2CH_2CH_3$ (1 2 3 4 5 6 7 8)

3-bromo-2-chloro-4-octyne
not 6-bromo-7-chloro-4-octyne
because 2 < 6

$CH_3CH(CH_3)C{\equiv}CCH_2CH_2Br$ (6 5 4 3 2 1)

1-bromo-5-methyl-3-hexyne
not 6-bromo-2-methyl-3-hexyne
because 1 < 2

A substituent receives the lowest possible number only if there is no functional group suffix, or if the same number for the functional group suffix is obtained in both directions.

The triple-bond-containing propargyl group is used in common nomenclature. It is analogous to the double-bond-containing allyl group that you saw in Section 3.2.

$HC{\equiv}CCH_2-$	$H_2C{=}CHCH_2-$
propargyl group	allyl group
$HC{\equiv}CCH_2Br$	$H_2C{=}CHCH_2OH$
propargyl bromide	allyl alcohol

PROBLEM 2 ◆

Draw the structure for each of the following compounds.

a. 1-chloro-3-hexyne
b. cyclooctyne
c. isopropylacetylene
d. propargyl chloride
e. 4,4-dimethyl-1-pentyne
f. dimethylacetylene

PROBLEM 3 ◆

Give the systematic name for each of the following compounds.

a. $BrCH_2CH_2C{\equiv}CCH_3$

b. $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HC{\equiv}C\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$

c. $CH_3OCH_2C{\equiv}CCH_2CH_3$

d. $CH_3CH_2\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{C}}HC{\equiv}CH$

PROBLEM 4 ◆

Draw the structures and give the common and systematic names for the seven alkynes with molecular formula C_6H_{10}.

PROBLEM 5

Which would you expect to be more stable, an internal alkyne or a terminal alkyne? Why?

5.2 PHYSICAL PROPERTIES OF UNSATURATED HYDROCARBONS

All hydrocarbons have similar physical properties. In other words, alkenes and alkynes have physical properties similar to those of alkanes (Section 2.9). All are insoluble in water and all are soluble in solvents with low polarity such as benzene and ether. They are less dense than water and, like other homologous series, have boiling points that increase with increasing molecular weight (Table 5.1). Alkynes are more linear than alkenes, and a triple bond is more polarizable than a double bond

TABLE 5.1 Boiling Points of the Smallest Hydrocarbons

	bp (°C)		bp (°C)		bp (°C)
CH_3CH_3 ethane	−88.6	$H_2C{=}CH_2$ ethene	−104	$HC{\equiv}CH$ ethyne	−84
$CH_3CH_2CH_3$ propane	−42.1	$CH_3CH{=}CH_2$ propene	−47	$CH_3C{\equiv}CH$ propyne	−23
$CH_3CH_2CH_2CH_3$ butane	−0.5	$CH_3CH_2CH{=}CH_2$ 1-butene	−6.5	$CH_3CH_2C{\equiv}CH$ 1-butyne	8
$CH_3(CH_2)_3CH_3$ pentane	36.1	$CH_3CH_2CH_2CH{=}CH_2$ 1-pentene	30	$CH_3CH_2CH_2C{\equiv}CH$ 1-pentyne	39
$CH_3(CH_2)_4CH_3$ hexane	68.7	$CH_3CH_2CH_2CH_2CH{=}CH_2$ 1-hexene	63.5	$CH_3CH_2CH_2CH_2C{\equiv}CH$ 1-hexyne	71
		$CH_3CH{=}CHCH_3$ *cis*-2-butene	3.7	$CH_3C{\equiv}CCH_3$ 2-butyne	27
		$CH_3CH{=}CHCH_3$ *trans*-2-butene	0.9	$CH_3CH_2C{\equiv}CCH_3$ 2-pentyne	55