CHEMISTRY

The Central Science

SEVENTH EDITION

ANNOTATED INSTRUCTOR'S EDITION

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25 The Chemistry of Life: Organic and Biological Chemistry

Contents

The element carbon forms a vast number of compounds. Over 10 million carbon-containing compounds are known, and about 90 percent of the new compounds synthesized each year contain carbon. The study of carbon compounds constitutes a separate branch of chemistry known as **organic chemistry**. This term arose from the eighteenth-century belief that organic compounds could be formed only by living systems. This idea was disproved in 1828 by the German chemist Friedrich Wöhler, who synthesized urea, H_2NCONH_2, an organic substance found in the urine of mammals, from inorganic starting materials.

The notion that organic chemicals and living organisms are connected is certainly true in one sense: Life as we know it could not exist without a vast array of complex, biologically important organic molecules. The study of the chemistry of living species is called *biological chemistry*, or **biochemistry**.

In this final chapter we present a brief view of some of the elementary aspects of organic chemistry and biochemistry. Many of you will study these subjects in greater detail by taking additional courses devoted entirely to these topics. As you read the material presented here, you will notice that many of the basic concepts that we developed earlier in this text are important in understanding the fundamentals of organic chemistry and biochemistry.

Teaching Note: The distinction between organic and inorganic molecules is somewhat vague. As a rule of thumb, inorganic carbon is carbon that is *not* bound to hydrogen, for example, H_2CO_3. Often, the species is completely devoid of hydrogen, such as in CN^- and CO_2.

Teaching Note: Carbon is the only element that forms extensive *extended* structures with itself. The observation is the basis of the speculation that life cannot be based on another element.

Learning Goal 1: List four groups of hydrocarbons and draw the structural formula from each group—in this case the alkanes.

Raymond B. Seymour, "Alkanes: Abundant, Pervasive, Important, and Essential," *J. Chem. Educ.* 1989, *66*, 59–63

The genetic information that provides both the similarities and the differences between these two tigers is transferred from one generation to the next by the replication of molecules of deoxyribonucleic acid, or DNA.

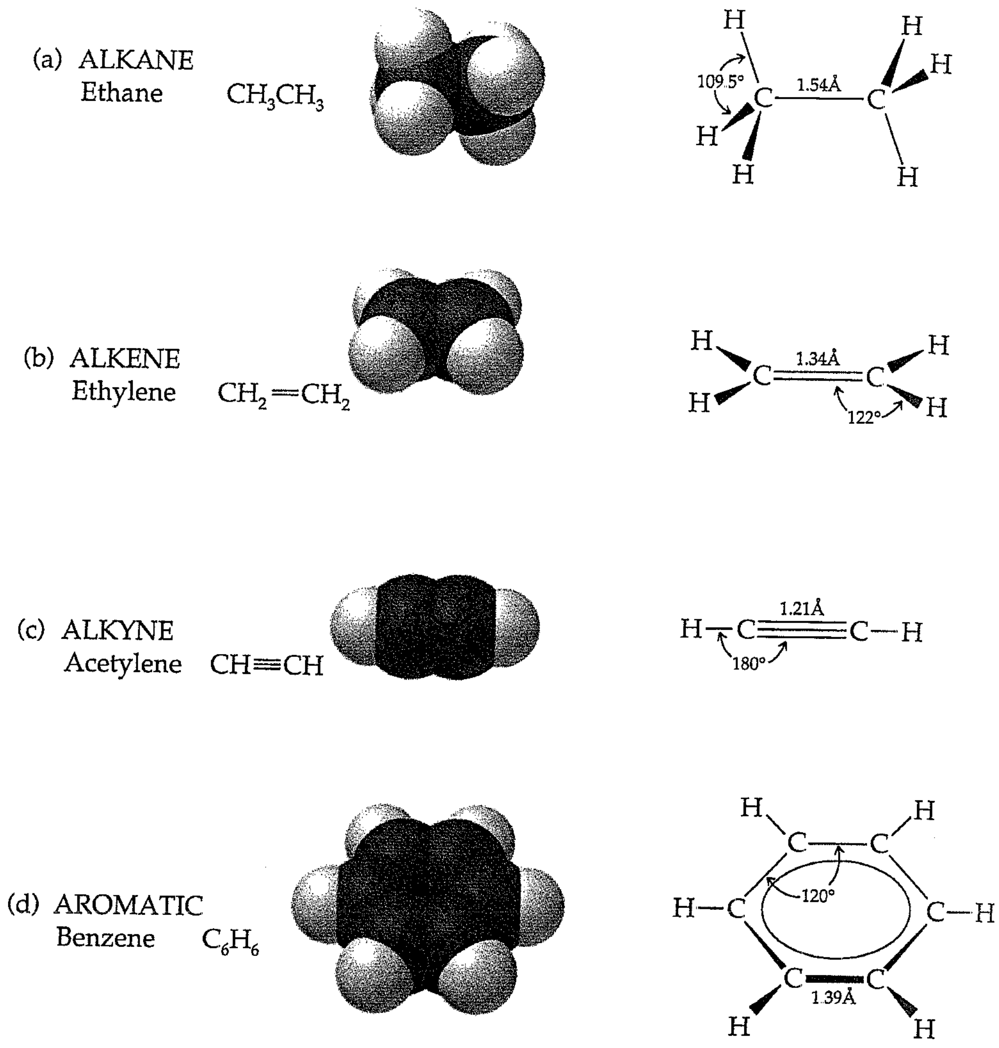
25.1 Introduction to Hydrocarbons

Because the compounds of carbon are so numerous, it is convenient to organize them into families that exhibit structural similarities. The simplest class of organic compounds is the *hydrocarbons*, compounds composed only of carbon and hydrogen. The key structural feature of hydrocarbons and of most other organic substances is the presence of stable carbon-carbon bonds. Carbon is the only element capable of forming stable, extended chains of atoms bonded through single, double, or triple bonds.

Hydrocarbons can be divided into four general types, depending on the kinds of carbon-carbon bonds in their molecules. Figure 25.1 shows an example of each of the four types: alkanes, alkenes, alkynes, and aromatic hydrocarbons. In these hydrocarbons as well as in other organic compounds, each C atom invariably has four bonds (four single bonds, two single bonds and one double bond, or one single bond and one triple bond).

Alkanes are hydrocarbons that contain only single bonds, as in ethane, C_2H_6. Because alkanes contain the largest possible number of hydrogen atoms per carbon atom, they are called *saturated hydrocarbons*. **Alkenes**, also known as olefins, are hydrocarbons that contain a C$=$C double bond, as in ethylene, C_2H_4. **Alkynes** contain a C$\equiv$C triple bond, as in acetylene, C_2H_2. In **aromatic hydrocarbons** the carbon atoms are connected in a planar ring structure, joined by both σ and π bonds between carbon atoms. Benzene, C_6H_6, is the best-known example of an aromatic hydrocarbon. Alkenes, alkynes, and aromatic

Figure 25.1



IGURE 25.1 Names, netrical structures, and ecular formulas for nples of each type of rocarbon.

hydrocarbons are called *unsaturated hydrocarbons* because they contain less hydrogen than an alkane having the same number of carbon atoms.

The members of these different classes of hydrocarbons exhibit different chemical behaviors, as we will see shortly. However, their physical properties are similar in many ways. Because carbon and hydrogen do not differ greatly in electronegativity (2.5 for carbon, 2.1 for hydrogen), hydrocarbon molecules are relatively nonpolar. Thus, they are almost completely insoluble in water, but they dissolve readily in other nonpolar solvents. Furthermore, their melting points and boiling points are determined by London dispersion forces. Thus, hydrocarbons tend to become less volatile with increasing molar mass. ∞ (Section 11.2) As a result, hydrocarbons of very low molecular weight, such as C_2H_6, are gases at room temperature; those of moderate molecular weight, such as C_6H_{14}, are liquids; and those of higher molecular weight are solids.

25.2 Alkanes

ing Goal 2: Write the las and names of the) members of the alkane

Table 25.1 lists several of the simplest alkanes. Many of these substances are familiar because of their widespread use. Methane is a major component of natural gas and is used for home heating and in gas stoves and hot-water heaters. Propane is the major component of bottled gas used for home heating

TABLE

Molecul Formula
CH_4
C_2H_6
C_3H_8
C_4H_{10}
C_5H_{12}
C_6H_{14}
C_7H_{16}
C_8H_{18}
C_9H_{20}
$C_{10}H_{22}$

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We formulas an alkan single bc in Table

Structu

The Lew tell us ar As we w bon ator each car The thre in Figure orbitals

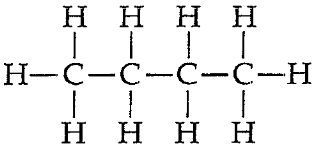
Rot occurs v ine grasp structure cause m

TABLE 25.1 **First Several Members of the Straight-Chain Alkane Series**

Molecular Formula	Condensed Structural Formula	Name	Boiling Point (°C)
CH_4	CH_4	Methane	−161
C_2H_6	CH_3CH_3	Ethane	−89
C_3H_8	$CH_3CH_2CH_3$	Propane	−44
C_4H_{10}	$CH_3CH_2CH_2CH_3$	Butane	−0.5
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	Pentane	36
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	Hexane	68
C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	Heptane	98
C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Octane	125
C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Nonane	151
$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Decane	174

and cooking in areas where natural gas is not available. Butane is used in disposable lighters and in fuel canisters for gas camping stoves and lanterns. Alkanes with from 5 to 12 carbon atoms per molecule are found in gasoline.

The formulas for the alkanes given in Table 25.1 are written in a notation called *condensed structural formulas*. This notation reveals the way in which atoms are bonded to one another but does not require drawing in all the bonds. For example, the Lewis structure and the condensed structural formula for butane, C_4H_{10}, are



$$\begin{array}{ccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

$CH_3CH_2CH_2CH_3$

Lewis structure

Condensed structural formula

We will frequently use either Lewis structures or condensed structural formulas to represent organic compounds. Notice that each carbon atom in an alkane has four single bonds, whereas each hydrogen atom forms one single bond. Notice also that each succeeding compound in the series listed in Table 25.1 has an additional CH_2 unit.

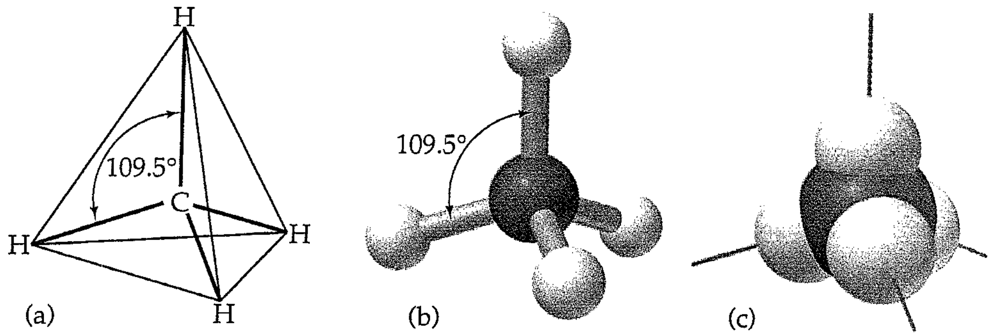
Structures of Alkanes

The Lewis structures and condensed structural formulas for alkanes do not tell us anything about the three-dimensional structures of these substances. As we would predict from the VSEPR model, the geometry about each carbon atom in an alkane is tetrahedral; that is, the four groups attached to each carbon are located at the vertices of a tetrahedron. ∞ (Section 9.2) The three-dimensional structures can be represented as shown for methane in Figure 25.2. The bonding may be described as involving sp^3 hybridized orbitals on the carbon. ∞ (Section 9.5)

Point of Emphasis: Carbon cannot exceed an octet in a stable compound.

Rotation about the carbon-carbon single bond is relatively easy, and it occurs very rapidly at room temperature. To visualize such rotation, imagine grasping the top left methyl group in Figure 25.3, which shows the structure of propane, and twisting it relative to the rest of the structure. Because motion of this sort occurs very rapidly in alkanes, long-chain alkanes

Teaching Note: Some energy is required for atoms to rotate about a single bond, but sufficient energy for this process exists at room temperature.



▸ **FIGURE 25.2** Representa-
:ons of the three-dimensional
rrangement of bonds about
arbon in methane.

are constantly undergoing motions that cause it to change its shape, something like a length of chain that is being shaken.

Structural Isomers

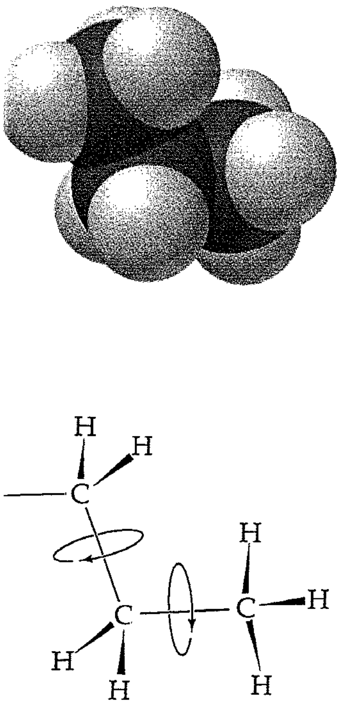
,earning Goal 3: Give
n example of structural
,omerism in alkanes.

:ommon Misconception:
tudents often interpret the
:rm *straight-chain* to mean
eometrically linear. Straight-
ıain hydrocarbons are actu-
lly bent at each carbon atom,
; predicted by the VSEPR
ıodel.

The alkanes listed in Table 25.1 are called *straight-chain hydrocarbons* because all the carbon atoms are joined in a continuous chain. Alkanes consisting of four or more carbon atoms can also form branched chains; hydrocarbons with branched chains are called *branched-chain hydrocarbons*. Figure 25.4 shows the condensed formulas and space-filling models for all the possible structures of alkanes containing four and five carbon atoms. Notice that there are two ways that four carbon atoms can be joined to give C_4H_{10}: as a straight chain (left) or a branched chain (right). For alkanes with five carbon atoms, C_5H_{12}, there are three different arrangements.

Compounds with the same molecular formula but with different bonding arrangements and hence different structures are called **structural isomers**. The structural isomers of a given alkane differ slightly from one another in physical properties. Note the melting and boiling points of the isomers of butane and pentane, given in Figure 25.4. The number of possible structural isomers increases rapidly with the number of carbon atoms in the alkane. For example, there are 18 possible isomers having the molecular formula, C_8H_{18}, and 75 possible isomers with the molecular formula, $C_{10}H_{22}$.

' FIGURE 25.3 Three-
imensional models for
ropane, C_3H_8, showing
)tations about the carbon-
ırbon single bonds.



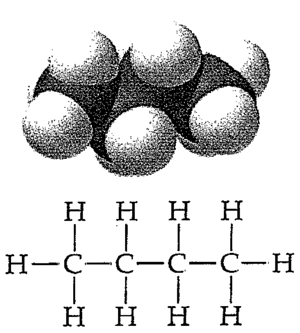
Nomenclature of Alkanes

The first names given to the structural isomers shown in Figure 25.4 are the so-called common names. The straight-chain isomer is called the normal isomer, abbreviated th the prefix *n*-. The isomer in which one CH_3 group is branched off the major chain is labeled the iso- isomer, for example, isobutane. However, as the number of isomers grows, it becomes impossible to find a suitable prefix to denote each isomer. The need for a systematic means of naming organic compounds was recognized early in the history of organic chemistry. In 1892 an organization called the International Union of Chemistry met in Geneva, Switzerland, to formulate rules for systematic naming of organic substances. Since that time the task of updating the rules for naming compounds has fallen to the International Union of Pure and Applied Chemistry (IUPAC). Chemists everywhere, regardless of their nationality or political affiliation, subscribe to a common system for naming compounds.

The IUPAC names for the isomers of butane and pentane are the ones given in parentheses for each compound in Figure 25.4. The following steps summarize the procedures used to arrive at these names and the names of

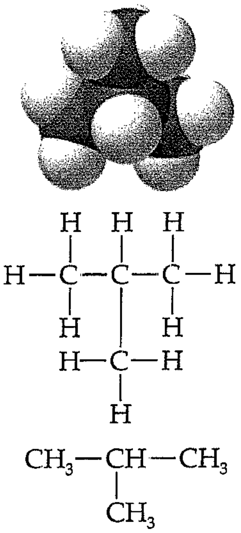
FIGURE 25.4 Possible structures, names, and melting and boiling points of alkanes of formula C_4H_{10} and C_5H_{12}.

Figure 25.4



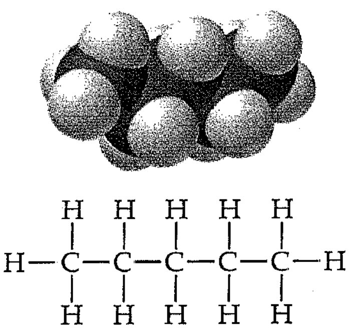
$CH_3CH_2CH_2CH_3$

n-Butane
(butane)
m.p. −135°C
b.p. −0.5°C



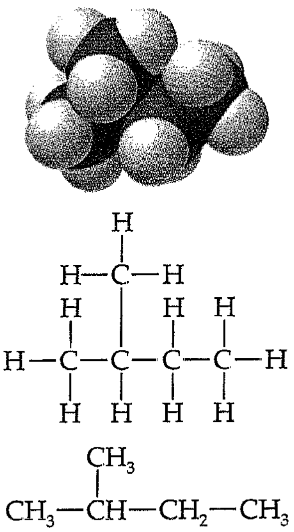
$$\mathrm{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3}$$

Isobutane
(2-methylpropane)
m.p. −145°C
b.p. −10°C



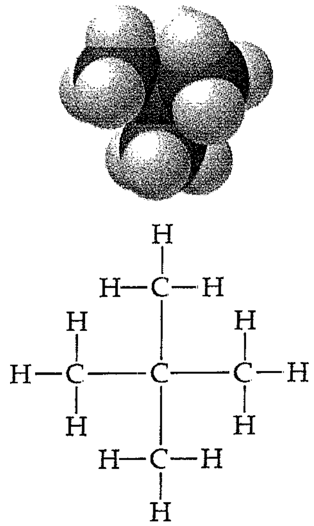
$CH_3CH_2CH_2CH_2CH_3$

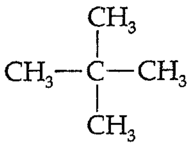
n-Pentane
(pentane)
m.p. −130°C
b.p. +36°C



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_3}$$

Isopentane
(2-methylbutane)
m.p. −160°C
b.p. +28°C





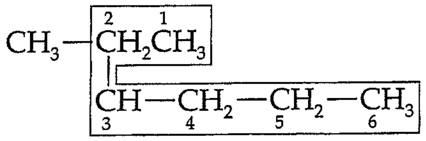
$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3}$$

Neopentane
(2,2-dimethylpropane)
m.p. −20°C
b.p. +9°C

other alkanes. We use a similar approach to write the names of other organic compounds.

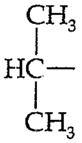
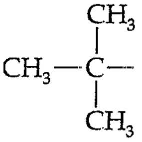
Learning Goal 4: Write the structural formula of an alkane given its systematic (IUPAC) name.

1. *Find the longest continuous chain of carbon atoms, and use the name of this chain as the base name of the compound.* The longest chain may not always be written in a straight line, as seen in the following example:



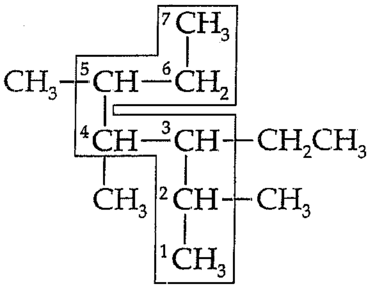
2-methyl*hexane*

TABLE 25.2 Condensed Structural Formulas and Common Names for Several Alkyl Groups

Group	Name
CH_3-	Methyl
CH_3CH_2-	Ethyl
$CH_3CH_2CH_2-$	Propyl
$CH_3CH_2CH_2CH_2-$	Butyl
 $\begin{array}{c}CH_3\\ \vert\\ HC-\\ \vert\\ CH_3\end{array}$	Isopropyl
 $\begin{array}{c}CH_3\\ \vert\\ CH_3-C-\\ \vert\\ CH_3\end{array}$	*t*-Butyl

Because this compound has a chain of six C atoms, it is named as a substituted hexane. Groups attached to the main chain are called *substituents* because they are substituted in place of an H atom on the main chain.

2. *Number the carbon atoms in the longest chain, beginning with the end of the chain that is nearest to a substituent.* In our example we number the C atoms from the upper left because that places the CH_3 substituent on the second C atom of the chain; if we number from the lower right, the CH_3 would be on the fifth C atom. The chain is numbered from the end that gives the lowest number for the substituent position.
3. *Name and give the location of each substituent group.* A substituent group that is formed by removing an H atom from an alkane is called an **alkyl group**. Alkyl groups are named by replacing the *-ane* ending of the alkane name with *-yl*. For example, the methyl group, CH_3, is derived from methane, CH_4. Likewise, the ethyl group, C_2H_5, is derived from ethane, C_2H_6. Table 25.2 lists several common alkyl groups. The name 2-methylhexane indicates the presence of a methyl, CH_3, group on the second carbon atom of a hexane (six carbon) chain.
4. *When two or more substituents are present, list them in alphabetical order.* When there are two or more of the same substituent, the number of substituents of that type is indicated by a prefix: *di-* (two), *tri-* (three), *tetra-* (four), *penta-* (five), and so forth. Notice how the following example is named:

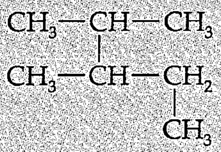


3-ethyl-2,4,5-trimethylheptane

Learning Goal 5: Name an alkane, given its structural formula.

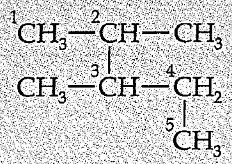
Sample Exercise 25.1

Name the following alkane:



$$\begin{array}{l}CH_3-CH-CH_3\\ \vert\\ CH_3-CH-CH_2\\ \vert\\ CH_3\end{array}$$

SOLUTION To name this compound properly, you must first find the longest continuous chain of carbon atoms. This chain, extending from the upper left CH_3 group to the lower right CH_3 group, is five carbon atoms long:

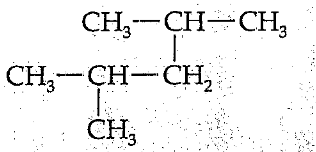


$$\begin{array}{l}{}^{1}CH_3-{}^{2}CH-CH_3\\ \vert\\ CH_3-{}^{3}CH-{}^{4}CH_2\\ \vert\\ {}^{5}CH_3\end{array}$$

The compound is thus named as a derivative of pentane. We might number the carbon atoms starting from either end. However, IUPAC rules state that the numbering should be done so that the numbers of carbons bearing side chains are as low as possible. This means that we should start numbering with the upper carbon. There is a methyl group on carbon 2, and one on carbon 3. The compound is thus called 2,3-dimethylpentane.

Practice Exercise

Name the following alkane:



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

Answer: 2,4-dimethylpentane

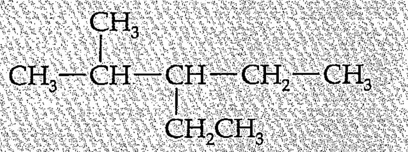
Sample Exercise 25.2

Write the condensed structural formula for 3-ethyl-2-methylpentane.

SOLUTION The longest continuous chain of carbon atoms in this compound is five. We can therefore begin by writing out a string of five C atoms:

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

We next place a methyl group on the second carbon, and an ethyl group on the third carbon atom of the chain. Hydrogens are then added to all the other carbon atoms to make the four bonds to each carbon. Thus, the structural formula is



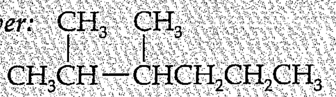
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

The formula can be written more concisely as $CH_3CH(CH_3)CH(C_2H_5)CH_2CH_3$.

Practice Exercise

Write the condensed structural formula for 2,3-dimethylhexane.

Answer:



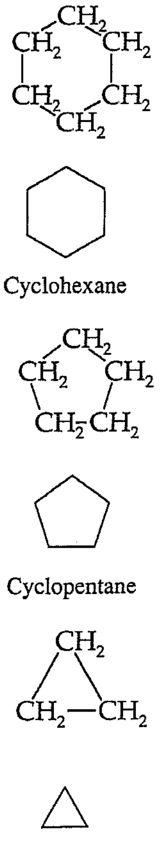
$$CH_3\overset{\displaystyle CH_3}{\overset{|}{CH}}-\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_2CH_3 \quad \text{or} \quad CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$$

Cycloalkanes

Alkanes can form not only branched chains, but rings or cycles as well. Alkanes with this form of structure are called **cycloalkanes**. Figure 25.5 illustrates a few examples of cycloalkanes. Cycloalkane structures are sometimes drawn as simple polygons in which each corner of the polygon represents a CH_2 group. This method of representation is similar to that used for benzene rings. ∞ (Section 8.7) In the case of aromatic structures each corner represents a CH group.

Carbon rings containing fewer than five carbon atoms are strained because the C—C—C bond angle in the smaller rings must be less than the 109.5° tetrahedral angle. The amount of strain increases as the rings get smaller. In cyclopropane, which has the shape of an equilateral triangle, the angle is only 60°; this molecule is therefore much more reactive than its straight-chain analog, propane.

▼ FIGURE 25.5 Condensed structural formulas for three cycloalkanes.



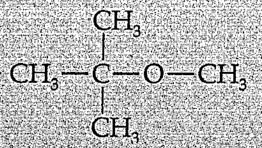
Cyclohexane

Cyclopentane

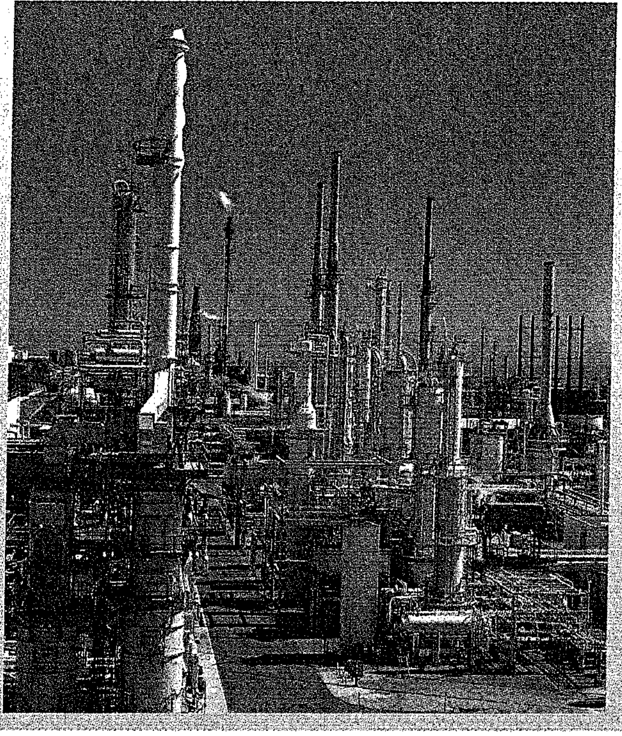
Cyclopropane

lar weight, such as ethylene and propene. These substances are used in a variety of reactions to form plastics and other chemicals.

The octane rating of gasoline is further improved by adding certain compounds called *antiknock agents*. Until the mid-1970s the principal antiknock agent was tetraethyl lead, $(C_2H_5)_4Pb$. Its use has been drastically curtailed because of the environmental hazards of lead and because it poisons catalytic converters. ∞ (Chemistry at Work, Section 14.6) Oxygenated hydrocarbons are now generally used as antiknock agents. One of the most cost-effective is methyl *t*-butyl ether (MTBE):



$$\begin{array}{c} \quad CH_3 \\ \quad | \\ CH_3—C—O—CH_3 \\ \quad | \\ \quad CH_3 \end{array}$$



▶ **FIGURE 25.7** Petroleum is separated into fractions by distillation and is subjected to catalytic cracking in a refinery, as shown here.

Reactions of Alkanes

Most alkanes are relatively unreactive. For example, at room temperature they do not react with acids, bases, or strong oxidizing agents, and they are not even attacked by boiling nitric acid. One reason for their low chemical reactivity is the strength of the C—C and C—H bonds.

Teaching Note: Hydrocarbon fuels such as gasoline and kerosene are largely composed of alkanes.

Alkanes are not completely inert, however. One of their most commercially important reactions is *combustion* in air, which is the basis of their use as fuels. ∞ (Section 3.2) For example, the complete combustion of ethane proceeds as follows:

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l) \qquad \Delta H = -2855 \text{ kJ}$$

In the following sections we will see two ways in which hydrocarbons can be modified to impart greater reactivity: the introduction of unsaturation into the carbon-carbon framework and the attachment of other reactive groups to the hydrocarbon backbone.

25.3 Unsaturated Hydrocarbons

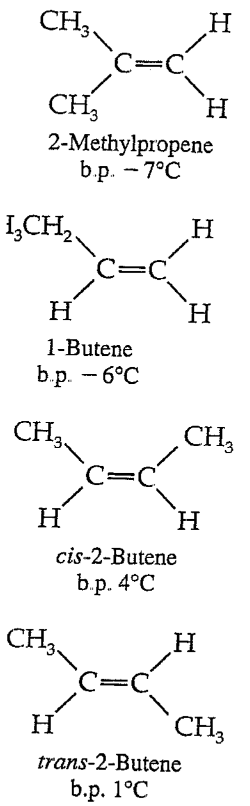
The presence of one or more multiple bonds makes unsaturated hydrocarbons significantly different from alkanes both in terms of their structures and their reactivity.

Learning Goal 6: List the four groups of hydrocarbons and draw the structural formula of an example from each group—in this case as applied to alkenes and alkynes.

Alkenes

Alkenes are unsaturated hydrocarbons that contain a C=C bond. The simplest alkene is $CH_2{=}CH_2$, called ethene or ethylene. The next member of

Teaching Note: *Ethene* and *propene* are IUPAC names; *ethylene* and *propylene* are historical or trivial names.



2-Methylpropene
b.p. −7°C

1-Butene
b.p. −6°C

cis-2-Butene
b.p. 4°C

trans-2-Butene
b.p. 1°C

IGURE 25.8 Structures, ies, and boiling points of nes with molecular nula C_4H_8.

the series is $CH_3—CH=CH_2$, called propene or propylene. For alkenes with four or more carbon atoms, several isomers exist for each molecular formula. For example, there are four isomers of C_4H_8, as shown in Figure 25.8. Notice both their structures and their names.

The names of alkenes are based on the longest continuous chain of carbon atoms that contains the double bond. The name given to the chain is obtained from the name of the corresponding alkane (Table 25.1) by changing the ending from *-ane* to *-ene*. For example, the compound on the top in Figure 25.8 has a double bond as part of a three-carbon chain; thus, the parent alkene is considered to be propene.

The location of the double bond along an alkene chain is indicated by a prefix number that designates the number of the carbon atom that is part of the double bond and is nearest an end of the chain. The chain is always numbered from the end that brings us to the double bond sooner and hence gives the smallest number prefix. In propene the only possible location for the double bond is between the first and second carbons; thus, a prefix indicating its location is unnecessary. For the compound on the top in Figure 25.8, numbering the carbon chain from the end closer to the double bond places a methyl group on the second carbon. Thus, the name of the isomer is 2-methylpropene. For the other compounds in Figure 25.8, the longest carbon chain contains four carbons, and there are two possible positions for the double bond, either after the first carbon (1-butene) or after the second carbon (2-butene).

If a substance contains two or more double bonds, each is located by a numerical prefix. The ending of the name is altered to identify the number of double bonds: diene (two), triene (three), and so forth. For example, $CH_2=CH—CH_2—CH=CH_2$ is 1,4-pentadiene.

Notice that the two isomers on the bottom in Figure 25.8 differ in the relative locations of their terminal methyl groups. These two compounds are examples of **geometrical isomers**, compounds that have the same molecular formula and the same groups bonded to one another but differ in the spatial arrangement of these groups. ∞ (Section 24.4) In the *cis* isomer the two methyl groups are on the same side of the double bond, whereas in the *trans* isomer they are on opposite sides. Geometrical isomers possess distinct physical properties and often differ significantly in their chemical behavior.

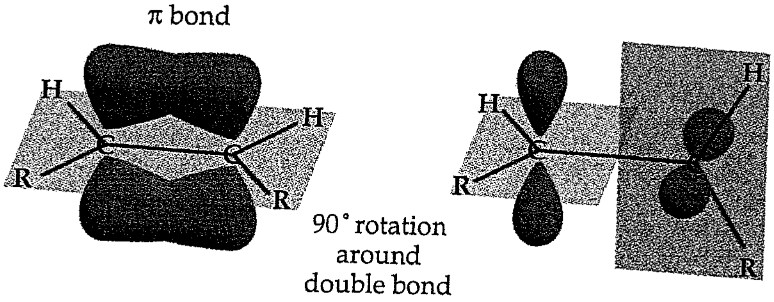
Geometrical isomerism in alkenes arises because, unlike the C—C bond, the C=C bond is resistant to twisting. Recall that the double bond between two carbon atoms consists of a σ and a π bond. ∞ (Section 9.6) Figure 25.9 shows a *cis* alkene. The carbon-carbon bond axis and the bonds to the hydrogen atoms and to the alkyl groups (designated R), are all in a plane. The p orbitals that overlap sideways to form the π bond are perpendicular to the molec-

rning Goal 7: Give an nple of structural and geo- rical isomerism in alkenes alkynes.

rning Goal 8: Write the :tural formula of an ne or alkyne, given its :matic (IUPAC) name.

ning Goal 9: Name an ne or alkyne, given its :tural formula.

Figure 25.9



:URE 25.9 Schematic :ation of rotation about a n-carbon double bond alkene. The overlap of orbitals that form the σ is lost in the rotation. is reason, rotation about 1-carbon double bonds ıot occur readily.

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Sam
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(a) C
(b) C

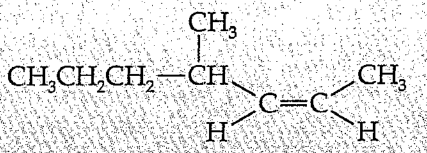
SOL
chair

ular plane. As Figure 25.9 shows, rotation around the carbon-carbon double bond requires the π bond to be broken, a process that requires considerable energy (about 250 kJ/mol). The rotation about a double bond is a key process in the chemistry of vision. ∞ (Chemistry and Life, Section 9.6)

Teaching Note: The cis and trans isomers of most alkenes are nearly identical in stability. Therefore, the resistance to twisting is a large activation energy resulting from breaking the π bond in the transition state.

Sample Exercise 25.3

Name the following compound:

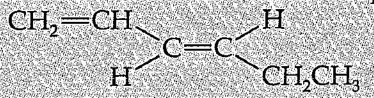


SOLUTION Because this compound possesses a double bond, it is an alkene. The longest continuous chain of carbons that contains the double bond is seven in length. The parent compound is therefore considered a heptene. The double bond begins at carbon 2 (numbering from the end closest to the double bond); thus the parent hydrocarbon chain is named 2-heptene. Continuing the numbering along the chain, a methyl group is bound at carbon atom 4. Thus the compound is 4-methyl-2-heptene. Finally we note that the geometrical configuration at the double bond is *cis*; that is, the alkyl groups are bonded to the double bond on the same side. For this reason, the full name is 4-methyl-*cis*-2-heptene.

Practice Exercise

Draw the structural formula for the compound *trans*-1,3-hexadiene.

Answer:



Alkynes

Alkynes are unsaturated hydrocarbons containing one or more $C\equiv C$ bonds. The simplest alkyne is acetylene, C_2H_2, a highly reactive molecule. When acetylene is burned in a stream of oxygen in an oxyacetylene torch, the flame reaches a very high temperature, about 3200 K. The oxyacetylene torch is widely used in welding, which requires high temperatures. Alkynes in general are highly reactive molecules. Because of their higher reactivity, they are not as widely distributed in nature as alkenes; however, they are important intermediates in many industrial processes.

Teaching Note: The IUPAC name of acetylene is *ethyne*.

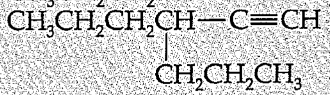
Alkynes are named by identifying the longest continuous chain in the molecule containing the triple bond and modifying the ending of the name as listed in Table 25.1 from *-ane* to *-yne*, as shown in Sample Exercise 25.4.

Sample Exercise 25.4

Name the following compounds:

(a) $CH_3CH_2CH_2-C\equiv C-CH_3$

(b)



$$\underset{\displaystyle CH_2CH_2CH_3}{CH_3CH_2CH_2\overset{}{C}H}-C\equiv CH$$

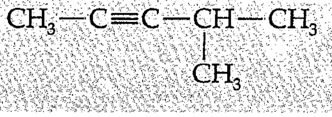
SOLUTION In **(a)** the longest chain of carbon atoms is six. There are no side chains. The triple bond begins at carbon 2 (remember, we always arrange the numbering so that the smallest possible number is assigned to the carbon containing the multiple bond). Thus, the name is 2-hexyne.

In **(b)** the longest continuous chain of carbon atoms is seven; but because this chain does not contain the triple bond we do not count it as derived from heptane. The longest chain containing the triple bond is six, and so this compound is named as a derivative of hexyne, 3-propyl-1-hexyne.

Practice Exercise

Draw the condensed structural formula for 4-methyl-2-pentyne.

Answer:

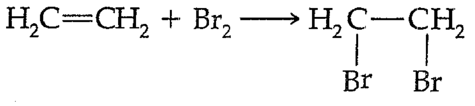


$$CH_3-C\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

Addition Reactions of Alkenes and Alkynes

Learning Goal 10: Give examples of addition reactions of alkenes and alkynes, showing the structural formulas of reactants and products.

The presence of carbon-carbon double or triple bonds in hydrocarbons markedly increases their chemical reactivity. The most characteristic reactions of alkenes and alkynes are **addition reactions,** in which a reactant is added to the two atoms that form the multiple bond. A simple example is the addition of a halogen such as Br_2 to ethene:



$$H_2C{=}CH_2 + Br_2 \longrightarrow H_2\underset{\displaystyle Br}{\underset{|}{C}}-\underset{\displaystyle Br}{\underset{|}{C}}H_2 \qquad [25.1]$$

The pair of electrons that form the π bond in ethylene is uncoupled and is used to form two new bonds to the two bromine atoms. The σ bond between the carbon atoms is retained.

Addition of H_2 to an alkene converts it to an alkane:

$$CH_3CH{=}CHCH_3 + H_2 \xrightarrow{\text{Ni, 500° C}} CH_3CH_2CH_2CH_3 \qquad [25.2]$$

The reaction between an alkene and H_2, referred to as *hydrogenation*, does not occur readily under ordinary temperature and pressure conditions. One reason for the lack of reactivity of H_2 toward alkenes is the high bond enthalpy of the H_2 bond. To promote the reaction, it is necessary to use a catalyst that assists in rupturing the H—H bond. The most widely used catalysts are finely divided metals on which H_2 is adsorbed. ∞ (Section 14.6)

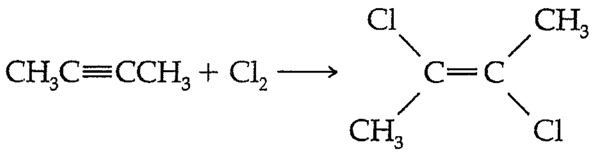
Hydrogen halides and water can also add to the double bond of alkenes, as illustrated by the following reactions of ethene:

$$CH_2{=}CH_2 + HBr \longrightarrow CH_3CH_2Br \qquad [25.3]$$

$$CH_2{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3CH_2OH \qquad [25.4]$$

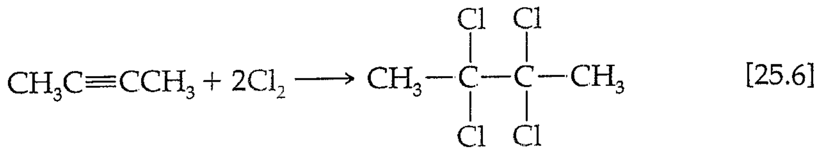
The addition of water is catalyzed by a strong acid such as H_2SO_4.

The addition reactions of alkynes resemble those of alkenes, as shown in the following examples:



[25.5]

2-Butyne *trans*-1,2-Dichloro-2-butene



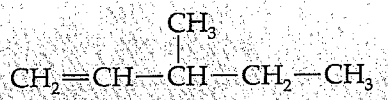
$$\mathrm{CH_3C{\equiv}CCH_3} + 2\mathrm{Cl_2} \longrightarrow \mathrm{CH_3-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-CH_3} \qquad [25.6]$$

2-Butyne 2,2,3,3-Tetrachlorobutane

Sample Exercise 25.5

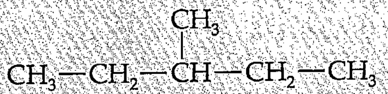
Predict the product of the hydrogenation of 3-methyl-1-pentene.

SOLUTION The name of the starting compound tells us that we have a chain of five carbon atoms with a double bond at one end (position 1) and a methyl group on the third carbon from that end (position 3):



$$\mathrm{CH_2{=}CH-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3}$$

The addition of H_2 across the double bond leads to the following alkane:



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

The longest chain in this alkane has five carbon atoms; its name is therefore 3-methylpentane.

Practice Exercise

Addition of HCl to an alkene leads to the formation of 2-chloropropane. What is the alkene? *Answer:* propene

Chemistry at Work The Accidental Discovery of Teflon

A *polymer* is a material with a high molecular weight that is formed from simple molecules called monomers. ∞ (Section 12.2) Polymers may be either natural or synthetic in origin. Later in this chapter we will see several examples of natural polymers, such as proteins and starch. In Section 12.2 we saw several examples of synthetic polymers, such as polyethylene and nylon. Another synthetic polymer is Teflon, which was discovered quite by accident.

In 1938 a scientist at Du Pont named Roy J. Plunkett made a rather curious observation: A tank of the gaseous compound *tetrafluoroethylene*, $\mathrm{CF_2{=}CF_2}$, that was supposed to be full seemed to have no gas in it. Rather than discarding the tank, Plunkett decided to explore further by cutting the tank open. He found that the inside of the tank was coated with a waxy white substance that was remarkably unreactive toward even the most corrosive chemical reagents. The compound was formed by the *addition polymerization* (Section 12.2) of tetrafluoroethylene:

$$n\mathrm{CF_2{=}CF_2} \xrightarrow{\text{polymerization}} \mathrm{-\!\!(CF_2-CF_2)_{\!n}\!-}$$

As it turned out, the properties of Teflon were ideal for an immediate and important application in the development of the first atomic bomb. Uranium hexafluoride, UF_6, which was used to separate fissionable ^{235}U by gaseous diffusion (see the Chemistry at Work box in Section 10.8), is an extremely corrosive material. Teflon was used as a gasket material in the gaseous diffusion plant. It is now used in a variety of applications, from nonstick cookware to space suits.

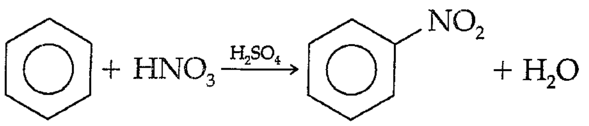
Plunkett's desire to know more about something that just didn't seem right is a wonderful example of how natural scientific curiosity can lead to remarkable discoveries. If you wish to read about more such accidental discoveries, we recommend Royston M. Roberts, *Serendipity: Accidental Discoveries in Science*, John Wiley and Sons, 1989.

Aromatic Hydrocarbons

Aromatic hydrocarbons are members of a large and important class of hydrocarbons. The simplest member of the series is benzene (see Figure 25.1), with molecular formula C_6H_6. As we have already noted, benzene is a planar, highly symmetrical molecule. The structure for benzene suggests a high degree of unsaturation. You might therefore expect benzene to resemble the unsaturated hydrocarbons and to be highly reactive. In fact, however, benzene is not at all similar to alkenes or alkynes in chemical behavior. The great stability of benzene and the other aromatic hydrocarbons as compared with alkenes and alkynes is due to stabilization of the π electrons through delocalization in the π orbitals. ∞ (Section 9.5)

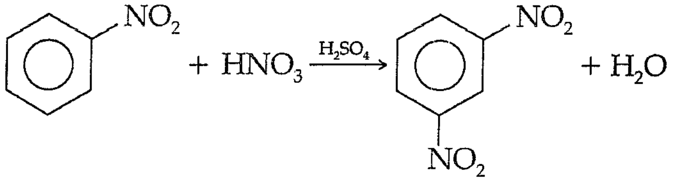
Each aromatic ring system is given a common name as shown in Figure 25.10. The aromatic rings are represented by hexagons with a circle inscribed inside to denote aromatic character. Each corner represents a carbon atom. Each carbon is bound to three other atoms—either three carbons or two carbons and a hydrogen. The hydrogen atoms are not shown.

Although aromatic hydrocarbons are unsaturated, they do not readily undergo addition reactions. The delocalized π bonding causes aromatic compounds to behave quite differently from alkenes and alkynes. For example, benzene does not add Cl_2 or Br_2 to its double bonds under ordinary conditions. In contrast, aromatic hydrocarbons undergo **substitution reactions** relatively easily. In a substitution reaction, one atom of a molecule is removed and replaced (substituted) by another atom or group of atoms. For example, when benzene is warmed in a mixture of nitric and sulfuric acids, hydrogen is replaced by the nitro group, NO_2:



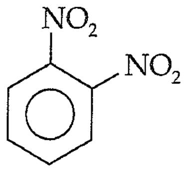
[25.7]

More vigorous treatment results in substitution of a second nitro group into the molecule:

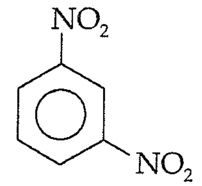


[25.8]

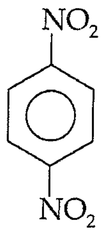
There are three possible isomers of benzene with two nitro groups attached. These three isomers are named *ortho-*, *meta-*, and *para-*dinitrobenzene:



ortho-Dinitrobenzene
m.p. 118°C

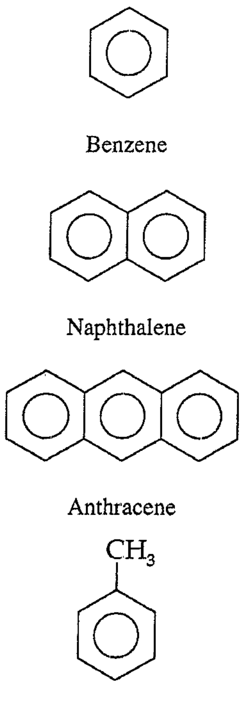


meta-Dinitrobenzene
m.p. 90°C



para-Dinitrobenzene
m.p. 174°C

Only the *meta* isomer is formed in the reaction of nitric acid with nitrobenzene.



Benzene

Naphthalene

Anthracene

Toluene
(methylbenzene)

▲ **FIGURE 25.10** Structures and names of several aromatic compounds.

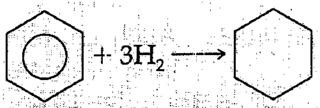
Learning Goal 11: Explain why aromatic hydrocarbons do not readily undergo addition reactions.

Learning Goal 12: Give two or three examples of substitution reactions of aromatic hydrocarbons.

Teaching Note: The English language definition of aromatic is "of or having an aroma; smelling sweet or spicy; fragrant or pungent." Historically, aromatic compounds were identified as such by their characteristic odor. The modern chemical definition of aromatic has to do with the cyclic delocalized bonding in a molecule rather than its odor.

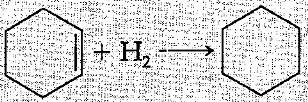
A Closer Look Aromatic Stabilization

We can obtain an estimate of the stabilization of the π electrons in benzene by comparing the energy required to add hydrogen to benzene to form a saturated compound with the energy required to hydrogenate certain alkenes. The hydrogenation of benzene to form cyclohexane can be represented as



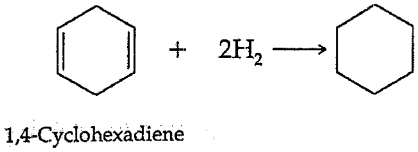
$\Delta H° = -208\ \text{kJ/mol}$

The enthalpy change in this reaction is −208 kJ/mol. The heat of hydrogenation of the cyclic alkene cyclohexene is −120 kJ/mol:



$\Delta H° = -120\ \text{kJ/mol}$

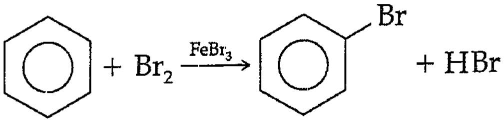
Similarly, the heat released on hydrogenating 1,4-cyclohexadiene is −232 kJ/mol:



$\Delta H° = -232\ \text{kJ/mo}$

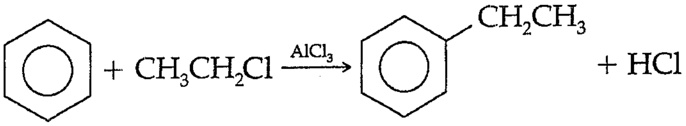
From these last two reactions, it appears that the heat of hydrogenating each double bond is roughly 116 kJ/mol for each bond. There is the equivalent of three double bonds in benzene. Therefore, we might expect that the heat of hydrogenating benzene would be about three times −116, or −348 kJ/mol, if benzene behaved as though it were "cyclohexatriene"; that is, if it behaved as though it had three double bonds in a ring. Instead, the heat released is much less than this, indicating that benzene is more stable than would be expected for three double bonds. The difference of 140 kJ/mol between −348 kJ/mol and the observed heat of hydrogenation, −208 kJ/mol, can be ascribed to stabilization of the π electrons through delocalization in the π orbitals that extend around the ring in an aromatic compound.

Another example of a substitution reaction is the bromination of benzene, which is carried out using $FeBr_3$ as a catalyst:



[25.9]

In a similar reaction, called the *Friedel-Crafts reaction,* alkyl groups can be substituted onto an aromatic ring by reaction of an alkyl halide with an aromatic compound in the presence of $AlCl_3$ as a catalyst:



[25.10]

25.4 Functional Groups; Alcohols and Ethers

The reactivity of organic compounds can be attributed to particular atoms or groups of atoms within the molecules. A site of reactivity in an organic molecule is called a **functional group** because it controls how the molecule behaves or functions. As we have seen, the presence of C═C double bonds or C≡C triple bonds in a hydrocarbon markedly increases its reactivity. Furthermore, these functional groups each undergo characteristic reactions. Each distinct kind of functional group undergoes the same kinds of reactions in every molecule, regardless of the size and complexity of the molecule. Thus, the chemistry of an organic molecule is largely determined by the functional groups it contains.

Learning Goal 13: Identify the groups or arrangement of atoms in a molecule that correspond to the following functional groups: alcohols; ethers; aldehydes and ketones; carboxylic acids; esters; amines and amides.

Table 25.4 lists the most common functional groups and gives examples of each. Notice that in addition to C═C double bonds or C≡C triple bonds, there are also many functional groups that contain elements other than just C and H. Many of the functional groups contain other nonmetals such as O and N.

Robert C. Mebane and Thomas R. Rybolt, "Chemistry in the Dyeing of Eggs," *J. Chem. Educ.* **1987**, *64*, 291–293.

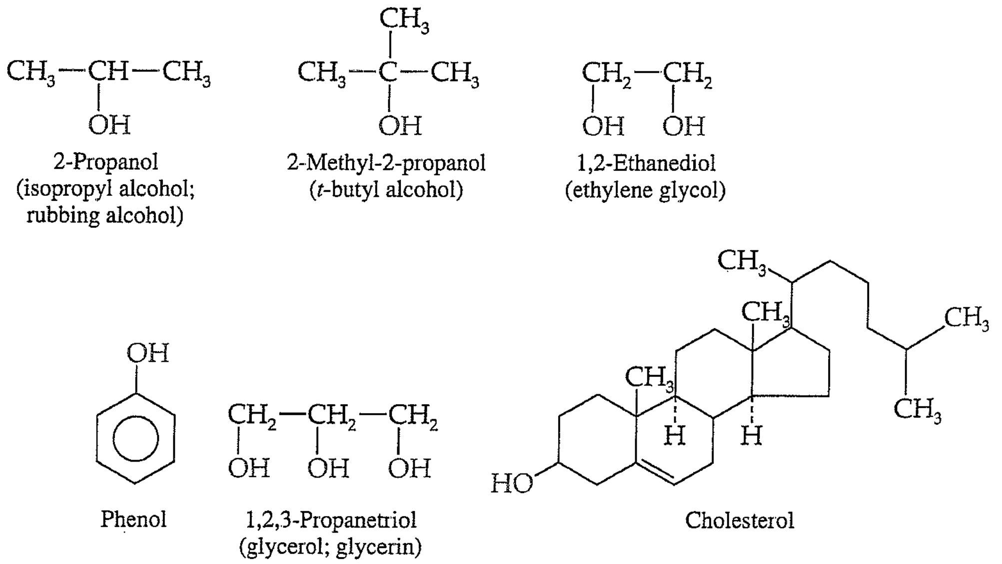
We can think of organic molecules as being composed of functional groups that are bonded to one or more alkyl groups. The alkyl groups, which are made of C—C and C—H single bonds, are the unreactive portions of the organic molecules. In describing general features of organic compounds, we can use the designation R to represent any alkyl group: methyl, ethyl, propyl, and so on. For example, alkanes, which contain no functional group, are represented as R—H. Alcohols, which contain the O—H, or alcohol functional group, are represented as R—OH. If two or more different alkyl groups are present in a molecule, we will designate them as R, R′, R″, and so forth. In this section we examine the structure and chemical properties of two functional groups, alcohols and ethers. In the next section we consider some additional functional groups that contain C═O bonds.

Alcohols (R—OH)

Point of Emphasis: Even though alcohols contain the −OH group, they are *not* hydroxides. The −OH is *covalently* bound to the carbon.

Alcohols are hydrocarbon derivatives in which one or more hydrogens of a parent hydrocarbon have been replaced by a *hydroxyl* or *alcohol* functional group, OH. Figure 25.11 shows the structural formulas and names of several alcohols. Note that the accepted name for an alcohol ends in *-ol*. The simple alcohols are named by changing the last letter in the name of the corresponding alkane to *-ol*—for example, ethan*e* becomes ethan*ol*. Where necessary, the location of the OH group is designated by an appropriate numeral prefix that indicates the number of the carbon atom bearing the OH group, as shown in the examples in Figure 25.11.

Because the O—H bond is polar, alcohols are much more soluble in polar solvents such as water than are hydrocarbons. The OH functional group can participate in hydrogen bonding. As a result, the boiling points of alcohols are much higher than those of their parent alkanes.



2-Propanol (isopropyl alcohol; rubbing alcohol)

2-Methyl-2-propanol (*t*-butyl alcohol)

1,2-Ethanediol (ethylene glycol)

Phenol

1,2,3-Propanetriol (glycerol; glycerin)

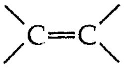
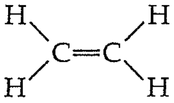
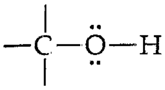
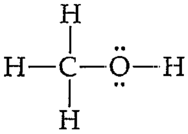
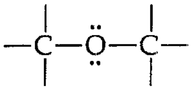
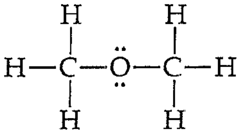
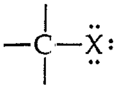
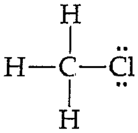
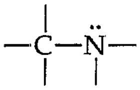
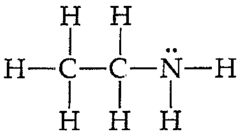
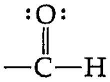
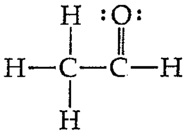
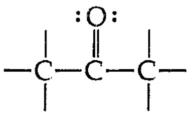
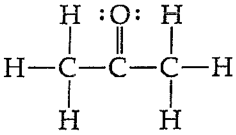
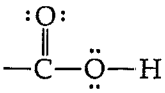
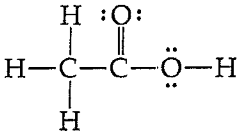
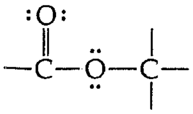
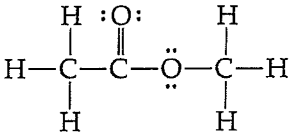
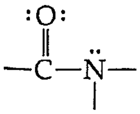
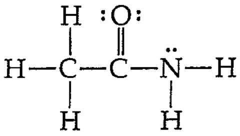
Cholesterol

▶ **FIGURE 25.11** Structural formulas of several important alcohols. Their common names are given in parentheses.

Figure 25.11

Table 25.4

TABLE 25.4 Common Functional Groups in Organic Compounds

Functional Group	Type of Compound	Suffix or Prefix	Example	Systematic Name (common name)
	Alkene	*ene*		Ethene (ethylene)
—C≡C—	Alkyne	*-yne*	H—C≡C—H	Ethyne (acetylene)
 $-\underset{\vert}{\overset{\vert}{C}}-\underset{\cdot\cdot}{\ddot{O}}-H$	Alcohol	*-ol*	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\underset{\cdot\cdot}{\ddot{O}}-H$	Methanol (methyl alcohol)
 $-\underset{\vert}{\overset{\vert}{C}}-\underset{\cdot\cdot}{\ddot{O}}-\underset{\vert}{\overset{\vert}{C}}-$	Ether	*ether*	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\underset{\cdot\cdot}{\ddot{O}}-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-H$	Dimethyl ether
 $-\underset{\vert}{\overset{\vert}{C}}-\underset{\cdot\cdot}{\ddot{X}}:$ (X = halogen)	Haloalkane	*halo-*	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\underset{\cdot\cdot}{\ddot{Cl}}:$	Chloromethane (methyl chloride)
 $-\underset{\vert}{\overset{\vert}{C}}-\underset{\vert}{\ddot{N}}-$	Amine	*-amine*	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\underset{\underset{H}{\vert}}{\ddot{N}}-H$	Ethylamine
 $-\overset{\overset{:O:}{\Vert}}{C}-H$	Aldehyde	*-al*	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{:O:}{\Vert}}{C}-H$	Ethanal (acetaldehyde)
 $-\underset{\vert}{\overset{\vert}{C}}-\overset{\overset{:O:}{\Vert}}{C}-\underset{\vert}{\overset{\vert}{C}}-$	Ketone	*-one*	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{:O:}{\Vert}}{C}-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-H$	2-Propanone (acetone)
 $-\overset{\overset{:O:}{\Vert}}{C}-\underset{\cdot\cdot}{\ddot{O}}-H$	Carboxylic acid	*-oic acid*	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{:O:}{\Vert}}{C}-\underset{\cdot\cdot}{\ddot{O}}-H$	Ethanoic acid (acetic acid)
 $-\overset{\overset{:O:}{\Vert}}{C}-\underset{\cdot\cdot}{\ddot{O}}-\underset{\vert}{\overset{\vert}{C}}-$	Ester	*-oate*	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{:O:}{\Vert}}{C}-\underset{\cdot\cdot}{\ddot{O}}-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-H$	Methyl ethanoate (methyl acetate)
 $-\overset{\overset{:O:}{\Vert}}{C}-\underset{\vert}{\ddot{N}}-$	Amide	*-amide*	 $H-\underset{\underset{H}{\vert}}{\overset{\overset{H}{\vert}}{C}}-\overset{\overset{:O:}{\Vert}}{C}-\underset{\underset{H}{\vert}}{\ddot{N}}-H$	Ethanamide (acetamide)