24

A chemical plant. Many small organic compounds form the basis of multibillion dollar pharmaceutical and polymer industries. The molecular models show acetic acid, benzene, ethylene, formaldehyde, and methanol.

Organic Chemistry

A LOOK AHEAD

- We begin by defining the scope and nature of organic chemistry. (24.1)
- Next, we examine aliphatic hydrocarbons. First, we study the nomenclature and reactions of alkanes. We examine the optical isomerism of substituted alkanes and also the properties of cycloalkanes. We then study unsaturated hydrocarbons—alkenes and alkynes—molecules that contain carbon-to-carbon double bonds and triple bonds. We focus on their nomenclature, properties, and geometric isomers. (24.2)
- Aromatic compounds all contain one or more benzene rings. They are, in general, more stable than aliphatic hydrocarbons. (24.3)
- Finally, we see that the reactivity of organic compounds can be largely accounted for by the presence of functional groups. We classify the oxygen- and nitrogen-containing functional groups in alcohols, ethers, aldehydes and ketones, carboxylic acids, esters, and amines. (24.4)

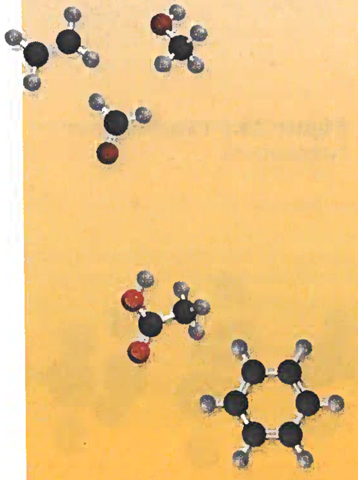
Interactive Activity Summary

1. Interactivity: Aliphatic Hydrocarbons (24.2)
2. Animations: Chirality (24.2)
3. Interactivity: Cyclohexane—Boat and Chair Formations (24.2)

Organic chemistry is the study of carbon compounds. The word "organic" was originally used by eighteenth-century chemists to describe substances obtained from living sources—plants and animals. These chemists believed that nature possessed a certain vital force and that only living things could produce organic compounds. This romantic notion was disproved in 1828 by Friedrich Wohler, a German chemist who prepared urea, an organic compound, from the reaction between the inorganic compounds lead cyanate and aqueous ammonia:

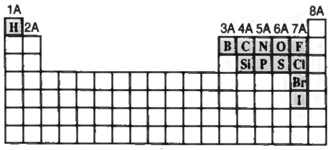
$$Pb(OCN)_2 + 2NH_3 + 2H_2O \longrightarrow \underset{\text{urea}}{2(NH_2)_2CO} + Pb(OH)_2$$

Today, well over 14 million synthetic and natural organic compounds are known. This number is significantly greater than the 100,000 or so known inorganic compounds.



24.1 Classes of Organic Compounds

Recall that the linking of like atoms is called catenation. The ability of carbon to catenate is discussed in Section 21.3.



Common elements in organic compounds.

Carbon can form more compounds than any other element because carbon atoms are able not only to form single, double, and triple carbon-carbon bonds, but also to link up with each other in chains and ring structures. *The branch of chemistry that deals with carbon compounds is* ***organic chemistry.***

Classes of organic compounds can be distinguished according to functional groups they contain. A ***functional group*** is *a group of atoms that is largely responsible for the chemical behavior of the parent molecule.* Different molecules containing the same kind of functional group or groups undergo similar reactions. Thus, by learning the characteristic properties of a few functional groups, we can study and understand the properties of many organic compounds. In the second half of this chapter we will discuss the functional groups known as alcohols, ethers, aldehydes and ketones, carboxylic acids, and amines.

Most organic compounds are derived from a group of compounds known as ***hydrocarbons*** because they are *made up of only hydrogen and carbon.* On the basis of structure, hydrocarbons are divided into two main classes—aliphatic and aromatic. ***Aliphatic hydrocarbons*** *do not contain the benzene group, or the benzene ring,* whereas ***aromatic hydrocarbons*** *contain one or more benzene rings.*

24.2 Aliphatic Hydrocarbons

Aliphatic hydrocarbons are divided into alkanes, alkenes, and alkynes, discussed next (Figure 24.1).

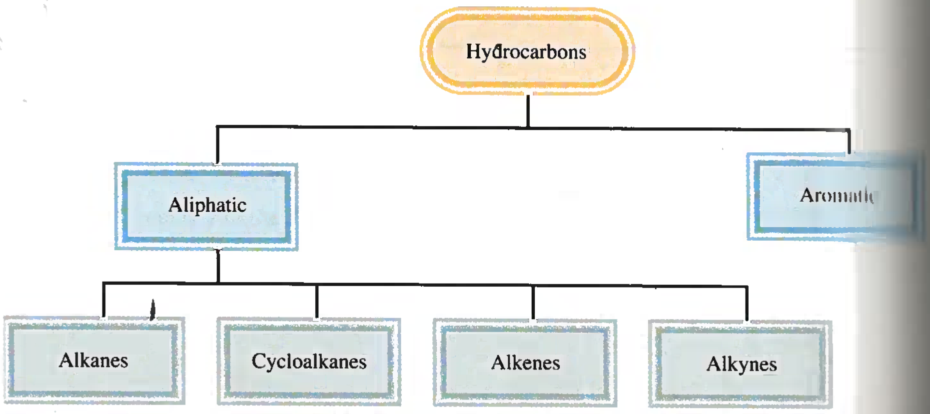
Interactivity:
Aliphatic Hydrocarbons
ARIS, Interactives

Alkanes

Alkanes *have the general formula* C_nH_{2n+2}, *where* $n = 1, 2, \ldots$. The essential characteristic of alkane hydrocarbon molecules is that *only single covalent bonds are present.* The alkanes are known as ***saturated hydrocarbons*** because they *contain the maximum number of hydrogen atoms that can bond with the number of carbon atoms present.*

The simplest alkane (that is, with $n = 1$) is methane CH_4, which is a natural product of the anaerobic bacterial decomposition of vegetable matter under water. Because it was first collected in marshes, methane became known as "marsh gas." A rather improbable but proven source of methane is termites. When these voracious insects consume wood, the microorganisms that inhabit their digestive system break down cellulose (the major component of wood) into methane, carbon dioxide, and other compounds. An estimated 170 million tons of methane are produced annually by

Figure 24.1 *Classification of hydrocarbons.*



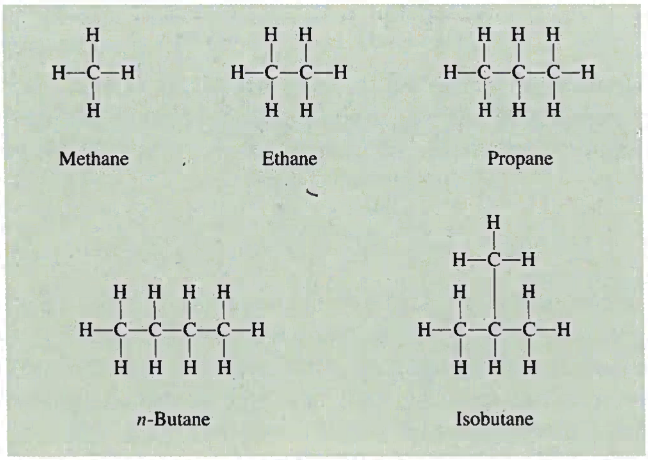


Figure 24.2 *Structures of the first four alkanes. Note that butane can exist in two structurally different forms, called structural isomers.*

termites! It is also produced in some sewage treatment processes. Commercially, methane is obtained from natural gas. The Chemistry in Action essay on p. 1016 describes an interesting compound formed by methane and water molecules.

Figure 24.2 shows the structures of the first four alkanes ($n = 1$ to $n = 4$). Natural gas is a mixture of methane, ethane, and a small amount of propane. We discussed the bonding scheme of methane in Chapter 10. Indeed the carbon atoms in all the alkanes can be assumed to be sp^3-hybridized. The structures of ethane and propane are straightforward, for there is only one way to join the carbon atoms in these molecules. Butane, however, has two possible bonding schemes resulting in the ***structural isomers*** *n*-butane (*n* stands for normal) and isobutane, *molecules that have the same molecular formula, but different structures.* Alkanes such as the structural isomers of butane are described as having the straight chain or branched chain structures. *n*-Butane is a straight-chain alkane because the carbon atoms are joined along one line. In a branched-chain alkane like isobutane, one or more carbon atoms are bonded to at least three other carbon atoms.

In the alkane series, as the number of carbon atoms increases, the number of structural isomers increases rapidly. For example, butane, C_4H_{10}, has two isomers; decane, $C_{10}H_{22}$, has 75 isomers; and the alkane $C_{30}H_{62}$ has over 400 million, or 4×10^8, possible isomers! Obviously, most of these isomers do not exist in nature nor have they been synthesized. Nevertheless, the numbers help to explain why carbon is found in so many more compounds than any other element.

Example 24.1 deals with the number of structural isomers of an alkane.

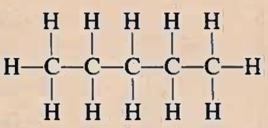
Termites are a natural source of methane.

Example 24.1

How many structural isomers can be identified for pentane, C_5H_{12}?

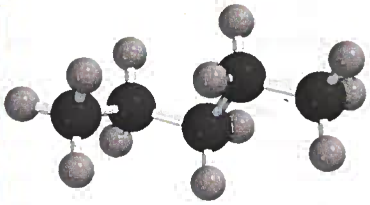
Strategy For small hydrocarbon molecules (eight or fewer C atoms), it is relatively easy to determine the number of structural isomers by trial and error.

Solution The first step is to write the straight-chain structure:

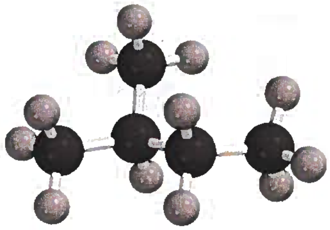


n-pentane
(b.p. 36.1°C)

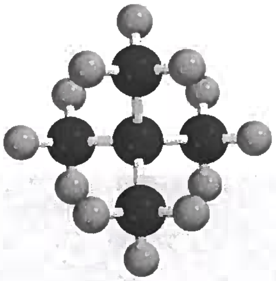
(Continued)



n-pentane



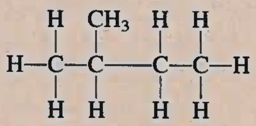
2-methylbutane



2,2-dimethylpropane

Similar problem: 24.11.

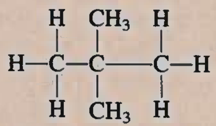
The second structure, by necessity, must be a branched chain:



$$\begin{array}{ccccccccc} & & H & & CH_3 & & H & & H \\ & & | & & | & & | & & | \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | \\ & & H & & H & & H & & H \end{array}$$

2-methylbutane
(b.p. 27.9°C)

Yet another branched-chain structure is possible:



$$\begin{array}{ccccccccc} & & H & & CH_3 & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & CH_3 & & H & & \end{array}$$

2,2-dimethylpropane
(b.p. 9.5°C)

We can draw no other structure for an alkane having the molecular formula C_5H_{12}. Thus, pentane has three structural isomers, in which the numbers of carbon and hydrogen atoms remain unchanged despite the differences in structure.

Practice Exercise How many structural isomers are there in the alkane C_6H_{14}?

Table 24.1 shows the melting and boiling points of the straight-chain isomers of the first 10 alkanes. The first four are gases at room temperature; and pentane through decane are liquids. As molecular size increases, so does the boiling point, because of the increasing dispersion forces (see Section 11.2).

Alkane Nomenclature

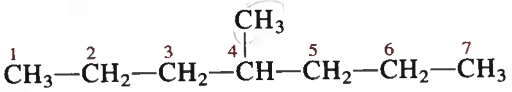
The nomenclature of alkanes and all other organic compounds is based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC). The first four alkanes (methane, ethane, propane, and butane) have nonsystematic names. As Table 24.1 shows, the number of carbon atoms is reflected in the Greek

TABLE 24.1 The First 10 Straight-Chain Alkanes

Name of Hydrocarbon	Molecular Formula	Number of Carbon Atoms	Melting Point (°C)	Boiling Point (°C)
Methane	CH_4	1	−182.5	−161.6
Ethane	$CH_3—CH_3$	2	−183.3	−88.6
Propane	$CH_3—CH_2—CH_3$	3	−189.7	−42.1
Butane	$CH_3—(CH_2)_2—CH_3$	4	−138.3	−0.5
Pentane	$CH_3—(CH_2)_3—CH_3$	5	−129.8	36.1
Hexane	$CH_3—(CH_2)_4—CH_3$	6	−95.3	68.7
Heptane	$CH_3—(CH_2)_5—CH_3$	7	−90.6	98.4
Octane	$CH_3—(CH_2)_6—CH_3$	8	−56.8	125.7
Nonane	$CH_3—(CH_2)_7—CH_3$	9	−53.5	150.8
Decane	$CH_3—(CH_2)_8—CH_3$	10	−29.7	174.0

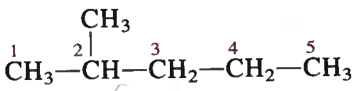
prefixes for the alkanes containing five to ten carbons. We now apply the IUPAC rules to the following examples:

1. The parent name of the hydrocarbon is that given to the longest continuous chain of carbon atoms in the molecule. Thus, the parent name of the following compound is heptane because there are seven carbon atoms in the longest chain



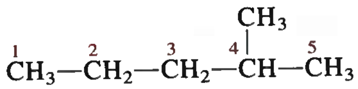
$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{\overset{CH_3}{|}}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH_3}$$

2. An alkane less one hydrogen atom is an *alkyl* group. For example, when a hydrogen atom is removed from methane, we are left with the CH_3 fragment, which is called a *methyl* group. Similarly, removing a hydrogen atom from the ethane molecule gives an *ethyl* group, or C_2H_5. Table 24.2 lists the names of several common alkyl groups. Any chain branching off the longest chain is named as an alkyl group.
3. When one or more hydrogen atoms are replaced by other groups, the name of the compound must indicate the locations of carbon atoms where replacements are made. The procedure is to number each carbon atom on the longest chain in the direction that gives the smaller numbers for the locations of all branches. Consider the two different systems for the *same* compound shown here:



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

2-methylpentane

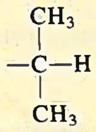
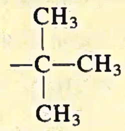


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{\overset{CH_3}{|}}{\overset{4}{CH}}-\overset{5}{CH_3}$$

4-methylpentane

The compound on the left is numbered correctly because the methyl group is located at carbon 2 of the pentane chain; in the compound on the right, the methyl group is located at carbon 4. Thus, the name of the compound is 2-methylpentane, and not 4-methylpentane. Note that the branch name and the parent name are written as a single word, and a hyphen follows the number.

TABLE 24.2 Common Alkyl Groups

Name	Formula
Methyl	$-CH_3$
Ethyl	$-CH_2-CH_3$
n-Propyl	$-CH_2-CH_2-CH_3$
n-Butyl	$-CH_2-CH_2-CH_2-CH_3$
Isopropyl	 $-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-H$
t-Butyl*	 $-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_3$

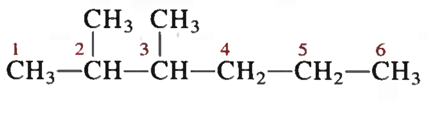
*The letter *t* stands for tertiary.

TABLE 24.3

Names of Common Substituent Groups

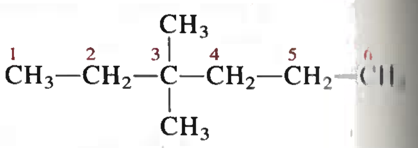
Functional Group	Name
$—NH_2$	Amino
—F	Fluoro
—Cl	Chloro
—Br	Bromo
—I	Iodo
$—NO_2$	Nitro
$—CH{=}CH_2$	Vinyl

4. When there is more than one alkyl branch of the same kind present, we use a prefix such as *di-*, *tri-*, or *tetra-* with the name of the alkyl group. Consider the following examples:



$\overset{1}{CH_3}-\overset{CH_3}{\overset{2|}{CH}}-\overset{CH_3}{\overset{3|}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_3}$

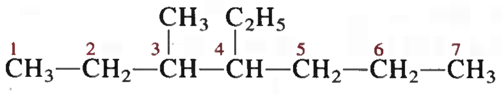
2,3-dimethylhexane



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

3,3-dimethylhexane

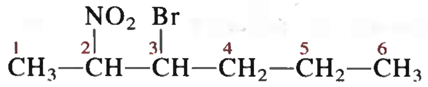
When there are two or more different alkyl groups, the names of the groups are listed alphabetically. For example,



$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{CH_3}{\overset{3|}{CH}}-\overset{C_2H_5}{\overset{4|}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH_3}$

4-ethyl-3-methylheptane

5. Of course, alkanes can have many different types of substituents. Table 24.3 lists the names of some substituents, including nitro and bromo. Thus, the compound

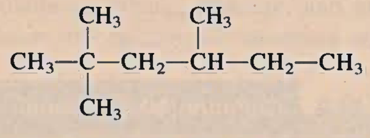


$\overset{1}{CH_3}-\overset{NO_2}{\overset{2|}{CH}}-\overset{Br}{\overset{3|}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_3}$

is called 3-bromo-2-nitrohexane. Note that the substituent groups are listed alphabetically in the name, and the chain is numbered in the direction that gives the lowest number to the first substituted carbon atom.

Example 24.2

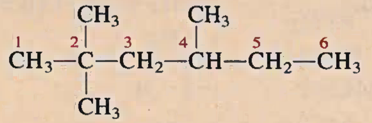
Give the IUPAC name of the following compound:



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

Strategy We follow the IUPAC rules and use the information in Table 24.2 to name the compound. How many C atoms are there in the longest chain?

Solution The longest chain has six C atoms so the parent compound is called hexane. Note that there are two methyl groups attached to carbon number 2 and one methyl group attached to carbon number 4.

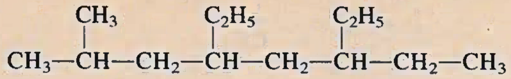


$\overset{1}{CH_3}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{2|}{C}}}}-\overset{3}{CH_2}-\overset{CH_3}{\overset{4|}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_3}$

Therefore, we call the compound 2,2,4-trimethylhexane.

Similar problem: 24.26.

Practice Exercise Give the IUPAC name of the following compound:



$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{C_2H_5}{\overset{|}{CH}}-CH_2-\overset{C_2H_5}{\overset{|}{CH}}-CH_2-CH_3$

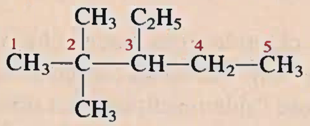
Example 24.3 shows that prefixes such as di-, tri-, and tetra- are used as needed, but are ignored when alphabetizing.

Example 24.3

Write the structural formula of 3-ethyl-2,2-dimethylpentane.

Strategy We follow the preceding procedure and the information in Table 24.2 to write the structural formula of the compound. How many C atoms are there in the longest chain?

Solution The parent compound is pentane, so the longest chain has five C atoms. There are two methyl groups attached to carbon number 2 and one ethyl group attached to carbon number 3. Therefore, the structure of the compound is



$$\overset{1}{CH_3}—\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}—\overset{C_2H_5}{\overset{3}{C}H}—\overset{4}{CH_2}—\overset{5}{CH_3}$$

Similar problem: 24.27.

Practice Exercise Write the structural formula of 5-ethyl-2,4,6-trimethyloctane.

Reactions of Alkanes

Alkanes are generally not considered to be very reactive substances. However, under suitable conditions they do react. For example, natural gas, gasoline, and fuel oil are alkanes that undergo highly exothermic combustion reactions:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -890.4 \text{ kJ/mol}$$
$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l) \qquad \Delta H^\circ = -3119 \text{ kJ/mol}$$

These, and similar combustion reactions, have long been utilized in industrial processes and in domestic heating and cooking.

Halogenation of alkanes—that is, the replacement of one or more hydrogen atoms by halogen atoms—is another type of reaction that alkanes undergo. When a mixture of methane and chlorine is heated above 100°C or irradiated with light of a suitable wavelength, methyl chloride is produced:

The systematic names of methyl chloride, methylene chloride, and chloroform are monochloromethane, dichloromethane, and trichloromethane, respectively.

$$CH_4(g) + Cl_2(g) \longrightarrow \underset{\text{methyl chloride}}{CH_3Cl(g)} + HCl(g)$$

If an excess of chlorine gas is present, the reaction can proceed further:

$$CH_3Cl(g) + Cl_2(g) \longrightarrow \underset{\text{methylene chloride}}{CH_2Cl_2(l)} + HCl(g)$$
$$CH_2Cl_2(l) + Cl_2(g) \longrightarrow \underset{\text{chloroform}}{CHCl_3(l)} + HCl(g)$$
$$CHCl_3(l) + Cl_2(g) \longrightarrow \underset{\text{carbon tetrachloride}}{CCl_4(l)} + HCl(g)$$

A great deal of experimental evidence suggests that the initial step of the first halogenation reaction occurs as follows:

$$Cl_2 + \text{energy} \longrightarrow Cl\cdot + Cl\cdot$$

Thus, the covalent bond in Cl_2 breaks and two chlorine atoms form. We know it is the Cl—Cl bond that breaks when the mixture is heated or irradiated because the bond enthalpy of Cl_2 is 242.7 kJ/mol, whereas about 414 kJ/mol are needed to break C—H bonds in CH_4.

A chlorine atom is a *radical,* which contains an unpaired electron (shown by a single dot). Chlorine atoms are highly reactive and attack methane molecules according to the equation

$$CH_4 + Cl\cdot \longrightarrow \cdot CH_3 + HCl$$

This reaction produces hydrogen chloride and the methyl radical $\cdot CH_3$. The methyl radical is another reactive species; it combines with molecular chlorine to give methyl chloride and a chlorine atom:

$$\cdot CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$$

The production of methylene chloride from methyl chloride and any further reactions can be explained in the same way. The actual mechanism is more complex than the scheme we have shown because "side reactions" that do not lead to the desired products often take place, such as

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2$$
$$\cdot CH_3 + \cdot CH_3 \longrightarrow C_2H_6$$

Alkanes in which one or more hydrogen atoms have been replaced by a halogen atom are called *alkyl halides*. Among the large number of alkyl halides, the best known are chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), methylene chloride (CH_2Cl_2), and the chlorofluorohydrocarbons.

Chloroform is a volatile, sweet-tasting liquid that was used for many years as an anesthetic. However, because of its toxicity (it can severely damage the liver, kidneys, and heart) it has been replaced by other compounds. Carbon tetrachloride, also a toxic substance, serves as a cleaning liquid, for it removes grease stains from clothing. Methylene chloride is used as a solvent to decaffeinate coffee and as a paint remover.

The preparation of chlorofluorocarbons and the effect of these compounds on ozone in the stratosphere were discussed in Chapter 17.

Optical Isomerism of Substituted Alkanes

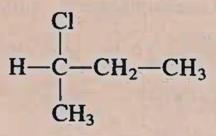
Optical isomerism was first discussed in Section 22.4.

Animation:
Chirality
ARIS, Animations

Optical isomers are compounds that are nonsuperimposable mirror images of each other. Figure 24.3 shows perspective drawings of the substituted methanes CH_2ClBr and CHFClBr and their mirror images. The mirror images of CH_2ClBr are superimposable but those of CHFClBr are not, no matter how we rotate the molecules. Thus, the CHFClBr molecule is chiral. Most simple chiral molecules contain at least one *asymmetric* carbon atom—that is, a carbon atom bonded to four different atoms or groups of atoms.

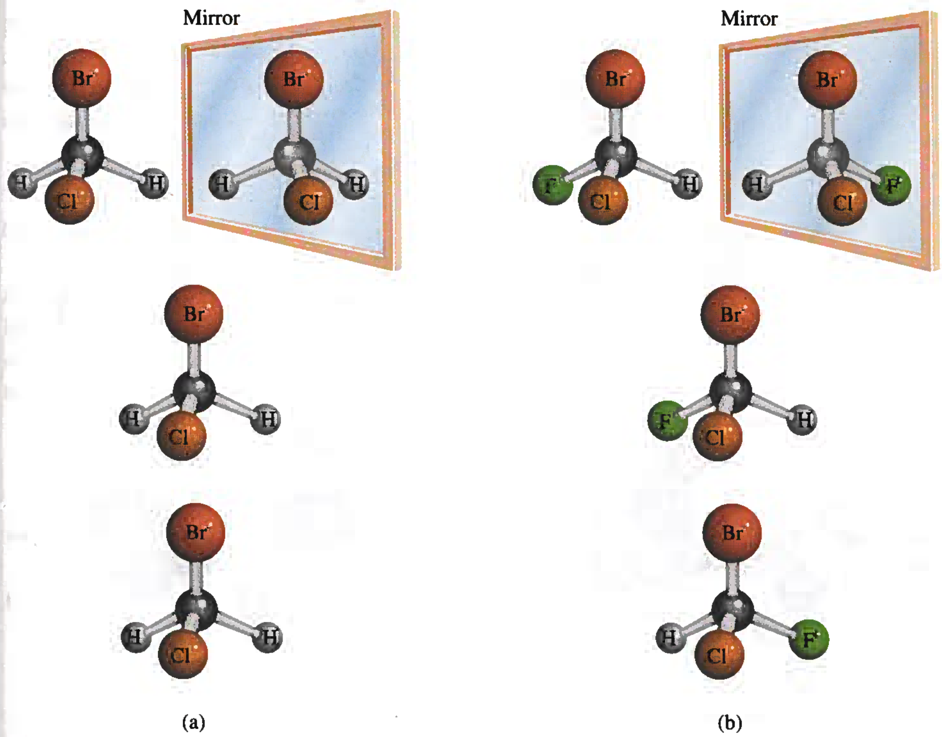
Example 24.4

Is the following molecule chiral?



$$H-\overset{\displaystyle Cl}{\underset{\displaystyle CH_3}{C}}-CH_2-CH_3$$

(Continued)



(a) (b)

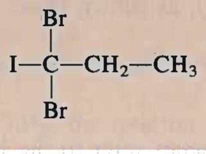
Figure 24.3 *(a) The CH_2ClBr molecule and its mirror image. Because the molecule and its mirror image are superimposable, the molecule is said to be achiral. (b) The CHFClBr molecule and its mirror image. Since the molecule and its mirror image are not superimposable, no matter how we rotate one with respect to the other, the molecule is said to be chiral.*

Strategy Recall the condition for chirality. Is the central C atom asymmetric; that is, does it have four different atoms or different groups attached to it?

Solution We note that the central carbon atom is bonded to a hydrogen atom, a chlorine atom, a $—CH_3$ group, and a $—CH_2—CH_3$ group. Therefore, the central carbon atom is asymmetric and the molecule is chiral.

Similar problem: 24.25.

Practice Exercise Is the following molecule chiral?



$$I—\overset{\displaystyle Br}{\underset{\displaystyle Br}{\overset{|}{\underset{|}{C}}}}—CH_2—CH_3$$

Cycloalkanes

Alkanes whose carbon atoms are joined in rings are known as ***cycloalkanes.*** They have the general formula C_nH_{2n}, where $n = 3, 4, \ldots$. The simplest cycloalkane is cyclopropane, C_3H_6 (Figure 24.4). Many biologically significant substances such as cholesterol, testosterone, and progesterone contain one or more such ring systems. Theoretical analysis shows that cyclohexane can assume two different geometries that are relatively free of strain (Figure 24.5). By "strain" we mean that bonds are compressed, stretched, or twisted out of normal geometric shapes as predicted by sp^3 hybridization. The most stable geometry is the *chair form.*

Interactivity:
Cyclohexane—Boat and Chair Formations
ARIS, Interactives

Alkenes

The ***alkenes*** (also called *olefins*) *contain at least one carbon-carbon double bond. Alkenes have the general formula C_nH_{2n}, where $n = 2, 3, \ldots$.* The simplest alkene

Figure 24.4 *Structures of the first four cycloalkanes and their simplified forms.*

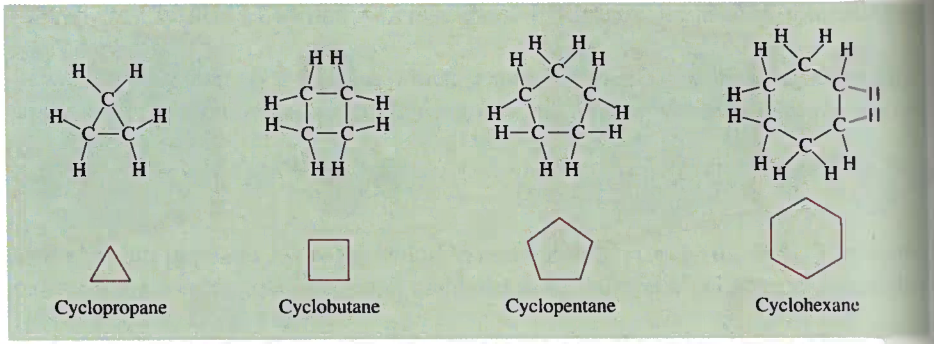
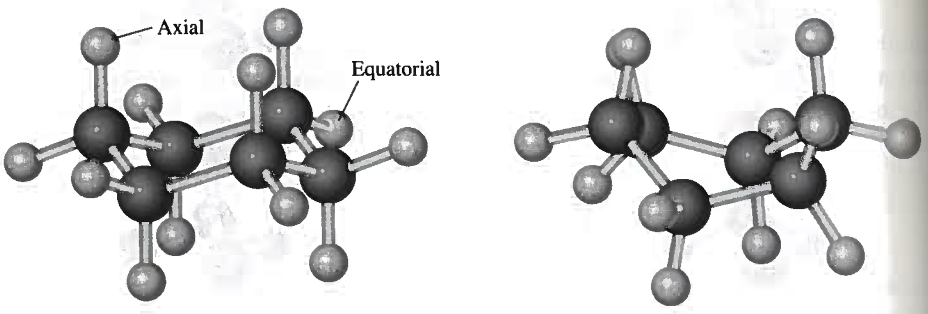


Figure 24.5 *The cyclohexane molecule can exist in various shapes. The most stable shape is the chair form and a less stable one is the boat form. Two types of H atoms are labeled axial and equatorial, respectively.*



Chair form

Boat form

is C_2H_4, ethylene, in which both carbon atoms are sp^2-hybridized and the double bond is made up of a sigma bond and a pi bond (see Section 10.5).

Alkene Nomenclature

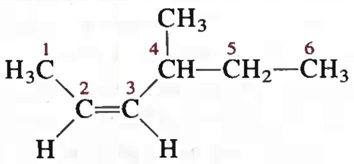
In naming alkenes we indicate the positions of the carbon-carbon double bonds. The names of compounds containing C=C bonds end with *-ene*. As with the alkanes, the name of the parent compound is determined by the number of carbon atoms in the longest chain (see Table 24.1), as shown here:

$CH_2{=}CH{-}CH_2{-}CH_3$ $H_3C{-}CH{=}CH{-}CH_3$

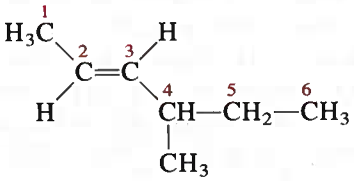
1-butene   2-butene

The numbers in the names of alkenes refer to the lowest numbered carbon atom in the chain that is part of the C=C bond of the alkene. The name "butene" means that there are four carbon atoms in the longest chain. Alkene nomenclature must specify whether a given molecule is *cis* or *trans* if it is a geometric isomer, such as

In the *cis* isomer, the two H atoms are on the same side of the C=C bond; in the *trans* isomer, the two H atoms are across from each other. Geometric isomerism was introduced in Section 22.4.



4-methyl-*cis*-2-hexene



4-methyl-*trans*-2-hexene

Properties and Reactions of Alkenes

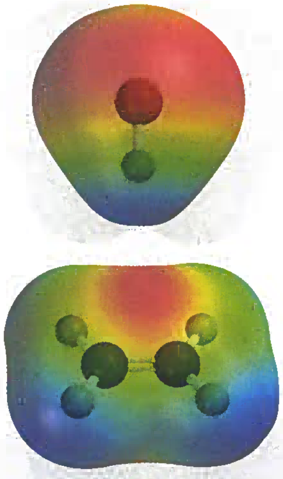
Ethylene is an extremely important substance because it is used in large quantities for the manufacture of organic polymers (to be discussed in Chapter 25) and in the preparation of many other organic chemicals. Ethylene is prepared industrially by the *cracking* process, that is, the thermal decomposition of a large hydrocarbon into smaller molecules. When ethane is heated to about 800°C, it undergoes the following reaction:

$$C_2H_6(g) \xrightarrow{\text{Pt catalyst}} CH_2{=}CH_2(g) + H_2(g)$$

Other alkenes can be prepared by cracking the higher members of the alkane family.

Alkenes are classified as ***unsaturated hydrocarbons,*** *compounds with double or triple carbon-carbon bonds that enable them to add hydrogen atoms.* Unsaturated hydrocarbons commonly undergo ***addition reactions,*** in which *one molecule adds to another to form a single product.* Hydrogenation (see p. 900) is an example of addition reaction. Other addition reactions to the C=C bond include

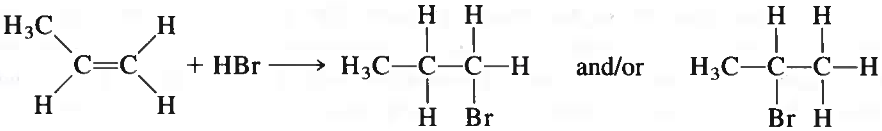
$$C_2H_4(g) + HX(g) \longrightarrow CH_3{-}CH_2X(g)$$
$$C_2H_4(g) + X_2(g) \longrightarrow CH_2X{-}CH_2X(g)$$



The addition reaction between HCl and ethylene. The initial interaction is between the positive end of HCl (blue) and the electron-rich region of ethylene (red), which is associated with the pi electrons of the C=C bond.

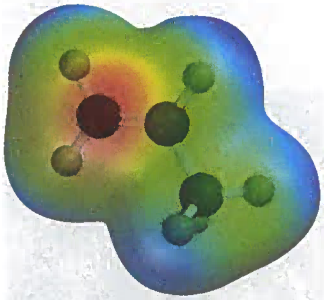
where X represents a halogen (Cl, Br, or I).

The addition of a hydrogen halide to an unsymmetrical alkene such as propene is more complicated because two products are possible:



propene 1-bromopropane 2-bromopropane

In reality, however, only 2-bromopropane is formed. This phenomenon was observed in all reactions between unsymmetrical reagents and alkenes. In 1871, Vladimir Markovnikov[†] postulated a generalization that enables us to predict the outcome of such an addition reaction. This generalization, now known as *Markovnikov's rule,* states that in the addition of unsymmetrical (that is, polar) reagents to alkenes, the positive portion of the reagent (usually hydrogen) adds to the carbon atom that already has the most hydrogen atoms.

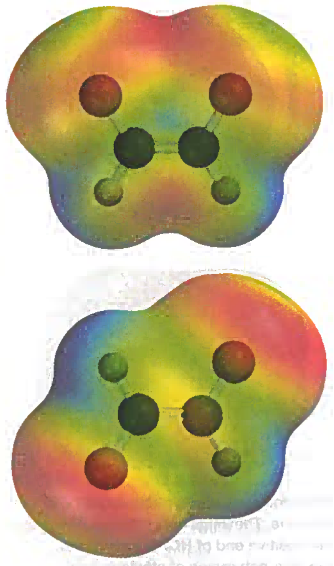


The electron density is higher on the carbon atom in the CH_2 group in propene.

Geometric Isomers of Alkenes

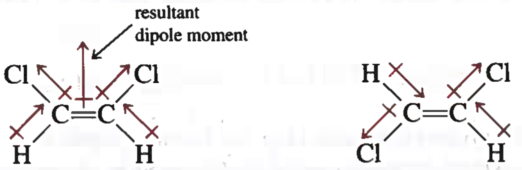
In a compound such as ethane, C_2H_6, the rotation of the two methyl groups about the carbon-carbon single bond (which is a sigma bond) is quite free. The situation is different for molecules that contain carbon-carbon double bonds, such as ethylene, C_2H_4. In addition to the sigma bond, there is a pi bond between the two carbon atoms. Rotation about the carbon-carbon linkage does not affect the sigma bond, but it does move the two $2p_z$ orbitals out of alignment for overlap and, hence, partially or totally destroys the pi bond (see Figure 10.16). This process requires an input of energy on the order of 270 kJ/mol. For this reason, the rotation of a carbon-carbon double bond is considerably restricted, but not impossible. Consequently, molecules containing carbon-carbon double bonds (that is, the alkenes) may have geometric isomers, which cannot be interconverted without breaking a chemical bond.

[†] Vladimir W. Markovnikov (1838–1904). Russian chemist. Markovnikov's observations of the addition reactions to alkenes were published a year after his death.



In *cis*-dichloroethylene (top), the bond moments reinforce one another and the molecule is polar. The opposite holds for *trans*-dichloroethylene and the molecule is nonpolar.

The molecule dichloroethylene, ClHC═CHCl, can exist as one of the two geometric isomers called *cis*-dichloroethylene and *trans*-dichloroethylene:



cis-dichloroethylene
$\mu = 1.89$ D
b.p. 60.3°C

trans-dichloroethylene
$\mu = 0$
b.p. 47.5°C

where the term *cis* means that two particular atoms (or groups of atoms) are adjacent to each other, and *trans* means that the two atoms (or groups of atoms) are across from each other. Generally, *cis* and *trans* isomers have distinctly different physical and chemical properties. Heat or irradiation with light is commonly used to bring about the conversion of one geometric isomer to another, a process called *cis-trans isomerization*, or geometric isomerization. As the above data show, dipole moment measurements can be used to distinguish between geometric isomers. In general, *cis* isomers possess a dipole moment, whereas *trans* isomers do not.

***Cis-Trans* Isomerization in the Vision Process** The molecules in the retina that respond to light are rhodopsin, which has two components called 11-*cis* retinal and opsin (Figure 24.6). Retinal is the light-sensitive component and opsin is a protein molecule. Upon receiving a photon in the visible region the 11-*cis* retinal isomerizes to the all-*trans* retinal by breaking a carbon-carbon pi bond. With the pi bond broken, the remaining carbon-carbon sigma bond is free to rotate and transforms into the all-*trans* retinal. At this point an electrical impulse is generated and transmitted to the brain, which forms a visual image. The all-*trans* retinal does not fit into the binding site on opsin and eventually separates from the protein. In time, the *trans* isomer is converted back to 11-*cis* retinal by an enzyme (in the absence of light) and rhodopsin is regenerated by the binding of the *cis* isomer to opsin and the visual cycle can begin again.

An electron micrograph of rod-shaped cells (containing rhodopsins) in the retina.

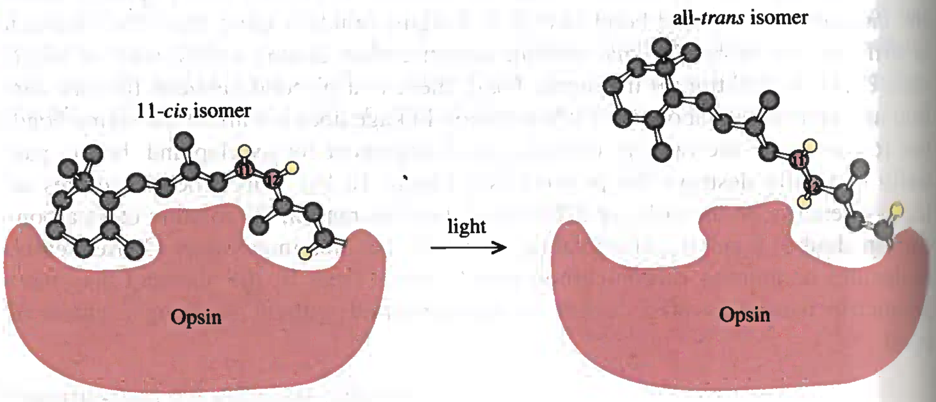


Figure 24.6 *The primary event in the vision process is the conversion of 11-cis retinal to the all-trans isomer on rhodopsin. The double bond at which the isomerization occurs is between carbon 11 and carbon-12. For simplicity, most of the H atoms are omitted. In the absence of light, this transformation takes place about once in a thousand years!*

Alkynes

***Alkynes** contain at least one carbon-carbon triple bond.* They have the *general formula* C_nH_{2n-2}, *where* $n = 2, 3, \ldots$.

Alkyne Nomenclature

Names of compounds containing C≡C bonds end with *-yne*. Again, the name of the parent compound is determined by the number of carbon atoms in the longest chain (see Table 24.1 for names of alkane counterparts). As in the case of alkenes, the names of alkynes indicate the position of the carbon-carbon triple bond, as, for example, in

$$\underset{\text{1-butyne}}{HC{\equiv}C{-}CH_2{-}CH_3} \qquad \underset{\text{2-butyne}}{H_3C{-}C{\equiv}C{-}CH_3}$$

Properties and Reactions of Alkynes

The reaction of calcium carbide with water produces acetylene, a flammable gas.

The simplest alkyne is ethyne, better known as acetylene (C_2H_2). The structure and bonding of C_2H_2 were discussed in Section 10.5. Acetylene is a colorless gas (b.p. −84°C) prepared by the reaction between calcium carbide and water:

$$CaC_2(s) + 2H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(aq)$$

Acetylene has many important uses in industry. Because of its high heat of combustion

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -2599.2\ \text{kJ/mol}$$

acetylene burned in an "oxyacetylene torch" gives an extremely hot flame (about 3000°C). Thus, oxyacetylene torches are used to weld metals (see p. 249).

The standard free energy of formation of acetylene is positive ($\Delta G_f^\circ = 209.2$ kJ/mol), unlike that of the alkanes. This means that the molecule is unstable (relative to its elements) and has a tendency to decompose:

$$C_2H_2(g) \longrightarrow 2C(s) + H_2(g)$$

In the presence of a suitable catalyst or when the gas is kept under pressure, this reaction can occur with explosive violence. To be transported safely, the gas must be dissolved in an organic solvent such as acetone at moderate pressure. In the liquid state, acetylene is very sensitive to shock and is highly explosive.

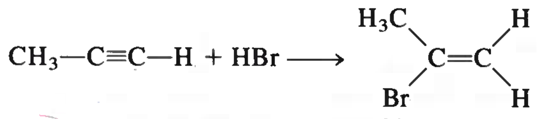
Acetylene, an unsaturated hydrocarbon, can be hydrogenated to yield ethylene:

$$C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$$

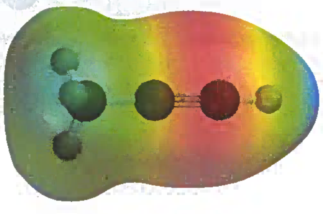
It undergoes the following addition reactions with hydrogen halides and halogens:

$$\begin{aligned} C_2H_2(g) + HX(g) &\longrightarrow CH_2{=}CHX(g) \\ C_2H_2(g) + X_2(g) &\longrightarrow CHX{=}CHX(g) \\ C_2H_2(g) + 2X_2(g) &\longrightarrow CHX_2{-}CHX_2(g) \end{aligned}$$

Methylacetylene (propyne), $CH_3{-}C{\equiv}C{-}H$, is the next member in the alkyne family. It undergoes reactions similar to those of acetylene. The addition reactions of propyne also obey Markovnikov's rule:



propyne 2-bromopropene



Propyne. Can you account for Markovnikov's rule in this molecule?

CHEMISTRY *in Action*

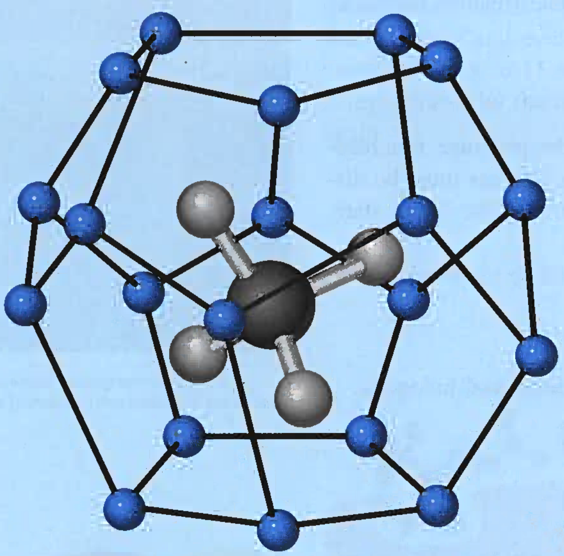
Ice That Burns

Ice that burns? Yes, there is such a thing. It is called *methane hydrate,* and there is enough of it to meet America's energy needs for years. But scientists have yet to figure out how to mine it without causing an environmental disaster.

Bacteria in the sediments on the ocean floor consume organic material and generate methane gas. Under high-pressure and low-temperature conditions, methane forms methane hydrate, which consists of single molecules of the natural gas trapped within crystalline cages formed by frozen water molecules. A lump of methane hydrate looks like a gray ice cube, but if one puts a lighted match to it, it will burn.

Oil companies have known about methane hydrate since the 1930s, when they began using high-pressure pipelines to transport natural gas in cold climates. Unless water is carefully removed before the gas enters the pipeline, chunks of methane hydrate will impede the flow of gas.

The total reserve of the methane hydrate in the world's oceans is estimated to be 10^{13} tons of carbon content, about twice the amount of carbon in all the coal, oil, and natural gas on land. However, harvesting the energy stored in methane hydrate presents a tremendous engineering challenge. It is believed that methane hydrate acts as a kind of cement to keep the ocean floor sediments together. Tampering with the hydrate deposits could cause underwater landslides, leading to the discharge of methane into the atmosphere. This event could have serious consequences for the environment, because methane is a potent greenhouse gas (see Section 17.5). In fact, scientists have speculated that the abrupt release of methane hydrates may have hastened the end of the last ice age about 10,000 years ago. As the great blanket of continental ice melted, global sea levels swelled by more than 90 m, submerging Arctic regions rich in hydrate deposits. The relatively warm ocean water would have melted the hydrates, unleashing tremendous amounts of methane, which led to global warming.

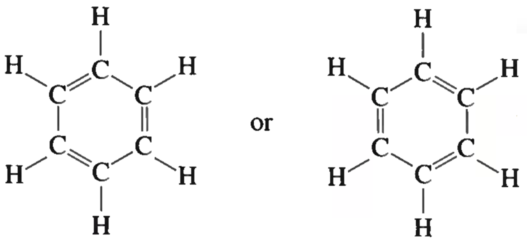


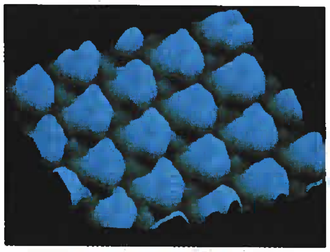
Methane hydrate. The methane molecule is trapped in a cage of frozen water molecules (blue spheres) held together by hydrogen bonds.

Methane hydrate burning in air.

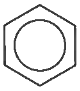
24.3 Aromatic Hydrocarbons

Benzene, the parent compound of this large family of organic substances, was discovered by Michael Faraday in 1826. Over the next 40 years, chemists were preoccupied with determining its molecular structure. Despite the small number of atoms in the molecule, there are quite a few ways to represent the structure of benzene without violating the tetravalency of carbon. However, most proposed structures were rejected because they did not explain the known properties of benzene. Finally, in 1865, August Kekulé[†] deduced that the benzene molecule could be best represented by a ring structure—a cyclic compound consisting of six carbon atoms:



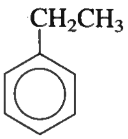

An electron micrograph of benzene molecules, which shows clearly the ring structure.

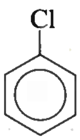
As we saw in Section 9.8, the properties of benzene are best represented by both of the above resonance structures. Alternatively, the properties of benzene can be explained in terms of delocalized molecular orbitals (see p. 438):

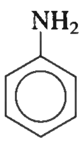


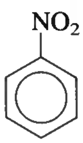
Nomenclature of Aromatic Compounds

The naming of monosubstituted benzenes, that is, benzenes in which one H atom has been replaced by another atom or a group of atoms, is quite straightforward, as shown here:

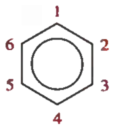

ethylbenzene


chlorobenzene


aminobenzene (aniline)

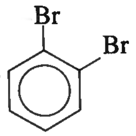

nitrobenzene

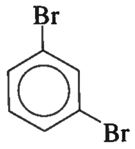
If more than one substituent is present, we must indicate the location of the second group relative to the first. The systematic way to accomplish this is to number the carbon atoms as follows:

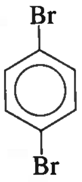


[†] August Kekulé (1829–1896). German chemist. Kekulé was a student of architecture before he became interested in chemistry. He supposedly solved the riddle of the structure of the benzene molecule after having a dream in which dancing snakes bit their own tails. Kekulé's work is regarded by many as the crowning achievement of theoretical organic chemistry of the nineteenth century.

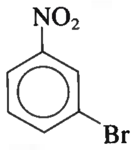
Three different dibromobenzenes are possible:


1,2-dibromobenzene
(*o*-dibromobenzene)


1,3-dibromobenzene
(*m*-dibromobenzene)


1,4-dibromobenzene
(*p*-dibromobenzene)

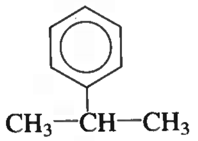
The prefixes *o*- (*ortho*-), *m*- (*meta*-), and *p*- (*para*-) are also used to denote the relative positions of the two substituted groups, as shown above for the dibromobenzenes. Compounds in which the two substituted groups are different are named accordingly. Thus,



is named 3-bromonitrobenzene, or *m*-bromonitrobenzene.

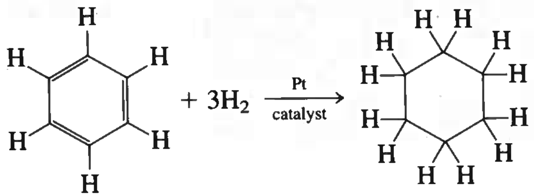
Finally, we note that the group containing benzene minus a hydrogen atom (C_6H_5) is called the *phenyl* group. Thus, the following molecule is called 2-phenylpropane:

This compound is also called isopropyl benzene (see Table 24.2).

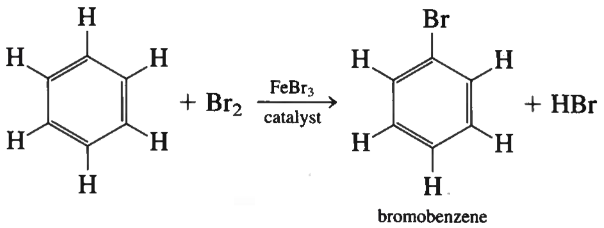


Properties and Reactions of Aromatic Compounds

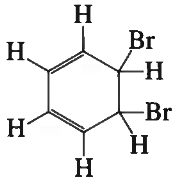
Benzene is a colorless, flammable liquid obtained chiefly from petroleum and coal tar. Perhaps the most remarkable chemical property of benzene is its relative inertness. Although it has the same empirical formula as acetylene (CH) and a high degree of unsaturation, it is much less reactive than either ethylene or acetylene. The stability of benzene is the result of electron delocalization. In fact, benzene can be hydrogenated, but only with difficulty. The following reaction is carried out at significantly higher temperatures and pressures than are similar reactions for the alkenes:


cyclohexane

We saw earlier that alkenes react readily with halogens to form addition products, because the pi bond in C=C can be broken easily. The most common reaction of halogens with benzene is the ***substitution reaction,*** in which *an atom or* *group of atoms replaces an atom or groups of atoms in another molecule.* For example,

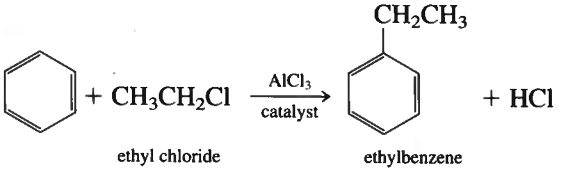


Note that if the reaction were an addition reaction, electron delocalization would be destroyed in the product



and the molecule would not have the aromatic characteristic of chemical unreactivity.

Alkyl groups can be introduced into the ring system by allowing benzene to react with an alkyl halide using $AlCl_3$ as the catalyst:



An enormously large number of compounds can be generated from substances in which benzene rings are fused together. Some of these *polycyclic* aromatic hydrocarbons are shown in Figure 24.7. The best known of these compounds is naphthalene, which is used in mothballs. These and many other similar compounds are present in coal tar. Some of the compounds with several rings are powerful carcinogens—they can cause cancer in humans and other animals.

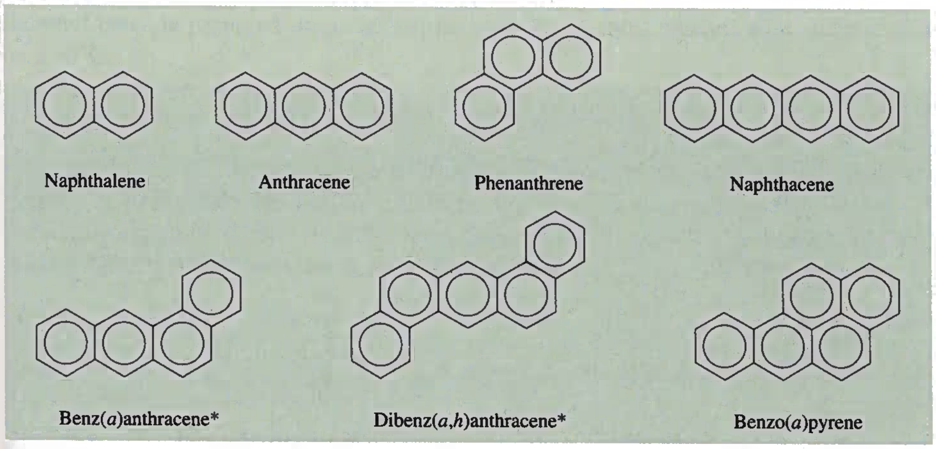
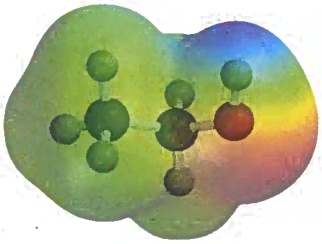


Figure 24.7 *Some polycyclic aromatic hydrocarbons. Compounds denoted by * are potent carcinogens. An enormous number of such compounds exist in nature.*

24.4 Chemistry of the Functional Groups

We now examine in greater depth some organic functional groups, groups that are responsible for most of the reactions of the parent compounds. In particular, we focus on oxygen-containing and nitrogen-containing compounds.

Alcohols



C_2H_5OH

All ***alcohols*** contain *the hydroxyl* functional *group, —OH.* Some common alcohols are shown in Figure 24.8. Ethyl alcohol, or ethanol, is by far the best known. It is produced biologically by the fermentation of sugar or starch. In the absence of oxygen, the enzymes present in bacterial cultures or yeast catalyze the reaction

$$C_6H_{12}O_6(aq) \xrightarrow{\text{enzymes}} \underset{\text{ethanol}}{2CH_3CH_2OH(aq)} + 2CO_2(g)$$

This process gives off energy, which microorganisms, in turn, use for growth and other functions.

Commercially, ethanol is prepared by an addition reaction in which water is combined with ethylene at about 280°C and 300 atm:

$$CH_2{=}CH_2(g) + H_2O(g) \xrightarrow{H_2SO_4} CH_3CH_2OH(g)$$

Ethanol has countless applications as a solvent for organic chemicals and as a starting compound for the manufacture of dyes, synthetic drugs, cosmetics, and explosives. It is also a constituent of alcoholic beverages. Ethanol is the only nontoxic (more properly, the least toxic) of the straight-chain alcohols; our bodies produce an enzyme, called *alcohol dehydrogenase,* which helps metabolize ethanol by oxidizing it to acetaldehyde:

$$CH_3CH_2OH \xrightarrow{\text{alcohol dehydrogenase}} \underset{\text{acetaldehyde}}{CH_3CHO} + H_2$$

This equation is a simplified version of what actually takes place; the H atoms are taken up by other molecules, so that no H_2 gas is evolved.

See Chemistry in Action on p. 143.

Ethanol can also be oxidized by inorganic oxidizing agents, such as acidified dichromate, to acetaldehyde and acetic acid:

$$CH_3CH_2OH \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3CHO \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3COOH$$

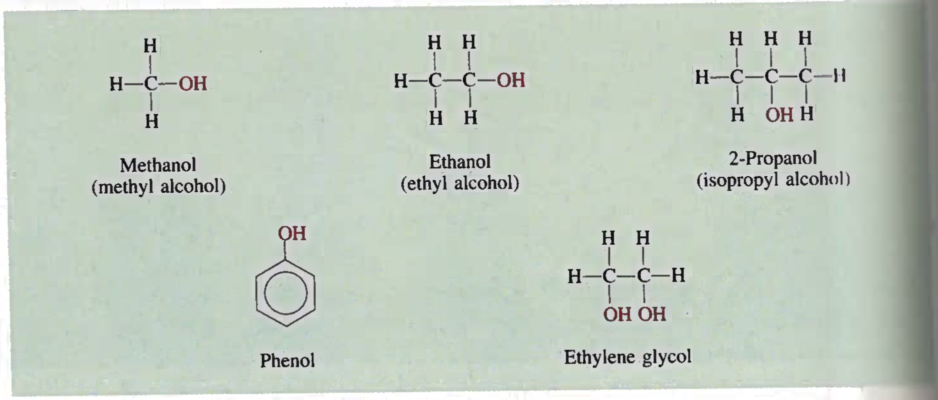


Figure 24.8 *Common alcohols. Note that all the compounds contain the OH group. The properties of phenol are quite different from those of the aliphatic alcohols.*

Ethanol is called an aliphatic alcohol because it is derived from an alkane (ethane). The simplest aliphatic alcohol is methanol, CH_3OH. Called *wood alcohol,* it was prepared at one time by the dry distillation of wood. It is now synthesized industrially by the reaction of carbon monoxide and molecular hydrogen at high temperatures and pressures:

$$CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{Fe_2O_3} \underset{\text{methanol}}{CH_3OH(l)}$$

Methanol is highly toxic. Ingestion of only a few milliliters can cause nausea and blindness. Ethanol intended for industrial use is often mixed with methanol to prevent people from drinking it. Ethanol containing methanol or other toxic substances is called *denatured alcohol.*

The alcohols are very weakly acidic; they do not react with strong bases, such as NaOH. The alkali metals react with alcohols to produce hydrogen:

$$2CH_3OH + 2Na \longrightarrow \underset{\text{sodium methoxide}}{2CH_3ONa} + H_2$$

However, the reaction is much less violent than that between Na and water:

$$2H_2O + 2Na \longrightarrow 2NaOH + H_2$$

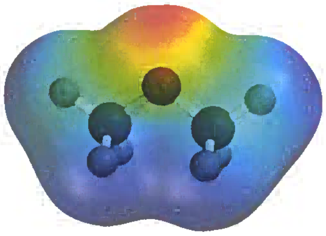
Alcohols react more slowly with sodium metal than does water.

Two other familiar aliphatic alcohols are 2-propanol (or isopropanol), commonly known as rubbing alcohol, and ethylene glycol, which is used as an antifreeze. Note that ethylene glycol has two —OH groups and so can form hydrogen bonds with water molecules more effectively than compounds that have only one —OH group (see Figure 24.8). Most alcohols—especially those with low molar masses—are highly flammable.

Ethers

***Ethers** contain the R—O—R′ linkage, where R and R′ are a hydrocarbon (aliphatic or aromatic) group.* They are formed by the reaction between an alkoxide (containing the RO^- ion) and an alkyl halide:

$$\underset{\text{sodium methoxide}}{NaOCH_3} + \underset{\text{methyl bromide}}{CH_3Br} \longrightarrow \underset{\text{dimethyl ether}}{CH_3OCH_3} + NaBr$$



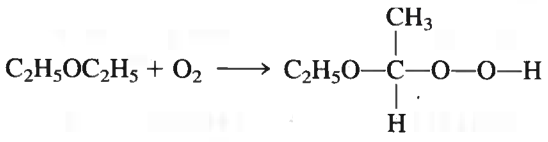
CH_3OCH_3

Diethyl ether is prepared on an industrial scale by heating ethanol with sulfuric acid at 140°C

$$C_2H_5OH + C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O$$

This reaction is an example of a ***condensation reaction,*** which is characterized by *the joining of two molecules and the elimination of a small molecule, usually water.*

Like alcohols, ethers are extremely flammable. When left standing in air, they have a tendency to slowly form explosive peroxides:

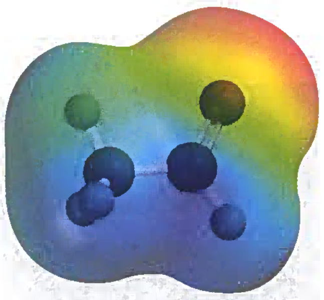


$$C_2H_5OC_2H_5 + O_2 \longrightarrow C_2H_5O\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}\text{—}O\text{—}O\text{—}H$$

diethyl ether 1-ethyoxyethyl hydroperoxide

Peroxides contain the —O—O— linkage; the simplest peroxide is hydrogen peroxide, H_2O_2. Diethyl ether, commonly known as "ether," was used as an anesthetic for many years. It produces unconsciousness by depressing the activity of the central nervous system. The major disadvantages of diethyl ether are its irritating effects on the respiratory system and the occurrence of postanesthetic nausea and vomiting. "Neothyl," or methyl propyl ether, $CH_3OCH_2CH_2CH_3$, is currently favored as an anesthetic because it is relatively free of side effects.

Aldehydes and Ketones

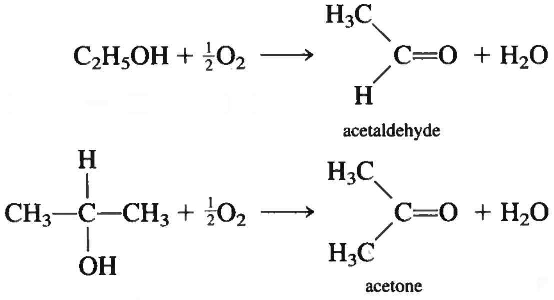


CH_3CHO

Under mild oxidation conditions, it is possible to convert alcohols to aldehydes and ketones:

$$CH_3OH + \tfrac{1}{2}O_2 \longrightarrow H_2C{=}O + H_2O$$

formaldehyde



$$C_2H_5OH + \tfrac{1}{2}O_2 \longrightarrow (H_3C)(H)C{=}O + H_2O$$

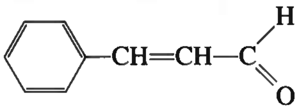
acetaldehyde

$$CH_3{-}CH(OH){-}CH_3 + \tfrac{1}{2}O_2 \longrightarrow (H_3C)_2C{=}O + H_2O$$

acetone

The functional group in these compounds is the *carbonyl group,* $>C{=}O$. In an ***aldehyde** at least one hydrogen atom is bonded to the carbon in the carbonyl group.* In a ***ketone,** the carbon atom in the carbonyl group is bonded to two hydrocarbon groups.*

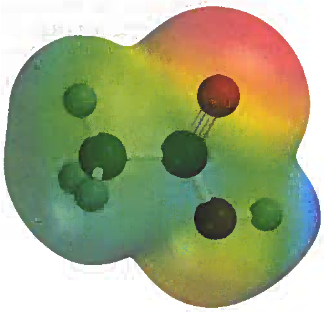
The simplest aldehyde, formaldehyde ($H_2C{=}O$) has a tendency to *polymerize,* that is, the individual molecules join together to form a compound of high molar mass. This action gives off much heat and is often explosive, so formaldehyde is usually prepared and stored in aqueous solution (to reduce the concentration). This rather disagreeable-smelling liquid is used as a starting material in the polymer industry (see Chapter 25) and in the laboratory as a preservative for animal specimens. Interestingly, the higher molar mass aldehydes, such as cinnamic aldehyde



Cinnamic aldehyde gives cinnamon its characteristic aroma.

have a pleasant odor and are used in the manufacture of perfumes.

Ketones generally are less reactive than aldehydes. The simplest ketone is acetone, a pleasant-smelling liquid that is used mainly as a solvent for organic compounds and nail polish remover.



CH_3COOH

Carboxylic Acids

Under appropriate conditions both alcohols and aldehydes can be oxidized to ***carboxylic acids,** acids that contain the carboxyl group, —COOH:*

$$CH_3CH_2OH + O_2 \longrightarrow CH_3COOH + H_2O$$
$$CH_3CHO + \tfrac{1}{2}O_2 \longrightarrow CH_3COOH$$

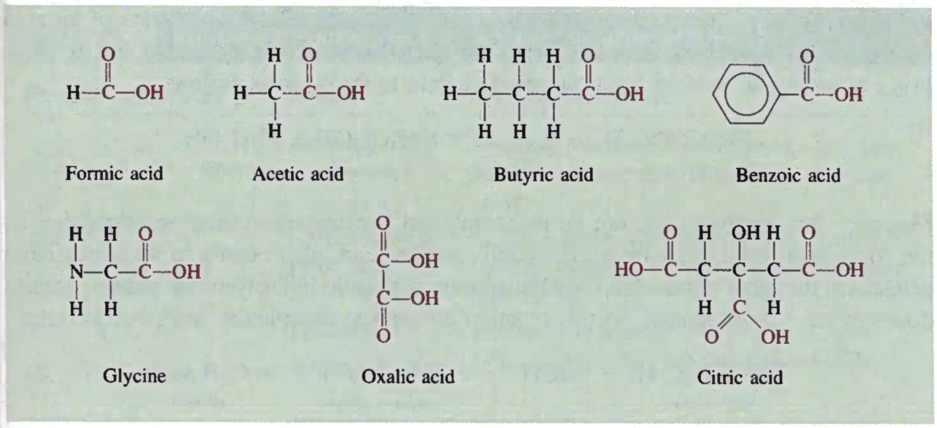


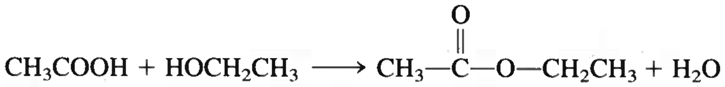
Figure 24.9 *Some common carboxylic acids. Note that they all contain the COOH group. (Glycine is one of the amino acids found in proteins.)*

These reactions occur so readily, in fact, that wine must be protected from atmospheric oxygen while in storage. Otherwise, it would soon turn to vinegar due to the formation of acetic acid. Figure 24.9 shows the structure of some of the common carboxylic acids.

The oxidization of ethanol to acetic acid in wine is catalyzed by enzymes.

Carboxylic acids are widely distributed in nature; they are found in both the plant and animal kingdoms. All protein molecules are made of amino acids, a special kind of carboxylic acid containing an amino group ($—NH_2$) and a carboxyl group ($—COOH$).

Unlike the inorganic acids HCl, HNO_3, and H_2SO_4, carboxylic acids are usually weak. They react with alcohols to form pleasant-smelling esters:



$$CH_3COOH + HOCH_2CH_3 \longrightarrow CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—O—CH_2CH_3 + H_2O$$

acetic acid ethanol ethyl acetate

This is a condensation reaction.

Other common reactions of carboxylic acids are neutralization

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

and formation of acid halides, such as acetyl chloride

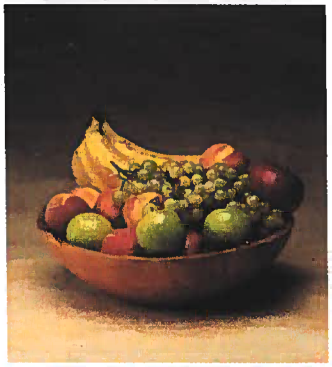
$$CH_3COOH + PCl_5 \longrightarrow \underset{\text{acetyl chloride}}{CH_3COCl} + HCl + \underset{\text{phosphoryl chloride}}{POCl_3}$$

Acid halides are reactive compounds used as intermediates in the preparation of many other organic compounds. They hydrolyze in much the same way as many nonmetallic halides, such as $SiCl_4$:

$$CH_3COCl(l) + H_2O(l) \longrightarrow CH_3COOH(aq) + HCl(g)$$
$$SiCl_4(l) + 3H_2O(l) \longrightarrow \underset{\text{silicic acid}}{H_2SiO_3(s)} + 4HCl(g)$$

Esters

Esters have the general formula R'COOR, where R' can be H or a hydrocarbon group and R is a hydrocarbon group. Esters are used in the manufacture of perfumes and as flavoring agents in the confectionery and soft-drink industries. Many fruits owe their characteristic smell and flavor to the presence of small quantities of esters. For example, bananas contain 3-methylbutyl acetate [$CH_3COOCH_2CH_2CH(CH_3)_2$], oranges contain octyl acetate ($CH_3COOCHCH_3C_6H_{13}$), and apples contain methyl butyrate ($CH_3CH_2CH_2COOCH_3$).



The odor of fruits is mainly due to the ester compounds in them.

The functional group in esters is the —COOR group. In the presence of an acid catalyst, such as HCl, esters undergo hydrolysis to yield a carboxylic acid and an alcohol. For example, in acid solution, ethyl acetate hydrolyzes as follows:

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O \rightleftharpoons \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethanol}}{C_2H_5OH}$$

However, this reaction does not go to completion because the reverse reaction, that is, the formation of an ester from an alcohol and an acid, also occurs to an appreciable extent. On the other hand, when NaOH solution is used in hydrolysis the sodium acetate does not react with ethanol, so this reaction does go to completion from left to right:

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{sodium acetate}}{CH_3COO^-Na^+} + \underset{\text{ethanol}}{C_2H_5OH}$$

For this reason, ester hydrolysis is usually carried out in basic solutions. Note that NaOH does not act as a catalyst; rather, it is consumed by the reaction. The term ***saponification*** (meaning *soapmaking*) was originally used to describe the alkaline hydrolysis of fatty acid esters to yield soap molecules (sodium stearate):

The action of soap is discussed on p. 533.

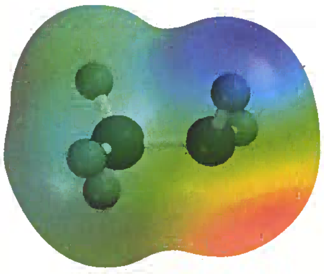
$$\underset{\text{ethyl stearate}}{C_{17}H_{35}COOC_2H_5} + NaOH \longrightarrow \underset{\text{sodium stearate}}{C_{17}H_{35}COO^-Na^+} + C_2H_5OH$$

Saponification has now become *a general term for alkaline hydrolysis of any type of ester.*

Amines

Amines are *organic bases having the general formula R_3N, where R may be H or a hydrocarbon group.* As with ammonia, the reaction of amines with water is

$$RNH_2 + H_2O \longrightarrow RNH_3^+ + OH^-$$



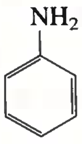
CH_3NH_2

where R represents a hydrocarbon group. Like all bases, the amines form salts when allowed to react with acids:

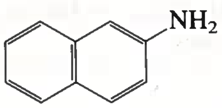
$$\underset{\text{ethylamine}}{CH_3CH_2NH_2} + HCl \longrightarrow \underset{\text{ethylammonium chloride}}{CH_3CH_2NH_3^+Cl^-}$$

These salts are usually colorless, odorless solids.

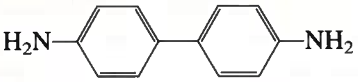
Aromatic amines are used mainly in the manufacture of dyes. Aniline, the simplest aromatic amine, itself is a toxic compound; a number of other aromatic amines such as 2-naphthylamine and benzidine are potent carcinogens:



aniline



2-naphthylamine



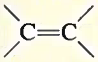
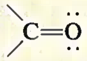
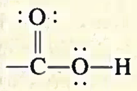
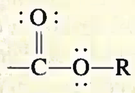
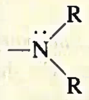
benzidine

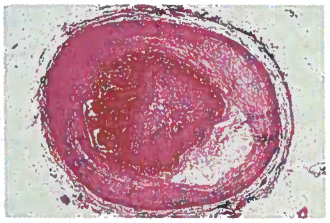
Summary of Functional Groups

Table 24.4 summarizes the common functional groups, including the C=C and C≡C groups. Organic compounds commonly contain more than one functional group. Generally, the reactivity of a compound is determined by the number and types of functional groups in its makeup.

Example 24.5 shows how we can use the functional groups to predict reactions.

TABLE 24.4 Important Functional Groups and Their Reactions

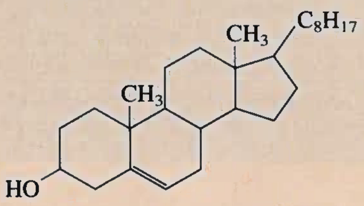
Functional Group	Name	Typical Reactions
	Carbon-carbon double bond	Addition reactions with halogens, hydrogen halides, and water; hydrogenation to yield alkanes
$-C\equiv C-$	Carbon-carbon triple bond	Addition reactions with halogens, hydrogen halides; hydrogenation to yield alkenes and alkanes
$-\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:$ (X = F, Cl, Br, I)	Halogen	Exchange reactions: $CH_3CH_2Br + KI \longrightarrow CH_3CH_2I + KBr$
$-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H$	Hydroxyl	Esterification (formation of an ester) with carboxylic acids; oxidation to aldehydes, ketones, and carboxylic acids
	Carbonyl	Reduction to yield alcohols; oxidation of aldehydes to yield carboxylic acids
 $-\overset{\overset{:O:}{\|}}{C}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-H$	Carboxyl	Esterification with alcohols; reaction with phosphorus pentachloride to yield acid chlorides
 $-\overset{\overset{:O:}{\|}}{C}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}-R$ (R = hydrocarbon)	Ester	Hydrolysis to yield acids and alcohols
 (R = H or hydrocarbon)	Amine	Formation of ammonium salts with acids



An artery becoming blocked by cholesterol.

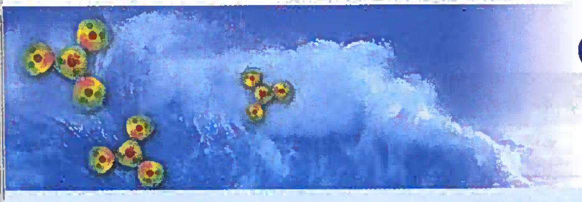
Example 24.5

Cholesterol is a major component of gallstones, and it is believed that the cholesterol level in the blood is a contributing factor in certain types of heart disease. From the following structure of the compound, predict its reaction with (a) Br_2, (b) H_2 (in the presence of a Pt catalyst), (c) CH_3COOH.



Strategy To predict the type of reactions a molecule may undergo, we must first identify the functional groups present (see Table 24.4).

(Continued on p. 1028)



CHEMISTRY *in Action*

The Petroleum Industry

In 2005 an estimated 40 percent of the energy needs of the United States were supplied by oil or petroleum. The rest was provided by natural gas (approximately 25 percent), coal (23 percent), hydroelectric power (4 percent), nuclear power (8 percent), and other sources (0.5 percent). In addition to energy, petroleum is the source of numerous organic chemicals used to manufacture drugs, clothing, and many other products.

Unrefined petroleum, a viscous, dark-brown liquid, is often called crude oil. A complex mixture of alkanes, alkenes, cycloalkanes, and aromatic compounds, petroleum was formed in Earth's crust over the course of millions of years by the anaerobic decomposition of animal and vegetable matter by bacteria.

Petroleum deposits are widely distributed throughout the world, but they are found mainly in North America, Mexico, Russia, China, Venezuela, and, of course, the Middle East. The actual composition of petroleum varies with location. In the United States, for example, Pennsylvania crude oils are mostly aliphatic hydrocarbons, whereas the major components of western crude oils are aromatic in nature.

Although petroleum contains literally thousands of hydrocarbon compounds, we can classify its components according to the range of their boiling points. These hydrocarbons can be separated on the basis of molar mass by fractional distillation. Heating crude oil to about 400°C converts the viscous oil into hot vapor and fluid. In this form it enters the fractionating tower. The vapor rises and condenses on various collecting trays according to the temperatures at which the various components of the vapor liquefy. Some gases are drawn off at the top of the column, and the unvaporized residual oil is collected at the bottom.

Gasoline is probably the best-known petroleum product. A mixture of volatile hydrocarbons, gasoline contains mostly alkanes, cycloalkanes, and a few aromatic hydrocarbons. Some of these compounds are far more suitable for fueling an automobile engine than others, and herein lies the problem of the further treatment and refinement of gasoline.

Most automobiles employ the four-stroke operation of the *Otto cycle* engine. A major engineering concern is to control the burning of the gasoline-air mixture inside each cylinder to obtain a smooth expansion of the gas mixture. If the mixture burns too rapidly, the piston receives a hard jerk rather than a smooth, strong push. This action produces a "knocking" or "pinging" sound, as well as a decrease in efficiency in the conversion of combustion energy to mechanical energy. It turns out that straight-chain hydrocarbons have the greatest tendency to produce knocking, whereas the branched-chain and aromatic hydrocarbons give the desired smooth push.

Gasolines are usually rated according to the *octane number*, a measure of their tendency to cause knocking. On this scale, a branched C_8 compound (2,2,4-trimethylpentane, or

Major Fractions of Petroleum

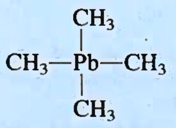
Fraction	Carbon Atoms*	Boiling Point Range (°C)	Uses
Natural gas	C_1–C_4	−161 to 20	Fuel and cooking gas
Petroleum ether	C_5–C_6	30–60	Solvent for organic compounds
Ligroin	C_7	20–135	Solvent for organic compounds
Gasoline	C_6–C_{12}	30–180	Automobile fuels
Kerosene	C_{11}–C_{16}	170–290	Rocket and jet engine fuels, domestic heating
Heating fuel oil	C_{14}–C_{18}	260–350	Domestic heating and fuel for electricity production
Lubricating oil	C_{15}–C_{24}	300–370	Lubricants for automobiles and machines

*The entries in this column indicate the numbers of carbon atoms in the compounds involved. For example, C_1–C_4 tells us that in natural gas the compounds contain 1 to 4 carbon atoms, and so on.

Crude oil.

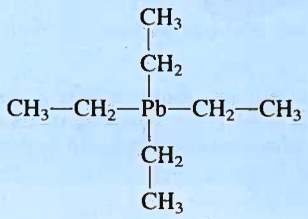
isooctane) has been arbitrarily assigned an octane number of 100, and that of *n*-heptane, a straight-chain compound, is zero. The higher the octane number of the hydrocarbon, the better its performance in the internal combustion engine. Aromatic hydrocarbons such as benzene and toluene have high octane numbers (106 and 120, respectively), as do aliphatic hydrocarbons with branched chains.

The octane rating of hydrocarbons can be improved by the addition of small quantities of compounds called *antiknocking agents.* Among the most widely used antiknocking agents are the following:



$$CH_3-\underset{CH_3}{\overset{CH_3}{Pb}}-CH_3$$

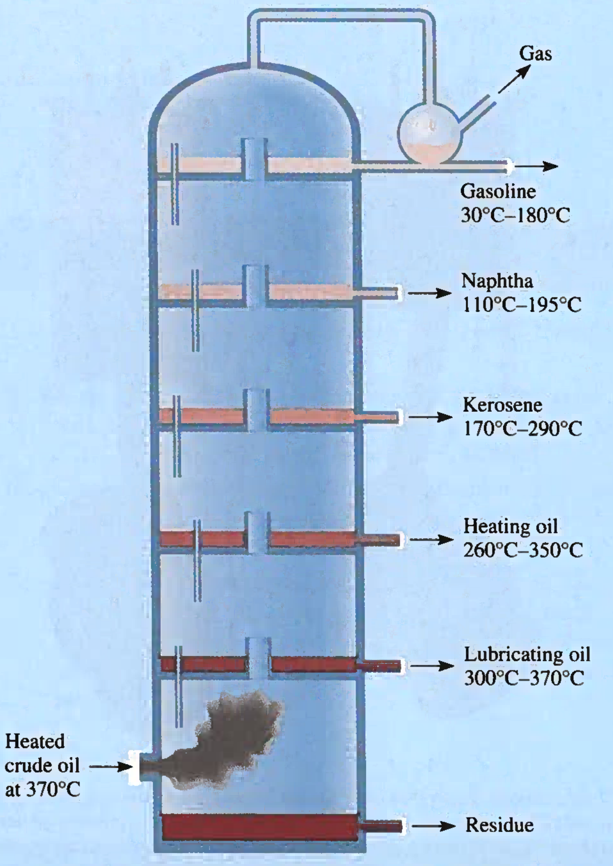
tetramethyllead



$$CH_3-CH_2-\underset{CH_2CH_3}{\overset{CH_3CH_2}{Pb}}-CH_2-CH_3$$

tetraethyllead

The addition of 2 to 4 g of either of these compounds to a gallon of gasoline increases the octane rating by 10 or more. However, lead is a highly toxic metal, and the constant discharge of automobile exhaust into the atmosphere has become a serious environmental problem. Federal regulations require that all automobiles made after 1974 use "unleaded" gasolines. The catalytic converters with which late-model automobiles are equipped can be "poisoned" by lead, another reason for its exclusion from gasoline. To minimize knocking, unleaded gasolines contain methyl *tert*-butyl ether (MTBE), which minimizes knocking and increases the oxygen content of gasoline, making the fuel burn cleaner. Unfortunately, in the late 1990s MTBE was found in drinking water supplies, primarily because of leaking gasoline storage tanks. The substance makes water smell and taste foul and is a possible human carcinogen. At this writing, some states have begun to phase out the use of MTBE in gasoline, although no suitable substitute has been found.

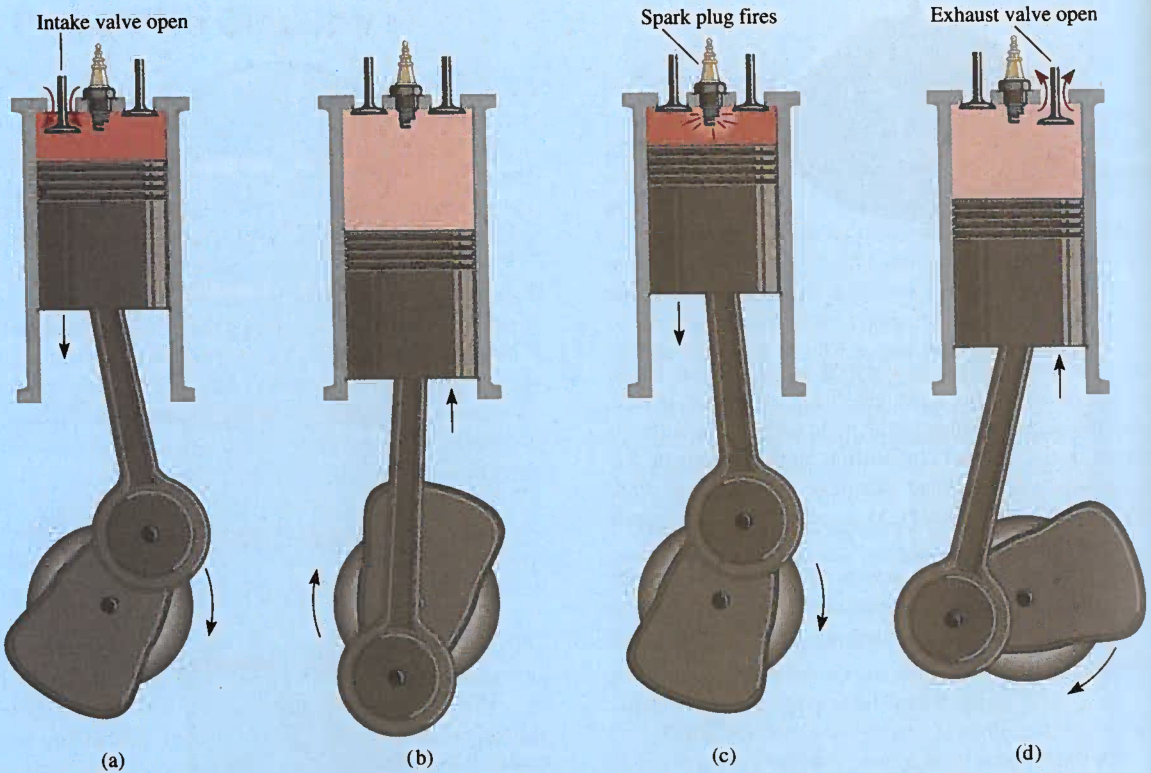


A fractional distillation column for separating the components of petroleum crude oil. As the hot vapor moves upward, it condenses and the various components of the crude oil are separated according to their boiling points and are drawn off as shown.

(Continued)

CHEMISTRY *in Action*

(Continued)



The four stages of operation of an internal combustion engine. This is the type of engine used in practically all automobiles and is described technically as a four-stroke Otto cycle engine. (a) The intake valve opens to let in a gasoline-air mixture. (b) During the compression stage the two valves are closed. (c) The spark plug fires and the piston is pushed outward. (d) Finally, as the piston is pushed downward, the exhaust valve opens to let out the exhaust gas.

Solution There are two functional groups in cholesterol: the hydroxyl group and the carbon-carbon double bond.

(a) The reaction with bromine results in the addition of bromine to the double-bonded carbons, which become single-bonded.

(b) This is a hydrogenation reaction. Again, the carbon-carbon double bond is converted to a carbon-carbon single bond.

(c) The acid reacts with the hydroxyl group to form an ester and water. Figure 24.10 shows the products of these reactions.

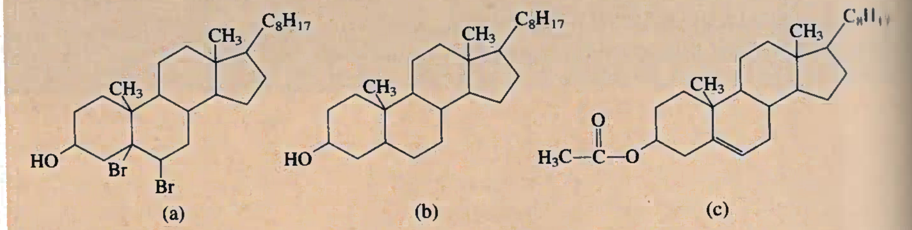


Figure 24.10 *The products formed by the reaction of cholesterol with (a) molecular bromine, (b) molecular hydrogen, and (c) acetic acid.*

Similar problem: 24.41.

(Continued)

Practice Exercise Predict the products of the following reaction:

$$CH_3OH + CH_3CH_2COOH \longrightarrow ?$$

The Chemistry in Action on p. 1026 shows the key organic compounds present in petroleum.

Summary of Facts and Concepts

1. Because carbon atoms can link up with other carbon atoms in straight and branched chains, carbon can form more compounds than any other element.
2. Organic compounds are derived from two types of hydrocarbons: aliphatic hydrocarbons and aromatic hydrocarbons.
3. Methane, CH_4, is the simplest of the alkanes, a family of hydrocarbons with the general formula C_nH_{2n+2}. Cyclopropane, C_3H_6, is the simplest of the cycloalkanes, a family of alkanes whose carbon atoms are joined in a ring. Alkanes and cycloalkanes are saturated hydrocarbons.
4. Ethylene, $CH_2{=}CH_2$, is the simplest of the olefins, or alkenes, a class of hydrocarbons containing carbon-carbon double bonds and having the general formula C_nH_{2n}.
5. Acetylene, $CH{\equiv}CH$, is the simplest of the alkynes, which are compounds that have the general formula C_nH_{2n-2} and contain carbon-carbon triple bonds.
6. Compounds that contain one or more benzene rings are called aromatic hydrocarbons. These compounds undergo substitution by halogens and alkyl groups.
7. Functional groups impart specific types of chemical reactivity to molecules. Classes of compounds characterized by their functional groups include alcohols, ethers, aldehydes and ketones, carboxylic acids and esters, and amines.

Key Words

Addition reactions, p. 1013
Alcohol, p. 1020
Aldehyde, p. 1022
Aliphatic hydrocarbon, p. 1004
Alkane, p. 1004
Alkene, p. 1011
Alkyne, p. 1015
Amine, p. 1024
Aromatic hydrocarbon, p. 1004
Carboxylic acid, p. 1022
Condensation reaction, p. 1021
Cycloalkane, p. 1011
Ester, p. 1023
Ether, p. 1021
Functional group, p. 1004
Hydrocarbon, p. 1004
Ketone, p. 1022
Organic chemistry, p. 1004
Saponification, p. 1024
Saturated hydrocarbon, p. 1004
Structural isomer, p. 1005
Substitution reaction, p. 1018
Unsaturated hydrocarbon, p. 1013

Questions and Problems

Classes of Organic Compounds

Review Questions

24.1 Explain why carbon is able to form so many more compounds than any other element.

24.2 What is the difference between aliphatic and aromatic hydrocarbons?

Aliphatic Hydrocarbons

Review Questions

24.3 What do "saturated" and "unsaturated" mean when applied to hydrocarbons? Give examples of a saturated hydrocarbon and an unsaturated hydrocarbon.

24.4 Give three sources of methane.

24.5 Alkenes exhibit geometric isomerism because rotation about the C=C bond is restricted. Explain.

24.6 Why is it that alkanes and alkynes, unlike alkenes, have no geometric isomers?

24.7 What is Markovnikov's rule?

24.8 Describe reactions that are characteristic of alkanes, alkenes, and alkynes.

24.9 What factor determines whether a carbon atom in a compound is chiral?

24.10 Give examples of a chiral substituted alkane and an achiral substituted alkane.

Problems

24.11 Draw all possible structural isomers for the following alkane: C_7H_{16}.

24.12 How many distinct chloropentanes, $C_5H_{11}Cl$, could be produced in the direct chlorination of *n*-pentane, $CH_3(CH_2)_3CH_3$? Draw the structure of each molecule.

24.13 Draw all possible isomers for the molecule C_4H_8.

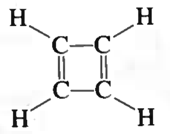
24.14 Draw all possible isomers for the molecule C_3H_5Br.

24.15 The structural isomers of pentane, C_5H_{12}, have quite different boiling points (see Example 24.1). Explain the observed variation in boiling point, in terms of structure.

24.16 Discuss how you can determine which of the following compounds might be alkanes, cycloalkanes, alkenes, or alkynes, without drawing their formulas: (a) C_6H_{12}, (b) C_4H_6, (c) C_5H_{12}, (d) C_7H_{14}, (e) C_3H_4.

24.17 Draw the structures of *cis*-2-butene and *trans*-2-butene. Which of the two compounds would have the higher heat of hydrogenation? Explain.

24.18 Would you expect cyclobutadiene to be a stable molecule? Explain.



24.19 How many different isomers can be derived from ethylene if two hydrogen atoms are replaced by a fluorine atom and a chlorine atom? Draw their structures and name them. Indicate which are structural isomers and which are geometric isomers.

24.20 Suggest two chemical tests that would help you distinguish between these two compounds:

(a) $CH_3CH_2CH_2CH_2CH_3$

(b) $CH_3CH_2CH_2CH=CH_2$

24.21 Sulfuric acid (H_2SO_4) adds to the double bond of alkenes as H^+ and $^-OSO_3H$. Predict the products when sulfuric acid reacts with (a) ethylene and (b) propene.

24.22 Acetylene is an unstable compound. It has a tendency to form benzene as follows:

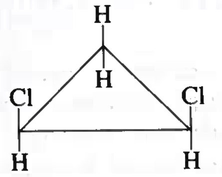
$$3C_2H_2(g) \longrightarrow C_6H_6(l)$$

Calculate the standard enthalpy change in kilojoules per mole for this reaction at 25°C.

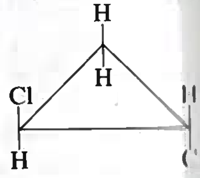
24.23 Predict products when HBr is added to (a) 1-butene and (b) 2-butene.

24.24 Geometric isomers are not restricted to compounds containing the C=C bond. For example, certain di substituted cycloalkanes can exist in the *cis* and the *trans* forms. Label the following molecules as the *cis* and *trans* isomer, of the same compound:

(a)



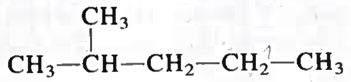
(b)



24.25 Which of the following amino acids are chiral (a) $CH_3CH(NH_2)COOH$, (b) $CH_2(NH_2)COOH$, (c) $CH_2(OH)CH(NH_2)COOH$?

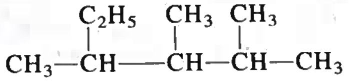
24.26 Name the following compounds:

(a)



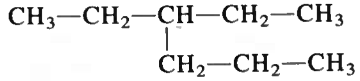
$$CH_3-\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-CH_2-CH_2-CH_3$$

(b)



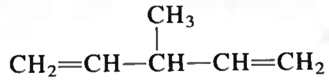
$$CH_3-\overset{\overset{\mathrm{C_2H_5}}{|}}{\mathrm{CH}}-\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-CH_3$$

(c)



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

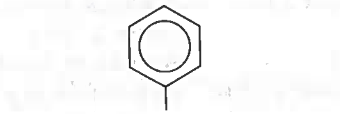
(d)



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

(e) $CH_3-C\equiv C-CH_2-CH_3$

(f)



24.27 Write structural formulas for the following organic compounds: (a) 3-methylhexane, (b) 1,3,5-trichlorocyclohexane, (c) 2,3-dimethylpentane, (d) 2-bromo-4-phenylpentane, (e) 3,4,5-trimethyloctane.

24.28 Write structural formulas for the following compounds: (a) *trans*-2-pentene, (b) 2-ethyl-1-butene, (c) 4-ethyl-*trans*-2-heptene, (d) 3-phenyl-butyne.

Aromatic Hydrocarbons

Review Questions

24.29 Comment on the extra stability of benzene compared to ethylene. Why does ethylene undergo addition reactions while benzene usually undergoes substitution reactions?

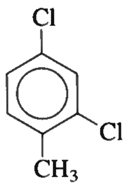
24.30 Benzene and cyclohexane molecules both contain six-membered rings. Benzene is a planar molecule, and cyclohexane is nonplanar. Explain.

Problems

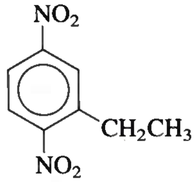
24.31 Write structures for the following compounds: (a) 1-bromo-3-methylbenzene, (b) 1-chloro-2-propylbenzene, (c) 1,2,4,5-tetramethylbenzene.

24.32 Name the following compounds:

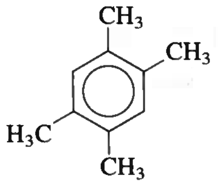
(a)



(b)



(c)



Chemistry of the Functional Groups

Review Questions

24.33 What are functional groups? Why is it logical and useful to classify organic compounds according to their functional groups?

24.34 Draw the Lewis structure for each of the following functional groups: alcohol, ether, aldehyde, ketone, carboxylic acid, ester, amine.

Problems

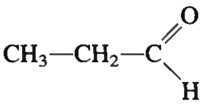
24.35 Draw structures for molecules with the following formulas: (a) CH_4O, (b) C_2H_6O, (c) $C_3H_6O_2$, (d) C_3H_8O.

24.36 Classify each of the following molecules as alcohol, aldehyde, ketone, carboxylic acid, amine, or ether:

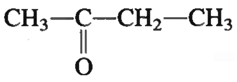
(a) $CH_3—O—CH_2—CH_3$

(b) $CH_3—CH_2—NH_2$

(c)

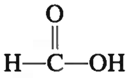


(d)



$CH_3—\underset{\underset{O}{\|}}{C}—CH_2—CH_3$

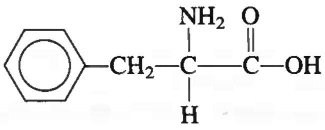
(e)



$H—\overset{\overset{O}{\|}}{C}—OH$

(f) $CH_3—CH_2CH_2—OH$

(g)



24.37 Generally aldehydes are more susceptible to oxidation in air than are ketones. Use acetaldehyde and acetone as examples and show why ketones such as acetone are more stable than aldehydes in this respect.

24.38 Complete the following equation and identify the products:

$$HCOOH + CH_3OH \longrightarrow$$

24.39 A compound has the empirical formula $C_5H_{12}O$. Upon controlled oxidation, it is converted into a compound of empirical formula $C_5H_{10}O$, which behaves as a ketone. Draw possible structures for the original compound and the final compound.

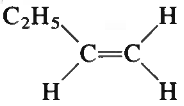
24.40 A compound having the molecular formula $C_4H_{10}O$ does not react with sodium metal. In the presence of light, the compound reacts with Cl_2 to form three compounds having the formula C_4H_9OCl. Draw a structure for the original compound that is consistent with this information.

24.41 Predict the product or products of each of the following reactions:

(a) $CH_3CH_2OH + HCOOH \longrightarrow$

(b) $H—C{\equiv}C—CH_3 + H_2 \longrightarrow$

(c)



$+ HBr \longrightarrow$

24.42 Identify the functional groups in each of the following molecules:

(a) $CH_3CH_2COCH_2CH_2CH_3$

(b) $CH_3COOC_2H_5$

(c) $CH_3CH_2OCH_2CH_2CH_2CH_3$

Additional Problems

24.43 Draw all the possible structural isomers for the molecule having the formula C_7H_7Cl. The molecule contains one benzene ring.

24.44 Given these data

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -1411 \text{ kJ/mol}$$

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -2599 \text{ kJ/mol}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -285.8 \text{ kJ/mol}$$

calculate the heat of hydrogenation for acetylene:

$$C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$$

24.45 State which member of each of the following pairs of compounds is the more reactive and explain why: (a) propane and cyclopropane, (b) ethylene and methane, (c) acetaldehyde and acetone.

24.46 State which of the following types of compounds can form hydrogen bonds with water molecules: (a) carboxylic acids, (b) alkenes, (c) ethers, (d) aldehydes, (e) alkanes, (f) amines.

24.47 An organic compound is found to contain 37.5 percent carbon, 3.2 percent hydrogen, and 59.3 percent fluorine by mass. The following pressure and volume data were obtained for 1.00 g of this substance at 90°C:

P (atm)	*V* (L)
2.00	0.332
1.50	0.409
1.00	0.564
0.50	1.028

The molecule is known to have no dipole moment. (a) What is the empirical formula of this substance? (b) Does this substance behave as an ideal gas? (c) What is its molecular formula? (d) Draw the Lewis structure of this molecule and describe its geometry. (e) What is the systematic name of this compound?

24.48 State at least one commercial use for each of the following compounds: (a) 2-propanol (isopropanol), (b) acetic acid, (c) naphthalene, (d) methanol, (e) ethanol, (f) ethylene glycol, (g) methane, (h) ethylene.

24.49 How many liters of air (78 percent N_2, 22 percent O_2 by volume) at 20°C and 1.00 atm are needed for the complete combustion of 1.0 L of octane, C_8H_{18}, a typical gasoline component that has a density of 0.70 g/mL?

24.50 How many carbon-carbon sigma bonds are present in each of the following molecules? (a) 2-butyne, (b) anthracene (see Figure 24.5), (c) 2,3-dimethylpentane

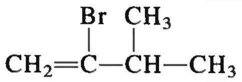
24.51 How many carbon-carbon sigma bonds are present in each of the following molecules? (a) benzene, (b) cyclobutane, (c) 3-ethyl-2-methylpentane

24.52 The combustion of 20.63 mg of compound Y, which contains only C, H, and O, with excess oxygen gave 57.94 mg of CO_2 and 11.85 mg of H_2O. (a) Calculate how many milligrams of C, H, and O were present in the original sample of Y. (b) Derive the empirical formula of Y. (c) Suggest a plausible structure for Y if the empirical formula is the same as the molecular formula.

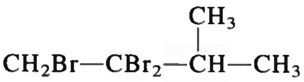
24.53 Draw all the structural isomers of compounds with the formula $C_4H_8Cl_2$. Indicate which isomers are chiral and give them systematic names.

24.54 The combustion of 3.795 mg of liquid B, which contains only C, H, and O, with excess oxygen gave 9.708 mg of CO_2 and 3.969 mg of H_2O. In a molar mass determination, 0.205 g of B vaporized at 1.00 atm and 200.0°C and occupied a volume of 89.8 mL. Derive the empirical formula, molar mass, and molecular formula of B and draw three plausible structures.

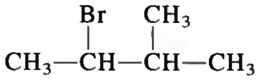
24.55 Beginning with 3-methyl-1-butyne, show how you would prepare the following compounds:

(a)


$CH_2{=}\underset{}{\overset{\displaystyle Br}{\overset{|}{C}}}{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_3$

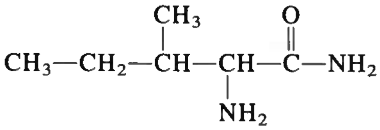
(b)


$CH_2Br{-}CBr_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_3$

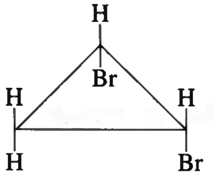
(c)


$CH_3{-}\overset{\displaystyle Br}{\overset{|}{C}H}{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_3$

24.56 Indicate the asymmetric carbon atoms in the following compounds:

(a)


$CH_3{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}\underset{\displaystyle NH_2}{\underset{|}{C}H}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH_2$

(b)


24.57 Suppose benzene contained three distinct single bonds and three distinct double bonds. How many different isomers would there be for dichlorobenzene ($C_6H_4Cl_2$)? Draw all your proposed structures.

24.58 Write the structural formula of an aldehyde that is a structural isomer of acetone.

24.59 Draw structures for the following compounds: (a) cyclopentane, (b) *cis*-2-butene, (c) 2-hexanol, (d) 1,4-dibromobenzene, (e) 2-butyne.

24.60 Name the classes to which the following compounds belong:

(a) C_4H_9OH

(b) $CH_3OC_2H_5$

(c) C_2H_5CHO

(d) C_6H_5COOH

(e) CH_3NH_2

24.61 Ethanol, C_2H_5OH, and dimethyl ether, CH_3OCH_3, are structural isomers. Compare their melting points, boiling points, and solubilities in water.

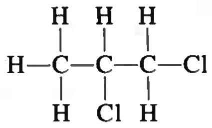
24.62 Amines are Brønsted bases. The unpleasant smell of fish is due to the presence of certain amines. Explain why cooks often add lemon juice to suppress the odor of fish (in addition to enhancing the flavor).

24.63 You are given two bottles, each containing a colorless liquid. You are told that one liquid is cyclohexane and the other is benzene. Suggest one chemical test that would allow you to distinguish between these two liquids.

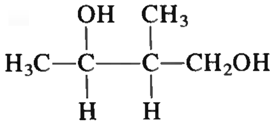
24.64 Give the chemical names of the following organic compounds and write their formulas: marsh gas, grain alcohol, wood alcohol, rubbing alcohol, antifreeze, mothballs, chief ingredient of vinegar.

24.65 The compound $CH_3—C\equiv C—CH_3$ is hydrogenated to an alkene using platinum as the catalyst. Predict whether the product is the pure *trans* isomer, the pure *cis* isomer, or a mixture of *cis* and *trans* isomers. Based on your prediction, comment on the mechanism of the heterogeneous catalysis.

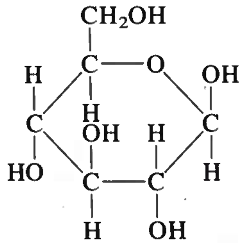
24.66 How many asymmetric carbon atoms are present in each of the following compounds?

(a) 

$H—CH_2—CHCl—CH_2—Cl$

(b) 

$H_3C—CH(OH)—CH(CH_3)—CH_2OH$

(c) 

24.67 Isopropanol is prepared by reacting propylene (CH_3CHCH_2) with sulfuric acid, followed by treatment with water. (a) Show the sequence of steps leading to the product. What is the role of sulfuric acid? (b) Draw the structure of an alcohol that is an isomer of isopropanol. (c) Is isopropanol a chiral molecule? (d) What property of isopropanol makes it useful as a rubbing alcohol?

24.68 When a mixture of methane and bromine vapor is exposed to light, the following reaction occurs slowly:

$$CH_4(g) + Br_2(g) \longrightarrow CH_3Br(g) + HBr(g)$$

Suggest a mechanism for this reaction. (*Hint*: Bromine vapor is deep red; methane is colorless.)

24.69 Under conditions of acid catalysis, alkenes react with water to form alcohols. As in the case with hydrogen halides, the addition reaction in the formation of alcohols is also governed by Markovnikov's rule. An alkene of approximate molar mass of 42 g reacts with water and sulfuric acid to produce a compound that reacts with acidic potassium dichromate solution to produce a ketone. Identify all the compounds in the preceding steps.

Special Problems

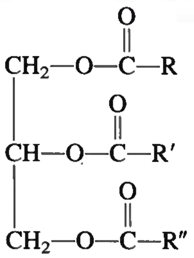
24.70 2-Butanone can be reduced to 2-butanol by reagents such as lithium aluminum hydride ($LiAlH_4$). (a) Write the formula of the product. Is it chiral? (b) In reality, the product does not exhibit optical activity. Explain.

24.71 Write the structures of three alkenes that yield 2-methylbutane on hydrogenation.

24.72 An alcohol was converted to a carboxylic acid with acidic potassium dichromate. A 4.46-g sample of the acid was added to 50.0 mL of 2.27 M NaOH and the excess NaOH required 28.7 mL of 1.86 M HCl for neutralization. What is the molecular formula of the alcohol?

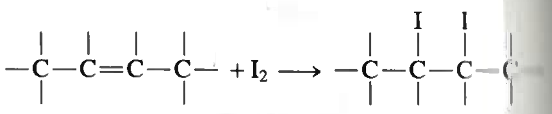
24.73 Write the structural formulas of the alcohols with the formula $C_6H_{13}O$ and indicate those that are chiral. Show only the C atoms and the —OH groups.

24.74 Fat and oil are names for the same class of compounds, called triglycerides, which contain three ester groups



A fat or oil

where R, R′, and R″ represent long hydrocarbon chains. (a) Suggest a reaction that leads to the formation of a triglyceride molecule, starting with glycerol and carboxylic acids (see p. 460 for structure of glycerol). (b) In the old days, soaps were made by hydrolyzing animal fat with lye (a sodium hydroxide solution). Write an equation for this reaction. (c) The difference between fats and oils is that at room temperature, the former are solids and the latter are liquids. Fats are usually produced by animals, whereas oils are commonly found in plants. The melting points of these substances are determined by the number of C=C bonds (or the extent of unsaturation) present—the larger the number of C=C bonds, the lower the melting point and the more likely that the substance is a liquid. Explain. (d) One way to convert liquid oil to solid fat is to hydrogenate the oil, a process by which some or all of the C=C bonds are converted to C—C bonds. This procedure prolongs shelf life of the oil by removing the more reactive C=C group and facilitates packaging. How would you carry out such a process (that is, what reagents and catalyst would you employ)? (e) The degree of unsaturation of oil can be determined by reacting the oil with iodine, which reacts with the C=C bond as follows:



$$-\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{C}-\overset{|}{\underset{|}{C}}- + I_2 \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{I}{\underset{|}{C}}-\overset{I}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

The procedure is to add a known amount of iodine to the oil and allow the reaction to go to completion. The amount of excess (unreacted) iodine is determined by titrating the remaining iodine with a standard sodium thiosulfate ($Na_2S_2O_3$) solution:

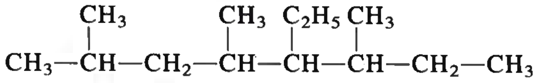
$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

The number of grams of iodine that react with 100 grams of oil is called the *iodine number.* In one case, 43.8 g of I_2 were treated with 35.3 g of corn oil. The excess iodine required 20.6 mL of a 0.142 M $Na_2S_2O_3$ for neutralization. Calculate the iodine number of the corn oil.

Answers to Practice Exercises

24.1 5.

24.2 4,6-diethyl-2-methyloctane

24.3 

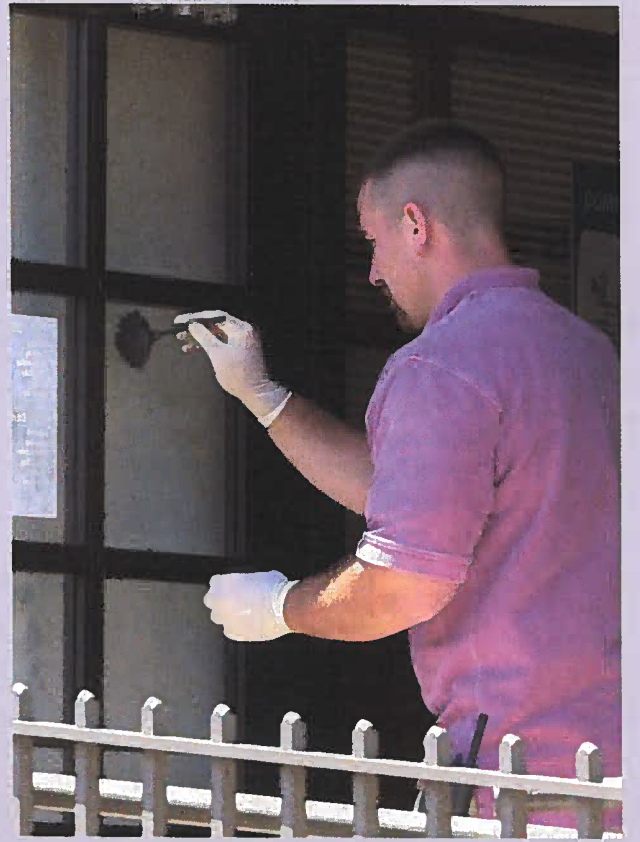
$$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{C_2H_5}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$$

24.4 No.

24.5 $CH_3CH_2COOCH_3$ and H_2O.

CHEMICAL

Mystery

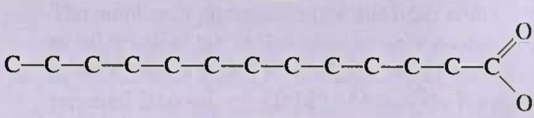


The Disappearing Fingerprints[†]

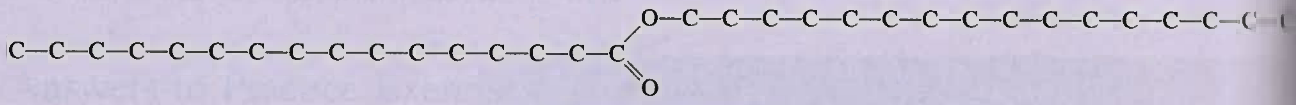
In 1993, a young girl was abducted from her home and taken away in a car. Later she managed to escape from her attacker and was rescued by a local resident and safely returned home unharmed. A few days later the police arrested a suspect and recovered the car. In building the case against the man, the law officers found that they lacked some crucial evidence. The girl's detailed description indicated that she must have been in the car, yet none of her fingerprints could be found. Fortunately, the police were able to link the girl to the car and its owner by matching fibers found in the car with those from the girl's nightgown.

What are fingerprints? Our fingertips are studded with sweat pores. When a finger touches something, the sweat from these pores is deposited on the surface, providing a mirror image of the ridge pattern, called a fingerprint. No two individuals have the same fingerprints. This fact makes fingerprint matching one of the most powerful methods for identifying crime suspects.

Why were the police not able to find the girl's fingerprints in the car? The residue that is deposited by fingerprints is about 99 percent water. The other 1 percent contains oils and fatty acids, esters, amino acids, and salts. Fingerprint samples from adults contain heavy oils and long carbon chains linked together by ester groups, but children's samples contain mostly unesterified and shorter fatty chains that are light and more volatile. (The hydrogen atoms are omitted for clarity.)



from a child's fingerprint



from an adult's fingerprint

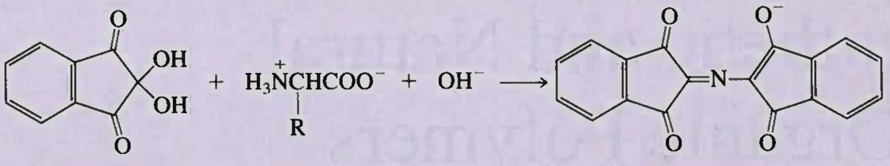
In general, adult fingerprints last at least several days, but children's fingerprints often vanish within 24 hours. For this reason, in cases involving children, crime scene investigation must be done very quickly.

[†] Adapted with permission from "The Disappearing Fingerprints" by Deborah Noble, *CHEM MATTERS*, February, 1997, p. 9. Copyright 1997 American Chemical Society.

Chemical Clues

When a finger touches a surface, it leaves an invisible pattern of oil called a latent fingerprint. Forensic investigators must develop a latent fingerprint into a visible print that can be photographed, then scanned and stored for matching purposes. The following are some of the common methods for developing latent fingerprints.

1. The dusting powder method: This is the traditional method in which fine powder (usually carbon black, which is an amorphous form of carbon obtained by the thermal decomposition of hydrocarbons) is brushed onto nonporous surfaces. The powder sticks to the sweat, making the ridge pattern visible. An improvement on this method is the use of fluorescent powders. What are the advantages of this modification?
2. The iodine method: When heated, iodine sublimes and its vapor reacts with the carbon-carbon double bonds in fats and oils, turning the ridge pattern to a yellow-brown color. This method is particularly well suited for fingerprints on porous objects like papers and cardboard. Write an equation showing the reaction of I_2 with fats and oils.
3. The ninhydrin method: This is one of the most popular methods for developing latent fingerprints on porous, absorbent surfaces like paper and wood. This method is based on a complex reaction between ninhydrin and amino acids (see Table 25.2) in the presence of a base to produce a compound, which turns purple when heated. The unbalanced equation is



ninhydrin amino acid Ruhemann's purple

where R is a substituent. Because the amino acids in sweat do not interact with the cellulose content of paper or wood, this technique enables prints that may be years old to be developed. Draw resonance structures of Ruhemann's purple, showing the movement of electrons with curved arrows.