CHAPTER 25

THE CHEMISTRY OF LIFE: ORGANIC AND BIOLOGICAL CHEMISTRY

A WARNING ON DIET SOFT DRINK CONTAINERS alerts those suffering from phenylketonuria of the presence of phenylalanine in the soft drink.

WHAT'S AHEAD

25.1 Some General Characteristics of Organic Molecules
We begin with a brief review of the structures and reactivities of organic compounds.

25.2 Introduction to Hydrocarbons
We consider the *hydrocarbons*, compounds containing only C and H.

25.3 Alkanes, Alkenes, and Alkynes
We next explore three classes of hydrocarbons: those in which all bonds are single bonds called *alkanes*, those with one or more C$=$C bonds called *alkenes*, and those with one or more C$\equiv$C bonds called *alkynes*. *Aromatic* hydrocarbons have at least one planar ring with delocalized π electrons. One reason for the huge number of organic compounds is the existence of *isomers*, compounds with identical compositions whose molecules have different structures.

25.4 Organic Functional Groups
We recognize that a central organizing principle of organic chemistry is the *functional group*, a group of atoms at which most of the compound's chemical reactions occur. Common organic functional groups that include oxygen and nitrogen atoms are described.

25.5 Chirality in Organic Chemistry
We learn that compounds with nonsuperimposable mirror images are *chiral*. Chirality plays very important roles in organic and biological chemistry.

25.6 Introduction to Biochemistry
We introduce the chemistry of living organisms, known as *biochemistry*, *biological chemistry*, or *chemical biology*. Important classes of compounds that occur in living systems are *proteins*, *carbohydrates*, *lipids*, and *nucleic acids*.

25.7 Proteins
We learn that proteins are polymers of *amino acids* linked with *amide* (also called *peptide*) bonds. Proteins are used for structural support (muscles, cartilage), molecular transporters (hemoglobin, which transports oxygen in blood), and enzymes (proteins that catalyze many metabolic reactions).

25.8 Carbohydrates
We observe that carbohydrates are sugars and polymers of sugars that are primarily used as fuel for organisms (glucose) or as structural supports in plants (cellulose).

25.9 Lipids
We recognize that lipids are a large class of molecules that are primarily used for energy storage in organisms (fats, oils).

25.10 Nucleic Acids
Finally, we learn that nucleic acids are polymers of nucleotides that comprise an organism's genetic information. *Deoxyribonucleic acid* (DNA) and *ribonucleic acid* (RNA) are polymers composed of *nucleotides*.

MANY CANS OF DIET SOFT DRINK CARRY THE WARNING "PHENYLKETONURICS: CONTAINS PHENYLALANINE." Phenylalanine is one of the essential amino acids, which means that we must have it in our diets to survive. However, in about one out of 10,000 to 20,000 Caucasian or Asian births, an enzyme that converts phenylalanine to another amino acid, tyrosine, is completely or nearly completely deficient because of a genetic defect. The result is that phenylalanine accumulates in the blood and in body tissues. The disease that results is called phenylketonuria (PKU), which causes mental retardation and seizures. Newborns are now routinely tested for PKU at about 3 days of age. The disease can be managed by a diet that provides just enough phenylalanine for proper nutrition, without exceeding the limit. Hence, the government requires warnings on diet drink containers.

Although biological systems are almost unimaginably complex, they are nevertheless constructed of molecules of quite modest size, put together in nature to form a host of complex, interacting structures. The example of phenylalanine and PKU illustrates the point that to understand biology, we need to understand the chemical behaviors of molecules of low molar mass. This chapter is about the molecules, composed mainly of carbon, hydrogen, oxygen, and nitrogen, that form the basis of both organic and biological chemistry.

The element carbon forms a vast number of compounds. Over 16 million carbon-containing compounds are known. Chemists make thousands of new compounds every year, about 90% of which contain carbon. The study of carbon compounds constitutes a separate branch of chemistry known as **organic chemistry**. This term arose from the eighteenth-century belief that organic compounds could be formed only by living systems. This idea was disproved in 1828 by the German chemist Friedrich Wöhler when he synthesized urea (H_2NCONH_2), an organic substance found in the urine of mammals, by heating ammonium cyanate (NH_4OCN), an inorganic substance.

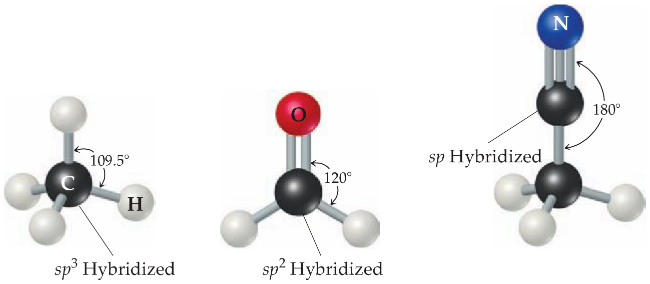
The study of the chemistry of living species is called *biological chemistry*, *chemical biology*, or **biochemistry**. In this final chapter we present a brief view of some of the elementary aspects of organic chemistry and biochemistry. Many of you will study these subjects in greater detail by taking additional courses devoted entirely to these topics. As you read the material that follows, you will notice that many of the concepts important for understanding the fundamentals of organic chemistry and biochemistry have been developed in earlier chapters.

25.1 SOME GENERAL CHARACTERISTICS OF ORGANIC MOLECULES

What is it about carbon that leads to the tremendous diversity in its compounds, and allows it to play such crucial roles in biology and society? Let's consider some general features of organic molecules, and as we do, let's review some principles that we learned in earlier chapters.

The Structures of Organic Molecules

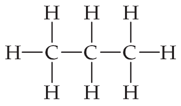
The three-dimensional structures of organic and biochemical molecules play an essential role in determining their physical and chemical behaviors. Because carbon has four valence electrons ([He]$2s^2 2p^2$), it forms four bonds in virtually all its compounds. When all four bonds are single bonds, the electron pairs are disposed in a tetrahedral arrangement. ∞ (Section 9.2) In the hybridization model the carbon $2s$ and $2p$ orbitals are then sp^3 hybridized. ∞ (Section 9.5) When there is one double bond, the arrangement is trigonal planar (sp^2 hybridization). With a triple bond, it is linear (sp hybridization). Examples are shown in Figure 25.1▼.



(a) Tetrahedral (b) Trigonal planar (c) Linear

▶ **Figure 25.1 Carbon geometries.** These molecular models show the three common geometries around carbon: (a) tetrahedral in methane (CH_4), where the carbon is bonded to four other atoms; (b) trigonal planar in formaldehyde (CH_2O), where the carbon is bonded to three other atoms; and (c) linear in acetonitrile (CH_3CN), where the top carbon is bonded to two atoms.

C—H bonds occur in almost every organic molecule. Because the valence shell of H can hold only two electrons, hydrogen forms only one covalent bond. As a result, hydrogen atoms are always located on the surface of organic molecules, as in the propane molecule:



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

The C—C bonds form the backbone, or skeleton, of the molecule, while the H atoms are on the surface, or "skin," of the molecule.

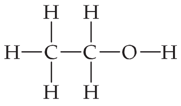
The bonding arrangements about individual atoms are important in determining overall molecular shape. In turn, the overall shapes of organic and biochemical molecules are important in determining how they will react with other molecules, and how rapidly. They also determine important physical properties.

The Stabilities of Organic Substances

In Section 8.8 we learned about the average strengths of various chemical bonds, including those that are characteristic of organic molecules, such as C—H, C—C, C—N, C—O, and C═O bonds. Carbon forms strong bonds with a variety of elements, especially H, O, N, and the halogens. Carbon also has an exceptional ability to bond to itself, forming a variety of molecules with chains or rings of carbon atoms. As we saw in Chapter 8, double bonds are generally stronger than single bonds, and triple bonds are stronger than double bonds. Increasing bond strength with bond order is accompanied by a shortening of the bond. Thus, carbon–carbon bond lengths decrease in the order $\mathrm{C{-}C} > \mathrm{C{=}C} > \mathrm{C{\equiv}C}$.

We know from calorimetric measurements that reaction of a simple organic substance such as methane (CH_4) with oxygen is highly exothermic. (Sections 5.6, 5.7, and 5.8) Indeed, the combustion of methane (natural gas) keeps many of our homes warm during the winter months! Although the reactions of most organic compounds with oxygen are exothermic, great numbers of them are stable indefinitely at room temperature in the presence of air because the activation energy required for combustion is large.

Most reactions with low or moderate activation barriers begin when a region of high electron density on one molecule encounters a region of low electron density on another molecule. The regions of high electron density may be due to the presence of a multiple bond or to the more electronegative atom in a polar bond. Because of their strength and lack of polarity, C—C single bonds are relatively unreactive. C—H bonds are also largely unreactive for the same reasons. The C—H bond is nearly nonpolar because the electronegativities of C (2.5) and H (2.1) are close. To better understand the implications of these facts, consider ethanol:

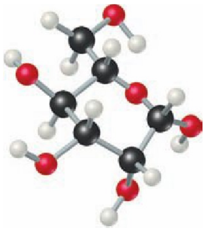


$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & & & \\ & & | & & | & & & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O} & - & \mathrm{H} \\ & & | & & | & & & & \\ & & \mathrm{H} & & \mathrm{H} & & & & \end{array}$$

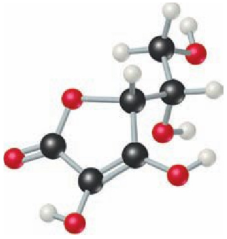
The differences in the electronegativity values of C (2.5) and O (3.5) and those of O and H (2.1) indicate that the C—O and O—H bonds are quite polar. Thus, the chemical reactions of ethanol involve these bonds. A group of atoms such as the C—O—H group, which determines how an organic molecule functions or reacts, is called a **functional group**. The functional group is the center of reactivity in an organic molecule.

GIVE IT SOME THOUGHT

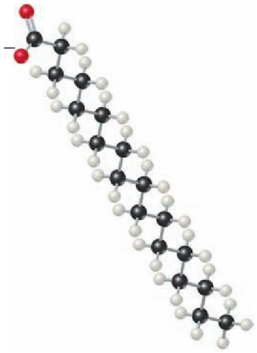
Which of these bond types is most likely to be the seat of a chemical reaction: C═N, C—C, or C—H?



Glucose ($C_6H_{12}O_6$)



Ascorbic acid ($HC_6H_7O_6$)



Stearate ($C_{17}H_{35}COO^-$)

▲ **Figure 25.2 Water-soluble organic molecules.** (a) Glucose ($C_6H_{12}O_6$), a simple sugar; (b) ascorbic acid ($HC_6H_7O_6$), known as vitamin C; (c) the stearate ion ($C_{17}H_{35}COO^-$), an ion that functions as a surfactant. (To fit this illustration in the allocated space, the scale at which the surfactant molecule is drawn is different from the scale used for the glucose and ascorbic acid molecules.)

Solubility and Acid–Base Properties of Organic Substances

In most organic substances, the most prevalent bonds are carbon–carbon and carbon–hydrogen, which have low polarity. For this reason, the overall polarity of organic molecules is often low. They are generally soluble in nonpolar solvents and not very soluble in water. (Section 13.3) Molecules that are soluble in polar solvents such as water are those that have polar groups on the surface of the molecule, such as found in glucose [Figure 25.2(a) ◀] or ascorbic acid [vitamin C, Figure 25.2(b)]. Surfactant organic molecules have a long, nonpolar part that extends into a nonpolar medium and a polar, ionic "head group" that extends into a polar medium, such as water [Figure 25.2(c)]. (Section 13.6) This type of structure is found in many biochemically important substances, as well as soaps and detergents.

Many organic substances contain acidic or basic groups. The most important acidic substances are the carboxylic acids, which bear the functional group $-COOH$. (Section 4.3 and Section 16.10) The most important basic substances are amines, which bear the $-NH_2$, $-NHR$, or $-NR_2$ groups, where R is an organic group consisting of some combination of $C-C$ and $C-H$ bonds, such as $-CH_3$ or $-C_2H_5$. (Section 16.7)

As you read this chapter, you will find many concept links to related materials in earlier chapters, many of them to the sections just discussed. *We strongly encourage you to follow these links and review the earlier materials*. Doing so will definitely enhance your understanding and appreciation of organic chemistry and biochemistry.

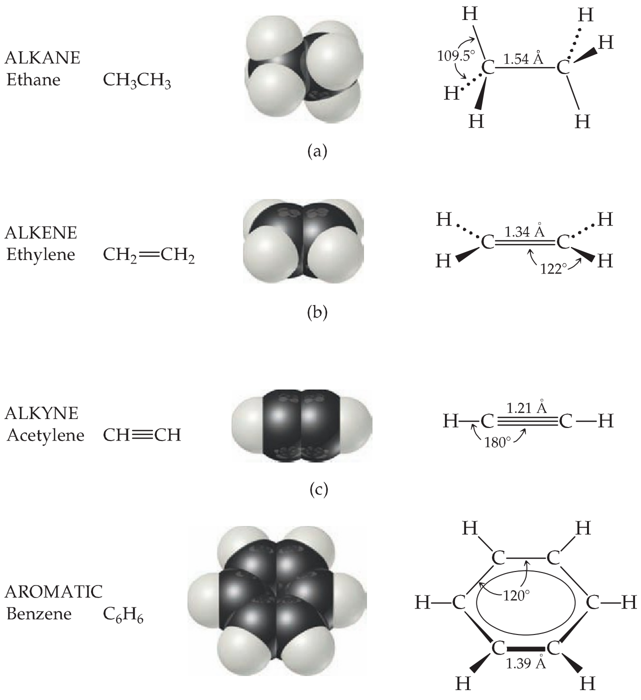
25.2 INTRODUCTION TO HYDROCARBONS

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

Hydrocarbons can be divided into four general types, depending on the kinds of carbon–carbon bonds in their molecules. Figure 25.3 ▶ shows an example of each of the four types: alkanes, alkenes, alkynes, and aromatic hydrocarbons. In these hydrocarbons, as well as in other organic compounds, each C atom invariably has four bonds (four single bonds, two single bonds and one double bond, or one single bond and one triple bond).

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

The members of these different classes of hydrocarbons exhibit different chemical behaviors, as we will see shortly. Their physical properties, however, are similar in many ways. Because carbon and hydrogen do not differ greatly in electronegativity, hydrocarbon molecules are relatively nonpolar. Thus, they are



(a)

(b)

(c)

(d)

▲ Figure 25.3 The four hydrocarbon types. Names, molecular formulas, and geometrical structures for examples of each type of hydrocarbon.

almost completely insoluble in water, but they dissolve readily in other nonpolar solvents. Their melting points and boiling points are determined by London dispersion forces. Hence, hydrocarbons tend to become less volatile with increasing molar mass. ∞ (Section 11.2) As a result, hydrocarbons of very low molecular weight, such as C_2H_6 (bp = −89 °C), are gases at room temperature; those of moderate molecular weight, such as C_6H_{14} (bp = 69 °C), are liquids; and those of high molecular weight, such as $C_{22}H_{46}$ (mp = 44 °C), are solids.

25.3 ALKANES, ALKENES, AND ALKYNES

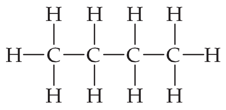
Table 25.1▼ lists several of the simplest alkanes. Many of these substances are familiar because they are used so widely. Methane is a major component of natural gas and is used for home heating and in gas stoves and water heaters. Propane is the major component of bottled gas used for home heating and cooking in areas where natural gas is not available. Butane is used in disposable lighters and in fuel canisters for gas camping stoves and lanterns. Alkanes with from 5 to 12 carbon atoms per molecule are found in gasoline.

The formulas for the alkanes given in Table 25.1 are written in a notation called *condensed structural formulas*. This notation reveals the way in which atoms are bonded to one another but does not require drawing in all the bonds.

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

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

For example, the Lewis structure and the condensed structural formulas for butane (C_4H_{10}) are



$$H_3C{-}CH_2{-}CH_2{-}CH_3$$

or

$$CH_3CH_2CH_2CH_3$$

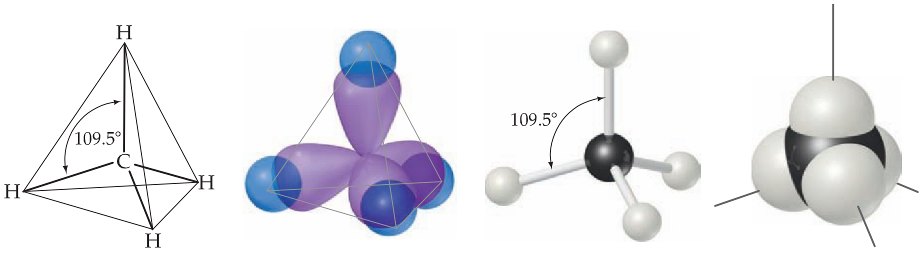
We will frequently use either Lewis structures or condensed structural formulas to represent organic compounds. Notice that each carbon atom in an alkane has four single bonds, whereas each hydrogen atom forms one single bond. Notice also that each succeeding compound in the series listed in Table 25.1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

GIVE IT SOME THOUGHT

How many C—H and C—C bonds are formed by the middle carbon atom of propane, Table 25.1?

Structures of Alkanes

The Lewis structures and condensed structural formulas for alkanes do not tell us anything about the three-dimensional structures of these substances. According to the VSEPR model, the geometry about each carbon atom in an alkane is tetrahedral; that is, the four groups attached to each carbon are located at the vertices of a tetrahedron. (Section 9.2) The three-dimensional structures can be represented as shown for methane in Figure 25.4▼. The bonding may be described as involving sp^3-hybridized orbitals on the carbon. (Section 9.5)

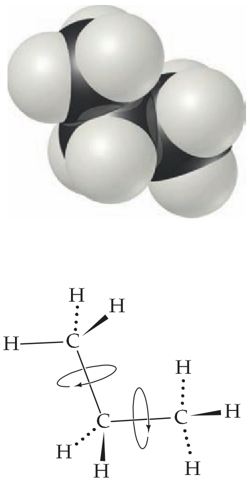


▲ **Figure 25.4** **Representations of the three-dimensional arrangement of bonds about carbon in methane.**

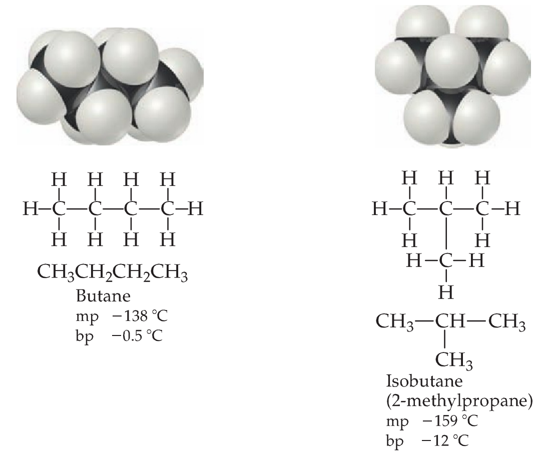
Rotation about a carbon–carbon single bond is relatively easy, and it occurs very rapidly at room temperature. To visualize such rotation, imagine grasping either methyl group in Figure 25.5▶, which shows the structure of propane, and spinning it relative to the rest of the structure. Because motion of this sort occurs very rapidly in alkanes, a long-chain alkane molecule is constantly undergoing motions that cause it to change its shape, something like a length of chain that is being shaken.

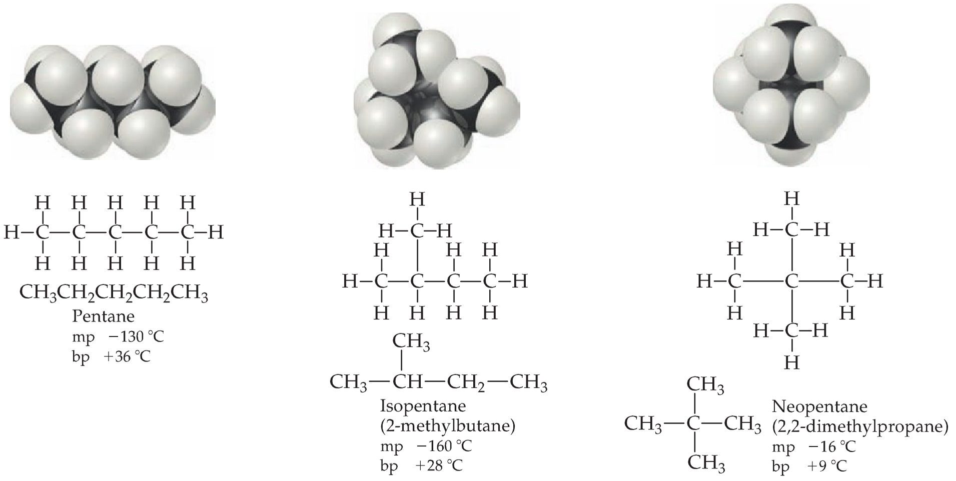
Structural Isomers

The alkanes listed in Table 25.1 are called *straight-chain hydrocarbons* because all the carbon atoms are joined in a continuous chain. Alkanes consisting of four or more carbon atoms can also form *branched chains* called *branched-chain hydrocarbons*. Figure 25.6▼ shows space-filling models, full structural formulas, and



▲ Figure 25.5 **Rotation about a C—C bond.** Either representation of propane (C_3H_8) can help you visualize rotation about a C—C single bond.





▲ Figure 25.6 **Hydrocarbon isomers.** There are two structural isomers having the formula C_4H_{10}: butane and isobutane. For the formula C_5H_{12}, there are three structural isomers: pentane, isopentane, and neopentane. In general, the number of structural isomers increases as the number of carbons in the hydrocarbon increases.

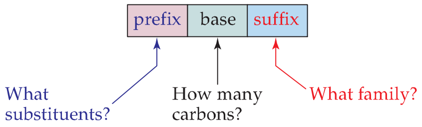
condensed structural formulas for all the possible structures of alkanes containing four or five carbon atoms. There are two ways that four carbon atoms can be joined to give C_4H_{10}: as a straight chain (left) or a branched chain (right). For alkanes with five carbon atoms (C_5H_{12}), there are three different arrangements.

Compounds with the same molecular formula but with different bonding arrangements (and hence different structures) are called **structural isomers**. The structural isomers of a given alkane differ slightly from one another in physical properties. Note the melting and boiling points of the isomers of butane and pentane, given in Figure 25.6. The number of possible structural isomers increases rapidly with the number of carbon atoms in the alkane. There are 18 possible isomers having the molecular formula C_8H_{18}, for example, and 75 possible isomers with the molecular formula $C_{10}H_{22}$.

Nomenclature of Alkanes

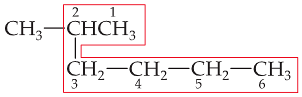
The first names given to the structural isomers shown in Figure 25.6 are the so-called common names. The isomer in which one CH_3 group is branched off the major chain is labeled the *iso-* isomer (for example, isobutane). As the number of isomers grows, however, it becomes impossible to find a suitable prefix to denote each isomer. The need for a systematic means of naming organic compounds was recognized early in the history of organic chemistry. In 1892 an organization called the International Union of Chemistry met in Geneva, Switzerland, to formulate rules for systematic naming of organic substances. Since that time the task of updating the rules for naming compounds has fallen to the International Union of Pure and Applied Chemistry (IUPAC). Chemists everywhere, regardless of their nationality, subscribe to a common system for naming compounds.

The IUPAC names for the isomers of butane and pentane are the ones given in parentheses for each compound in Figure 25.6. These names as well as those of other organic compounds have three parts to them:



The following steps summarize the procedures used to arrive at the names of alkanes, which all have names ending with the suffix *-ane*. We use a similar approach to write the names of other organic compounds.

1. *Find the longest continuous chain of carbon atoms, and use the name of this chain (Table 25.1) as the base name of the compound.* The longest chain may not always be written in a straight line, as seen in the following example:



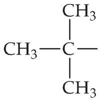
2-Methyl*hexane*

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

2. *Number the carbon atoms in the longest chain, beginning with the end of the chain that is nearest to a substituent.* In our example we number the C atoms from the upper right because that places the CH_3 substituent on the second C atom of the chain; if we number from the lower right, the CH_3 would be on the fifth C atom. The chain is numbered from the end that gives the lowest number for the substituent position.

3. *Name and give the location of each substituent group.* A substituent group that is formed by removing an H atom from an alkane is called an **alkyl group**. Alkyl groups are named by replacing the *-ane* ending of the alkane name with *-yl*. The methyl group (CH_3), for example, is derived from methane (CH_4). Likewise, the ethyl group (C_2H_5) is derived from ethane (C_2H_6). Table 25.2 ▶ lists several common alkyl groups. The name 2-methylhexane indicates the presence of a methyl (CH_3) group on the second carbon atom of a hexane (six-carbon) chain.

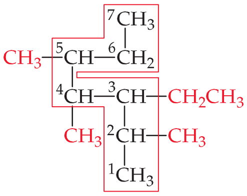
TABLE 25.2 ■ Condensed Structural Formulas and Common Names for Several Alkyl Groups

Group	Name
CH_3—	Methyl
CH_3CH_2—	Ethyl
$CH_3CH_2CH_2$—	Propyl
$CH_3CH_2CH_2CH_2$—	Butyl
 $\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{HC}}}\text{—}$	Isopropyl
 $\mathrm{CH_3}\text{—}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\text{—}$	*tert*-Butyl

GIVE IT SOME THOUGHT

What is the chemical formula of the propyl group?

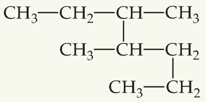
4. *When two or more substituents are present, list them in alphabetical order.* When there are two or more of the same substituent, the number of substituents of that type is indicated by a prefix: *di-* (two), *tri-* (three), *tetra-* (four), *penta-* (five), and so forth. Notice how the following example is named:



3-Ethyl-2,4,5-trimethylheptane

SAMPLE EXERCISE 25.1 | Naming Alkanes

Give the systematic name for the following alkane:

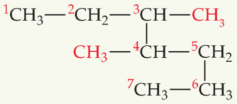


SOLUTION

Analyze: We are given the structural formula of an alkane and asked to give its name.

Plan: Because the hydrocarbon is an alkane, its name ends in *-ane*. The name of the parent hydrocarbon is based on the longest continuous chain of carbon atoms, as summarized in Table 25.1. Branches are alkyl groups, named after the number of C atoms in the branch and located by counting C atoms along the longest continuous chain.

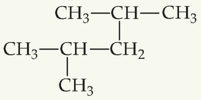
Solve: The longest continuous chain of C atoms extends from the upper left CH_3 group to the lower left CH_3 group and is seven C atoms long:



The parent compound is thus heptane. There are two CH_3 (methyl) groups that branch off the main chain. Hence, this compound is a dimethylheptane. To specify the location of the two methyl groups, we must number the C atoms from the end that gives the lowest number possible to the carbons bearing side chains. This means that we should start numbering with the upper left carbon. There is a methyl group on carbon 3, and one on carbon 4. The compound is thus 3,4-dimethylheptane.

PRACTICE EXERCISE

Name the following alkane:



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

Answer: 2,4-dimethylpentane

SAMPLE EXERCISE 25.2 | Writing Condensed Structural Formulas

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

SOLUTION

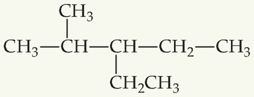
Analyze: We are given the systematic name for a hydrocarbon and asked to write its structural formula.

Plan: Because the compound's name ends in *-ane*, it is an alkane, meaning that all the carbon–carbon bonds are single bonds. The parent hydrocarbon is pentane, indicating five C atoms (Table 25.1). There are two alkyl groups specified, an ethyl group (two carbon atoms, C_2H_5) and a methyl group (one carbon atom, CH_3). Counting from left to right along the five-carbon chain, the ethyl group will be attached to the third C atom and the methyl group will be attached to the second C atom.

Solve: We begin by writing a string of five C atoms attached to each other by single bonds. These represent the backbone of the parent pentane chain:

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

We next place a methyl group on the second C and an ethyl group on the third C atom of the chain. We then add hydrogens to all the other C atoms to make the four bonds to each carbon, giving the following condensed structure:



$$\begin{array}{ccccc} & CH_3 & & & \\ & | & & & \\ CH_3- & CH & - & CH & -CH_2-CH_3 \\ & & & | & \\ & & & CH_2CH_3 & \end{array}$$

The formula can be written even more concisely in the following style:

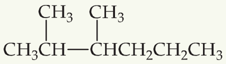
$$CH_3CH(CH_3)CH(C_2H_5)CH_2CH_3$$

In this formula the branching alkyl groups are indicated in parentheses.

PRACTICE EXERCISE

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

Answer:



$$\begin{array}{ccccc} & CH_3 & & CH_3 & \\ & | & & | & \\ CH_3 & CH & - & CH & CH_2CH_2CH_3 \end{array}$$

or $CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$

Cycloalkanes

Alkanes can form rings or cycles. Alkanes with this form of structure are called **cycloalkanes**. Figure 25.7 ▶ illustrates a few cycloalkanes. Cycloalkane structures are sometimes drawn as simple polygons in which each corner of the polygon represents a CH_2 group. This method of representation is similar to that used for benzene rings. ∞ (Section 8.6) (Remember from our benzene discussion that in aromatic structures each vertex represents a CH group, not a CH_2 group.)

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

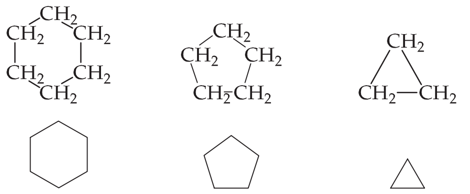

Cyclohexane Cyclopentane Cyclopropane

Figure 25.7 Condensed structural formulas and line structures for three cycloalkanes.

Cycloalkanes, particularly the small-ring compounds, sometimes behave chemically like unsaturated hydrocarbons, which we will discuss shortly. The general formula for cycloalkanes, C_nH_{2n}, differs from the general formula for straight-chain alkanes, C_nH_{2n+2}.

Reactions of Alkanes

Because they contain only C—C and C—H bonds, most alkanes are relatively unreactive. At room temperature, for example, they do not react with acids, bases, or strong oxidizing agents, and they are not even attacked by boiling nitric acid. Their low chemical reactivity is due primarily to the strength and lack of polarity of C—C and C—H bonds.

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

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

In the following sections we will see that hydrocarbons can be modified to impart greater reactivity by introducing unsaturation into the carbon–carbon framework and by attaching other reactive groups to the hydrocarbon backbone.

Chemistry Put to Work GASOLINE

Petroleum, or crude oil, is a complex mixture of organic compounds, mainly hydrocarbons, with smaller quantities of other organic compounds containing nitrogen, oxygen, or sulfur. The tremendous demand for petroleum to meet the world's energy needs has led to the tapping of oil wells in such forbidding places as the North Sea and northern Alaska.

The usual first step in the *refining*, or processing, of petroleum is to separate it into fractions on the basis of boiling point. The fractions commonly taken are shown in Table 25.3▼. Because gasoline is the most commercially important of these fractions, various processes are used to maximize its yield.

Gasoline is a mixture of volatile hydrocarbons containing varying amounts of aromatic hydrocarbons in addition to alkanes. In a traditional automobile engine a mixture of air and gasoline vapor is compressed by a piston and then ignited by a spark plug. The burning of the gasoline should create a strong, smooth expansion of gas, forcing the piston outward and imparting force along the drive shaft of the engine. If the gas

TABLE 25.3 ■ Hydrocarbon Fractions from Petroleum

Fraction	Size Range of Molecules	Boiling-Point Range (°C)	Uses
Gas	C_1 to C_5	−160 to 30	Gaseous fuel, production of H_2
Straight-run gasoline	C_5 to C_{12}	30 to 200	Motor fuel
Kerosene, fuel oil	C_{12} to C_{18}	180 to 400	Diesel fuel, furnace fuel, cracking
Lubricants	C_{16} and up	350 and up	Lubricants
Paraffins	C_{20} and up	Low-melting solids	Candles, matches
Asphalt	C_{36} and up	Gummy residues	Surfacing roads

continues on next page

continued

▲ **Figure 25.8** **Octane rating.** The octane rating of gasoline measures its resistance to knocking when burned in an engine. The octane rating of this gasoline is 89, as shown on the face of the pump.

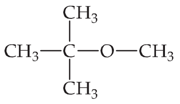
burns too rapidly, the piston receives a single hard slam rather than a strong, smooth push. The result is a "knocking" or "pinging" sound and a reduction in the efficiency with which energy produced by the combustion is converted to work.

The *octane number* of a gasoline is a measure of its resistance to knocking. Gasolines with high octane numbers burn more smoothly and are thus more effective fuels (Figure 25.8▲). Branched alkanes and aromatic hydrocarbons have higher octane numbers than the straight-chain alkanes. The octane number of gasoline is obtained by comparing its knocking characteristics with those of "isooctane" (2,2,4-trimethylpentane) and heptane. Isooctane is assigned an octane number of 100, whereas heptane is assigned 0. Gasoline with the same knocking characteristics as a mixture of 91% isooctane and 9% heptane is rated as 91 octane.

The gasoline obtained directly from fractionation of petroleum (called *straight-run* gasoline) contains mainly straight-chain hydrocarbons and has an octane number around 50. It is therefore subjected to a process called *reforming*, which converts the straight-chain alkanes into more desirable branched-chain ones (Figure 25.9▶). *Cracking* is used to produce aromatic hydrocarbons and to convert some of the less volatile kerosene and fuel-oil fraction into compounds with lower molecular weights that are suitable for use as automobile fuel. In the cracking process the hydrocarbons are mixed with a catalyst and heated to 400 °C to 500 °C. The catalysts used are naturally occurring clay minerals or synthetic Al_2O_3–SiO_2 mixtures. In addition to forming molecules more suitable for gasoline, cracking results in the formation of hydrocarbons of lower molecular weight, such as ethylene and propene. These substances are used in a variety of reactions to form plastics and other chemicals.

▲ **Figure 25.9** **Fractional distillation.** Petroleum is separated into fractions by distillation and is subjected to catalytic cracking in a refinery, as shown here.

Adding certain compounds called *antiknock agents* or octane enhancers increases the octane rating of gasoline. Until the mid-1970s the principal antiknock agent was tetraethyl lead, $(C_2H_5)_4Pb$. It is no longer used, however, because of the environmental hazards of lead and because it poisons catalytic converters. (Section 14.7: "Chemistry Put to Work: Catalytic Converters") Aromatic compounds such as toluene ($C_6H_5CH_3$) and oxygenated hydrocarbons such as ethanol (CH_3CH_2OH) and methyl *tert*-butyl ether (MTBE, shown below) are now generally used as antiknock agents.

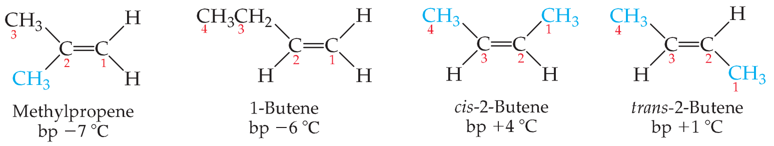


$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3$$

The use of MTBE has been banned in several states, however, because it finds its way into drinking-water supplies from spills and leaking storage tanks, giving the water a bad smell and taste and perhaps producing adverse health effects.
Related Exercises: 25.29 and 25.30

Alkenes

Alkenes are unsaturated hydrocarbons that contain at least one $C{=}C$ bond. The simplest alkene is $CH_2{=}CH_2$, called ethene (IUPAC) or ethylene. Ethylene is a plant hormone. It plays important roles in seed germination and fruit ripening. The next member of the series is $CH_3{-}CH{=}CH_2$, called propene or propylene. For alkenes with four or more carbon atoms, several isomers exist for each molecular formula. For example, there are four isomers of C_4H_8, as shown in Figure 25.10▶. Notice both their structures and their names.



Methylpropene
bp −7 °C

1-Butene
bp −6 °C

cis-2-Butene
bp +4 °C

trans-2-Butene
bp +1 °C

▲ **Figure 25.10** **C_4H_8 structural isomers.** Full structural formulas, names, and boiling points of alkenes having the molecular formula C_4H_8.

The names of alkenes are based on the longest continuous chain of carbon atoms that contains the double bond. The name given to the chain is obtained from the name of the corresponding alkane (Table 25.1) by changing the ending from -*ane* to -*ene*. The compound on the left in Figure 25.10, for example, has a double bond as part of a three-carbon chain; thus, the parent alkene is propene.

The location of the double bond along an alkene chain is indicated by a prefix number that designates the number of the carbon atom that is part of the double bond and is nearest an end of the chain. The chain is always numbered from the end that brings us to the double bond sooner and hence gives the smallest-numbered prefix. In propene the only possible location for the double bond is between the first and second carbons; thus, a prefix indicating its location is unnecessary. For butene (Figure 25.10) there are two possible positions for the double bond, either after the first carbon (1-butene) or after the second carbon (2-butene).

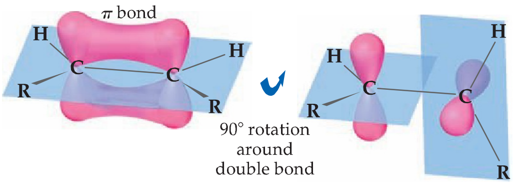
GIVE IT SOME THOUGHT

How many distinct locations are there for one double bond in a five-carbon linear chain?

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

The two isomers on the right in Figure 25.10 differ in the relative locations of their terminal methyl groups. These two compounds are **geometric isomers**, compounds that have the same molecular formula and the same groups bonded to one another, but differ in the spatial arrangement of these groups. ∞ (Section 24.4) In the *cis* isomer the two methyl groups are on the same side of the double bond, whereas in the *trans* isomer they are on opposite sides. Geometric isomers possess distinct physical properties and often differ significantly in their chemical behavior.

Geometric isomerism in alkenes arises because, unlike the C—C bond, the C═C bond resists twisting. Recall that the double bond between two carbon atoms consists of a σ and a π bond. ∞ (Section 9.6) Figure 25.11 ▶ shows a *cis* alkene. The carbon–carbon bond axis and the bonds to the hydrogen atoms and to the alkyl groups (designated R) are all in a plane. The *p* orbitals that overlap sideways to form the π bond are perpendicular to the molecular plane. As Figure 25.11 shows, rotation around the carbon–carbon double bond requires the π bond to be broken, a process that requires considerable energy (about 250 kJ/mol). While rotation about a double bond does not occur easily, it is a key process in the chemistry of vision. ∞ (Section 9.6: "Chemistry and Life: Chemistry of Vision")



▲ **Figure 25.11** **Rotation about a carbon–carbon double bond.** In an alkene, the overlap of the *p* orbitals that form the π bond is lost in the rotation. For this reason, rotation about carbon–carbon double bonds does not occur readily.

SAMPLE EXERCISE 25.3 | Drawing Isomers

Draw all the structural and geometric isomers of pentene, C_5H_{10}, that have an unbranched hydrocarbon chain.

SOLUTION

Analyze: We are asked to draw all the isomers (both structural and geometric) for an alkene with a five-carbon chain.

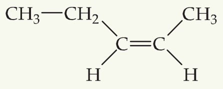
Plan: Because the compound is named pentene and not pentadiene or pentatriene, we know that the five-carbon chain contains only one carbon–carbon double bond. Thus, we can begin by first placing the double bond in various locations along the chain, remembering that the chain can be numbered from either end. After finding the different distinct locations for the double bond, we can consider whether the molecule can have *cis* and *trans* isomers.

Solve: There can be a double bond after either the first carbon (1-pentene) or second carbon (2-pentene). These are the only two possibilities because the chain can be numbered from either end. (Thus, what we might erroneously call 4-pentene is actually 1-pentene, as seen by numbering the carbon chain from the other end.)

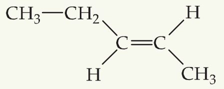
Because the first C atom in 1-pentene is bonded to two H atoms, there are no *cis-trans* isomers. On the other hand, there are *cis* and *trans* isomers for 2-pentene. Thus, the three isomers for pentene are

$CH_3—CH_2—CH_2—CH{=}CH_2$

1-Pentene



cis-2-Pentene



trans-2-Pentene

(You should convince yourself that *cis-* or *trans*-3-pentene is identical to *cis-* or *trans*-2-pentene, respectively.)

PRACTICE EXERCISE

How many straight-chain isomers are there of hexene, C_6H_{12}?
Answer: five (1-hexene, *cis*-2-hexene, *trans*-2-hexene, *cis*-3-hexene, *trans*-3-hexene)

Alkynes

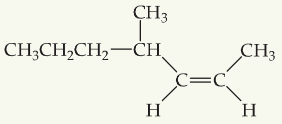
Alkynes are unsaturated hydrocarbons containing one or more C≡C bonds. The simplest alkyne is acetylene (C_2H_2), a highly reactive molecule. When acetylene is burned in a stream of oxygen in an oxyacetylene torch, the flame reaches about 3200 K. The oxyacetylene torch is widely used in welding, which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

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

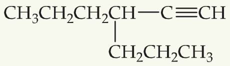
SAMPLE EXERCISE 25.4 | Naming Unsaturated Hydrocarbons

Name the following compounds:

(a)



(b)



$CH_3CH_2CH_2\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{CH}}—C{\equiv}CH$

SOLUTION

Analyze: We are given the structural formulas for two compounds, the first an alkene and the second an alkyne, and asked to name the compounds.

Plan: In each case the name is based on the number of carbon atoms in the longest continuous carbon chain that contains the multiple bond. In the case of the alkene, care must be taken to indicate whether *cis-trans* isomerism is possible and, if so, which isomer is given.

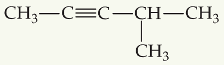
Solve:

(a) The longest continuous chain of carbons that contains the double bond is seven in length. The parent compound is therefore heptene. Because the double bond begins at carbon 2 (numbering from the end closest to the double bond), the parent hydrocarbon chain is named 2-heptene. A methyl group is found at carbon atom 4. Thus, the compound is 4-methyl-2-heptene. The geometrical configuration at the double bond is *cis* (that is, the alkyl groups are bonded to the double bond on the same side). Thus, the full name is 4-methyl-*cis*-2-heptene.
(b) The longest continuous chain of carbon atoms containing the triple bond is six, so this compound is a derivative of hexyne. The triple bond comes after the first carbon (numbering from the right), making it a derivative of 1-hexyne. The branch from the hexyne chain contains three carbon atoms, making it a propyl group. Because it is located on the third carbon atom of the hexyne chain, the molecule is 3-propyl-1-hexyne.

PRACTICE EXERCISE

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

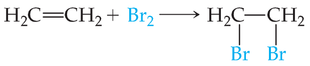
Answer:



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

Addition Reactions of Alkenes and Alkynes

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



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

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

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

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

The reaction between an alkene and H_2, referred to as *hydrogenation*, does not occur readily under ordinary conditions of temperature and pressure. One reason for the lack of reactivity of H_2 toward alkenes is the high bond enthalpy of the H_2 bond. To promote the reaction, it is necessary to use a catalyst that assists in rupturing the H—H bond. The most widely used catalysts are finely divided metals on which H_2 is adsorbed. ∞ (Section 14.7)

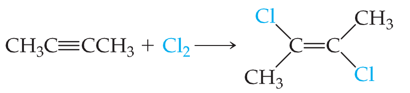
Hydrogen halides and water can also add to the double bond of alkenes, as illustrated by the following reactions of ethylene:

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

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

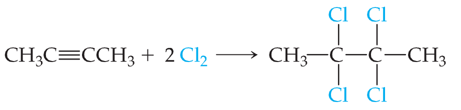
The addition of water is catalyzed by a strong acid, such as H_2SO_4.

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



[25.5]

2-Butyne *trans*-2,3-Dichloro-2-butene



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

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

SAMPLE EXERCISE 25.5 | Identifying the Product of a Hydrogenation Reaction

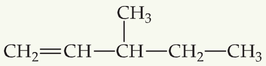
Write the structural formula for the product of the hydrogenation of 3-methyl-1-pentene.

SOLUTION

Analyze: We are asked to predict the compound formed when a particular alkene undergoes hydrogenation (reaction with H_2).

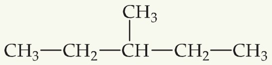
Plan: To determine the structural formula of the reaction product, we must first write the structural formula or Lewis structure of the reactant. In the hydrogenation of the alkene, H_2 adds to the double bond, producing an alkane. (That is, each carbon atom of the double bond forms a bond to an H atom, and the double bond is converted to a single bond.)

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



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

Hydrogenation—the addition of two H atoms to the carbons of the double bond—leads to the following alkane:



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

Comment: The longest chain in the product alkane has five carbon atoms; its name is therefore 3-methylpentane.

PRACTICE EXERCISE

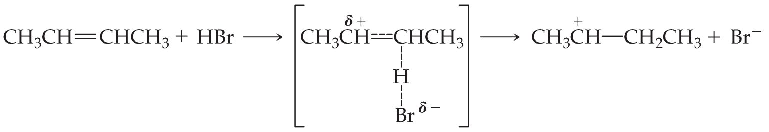
Addition of HCl to an alkene forms 2-chloropropane. What is the alkene?
Answer: propene

Mechanism of Addition Reactions

As the understanding of chemistry has grown, chemists have been able to advance from simply cataloging reactions known to occur to explaining *how* they occur. An explanation of how a reaction proceeds is called a *mechanism*. ∞ (Section 14.6)

In Equation 25.3 we considered the addition reaction between HBr and an alkene. This reaction is thought to proceed in two steps. In the first step, which is rate determining [∞ (Section 14.6)], the HBr molecule attacks the electron-rich double bond, transferring a proton to one of the two alkene carbons.

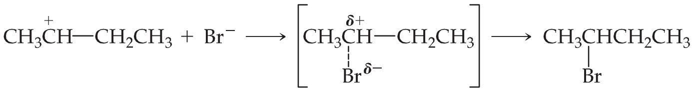
In the reaction of 2-butene with HBr, for example, the first step proceeds as follows:



$$CH_3CH{=}CHCH_3 + HBr \longrightarrow \left[\begin{array}{l} CH_3\overset{\delta+}{C}H{\cdots}CHCH_3 \\ \qquad\ \vdots \\ \qquad\ H \\ \qquad\ \vdots \\ \qquad\ Br^{\delta-} \end{array}\right] \longrightarrow CH_3\overset{+}{C}H{-}CH_2CH_3 + Br^- \qquad [25.7]$$

The pair of electrons that formed the π bond between the carbon atoms in the alkane is used to form the new C—H bond.

The second step, involving the addition of Br^- to the positively charged carbon, is faster:



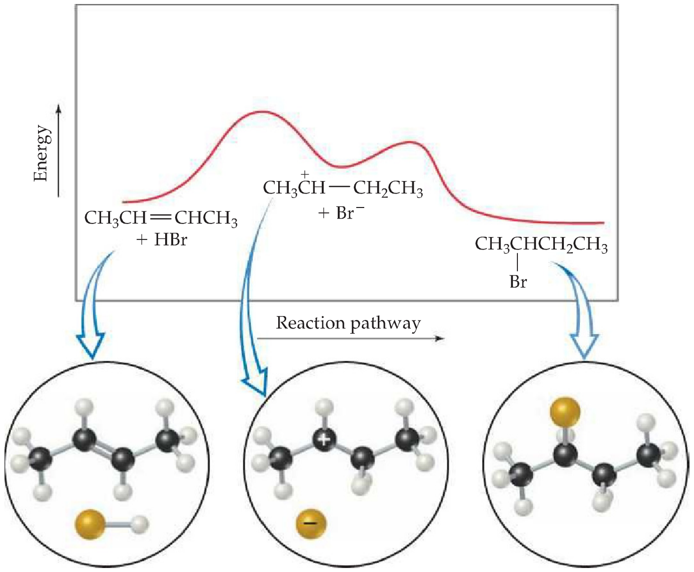
$$CH_3\overset{+}{C}H{-}CH_2CH_3 + Br^- \longrightarrow \left[\begin{array}{l} CH_3\overset{\delta+}{C}H{-}CH_2CH_3 \\ \qquad\ \vdots \\ \qquad\ Br^{\delta-} \end{array}\right] \longrightarrow \begin{array}{l} CH_3CHCH_2CH_3 \\ \qquad\ | \\ \qquad\ Br \end{array} \qquad [25.8]$$

In this reaction the bromide ion (Br^-) donates a pair of electrons to the carbon, forming the new C—Br bond.

Because the first rate-determining step in the reaction involves both the alkene and acid, the rate law for the reaction is second order, first order each in the alkene and HBr:

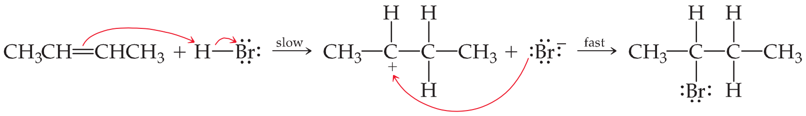
$$\text{Rate} = -\frac{\Delta[CH_3CH{=}CHCH_3]}{\Delta t} = k[CH_3CH{=}CHCH_3][HBr] \qquad [25.9]$$

The energy profile for the reaction is shown in Figure 25.12▼. The first energy maximum represents the transition state in the first step of the mechanism. The second maximum represents the transition state for the second step. Notice that there is an energy minimum between the first and second steps of the reaction. This energy minimum corresponds to the energies of the intermediate species, $CH_3\overset{+}{C}H{-}CH_2CH_3$ and Br^-.



◀ **Figure 25.12 Energy profile for addition of HBr to 2-butene.** The chemical formulas given in brackets in Equations 25.7 and 25.8 are the transition states.

To show electron movement in reactions like these, chemists often use curved arrows, which point in the direction of the electron flow (from a negative charge toward a positive charge). For the addition of HBr to 2-butene, the shifts in electron positions are

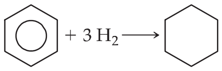


$$\mathrm{CH_3CH{=}CHCH_3} + \mathrm{H{-}\ddot{B}r}: \xrightarrow{\text{slow}} \mathrm{CH_3{-}\overset{H}{\underset{+}{C}}{-}\overset{H}{\underset{H}{C}}{-}CH_3} + :\mathrm{\ddot{B}r}:^- \xrightarrow{\text{fast}} \mathrm{CH_3{-}\overset{H}{\underset{:Br:}{C}}{-}\overset{H}{\underset{H}{C}}{-}CH_3}$$

Aromatic Hydrocarbons

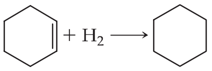
Aromatic hydrocarbons are a large and important class of hydrocarbons. The simplest member of the series is benzene (C_6H_6), whose structure is shown in Figure 25.3. The planar, highly symmetrical structure of benzene, with its 120° bond angles, suggests a high degree of unsaturation. You might therefore expect benzene to resemble the unsaturated hydrocarbons and to be highly reactive. The chemical behavior of benzene, however, is unlike that of alkenes or alkynes. Benzene and the other aromatic hydrocarbons are much more stable than alkenes and alkynes because the π electrons are delocalized in the π orbitals. ∞ (Section 9.6)

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



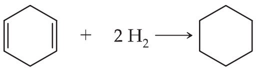
$$\Delta H^\circ = -208 \text{ kJ/mol}$$

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



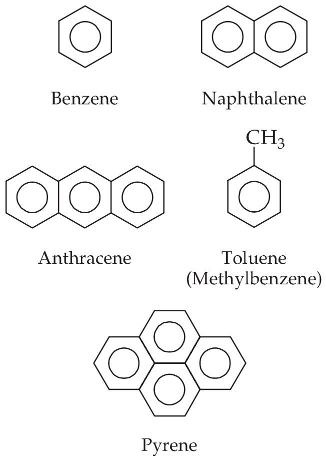
$$\Delta H^\circ = -120 \text{ kJ/mol}$$

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



$$\Delta H^\circ = -232 \text{ kJ/mol}$$

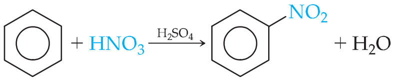
From these last two reactions, it appears that the heat of hydrogenating each double bond is roughly 116 kJ/mol for each bond. Benzene contains the equivalent of three double bonds. We might expect, therefore, that the heat of hydrogenating benzene would be about 3 times −116, or −348 kJ/mol, if benzene behaved as though it were "cyclohexatriene"; that is, if it behaved as though it had three isolated double bonds in a ring. Instead, the heat released is 140 kJ less than this, indicating that benzene is more stable than would be expected for three double bonds. The difference of 140 kJ/mol between the "expected" heat of hydrogenation, −348 kJ/mol, and the observed heat of hydrogenation, −208 kJ/mol, is due to stabilization of the π electrons through delocalization in the π orbitals that extend around the ring in this aromatic compound.



Benzene
Naphthalene
Anthracene
Toluene (Methylbenzene)
Pyrene

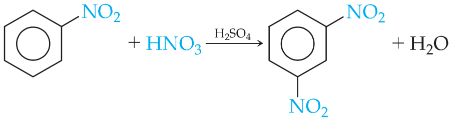
▲ **Figure 25.13 Condensed structural formulas and common names of several aromatic compounds.** The aromatic rings are represented by hexagons with a circle inscribed inside to denote aromatic character. Each corner represents a carbon atom. Each carbon is bound to three other atoms—either three carbons or two carbons and a hydrogen. The hydrogen atoms are not shown.

Each aromatic ring system is given a common name as shown in Figure 25.13 ◀. Although aromatic hydrocarbons are unsaturated, *they do not readily undergo addition reactions*. The delocalized π bonding causes aromatic compounds to behave quite differently from alkenes and alkynes. Benzene, for example, does not add Cl_2 or Br_2 to its double bonds under ordinary conditions. In contrast, aromatic hydrocarbons undergo **substitution reactions** relatively easily. In a substitution reaction one atom of a molecule is removed and replaced (substituted) by another atom or group of atoms. When benzene is warmed in a mixture of nitric and sulfuric acids, for example, hydrogen is replaced by the nitro group, NO_2:



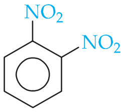
[25.10]

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

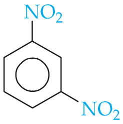


[25.11]

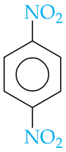
There are three possible isomers of benzene with two nitro groups attached. These three isomers are named *ortho*-, *meta*-, and *para*-dinitrobenzene:



ortho-Dinitrobenzene
mp 118 °C



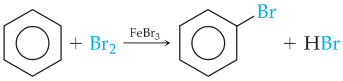
meta-Dinitrobenzene
mp 90 °C



para-Dinitrobenzene
mp 174 °C

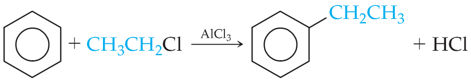
Mainly the *meta* isomer is formed in the reaction of nitric acid with nitrobenzene.

The bromination of benzene, which is carried out using $FeBr_3$ as a catalyst, is another substitution reaction:



[25.12]

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



[25.13]

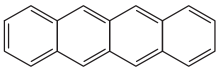
GIVE IT SOME THOUGHT

When naphthalene is reacted with nitric and sulfuric acids, two compounds containing one nitro group are formed. Draw the structures of these two compounds.

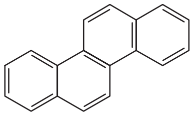
Chemistry and Life

POLYCYCLIC AROMATIC HYDROCARBONS

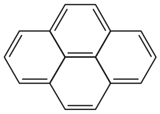
If you look up the U.S. Environmental Protection Agency's list of priority pollutants, you will find "PAHs" among the top 25. PAHs are "polycyclic aromatic hydrocarbons," a term which refers to an entire class of molecules whose structures are fused benzene rings, such as naphthalene and anthracene (Figure 25.13). Traditionally, molecules with three fused benzene rings or more are considered PAHs; some examples are shown below.



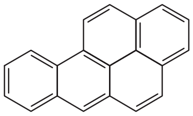
Tetracene



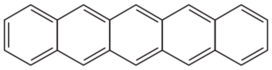
Chrysene



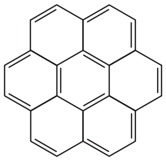
Pyrene



Benzo[a]pyrene



Pentacene



Coronene

You will notice that only one representative resonance structure is shown for each molecule, and that all these molecules resemble graphite. (Section 11.8) PAHs are found in coal and tars, and occur as side products of combustion of carbon-containing compounds. Therefore, PAHs can be found as particulate matter in air, water, and adsorbed to sediments and soil. They are relatively insoluble in water, as you would expect; the larger the molecule, the less water soluble, but more fat soluble, it is. Many PAHs are carcinogenic, meaning that they are known to cause cancer. Benzo[a]pyrene was the first chemical carcinogen discovered; it is one of the many components of cigarette smoke.

In spite of the toxicity of PAHs, there is great scientific interest in their electronic properties. Tetracene and pentacene are large enough that their delocalized π electrons provide a very high conductivity in the plane of the rings, but these molecules are also small enough that they are chemically easier to work with compared to larger PAHs. Tetracene is yellow, and pentacene is dark blue, due to their delocalized π electron systems. (Section 9.6) Pentacene is being explored as a component in organic thin-film transistors and solar energy conversion devices. (Section 12.3)

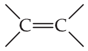
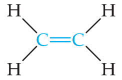
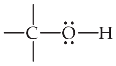
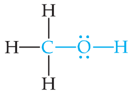
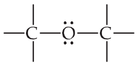
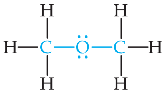
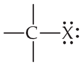
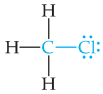
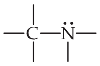
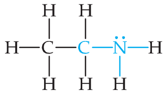
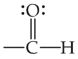
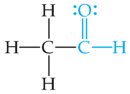
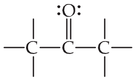
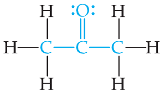
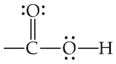
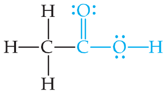
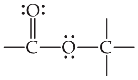
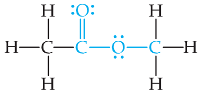
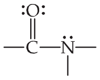
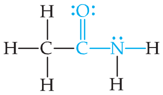
25.4 ORGANIC FUNCTIONAL GROUPS

The reactivity of organic compounds can be attributed to particular atoms or groups of atoms within the molecules. A site of reactivity in an organic molecule is called a *functional group* because it controls how the molecule behaves or functions. (Section 25.1) As we have seen, the presence of $C{=}C$ double bonds or $C{\equiv}C$ triple bonds in a hydrocarbon markedly increases its reactivity. Furthermore, these functional groups each undergo characteristic reactions. Each distinct kind of functional group often undergoes the same kinds of reactions in every molecule, regardless of the size and complexity of the molecule. Thus, the chemistry of an organic molecule is largely determined by the functional groups it contains.

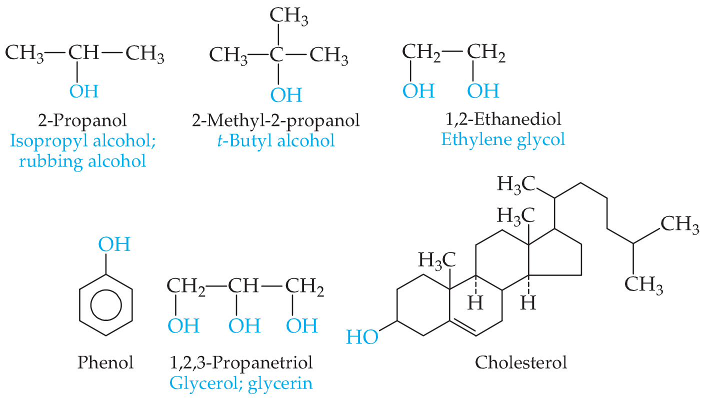
Table 25.4 ▶ lists the most common functional groups and gives examples of each. Notice that in addition to $C{=}C$ double bonds or $C{\equiv}C$ triple bonds, there are also many functional groups that contain elements other than just C and H. Many of the functional groups contain other nonmetals such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

We can think of organic molecules as being composed of functional groups that are bonded to one or more alkyl groups. The alkyl groups, which are made of $C{-}C$ and $C{-}H$ single bonds, are the less reactive portions of the organic molecules. In describing general features of organic compounds, chemists often use the designation R to represent any alkyl group: methyl, ethyl, propyl, and so on. Alkanes, for example, which contain no functional group, are represented as $R{-}H$. Alcohols, which contain the $-OH$, or alcohol functional group, are represented as $R{-}OH$. If two or more different alkyl groups are present in a

TABLE 25.4 ■ Common Functional Groups in Organic Compounds

Functional Group	Type of Compound	Suffix or Prefix	Example	Systematic Name (common name)
	Alkene	*-ene*		Ethene (Ethylene)
$-C{\equiv}C-$	Alkyne	*-yne*	$H-C{\equiv}C-H$	Ethyne (Acetylene)
	Alcohol	*-ol*		Methanol (Methyl alcohol)
	Ether	*ether*		Dimethyl ether
 (X = halogen)	Haloalkane	*halo-*		Chloromethane (Methyl chloride)
	Amine	*-amine*		Ethylamine
	Aldehyde	*-al*		Ethanal (Acetaldehyde)
	Ketone	*-one*		Propanone (Acetone)
	Carboxylic acid	*-oic acid*		Ethanoic acid (Acetic acid)
	Ester	*-oate*		Methyl ethanoate (Methyl acetate)
	Amide	*-amide*		Ethanamide (Acetamide)

molecule, we will designate them as R, R′, R″, and so forth. In this section we examine the structure and chemical properties of two functional groups, alcohols and ethers. Later in this section we consider some additional functional groups that contain C═O bonds.



▲ **Figure 25.14 Structural formulas of six important alcohols.** Common names are given in blue.

Alcohols

Alcohols are hydrocarbon derivatives in which one or more hydrogens of a parent hydrocarbon have been replaced by a *hydroxyl* or *alcohol* functional group, —OH. Figure 25.14◀ shows the structural formulas and names of several alcohols. Note that the name for an alcohol ends in -*ol*. The simple alcohols are named by changing the last letter in the name of the corresponding alkane to -*ol*—for example, ethan*e* becomes ethan*ol*. Where necessary, the location of the OH group is designated by an appropriate numeral prefix that indicates the number of the carbon atom bearing the OH group, as shown in many of the examples in Figure 25.14.

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

Figure 25.15◀ shows several familiar commercial products that consist entirely or in large part of an organic alcohol. Let's consider how some of the more important alcohols are formed and used.

The simplest alcohol, methanol (methyl alcohol), has many important industrial uses and is produced on a large scale. Carbon monoxide and hydrogen are heated together under pressure in the presence of a metal oxide catalyst:

$$CO(g) + 2\,H_2(g) \xrightarrow[400\,^\circ C]{200-300\text{ atm}} CH_3OH(g) \qquad [25.14]$$

Because methanol has a very high octane rating as an automobile fuel, it is used as a gasoline additive and as a fuel in its own right.

Ethanol (ethyl alcohol, C_2H_5OH) is a product of the fermentation of carbohydrates such as sugar and starch. In the absence of air, yeast cells convert carbohydrates into a mixture of ethanol and CO_2, as shown in Equation 25.15. In the process, yeast derives energy necessary for growth.

$$C_6H_{12}O_6(aq) \xrightarrow{\text{yeast}} 2\,C_2H_5OH(aq) + 2\,CO_2(g) \qquad [25.15]$$

This reaction is carried out under carefully controlled conditions to produce beer, wine, and other beverages in which ethanol is the active ingredient.

Many polyhydroxyl alcohols (those containing more than one OH group) are known. The simplest of these is 1,2-ethanediol (ethylene glycol, $HOCH_2CH_2OH$). This substance is the major ingredient in automobile antifreeze. Another common polyhydroxyl alcohol is 1,2,3-propanetriol [glycerol, $HOCH_2CH(OH)CH_2OH$]. It is a viscous liquid that dissolves readily in water and is widely used as a skin softener in cosmetic preparations. It is also used in foods and candies to keep them moist.

Phenol is the simplest compound with an OH group attached to an aromatic ring. One of the most striking effects of the aromatic group is the greatly increased acidity of the OH group. Phenol is about 1 million times more acidic in water than a typical nonaromatic alcohol such as ethanol. Even so, it is not a very strong acid ($K_a = 1.3 \times 10^{-10}$). Phenol is used industrially to make several kinds of plastics and dyes. It is also used as a topical anesthetic in many sore throat sprays.

Cholesterol, shown in Figure 25.14, is a biochemically important alcohol. The OH group forms only a small component of this rather large molecule, so cholesterol is only slightly soluble in water (0.26 g per 100 mL of H_2O). Cholesterol is a normal component of our bodies; when present in excessive amounts, however,

▲ **Figure 25.15 Everyday alcohols.** Many of the products we use every day—from rubbing alcohol and throat lozenges to hair spray and antifreeze—are composed either entirely or mainly of alcohols.

it may precipitate from solution. It precipitates in the gallbladder to form crystalline lumps called *gallstones*. It may also precipitate against the walls of veins and arteries and thus contribute to high blood pressure and other cardiovascular problems. The amount of cholesterol in our blood is determined by how much cholesterol we eat and by total dietary intake. There is evidence that excessive caloric intake leads the body to synthesize excessive cholesterol.

Ethers

Compounds in which two hydrocarbon groups are bonded to one oxygen are called **ethers**. Ethers can be formed from two molecules of alcohol by splitting out a molecule of water. The reaction is catalyzed by sulfuric acid, which takes up water to remove it from the system:

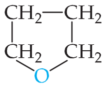
$$CH_3CH_2{-}OH + H{-}OCH_2CH_3 \xrightarrow{H_2SO_4} CH_3CH_2{-}O{-}CH_2CH_3 + H_2O \quad [25.16]$$

A reaction in which water is split out from two substances is called a *condensation reaction*. ∞ (Sections 12.4 and 22.8)

Ethers are used as solvents. Both diethyl ether and the cyclic ether tetrahydrofuran are common solvents for organic reactions:

$CH_3CH_2{-}O{-}CH_2CH_3$

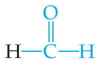
Diethyl ether



Tetrahydrofuran (THF)

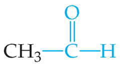
Aldehydes and Ketones

Several of the functional groups listed in Table 25.4 contain a C=O double bond. This particular group of atoms is called a **carbonyl group**. The carbonyl group, together with the atoms that are attached to the carbon of the carbonyl group, defines several important functional groups that we consider in this section. In **aldehydes** the carbonyl group has at least one hydrogen atom attached, as in the following examples:



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

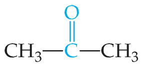
Methanal
Formaldehyde



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

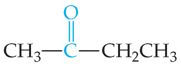
Ethanal
Acetaldehyde

In **ketones** the carbonyl group occurs at the interior of a carbon chain and is therefore flanked by carbon atoms:



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

Propanone
Acetone



$CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2CH_3$

2-Butanone
Methyl ethyl ketone

Aldehydes and ketones can be prepared by carefully controlled oxidation of alcohols. It is fairly easy to oxidize alcohols. Complete oxidation results in formation of CO_2 and H_2O, as in the burning of methanol:

$$CH_3OH(g) + \tfrac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

Controlled partial oxidation to form other organic substances, such as aldehydes and ketones, is carried out by using various oxidizing agents such as air, hydrogen peroxide (H_2O_2), ozone (O_3), and potassium dichromate ($K_2Cr_2O_7$).

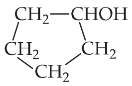
(a)

(b)

▲ **Figure 25.16 Everyday carboxylic acids and esters.** (a) Spinach and some cleaners contain oxalic acid; vinegar contains acetic acid; vitamin C is ascorbic acid; citrus fruits contain citric acid; and aspirin is acetylsalicylic acid (which is both an acid and an ester). (b) Many sunburn lotions contain the ester benzocaine; some nail polish remover is ethyl acetate; vegetable oils are also esters.

GIVE IT SOME THOUGHT

Write the condensed formula for the ketone that would result from partial oxidation of this alcohol.



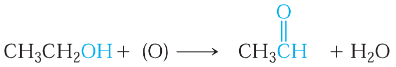
Many compounds found in nature possess an aldehyde or ketone functional group. Vanilla and cinnamon flavorings are naturally occurring aldehydes. Two isomers of the ketone carvone impart the characteristic flavors of spearmint leaves or caraway seeds.

Ketones are less reactive than aldehydes and are used extensively as solvents. Acetone, which boils at 56 °C, is the most widely used ketone. The carbonyl functional group imparts polarity to the solvent. Acetone is completely miscible with water, yet it dissolves a wide range of organic substances. 2-Butanone ($CH_3COCH_2CH_3$), which boils at 80 °C, is also used industrially as a solvent.

Carboxylic Acids and Esters

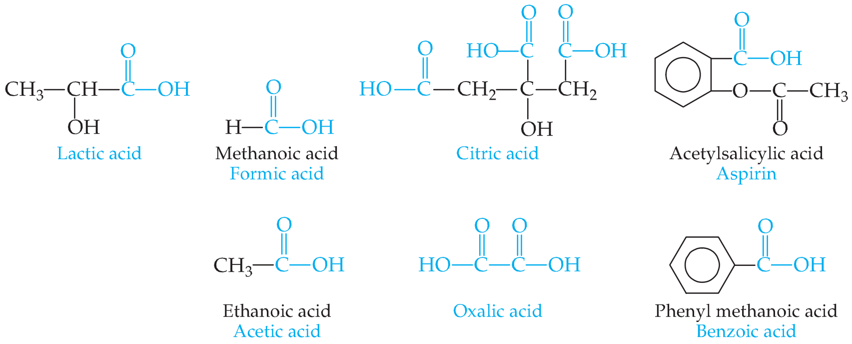
We discussed carboxylic acids in Sections 4.3 and 16.10. **Carboxylic acids** contain the *carboxyl* functional group, which is often written as COOH. These weak acids are widely distributed in nature and are common in consumer products [Figure 25.16(a)◀]. They are also important in the manufacture of polymers used to make fibers, films, and paints. Figure 25.17▼ shows the structural formulas of several carboxylic acids. Notice that oxalic acid and citric acid contain two and three carboxyl groups, respectively. The common names of many carboxylic acids are based on their historical origins. Formic acid, for example, was first prepared by extraction from ants; its name is derived from the Latin word *formica*, meaning "ant."

Carboxylic acids can be produced by oxidation of alcohols in which the OH group is attached to a CH_2 group, such as ethanol or propanol. Under appropriate conditions the corresponding aldehyde may be isolated as the first product of oxidation. These transformations are shown for ethanol in the following equations, in which (O) represents an oxidant that can provide oxygen atoms:

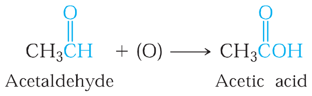


$$CH_3CH_2OH + (O) \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}H + H_2O \qquad [25.17]$$

Ethanol Acetaldehyde



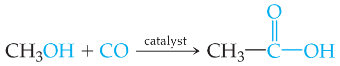
▶ **Figure 25.17 Structural formulas of common carboxylic acids.** The IUPAC names are given in black type for the monocarboxylic acids, but they are generally referred to by their common names (blue type).



$$\underset{\text{Acetaldehyde}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}H} + (O) \longrightarrow \underset{\text{Acetic acid}}{CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH} \qquad [25.18]$$

The air oxidation of ethanol to acetic acid is responsible for causing wines to turn sour, producing vinegar.

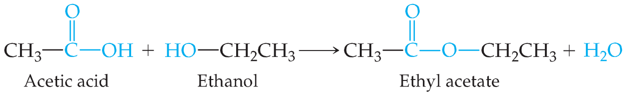
Acetic acid can also be produced by the reaction of methanol with carbon monoxide in the presence of a rhodium catalyst:



$$CH_3OH + CO \xrightarrow{\text{catalyst}} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \qquad [25.19]$$

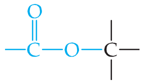
This reaction involves, in effect, the insertion of a carbon monoxide molecule between the CH_3 and OH groups. A reaction of this kind is called *carbonylation*.

Carboxylic acids can undergo condensation reactions with alcohols to form **esters**:



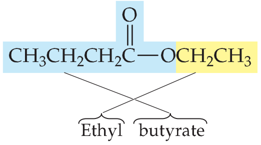
$$\underset{\text{Acetic acid}}{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH} + \underset{\text{Ethanol}}{HO{-}CH_2CH_3} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2CH_3} + H_2O \qquad [25.20]$$

Esters are compounds in which the H atom of a carboxylic acid is replaced by a carbon-containing group:



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

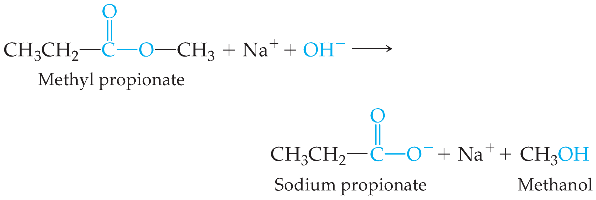
Figure 25.16(b) shows some common esters, which are named by using first the group from which the alcohol is derived and then the group from which the acid is derived. For example:



$$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_2CH_3$$

Esters generally have very pleasant odors. They are largely responsible for the pleasant aromas of fruit. Pentyl acetate ($CH_3COOCH_2CH_2CH_2CH_2CH_3$), for example, is responsible for the odor of bananas.

When esters are treated with an acid or a base in aqueous solution, they are hydrolyzed; that is, the molecule is split into its alcohol and acid components:



$$\underset{\text{Methyl propionate}}{CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_3} + Na^+ + OH^- \longrightarrow$$

$$\underset{\text{Sodium propionate}}{CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-} + Na^+ + \underset{\text{Methanol}}{CH_3OH} \qquad [25.21]$$

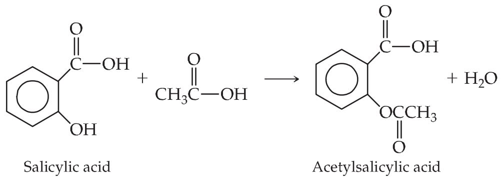
In this example the hydrolysis was carried out in basic medium. The products of the reaction are the sodium salt of the carboxylic acid and the alcohol.

Chemistry Put to Work PORTRAIT OF AN ORGANIC CHEMICAL

Few other chemicals have been associated with human history for as long as acetic acid has. It is the primary ingredient of vinegar, formed by the oxidation of ethyl alcohol in dilute solutions formed from fruit juices. The oxidation of ethyl alcohol, which is the process responsible for the spoilage of wine and ciders, is aided by bacteria. When such "spoiled" solutions are distilled, the result is vinegar, a dilute (4–8%) solution of acetic acid.

A more complete fractional distillation of vinegar can yield nearly pure acetic acid—a clear, colorless liquid that boils at 118 °C and freezes at 16.7 °C. Because acetic acid solidifies when stored at temperatures not much below room temperature, the term "glacial acetic acid" came to be applied to pure or nearly pure acetic acid. Although vinegar is relatively harmless and is a common household solution used in cooking and cleaning, pure acetic acid is highly corrosive and capable of causing severe burns. You may be surprised to learn that the pure acid is also flammable.

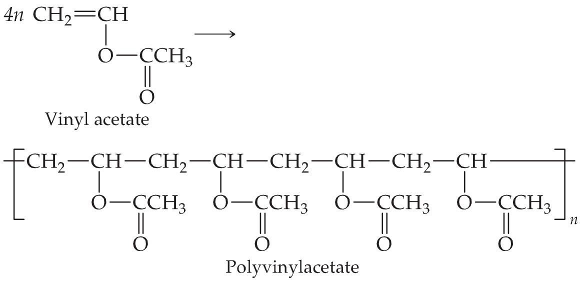
Acetic acid is an important industrial chemical. More than 3×10^9 kg are produced in the United States each year, either by the process shown in Equation 25.19 or by a similar process. The most important uses are for the formation of acetate esters, as illustrated in Equation 25.20. For example, aspirin (acetylsalicylic acid) is formed by the reaction of acetic acid with salicylic acid, which also happens to have a hydroxyl group attached to the benzene ring:



Notice that this is a condensation reaction, in which water is split out. The key to this reaction is that the OH group on the benzene ring undergoes the condensation reaction more readily than the OH group of the carboxylic acid. As we will learn later in this chapter, cellulose, which is found in cotton and wood, is a polymeric material containing multiple hydroxyl groups. The condensation reaction of cellulose with acetic acid yields cellulose acetate, which has many uses. When spun into fibers, to name just one use, cellulose acetate forms rayon-like material (Figure 25.18▲).

▲ **Figure 25.18 Cellulose acetate fiber.** The blue garment, woven from cellulose acetate fiber, has a silky, vibrant texture compared with the white garment, woven from simple cotton fiber.

Reaction of acetic acid with vinyl alcohol yields vinyl acetate. When vinyl acetate is polymerized, the product is polyvinyl acetate, which is used in water-based latex paints and in glues for paper and wood:



$$4n\ \mathrm{CH_2{=}\underset{\displaystyle O{-}\underset{\displaystyle \overset{\|}{O}}{C}CH_3}{\underset{|}{C}H}} \longrightarrow \left[\mathrm{CH_2{-}\underset{\displaystyle O{-}\underset{\displaystyle \overset{\|}{O}}{C}CH_3}{\underset{|}{C}H}{-}CH_2{-}\underset{\displaystyle O{-}\underset{\displaystyle \overset{\|}{O}}{C}CH_3}{\underset{|}{C}H}{-}CH_2{-}\underset{\displaystyle O{-}\underset{\displaystyle \overset{\|}{O}}{C}CH_3}{\underset{|}{C}H}{-}CH_2{-}\underset{\displaystyle O{-}\underset{\displaystyle \overset{\|}{O}}{C}CH_3}{\underset{|}{C}H}{-}}\right]_n$$

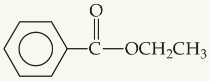
Related Exercises: 25.49, 25.50

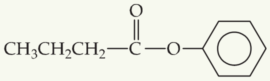
The hydrolysis of an ester in the presence of a base is called **saponification**, a term that comes from the Latin word for soap (*sapon*). Naturally occurring esters include fats and oils. In the soap-making process an animal fat or a vegetable oil is boiled with a strong base, usually NaOH. The resultant soap consists of a mixture of sodium salts of long-chain carboxylic acids (called fatty acids), which form during the saponification reaction (Figure 25.19◀).

◀ **Figure 25.19 Saponification.** Saponification of fats and oils has long been used to make soap. This etching shows a step in the soap-making process during the mid-nineteenth century.

SAMPLE EXERCISE 25.6 Naming Esters and Predicting Hydrolysis Products

In a basic aqueous solution, esters react with hydroxide ion to form the salt of the carboxylic acid and the alcohol from which the ester is constituted. Name each of the following esters, and indicate the products of their reaction with aqueous base.

(a)


(b)


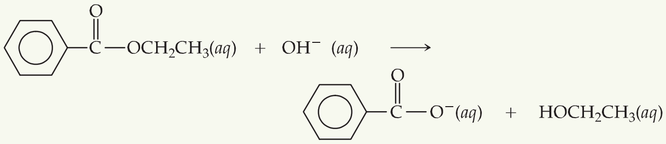
SOLUTION

Analyze: We are given two esters and asked to name them and to predict the products formed when they undergo hydrolysis (split into an alcohol and carboxylate ion) in basic solution.

Plan: Esters are formed by the condensation reaction between an alcohol and a carboxylic acid. To name an ester, we must analyze its structure and determine the identities of the alcohol and acid from which it is formed. We can identify the alcohol by adding an OH to the alkyl group attached to the O atom of the carboxyl (COO) group. We can identify the acid by adding an H group to the O atom of the carboxyl group. We have learned that the first part of an ester name indicates the alcohol portion and the second indicates the acid portion. The name conforms to how the ester undergoes hydrolysis in base, reacting with base to form an alcohol and a carboxylate anion.

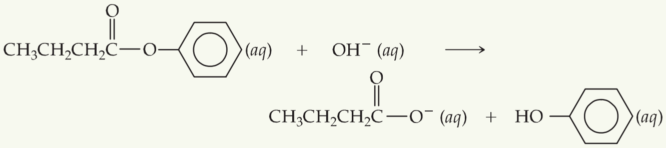
Solve:

(a) This ester is derived from ethanol (CH_3CH_2OH) and benzoic acid (C_6H_5COOH). Its name is therefore ethyl benzoate. The net ionic equation for reaction of ethyl benzoate with hydroxide ion is



The products are benzoate ion and ethanol.

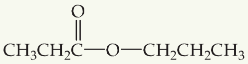
(b) This ester is derived from phenol (C_6H_5OH) and butanoic acid (commonly called butyric acid) ($CH_3CH_2CH_2COOH$). The residue from the phenol is called the phenyl group. The ester is therefore named phenyl butyrate. The net ionic equation for the reaction of phenyl butyrate with hydroxide ion is



The products are butyrate ion and phenol.

PRACTICE EXERCISE

Write the structural formula for the ester formed from propyl alcohol and propionic acid.

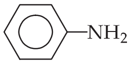
Answer:

$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}—O—CH_2CH_2CH_3$

Amines and Amides

Amines are organic bases. (Section 16.7) They have the general formula R_3N, where R may be H or a hydrocarbon group, as in the following examples:

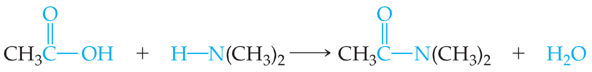
$CH_3CH_2NH_2$ Ethylamine

$(CH_3)_3N$ Trimethylamine



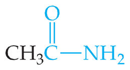
Phenylamine
Aniline

Amines containing a hydrogen bonded to nitrogen can undergo condensation reactions with carboxylic acids to form **amides**:



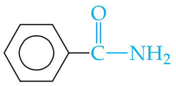
$$CH_3\overset{O}{\overset{\|}{C}}-OH + H-N(CH_3)_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-N(CH_3)_2 + H_2O \tag{25.22}$$

We may consider the amide functional group to be derived from a carboxylic acid with an NR_2 group replacing the OH of the acid, as in these additional examples:



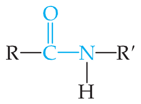
$$CH_3\overset{O}{\overset{\|}{C}}-NH_2$$

Ethanamide
Acetamide



Phenylmethanamide
Benzamide

The amide linkage

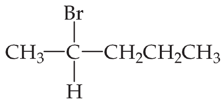


$$R-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R'$$

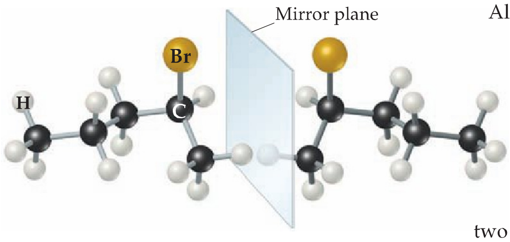
where R and R′ are organic groups, is the key functional group in the structures of proteins, as we will see in Section 25.7.

25.5 CHIRALITY IN ORGANIC CHEMISTRY

A molecule possessing a nonsuperimposable mirror image is termed **chiral** (Greek *cheir*, "hand"). (Section 24.4) *Compounds containing carbon atoms with four different attached groups are inherently chiral*. A carbon atom with four different attached groups is called a *chiral center*. For example, the structural formula of 2-bromopentane is



$$CH_3-\underset{H}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_2CH_2CH_3$$



▲ **Figure 25.20 The two enantiomeric forms of 2-bromopentane.** The mirror-image isomers are not superimposable on each other.

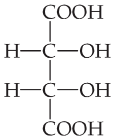
All four groups attached to the second carbon are different, making that carbon a chiral center. Figure 25.20◀ illustrates the two nonsuperimposable mirror images of this molecule. If you imagine trying to move the left-hand molecule to the right and turning it in every possible way, you will conclude that it cannot be superimposed on the right-hand molecule. Nonsuperimposable mirror images are called optical isomers or *enantiomers*. (Section 24.4) Organic chemists use the labels *R* and *S* to distinguish the two forms. We need not go into the rules for deciding on the labels.

Enantiomers, such as the two forms of 2-bromopentane shown in Figure 25.20, have identical physical properties, such as melting and boiling points, and identical chemical properties when they react with nonchiral reagents. Only in a chiral environment do they exhibit different behaviors. One of the more interesting properties of chiral substances is that their solutions may rotate the plane of polarized light, as explained in Section 24.4.

Chirality is very common in organic substances. It is not often observed, however, because when a chiral substance is synthesized in a typical chemical reaction, the two enantiomeric species are formed in precisely the same quantity.

The resulting mixture of isomers is called a *racemic* mixture. A racemic mixture of enantiomers does not rotate the plane of polarized light because the two forms rotate the light to equal extents in opposite directions. ∞ (Section 24.4)

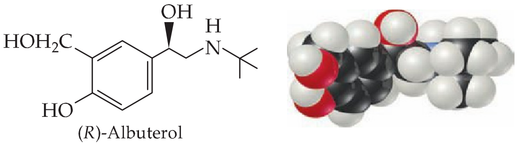
Naturally occurring substances often are found as just one enantiomer. An example is tartaric acid, which has the structural formula*



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{COOH} \end{array}$$

This compound has not one, but two chiral centers. Both the inner carbon atoms are attached to four different groups. Tartaric acid is found in nature, either as the free acid or as a salt of calcium or potassium, in fruit extracts and especially as crystals deposited during wine fermentation. The naturally occurring form is optically active in solution. Tartaric acid is typical; many biologically important molecules are chiral. In Section 25.7 we will examine the amino acids, all of which (except for glycine) are chiral and found in nature as just one of the enantiomers.

Many drugs of importance in human medicine are chiral substances. When a drug is administered as a racemic mixture, it often turns out that only one of the enantiomers has beneficial results. The other is either inert or nearly so, or may even have a harmful effect. For this reason, a great deal of attention has been given in recent years to methods for synthesizing the desired enantiomer of chiral drugs. Synthesizing just one enantiomer of a chiral substance can be very difficult and costly, but the rewards are worth the effort. Worldwide sales of single-enantiomer drugs amount to over $125 billion annually! As an example of the different behavior of enantiomers, the drug *(R)*-albuterol (Figure 25.21▶) is an effective bronchodilator used to relieve the symptoms of asthma. The enantiomer *(S)*-albuterol is not only ineffective as a bronchodilator but actually counters the effects of *(R)*-albuterol. As another example, the nonsteroidal analgesic ibuprofen (marketed under the trade names Advil™, Motrin™, and Nuprin™) is a chiral molecule usually sold as the racemic mixture. However, a preparation consisting of just the more active enantiomer, *(S)*-ibuprofen (Figure 25.22▼), relieves pain and reduces inflammation more rapidly than the racemic mixture. For this reason, the chiral version of the drug may in time come to replace the racemic mixture.

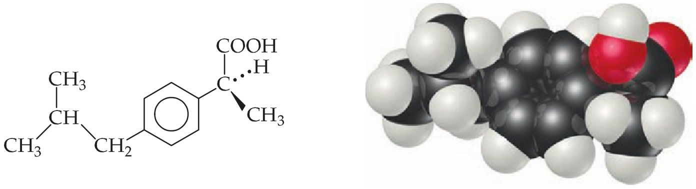


(*R*)-Albuterol

▲ **Figure 25.21** ***(R)*-Albuterol.** This compound, which acts as a bronchodilator in patients with asthma, is one member of a pair of optical isomers. The other member, *(S)*-albuterol, does not have the same physiological effect.

GIVE IT SOME THOUGHT

What are the requirements on the four groups attached to a carbon atom in order that it be a chiral center?



▲ **Figure 25.22** ***(S)*-Ibuprofen.** For relieving pain and reducing inflammation, the ability of this enantiomer far outweighs that of the (R) isomer.

**Louis Pasteur discovered chirality while he was studying crystalline samples of salts of tartaric acid.*

25.6 INTRODUCTION TO BIOCHEMISTRY

The several types of organic functional groups discussed in Section 25.4 generate a vast array of molecules with very specific chemical reactivities. Nowhere is this specificity more apparent than in *biochemistry*—the chemistry of living organisms.

Before we discuss specific biochemical molecules, we can make some general observations. As we will see, many biologically important molecules are quite large. The synthesis of these molecules is a remarkable aspect of biochemistry, one that places large demands on the chemical systems in living organisms. Organisms build biomolecules from much smaller and simpler substances that are readily available in the biosphere. The synthesis of large molecules requires energy because most of the reactions are endothermic. The ultimate source of this energy is the Sun. Mammals and other animals have essentially no capacity for using solar energy directly; rather, they depend on plant photosynthesis to supply the bulk of their energy needs. ∞ (Section 24.2)

In addition to requiring large amounts of energy, living organisms are highly organized. The complexity of all the substances that make up even the simplest single-cell organisms and the relationships among all the many chemical processes that occur are truly amazing. In thermodynamic terms this high degree of organization means that the entropy of living systems is much lower than the entropy of the random mix of raw materials from which the systems formed. Thus, living systems must continuously work against the spontaneous tendency toward increased entropy that is characteristic of all organized systems. Maintaining a high degree of order places additional energetic requirements on organisms. (You may want to review the second law of thermodynamics in Section 19.3 and the "Chemistry and Life" box there.)

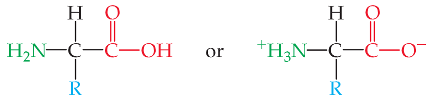
We have introduced you to some important biochemical applications of fundamental chemical ideas in the "Chemistry and Life" essays that appear throughout this text. A complete listing of the topics covered and their locations in the text are included in the table of contents. The remainder of this chapter will serve as only a brief introduction to other aspects of biochemistry. Nevertheless, you will see some patterns emerging. Hydrogen bonding ∞ (Section 11.2), for example, is critical to the function of many biochemical systems, and the geometry of molecules can govern their biological importance and activity. Many of the large molecules in living systems are polymers (Section 12.6) of much smaller molecules. These **biopolymers** can be classified into three broad categories: proteins, polysaccharides (carbohydrates), and nucleic acids. Lipids are another common class of molecules in living systems, but they are usually large molecules, not biopolymers.

25.7 PROTEINS

Proteins are macromolecular substances present in all living cells. About 50% of your body's dry weight is protein. Proteins serve as the major structural components in animal tissues; they are a key part of skin, nails, cartilage, and muscles. Other proteins catalyze reactions, transport oxygen, serve as hormones to regulate specific body processes, and perform other tasks. Whatever their function, all proteins are chemically similar, being composed of the same basic building blocks, called **amino acids**.

Amino Acids

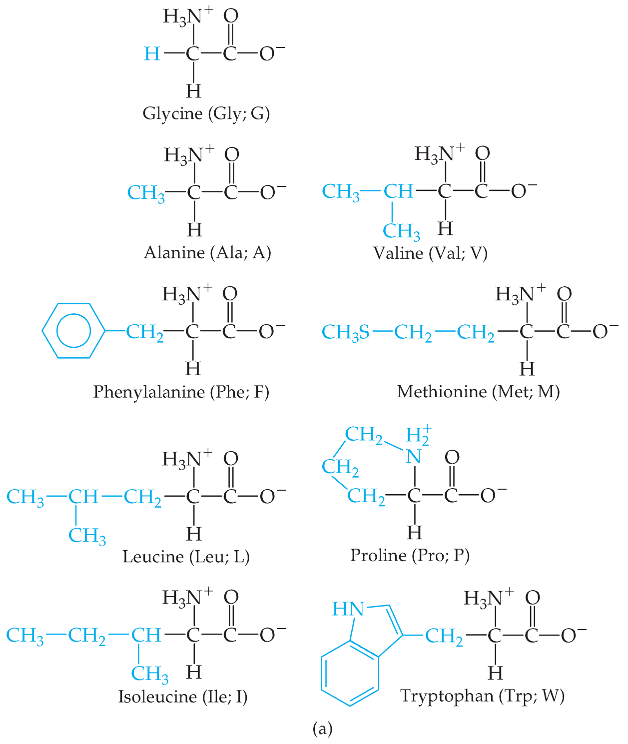
The building blocks of all proteins are α-amino acids, which are substances in which the amino group is located on the carbon atom immediately adjacent to the carboxylic acid group. Thus, there is always one carbon atom between the amino group and the carboxylic acid group. The general formula for an α-amino acid is represented in the following ways:



$$\mathrm{H_2N{-}\underset{\displaystyle R}{\overset{\displaystyle H}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH} \quad \text{or} \quad \mathrm{{}^{+}H_3N{-}\underset{\displaystyle R}{\overset{\displaystyle H}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O^{-}}$$

The doubly ionized form, called the zwitterion, usually predominates at near-neutral values of pH. This form is a result of the transfer of a proton from the carboxylic acid group to the basic amine group. ∞ (Section 16.10: "Chemistry and Life: The Amphiprotic Behavior of Amino Acids")

Amino acids differ from one another in the nature of their R groups. Twenty-two amino acids have been identified in nature. Figure 25.23▼ shows the structural formulas of the 20 amino acids found in the proteins of our bodies. Those amino acids for which the side group is relatively nonpolar are shown in Figure 25.23(a). Those that contain a relatively polar or charged side group are shown in Figure 25.23(b)▼. Our bodies can synthesize ten of the amino acids in sufficient amounts for our needs. The other ten must be ingested and are called *essential amino acids* because they are necessary components of our diet.



Glycine (Gly; G)

Alanine (Ala; A)

Valine (Val; V)

Phenylalanine (Phe; F)

Methionine (Met; M)

Leucine (Leu; L)

Proline (Pro; P)

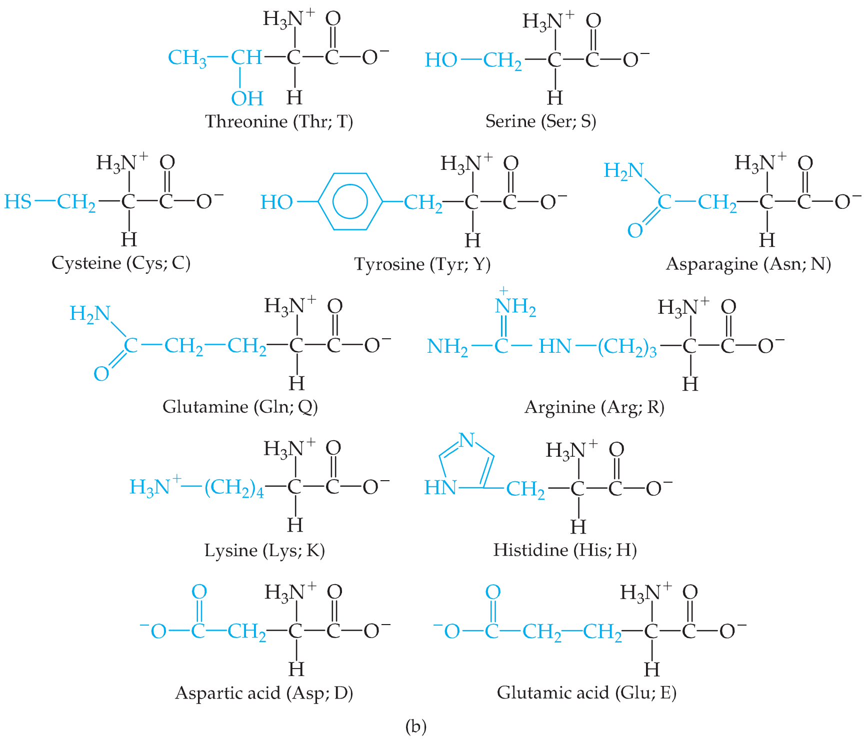
Isoleucine (Ile; I)

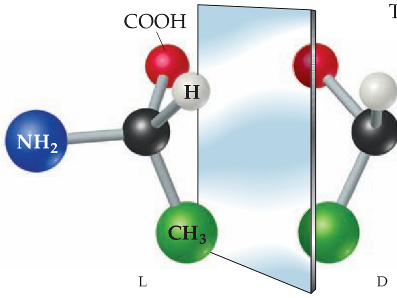
Tryptophan (Trp; W)

(a)

▲ **Figure 25.23(a) The 9 amino acids found in the human body that contain relatively nonpolar, hydrophobic side groups.** The acids are shown in the zwitterionic form in which they exist in water at near-neutral pH. The names for each amino acid are given with their three-letter codes and one-letter codes in parentheses.

▶ **Figure 25.23(b)** **The 11 amino acids found in the human body that contain polar side groups.** The acids are shown in the zwitterionic form in which they exist in water a near-neutral pH. The names for each amino acid are given with their three-letter codes and one-letter codes in parentheses.



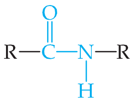


▲ **Figure 25.24** **Alanine enantiomers.** The middle carbon of alanine is chiral, and therefore there are two enantiomers, which by definition are nonsuperimposable mirror images of each other.

The α-carbon atom of the amino acids, which bears both the ammonium and carboxylate groups, has four different groups attached to it. The amino acids are thus chiral (except for glycine, which has two hydrogens attached to the central carbon). Figure 25.24 ◀ shows the two enantiomers of the amino acid alanine. For historical reasons, the two enantiomeric forms of amino acids are often distinguished by the labels D (from the Latin *dexter*, "right") and L (from the Latin *laevus*, "left"). Nearly all amino acids normally found in living organisms are "left-handed"; that is, all have the L configuration at the chiral center (except for glycine, which is not chiral because its central carbon has two hydrogens attached). The principal exception to the dominance of L amino acids in nature are the proteins that make up the cell walls of bacteria, which can contain considerable quantities of the D isomers.

Polypeptides and Proteins

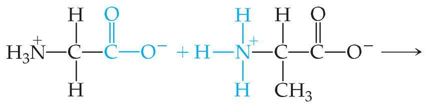
Amino acids are linked together into proteins by amide groups, one of the functional groups introduced in Section 25.4:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-R \qquad [25.23]$$

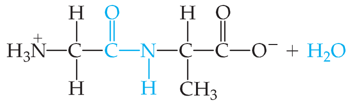
Each of these amide groups is called a **peptide bond** when it is formed by amino acids. A peptide bond is formed by a condensation reaction between the carboxyl group of one amino acid and the amino group of another amino acid.

Alanine and glycine, for example, can react to form the dipeptide glycylalanine:



$H_3\overset{+}{N}-CH_2-COO^- + H-\overset{+}{N}H_2-CH(CH_3)-COO^- \longrightarrow$

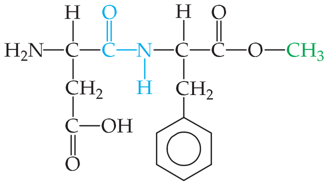
Glycine (Gly; G) Alanine (Ala; A)

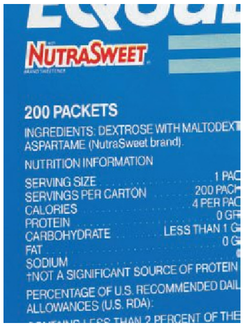


$H_3\overset{+}{N}-CH_2-CO-NH-CH(CH_3)-COO^- + H_2O$

Glycylalanine (Gly–Ala; GA)

The amino acid that furnishes the carboxyl group for peptide-bond formation is named first, with a -*yl* ending; then the amino acid furnishing the amino group is named. Based on the three-letter codes for the amino acids from Figure 25.23, glycylalanine can be abbreviated Gly-Ala, or as GA using the one-letter codes for the amino acids. In this notation it is understood that the unreacted amino group is on the left and the unreacted carboxyl group on the right. The artificial sweetener *aspartame* (Figure 25.25▶) is the methyl ester of the dipeptide of aspartic acid and phenylalanine:





▲ **Figure 25.25** **Sweet stuff.** The artificial sweetener aspartame is the methyl ester of a dipeptide.

SAMPLE EXERCISE 25.7 | Drawing the Structural Formula of a Tripeptide

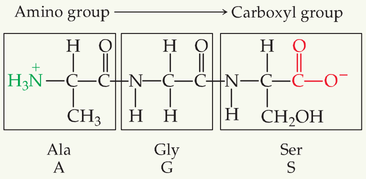
Draw the full structural formula for alanylglycylserine, or AGS.

SOLUTION

Analyze: We are given the name of a substance with peptide bonds and asked to write its full structural formula.

Plan: The name of this substance suggests that three amino acids—alanine, glycine, and serine—have been linked together, forming a *tripeptide*. Note that the ending -*yl* has been added to each amino acid except for the last one, serine. By convention, the sequence of amino acids that make up peptides and proteins are written from the nitrogen end to the carbon end: the first-named amino acid (alanine, in this case) has a free amino group and the last-named one (serine) has a free carboxyl group. Thus, we can construct the structural formula of the tripeptide from its amino acid building blocks (Figure 25.23).

Solve: We first combine the carboxyl group of alanine with the amino group of glycine to form a peptide bond and then the carboxyl group of glycine with the amino group of serine to form another peptide group. The resulting tripeptide consists of three "building blocks" connected by peptide bonds:

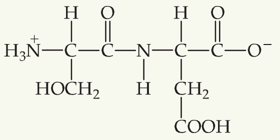


$H_3\overset{+}{N}-CH(CH_3)-CO-NH-CH_2-CO-NH-CH(CH_2OH)-COO^-$

We can abbreviate this tripeptide as Ala-Gly-Ser, or AGS.

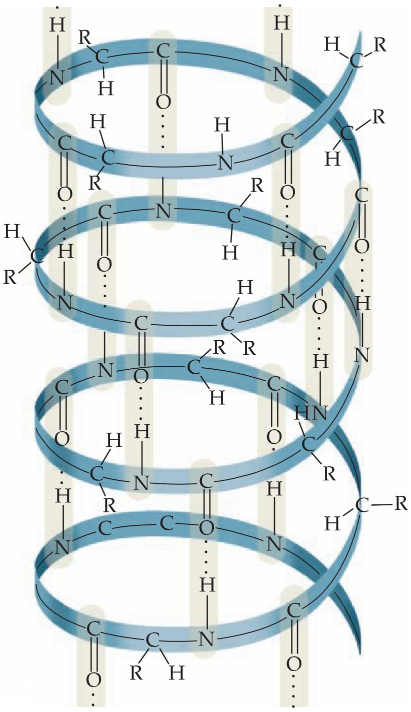
PRACTICE EXERCISE

Name the dipeptide that has the following structure, and give its abbreviation:

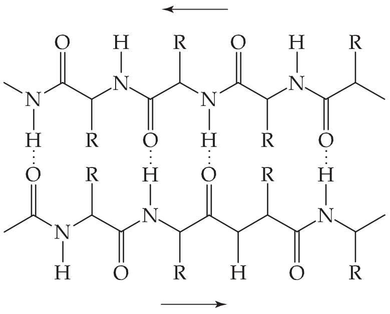


$$H_3\overset{+}{N}-CH(HOCH_2)-C(=O)-N(H)-CH(CH_2COOH)-C(=O)-O^-$$

Answer: serylaspartic acid; Ser-Asp, or SD.



▲ **Figure 25.26** **α-Helix structure for a protein.** The symbol R represents any one of the several side chains shown in Figure 25.23.



▲ **Figure 25.27** **β-Sheet structure for a protein.** The symbol R represents any one of the several side chains shown in Figure 25.23.

Polypeptides are formed when a large number of amino acids are linked together by peptide bonds. Proteins are linear (that is, unbranched) polypeptide molecules with molecular weights ranging from about 6000 to over 50 million amu. Because up to 22 different amino acids are linked together in proteins and because proteins consist of hundreds of amino acids, the number of possible arrangements of amino acids within proteins is virtually limitless.

Protein Structure

The arrangement, or sequence, of amino acids along a protein chain is called its **primary structure**. The primary structure gives the protein its unique identity. A change in even one amino acid can alter the biochemical characteristics of the protein. For example, sickle-cell anemia is a genetic disorder resulting from a single replacement in a protein chain in hemoglobin. The chain that is affected contains 146 amino acids. The substitution of a single amino acid with a hydrocarbon side chain for one that has an acidic functional group in the side chain alters the solubility properties of the hemoglobin, and normal blood flow is impeded. ∞ (Section 13.6: "Chemistry and Life: Sickle-Cell Anemia")

Proteins in living organisms are not simply long, flexible chains with random shapes. Rather, the chains self-assemble into particular structures based on the same kinds of intermolecular forces we learned about in Chapter 11. The **secondary structure** of a protein refers to how segments of the protein chain are oriented in a regular pattern.

One of the most important and common secondary structure arrangements is the **α helix**, first proposed by Linus Pauling and R. B. Corey. The helix arrangement is shown in schematic form in Figure 25.26◀. Imagine winding a long protein chain in a helical fashion around a long cylinder. The helix is held in position by hydrogen-bond interactions between N—H bonds and the oxygens of nearby carbonyl groups in the amide backbone of the protein; the R groups are not involved. The pitch of the helix and the diameter of the cylinder must be such that (1) no bond angles are strained and (2) the N—H and C=O functional groups on adjacent turns are in proper position for hydrogen bonding. An arrangement of this kind is possible for some amino acids along the chain, but not for others. Large protein molecules may contain segments of the chain that have the α-helical arrangement interspersed with sections in which the chain is in a random coil.

Another common structural motif in proteins is the beta (β) sheet. Beta sheets are made of two strands of peptides that hydrogen bond their backbone amide groups more like a zipper than an alpha-helical spiral (Figure 25.27◀). A single protein chain can form a β sheet if it has a flexible loop connecting the two β sheet partners.

GIVE IT SOME THOUGHT

If you heat a protein to break the intramolecular hydrogen bonds, will you maintain the α helical or β sheet structure?

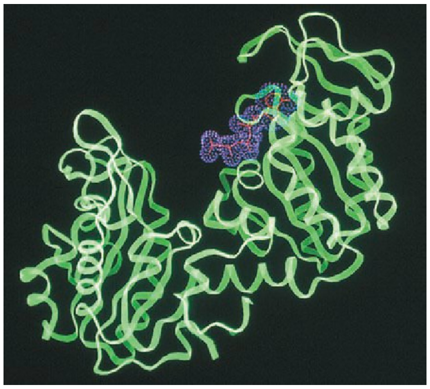
Proteins are not active biologically unless they are in a particular shape in solution. The process by which the protein adopts its biologically active shape is called **folding**. The overall shape of a protein in its folded form—determined by all the bends, kinks, and sections of rodlike α-helical, β-sheet, or flexible coil components—is called the **tertiary structure**. Figure 24.11 shows the tertiary structure of myoglobin, a protein with a molecular weight of about 18,000 amu and containing one heme group. (Section 24.2) Notice that some sections of the protein consist of α-helices.

Myoglobin is a *globular protein*, one that folds into a compact, roughly spherical shape. Globular proteins are generally soluble in water and are mobile within cells. They have nonstructural functions, such as combating the invasion of foreign objects, transporting and storing oxygen, and acting as catalysts. The *fibrous proteins* form a second class of proteins. In these substances the long coils align themselves in a more-or-less parallel fashion to form long, water-insoluble fibers. Fibrous proteins provide structural integrity and strength to many kinds of tissue and are the main components of muscle, tendons, and hair. The largest known proteins, in excess of 27,000 amino acids long, are muscle proteins called the titins.

The tertiary structure of a protein is maintained by many different interactions. Certain foldings of the protein chain lead to lower-energy (more stable) arrangements than do other folding patterns. For example, a globular protein dissolved in aqueous solution folds in such a way that the nonpolar hydrocarbon portions are tucked within the molecule, away from the polar water molecules. Most of the more polar acidic and basic side chains, however, project into the solution where they can interact with water molecules through ion–dipole, dipole–dipole, or hydrogen-bonding interactions.

One of the most important classes of proteins is *enzymes*, large protein molecules that serve as catalysts. (Section 14.7) Enzymes usually catalyze only very specific reactions. Their tertiary structure generally dictates that only certain substrate molecules can interact with the active site of the enzyme (Figure 25.28 ▶).

▼ Figure 25.28 **An enzyme and its substrate.** A computer-generated structure of an enzyme showing the carbon backbone as a green ribbon. The substrate (violet) is shown at the active site.



Chemistry and Life THE ORIGINS OF CHIRALITY IN LIVING SYSTEMS

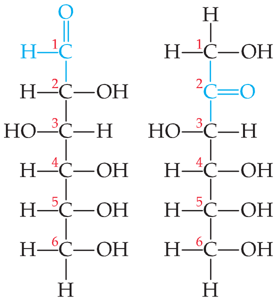
The presence of a "handedness" in the molecules that make up living systems is a key feature of life on Earth. The insistence of nature on just one chiral form in the molecules of life is called *homochirality*. How did the dominance of the L-amino acids arise? Why are the naturally occurring helices of protein and DNA, which we will discuss in Section 25.10, all right-turn helices? Homochirality could have arisen by chance in the course of evolution or because it was "seeded" in some way at the beginnings of life. One theory is that chirality was introduced early in Earth's evolutionary history, through seeding by chiral amino acids that fell on the planet from outer space.

Examination of the Murchison meteorite, which fell to Earth in 1969, has revealed the presence of amino acids. For some of the acids, there appears to be a surplus of the L form. One theory proposes that the chiral amino acids could have been synthesized in interstellar space by the action of circularly polarized starlight.* Astronomers in Australia have recently observed circular polarization in the infrared light from a region of intense star birth in the Orion nebula. These workers calculate that a similar degree of circular polarization could be present in the visible and ultraviolet light from this source. Light that has the energy required to break chemical bonds, if circularly polarized, could give rise to new chiral molecules with a preference for one enantiomer over the other. Perhaps the homochirality we observe on Earth today arose, through a process of amplification and refinement in the course of evolutionary development, from molecules that were formed in interstellar space when the planet was young.

**Circularly polarized light is like plane-polarized light, as shown in Figure 24.21, except that the plane continuously rotates either to the left or to the right. Thus, in a sense, circularly polarized light is chiral.*

25.8 CARBOHYDRATES

Carbohydrates are an important class of naturally occurring substances found in both plant and animal matter. The name **carbohydrate** (hydrate of carbon) comes from the empirical formulas for most substances in this class, which can be written as $C_x(H_2O)_y$. For example, **glucose**, the most abundant carbohydrate, has the molecular formula $C_6H_{12}O_6$, or $C_6(H_2O)_6$. Carbohydrates are not really hydrates of carbon; rather, they are polyhydroxy aldehydes and ketones. Glucose, for example, is a six-carbon aldehyde sugar; whereas *fructose*, the sugar that occurs widely in fruit, is a six-carbon ketone sugar (Figure 25.29 ◀).

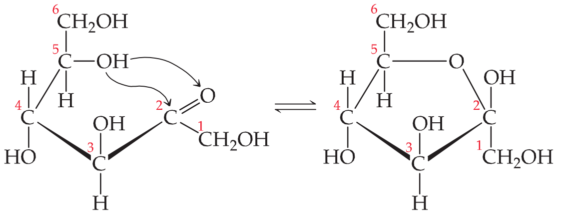

Glucose Fructose

▲ **Figure 25.29 Linear structure of glucose and fructose.**

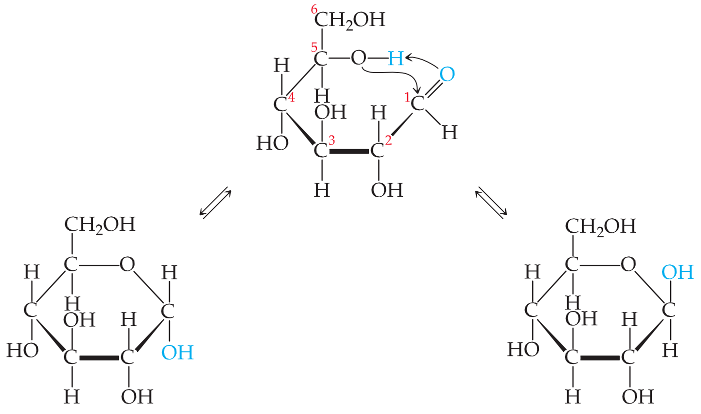
Glucose, having both alcohol and aldehyde functional groups and having a reasonably long and flexible backbone, can react with itself to form a six-member-ring structure, as shown in Figure 25.30 ▼. In fact, only a small percentage of the glucose molecules are in the open-chain form in aqueous solution. Although the ring is often drawn as if it were planar, the molecules are actually nonplanar because of the tetrahedral bond angles around the C and O atoms of the ring.

Figure 25.30 shows that the ring structure of glucose can have two relative orientations. In the α form the OH group on carbon 1 and the CH_2OH group on carbon 5 point in opposite directions. In the β form they point in the same direction. Although the difference between the α and β forms might seem small, it has enormous biological consequences. As we will soon see, this one small change in structure accounts for the vast difference in properties between starch and cellulose.

Fructose can cyclize to form either five- or six-member rings. The five-member ring forms when the OH group on carbon 5 reacts with the carbonyl group on carbon 2:



The six-member ring results from the reaction between the OH group on carbon 6 and the carbonyl group on carbon 2.


α-Glucose β-Glucose

▶ **Figure 25.30 Cyclic glucose.** The carbonyl group of a glucose molecule can react with one of the hydroxyl groups to form either of two six-member-ring structures, designated α and β.

SAMPLE EXERCISE 25.8 | Identifying Chiral Centers

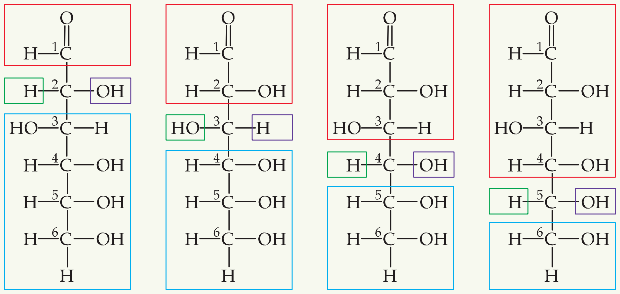
How many chiral carbon atoms are there in the open-chain form of glucose (Figure 25.29)?

SOLUTION

Analyze: We are given the structure of glucose and asked to determine the number of chiral carbons in the molecule.

Plan: A chiral carbon has four different groups attached (Section 25.5). We need to identify those carbon atoms in glucose.

Solve: The carbon atoms numbered 2, 3, 4, and 5 each have four different groups attached to them, as indicated here:



Thus, there are four chiral carbon atoms in the glucose molecule.

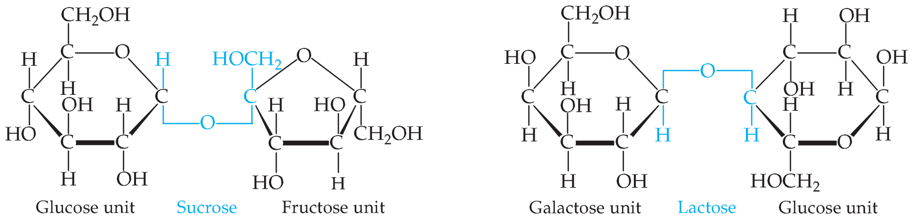
PRACTICE EXERCISE

How many chiral carbon atoms are there in the open-chain form of fructose (Figure 25.29)?
Answer: three

Disaccharides

Both glucose and fructose are examples of **monosaccharides**, simple sugars that cannot be broken into smaller molecules by hydrolysis with aqueous acids. Two monosaccharide units can be linked together by a condensation reaction to form a *disaccharide*. The structures of two common disaccharides, *sucrose* (table sugar) and *lactose* (milk sugar), are shown in Figure 25.31 ▼.

The word *sugar* makes us think of sweetness. All sugars are sweet, but they differ in the degree of sweetness we perceive when we taste them. Sucrose is about six times sweeter than lactose, slightly sweeter than glucose, but only about half as sweet as fructose. Disaccharides can be reacted with water (hydrolyzed) in the presence of an acid catalyst to form monosaccharides.

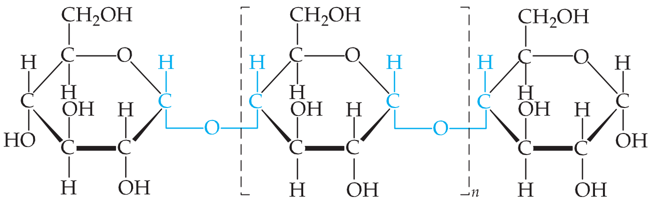


▲ **Figure 25.31 Two disaccharides.** The structures of sucrose (left) and lactose (right).

When sucrose is hydrolyzed, the mixture of glucose and fructose that forms, called *invert sugar*,* is sweeter to the taste than the original sucrose. The sweet syrup present in canned fruits and candies is largely invert sugar formed from hydrolysis of added sucrose.

Polysaccharides

Polysaccharides are made up of many monosaccharide units joined together by a bonding arrangement similar to those shown for the disaccharides in Figure 25.31. The most important polysaccharides are starch, glycogen, and cellulose, which are formed from repeating glucose units.



▲ **Figure 25.32 Structure of a starch molecule.** The molecule consists of many units of the kind enclosed in brackets, joined by linkages of the α form. (That is, the C—O bonds on the linking carbons are on the opposite side of the ring from the CH_2OH groups.)

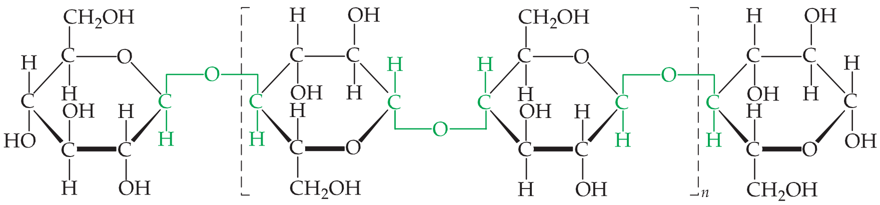
Starch is not a pure substance. The term refers to a group of polysaccharides found in plants. Starches serve as a major method of food storage in plant seeds and tubers. Corn, potatoes, wheat, and rice all contain substantial amounts of starch. These plant products serve as major sources of needed food energy for humans. Enzymes within the digestive system catalyze the hydrolysis of starch to glucose.

Some starch molecules are unbranched chains, whereas others are branched. Figure 25.32◀ illustrates an unbranched starch structure. Notice, in particular, that the glucose units are in the α form (that is, the bridging oxygen atom is opposite the CH_2OH group on the adjacent carbon).

Glycogen is a starchlike substance synthesized in the animal body. Glycogen molecules vary in molecular weight from about 5000 to more than 5 million amu. Glycogen acts as a kind of energy bank in the body. It is concentrated in the muscles and liver. In muscles it serves as an immediate source of energy; in the liver it serves as a storage place for glucose and helps to maintain a constant glucose level in the blood.

Cellulose forms the major structural unit of plants. Wood is about 50% cellulose; cotton fibers are almost entirely cellulose. Cellulose consists of an unbranched chain of glucose units, with molecular weights averaging more than 500,000 amu. The structure of cellulose is shown in Figure 25.33▼. At first glance this structure looks very similar to that of starch. In cellulose, however, the glucose units are in the β form (that is, the bridging oxygen atom is on the same side as the CH_2OH groups).

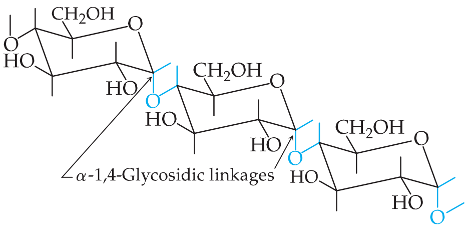
The distinction between starch and cellulose is made clearer when we examine their structures in a more realistic three-dimensional representation, as shown in Figure 25.34▶. The individual glucose units have different relationships to one another in the two structures. Because of this fundamental difference, enzymes



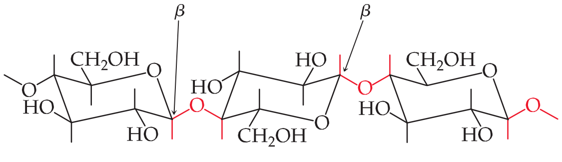
▲ **Figure 25.33 Structure of cellulose.** Like starch, cellulose is a polymer. The repeating unit is shown between brackets. The linkage in cellulose is of the β form, different from that in starch (see Figure 25.32).

**The term* invert sugar *comes from the fact that rotation of the plane of polarized light by the glucose-fructose mixture is in the opposite direction, or inverted, from that of the sucrose solution.*

that readily hydrolyze starches do not hydrolyze cellulose. Thus, you might eat a pound of cellulose and receive no caloric value from it whatsoever, even though the heat of combustion per unit weight is essentially the same for both cellulose and starch. A pound of starch, in contrast, would represent a substantial caloric intake. The difference is that the starch is hydrolyzed to glucose, which is eventually oxidized with release of energy. However, enzymes in the body do not readily hydrolyze cellulose, so it passes through the digestive system relatively unchanged. Many bacteria contain enzymes, called cellulases, that hydrolyze cellulose. These bacteria are present in the digestive systems of grazing animals, such as cattle, that use cellulose for food.



(a) Starch



(b) Cellulose

▲ **Figure 25.34 Structural differences in starch and cellulose.** These representations show the geometrical arrangements of bonds about each carbon atom. The glucose rings are oriented differently with respect to one another in the two structures.

GIVE IT SOME THOUGHT

Which type of linkage would you expect to join the sugar molecules of glycogen?

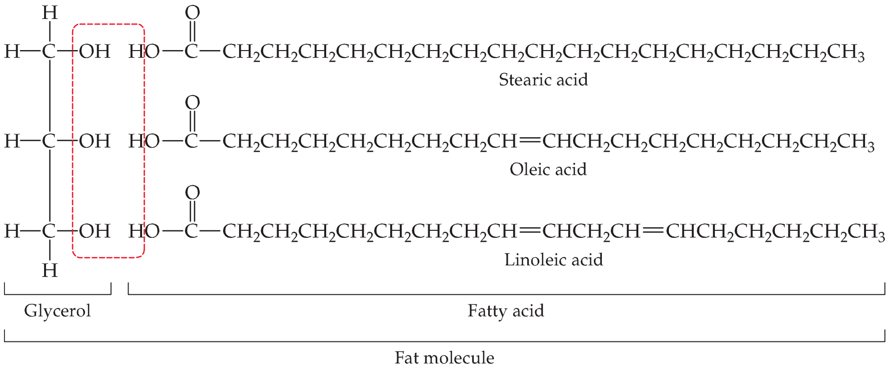
25.9 LIPIDS

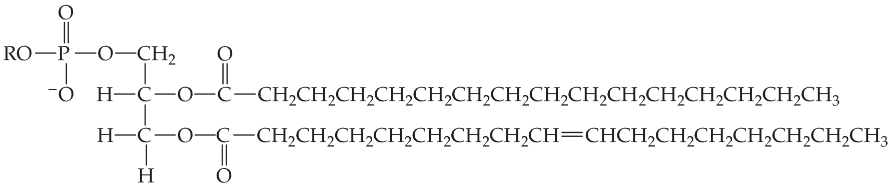
Lipids are another important class of biological molecules. Lipids are nonpolar and are used by organisms for long-term energy storage (fats, oils) and as elements of biological structures (phospholipids, cell membranes, waxes).

In vertebrate organisms such as ourselves, excess glycogen is converted into fats for long-term storage. Plants will more typically store energy in the form of oils. Both fats and oils are chemically derived from glyercol and three long-chain fatty acids (Figure 25.35▼); fatty acids are carboxylic acids (RCOOH) in which R is a hydrocarbon chain with at least four carbons.

In saturated fatty acids (and the saturated fats derived from them) the R groups are alkanes. Saturated fatty acids, such as shortening, are commonly solids at room temperature and are less reactive than unsaturated fats. In unsaturated fatty acids (and the unsaturated fats derived from them) the R groups are alkenes. The *cis* and *trans* nomenclature we learned earlier for alkenes is the same here: *Trans* fats have Hs on the opposite sides of the $C{=}C$ double bond, and *cis* fats have Hs on the same sides of the $C{=}C$ double bond. Unsaturated fats (such as olive oil and peanut oil) are usually liquid at room temperature and are more often found in plants. For example, the major component (approximately 60–80%) of olive oil is oleic acid, *cis*-$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$.

▼ **Figure 25.35 Structures of selected fats.** Fats are derived from glycerol and fatty acid molecules.





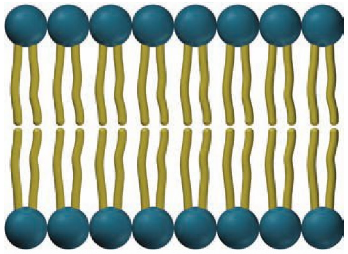
▲ **Figure 25.36** **Structure of phospholipids.** Phospholipids are closely related to fats. They form bilayers that are the key components of cell membranes.

Oleic acid is also an example of a *monounsaturated* fatty acid, meaning that there is one carbon–carbon double bond in the chain. In contrast, *polyunsaturated* fatty acids have more than one carbon–carbon double bond in the chain.

For humans, *trans* fats are not nutritionally required, which is why some governments are moving to ban them in foods. How, then, did *trans* fats end up in our food? The process that converts unsaturated fats (such as oils) into saturated fats (such as shortening) is hydrogenation. (Section 25.3) The by-products of this hydrogenation process include *trans* fats. If we eat food that has been cooked in *trans* fats, we inevitably ingest some *trans* fats.

Some fatty acids that are essential for human health must be available in our diets, because our metabolism is incapable of synthesizing them from other substances. These essential fatty acids are ones that have the carbon–carbon double bonds either three carbons or six carbons away from the —CH_3 end of the chain. These are called omega-3 and omega-6 fatty acids, where omega refers to the last carbon in the chain (the carboxylic acid carbon is considered the first, or alpha, one).

Phospholipids are similar in chemical structure to fats and oils, with the important addition of a charged phosphate group to the glycerol (Figure 25.36▲). In water, phospholipids cluster together with their charged polar heads facing the water and their nonpolar tails facing inward. (Section 13.6) The phospholipids thus form a bilayer that is a key component of cell membranes (Figure 25.37◀).



▲ **Figure 25.37** **The cell membrane.** Living cells are encased in membranes that are typically made of phospholipid bilayers. The bilayer structure is stabilized by the favorable interactions of the hydrophobic tails of the phospholipids away from water, while the charged headgroups face the water that is both outside and inside the cell.

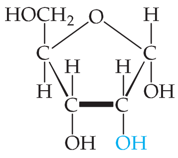
25.10 NUCLEIC ACIDS

Nucleic acids are a class of biopolymers that are the chemical carriers of an organism's genetic information. **Deoxyribonucleic acids (DNA)** are huge molecules [Figure 1.2(c)] whose molecular weights may range from 6 million to 16 million amu. **Ribonucleic acids (RNA)** are smaller molecules, with molecular weights in the range of 20,000 to 40,000 amu. Whereas DNA is found primarily in the nucleus of the cell, RNA is found mostly outside the nucleus in the *cytoplasm*, the nonnuclear material enclosed within the cell membrane. The DNA stores the genetic information of the cell and specifies which proteins the cell can synthesize. The RNA carries the information stored by DNA out of the nucleus of the cell into the cytoplasm, where the information is used in protein synthesis.

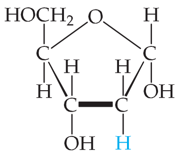
The monomers of nucleic acids, called **nucleotides**, are formed from the following units:

1. A phosphoric acid molecule, H_3PO_4
2. A five-carbon sugar
3. A nitrogen-containing organic base

The sugar component of RNA is *ribose*, whereas that in DNA is *deoxyribose*.



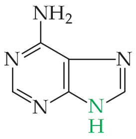
Ribose



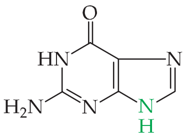
Deoxyribose

*Deoxy*ribose differs from ribose only in having one fewer oxygen atom at carbon 2.

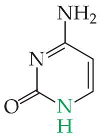
The following nitrogen bases are found in DNA and RNA:



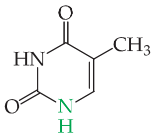
Adenine (A)
DNA
RNA



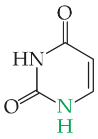
Guanine (G)
DNA
RNA



Cytosine (C)
DNA
RNA



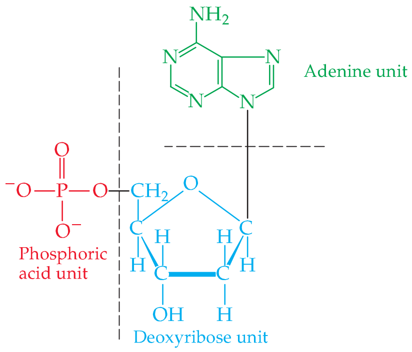
Thymine (T)
DNA



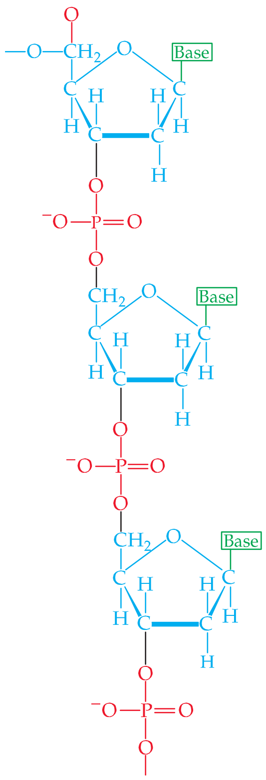
Uracil (U)
RNA

The base is attached to a ribose or deoxyribose molecule through a bond to the nitrogen atom shown in color above. An example of a nucleotide in which the base is adenine and the sugar is deoxyribose is shown in Figure 25.38▼.

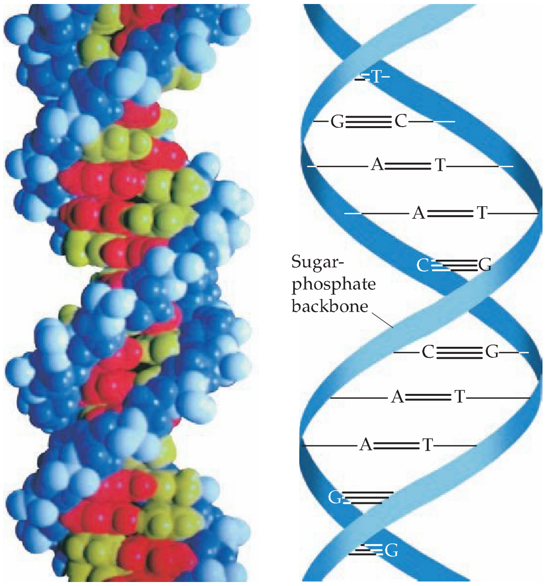
Nucleic acids are polynucleotides formed by condensation reactions between an OH group of the phosphoric acid unit on one nucleotide and an OH group of the sugar of another nucleotide. Figure 25.39▶ shows a portion of the polymeric chain of a DNA molecule.



▲ **Figure 25.38 A nucleotide.** Structure of deoxyadenylic acid, a nucleotide formed from phosphoric acid, deoxyribose, and the organic base adenine.



◀ **Figure 25.39 Structure of a polynucleotide.** Because the sugar in each nucleotide is deoxyribose, this polynucleotide is of the form found in DNA.

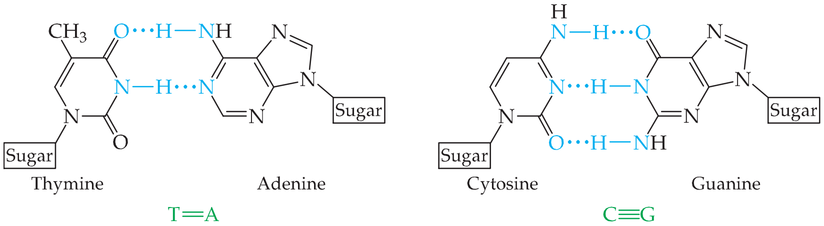


(a) (b)

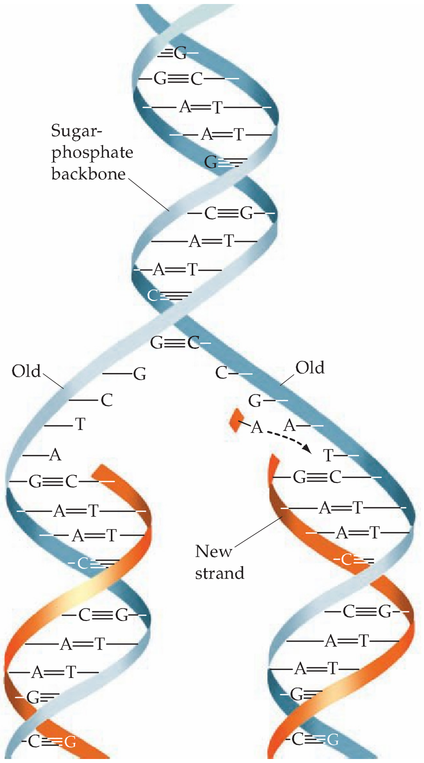
▶ **Figure 25.40** **Two views of DNA.** (a) A computer-generated model of a DNA double helix. The dark blue and light blue atoms represent the sugar-phosphate chains that wrap around the outside. Inside the chains are the bases, shown in red and yellow-green. (b) A schematic illustration of the double helix showing the hydrogen-bond interactions between complementary base pairs.

DNA molecules consist of two deoxyribonucleic acid chains or strands that are wound together in the form of a **double helix**, as shown in Figure 25.40▲. The drawing in Figure 25.40(b) has been simplified to show the essential features of the structure. The sugar and phosphate groups form the backbone of each strand. The bases (represented by the letters T, A, C, and G) are attached to the sugars. The two strands are held together by attractions between the bases in one strand and those in the other strand. These attractions involve London dispersion interactions, dipole-dipole and hydrogen bonds. ∞ (Section 11.2) As shown in Figure 25.41▼, the structures of thymine (T) and adenine (A) make them perfect partners for hydrogen bonding. Likewise, cytosine (C) and guanine (G) form ideal hydrogen-bonding partners. In the double-helix structure, therefore, each thymine on one strand is opposite an adenine on the other strand. Likewise, each cytosine is opposite a guanine. The double-helix structure with complementary bases on the two strands is the key to understanding how DNA functions.

The two strands of DNA unwind during cell division, and new complementary strands are constructed on the unraveling strands (Figure 25.42▶).



▲ **Figure 25.41** **Hydrogen bonding between complementary base pairs.** The hydrogen bonds are responsible for formation of the double-stranded helical structure of DNA.

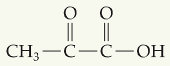


◀ **Figure 25.42** **DNA replication.** The original DNA double helix partially unwinds, and new nucleotides line up on each strand in complementary fashion. Hydrogen bonds help align the new nucleotides with the original DNA chain. When the new nucleotides are joined by condensation reactions, two identical double-helix DNA molecules result.

This process results in two identical double-helix DNA structures, each containing one strand from the original structure and one newly synthesized strand. This replication process allows genetic information to be transmitted when cells divide. The structure of DNA is also the key to understanding protein synthesis, the means by which viruses infect cells, and many other problems of central importance to modern biology. These themes are beyond the scope of this book. If you take courses in the life sciences, however, you will learn a good deal about such matters.

SAMPLE INTEGRATIVE EXERCISE | **Putting Concepts Together**

Pyruvic acid has the following structure:



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

It is formed in the body from carbohydrate metabolism. In the muscle it is reduced to lactic acid in the course of exertion. The acid-dissociation constant for pyruvic acid is 3.2×10^{-3}. **(a)** Why does pyruvic acid have a higher acid-dissociation constant than acetic acid? **(b)** Would you expect pyruvic acid to exist primarily as the neutral acid or as dissociated ions in muscle tissue, assuming a pH of about 7.4 and an acid concentration of 2×10^{-4} *M*? **(c)** What would you predict for the solubility properties of pyruvic acid? Explain. **(d)** What is the hybridization of each carbon atom in pyruvic acid? **(e)** Assuming H atoms as the reducing agent, write a balanced chemical equation for the reduction of pyruvic acid to lactic acid (Figure 25.17). (Although H atoms do not exist as such in biochemical systems, biochemical reducing agents deliver hydrogen for such reductions.)

SOLUTION

(a) The acid ionization constant for pyruvic acid should be somewhat greater than that of acetic acid because the carbonyl function on the α-carbon atom exerts an electron-withdrawing effect on the carboxylic acid group. In the C—O—H bond system the electrons are shifted from hydrogen, facilitating loss of the hydrogen as a proton. (Section 16.10)

(b) To determine the extent of ionization, we first set up the ionization equilibrium and equilibrium-constant expression. Using HPv as the symbol for the acid, we have

$$\mathrm{HPv} \rightleftharpoons \mathrm{H^+} + \mathrm{Pv^-}$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{Pv^-}]}{[\mathrm{HPv}]} = 3.2 \times 10^{-3}$$

Let $[\mathrm{Pv^-}] = x$. Then the concentration of undissociated acid is $2 \times 10^{-4} - x$. The concentration of $[\mathrm{H^+}]$ is fixed at 4.0×10^{-8} (the antilog of the pH value). Substituting, we obtain

$$3.2 \times 10^{-3} = \frac{[4.0 \times 10^{-8}][x]}{[2 \times 10^{-4} - x]}$$

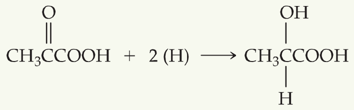
Solving for x, we obtain $x[3.2 \times 10^{-3} + 4.0 \times 10^{-8}] = 6.4 \times 10^{-7}$.

The second term in the brackets is negligible compared to the first, so $x = [\mathrm{Pv^-}] = 6.4 \times 10^{-7}/3.2 \times 10^{-3} = 2 \times 10^{-4}\ M$. This is the initial concentration of acid, which means that essentially all the acid has dissociated. We might have expected this result because the acid is quite dilute and the acid-dissociation constant is fairly high.

(c) Pyruvic acid should be quite soluble in water because it has polar functional groups and a small hydrocarbon component. It is miscible with water, ethanol, and diethyl ether.

(d) The methyl group carbon has sp^3 hybridization. The carbon carrying the carbonyl group has sp^2 hybridization because of the double bond to oxygen. Similarly, the carboxylic acid carbon is sp^2 hybridized.

(e) The balanced chemical equation for this reaction is



$$\mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{COOH} + 2\,(\mathrm{H}) \longrightarrow \mathrm{CH_3}\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}}\mathrm{COOH}$$

Essentially, the ketonic functional group has been reduced to an alcohol.

Strategies in Chemistry WHAT NOW?

If you are reading this box, you have made it to the end of our text. We congratulate you on the tenacity and dedication that you have exhibited to make it this far!

As an epilogue, we offer the ultimate study strategy in the form of a question: What do you plan to do with the knowledge of chemistry that you have gained thus far in your studies? Many of you will enroll in additional courses in chemistry as part of your required curriculum. For others, this will be the last formal course in chemistry that you will take. Regardless of the career path you plan to take—whether it is chemistry, one of the biomedical fields, engineering, the liberal arts, or another field—we hope that this text has increased your appreciation of the chemistry in the world around you. If you pay attention, you will be aware of encounters with chemistry on a daily basis, from food and pharmaceutical labels to gasoline pumps, sports equipment to news reports.

We have also tried to give you a sense that chemistry is a dynamic, continuously changing science. Research chemists synthesize new compounds, develop new reactions, uncover chemical properties that were previously unknown, find new applications for known compounds, and refine theories. The understanding of biological systems in terms of the underlying chemistry has become increasingly important as new levels of complexity are uncovered. You may wish to participate in the fascinating venture of chemical research by taking part in an undergraduate research program. Given all the answers that chemists seem to have, you may be surprised at the large number of questions that they still find to ask.

Finally, we hope you have enjoyed using this textbook. We certainly enjoyed putting so many of our thoughts about chemistry on paper. We truly believe it to be the central science, one that benefits all who learn about it and from it.

CHAPTER REVIEW

SUMMARY AND KEY TERMS

Introduction and Section 25.1 This chapter introduces **organic chemistry**, which is the study of carbon compounds (typically compounds containing carbon–carbon bonds), and **biochemistry**, which is the study of the chemistry of living organisms. We have encountered many aspects of organic chemistry in earlier chapters. Carbon forms four bonds in its stable compounds. The C—C single bonds and the C—H bonds tend to have low reactivity. Those bonds that have a high electron density (such as multiple bonds or bonds with an atom of high electronegativity) tend to be the sites of reactivity in an organic compound. These sites of reactivity are called **functional groups**.

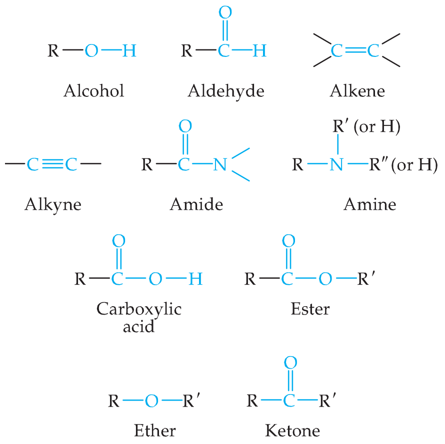
Section 25.2 The simplest types of organic compounds are hydrocarbons, those composed of only carbon and hydrogen. There are four major kinds of hydrocarbons: alkanes, alkenes, alkynes, and aromatic hydrocarbons. **Alkanes** are composed of only C—H and C—C single bonds. **Alkenes** contain one or more carbon–carbon double bonds. **Alkynes** contain one or more carbon–carbon triple bonds. **Aromatic hydrocarbons** contain cyclic arrangements of carbon atoms bonded through both σ and delocalized π bonds. Alkanes are saturated hydrocarbons; the others are unsaturated.

Section 25.3 Alkanes may form straight-chain, branched-chain, and cyclic arrangements. Isomers are substances that possess the same molecular formula, but differ in the arrangements of atoms. In **structural isomers** the bonding arrangements of the atoms differ. Different isomers are given different systematic names. The naming of hydrocarbons is based on the longest continuous chain of carbon atoms in the structure. The locations of **alkyl groups**, which branch off the chain, are specified by numbering along the carbon chain. Alkanes with ring structures are called **cycloalkanes**. Alkanes are relatively unreactive. They do, however, undergo combustion in air, and their chief use is as sources of heat energy produced by combustion.

The names of alkenes and alkynes are based on the longest continuous chain of carbon atoms that contains the multiple bond, and the location of the multiple bond is specified by a numerical prefix. Alkenes exhibit not only structural isomerism but geometric (cis-trans) isomerism as well. In **geometric isomers** the bonds are the same, but the molecules have different geometries. Geometric isomerism is possible in alkenes because rotation about the C═C double bond is restricted.

Alkenes and alkynes readily undergo **addition reactions** to the carbon–carbon multiple bonds. Additions of acids, such as HBr, proceed via a rate-determining step in which a proton is transferred to one of the alkene or alkyne carbon atoms. Addition reactions are difficult to carry out with aromatic hydrocarbons, but **substitution reactions** are easily accomplished in the presence of catalysts.

Section 25.4 The chemistry of organic compounds is dominated by the nature of their functional groups. The functional groups we have considered are



R, R′, and R″ represent hydrocarbon groups—for example, methyl (CH_3) or phenyl (C_6H_5).

Alcohols are hydrocarbon derivatives containing one or more OH groups. **Ethers** are formed by a condensation reaction of two molecules of alcohol. Several functional groups contain the **carbonyl** (C═O) **group**, including **aldehydes**, **ketones**, **carboxylic acids**, **esters**, and **amides**. Aldehydes and ketones can be produced by oxidation of certain alcohols. Further oxidation of the aldehydes produces carboxylic acids. Carboxylic acids can form esters by a condensation reaction with alcohols, or they can form amides by a condensation reaction with amines. Esters undergo hydrolysis (**saponification**) in the presence of strong bases.

Section 25.5 Molecules that possess nonsuperimposable mirror images are termed **chiral**. The two nonsuperimposable forms of a chiral molecule are called *enantiomers*. In carbon compounds a chiral center is created when all four groups bonded to a central carbon atom are different, as in 2-bromobutane. Many of the molecules occurring in living systems, such as the amino acids, are chiral and exist in nature in only one enantiomeric form. Many drugs of importance in human medicine are chiral, and the enantiomers may produce very different biochemical effects. For this reason, synthesis of only the effective isomers of chiral drugs has become a high priority.

Sections 25.6 and 25.7 Many of the molecules that are essential for life are large natural polymers that are constructed from smaller molecules called monomers. Three of these **biopolymers** were considered in this chapter: proteins, polysaccharides (carbohydrates), and nucleic acids.

Proteins are polymers of **amino acids**. They are the major structural materials in animal systems. All naturally occurring proteins are formed from 22 amino acids are formed from 22 amino acids, although only 20 are common. The amino acids are linked by **peptide bonds**. A **polypeptide** is a polymer formed by linking many amino acids by peptide bonds.

Amino acids are chiral substances. Usually only one of the enantiomers is found to be biologically active. Protein structure is determined by the sequence of amino acids in the chain (its **primary structure**), the coiling or stretching of the chain (its **secondary structure**), and the overall shape of the complete molecule (its **tertiary structure**). Two important secondary structures are the **α helix** and the **β sheet**. The process by which a protein assumes its biologically active tertiary structure is called **folding**.

Sections 25.8 and 25.9 **Carbohydrates**, which are polyhydroxy aldehydes and ketones, are the major structural constituents of plants and are a source of energy in both plants and animals. **Glucose** is the most common **monosaccharide**, or simple sugar. Two monosaccharides can be linked together by means of a condensation reaction to form a disaccharide. **Polysaccharides** are complex carbohydrates made up of many monosaccharide units joined together. The three most important polysaccharides are **starch**, which is found in plants; **glycogen**, which is found in mammals; and **cellulose**, which is also found in plants. **Lipids** are small molecules derived from glycerol and fatty acids that comprise fats, oils, and **phospholipids**. Fatty acids can be *saturated, unsaturated, cis,* or *trans* depending on their chemical formulas and structures.

Section 25.10 **Nucleic acids** are biopolymers that carry the genetic information necessary for cell reproduction; they also control cell development through control of protein synthesis. The building blocks of these biopolymers are **nucleotides**. There are two types of nucleic acids, the **ribonucleic acids (RNA)** and the **deoxyribonucleic acids (DNA)**. These substances consist of a polymeric backbone of alternating phosphate and ribose or deoxyribose sugar groups, with organic bases attached to the sugar molecules. The DNA polymer is a double-stranded helix (a **double helix**) held together by hydrogen bonding between matching organic bases situated across from one another on the two strands. The hydrogen bonding between specific base pairs is the key to gene replication and protein synthesis.

KEY CONCEPTS

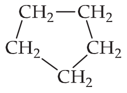
- Draw hydrocarbon structures based on their names and name hydrocarbons based on their structures.
- Know the structures of the functional groups: alkene, alkyne, alcohol, carbonyl, ether, aldehyde, ketone, carboxylic acid, amine, amide.
- Distinguish between addition reactions and substitution reactions.
- Understand what makes a compound chiral and be able to recognize a chiral substance.
- Recognize the amino acids and understand how they form peptides and proteins via amide bond formation.
- Understand the difference between primary, secondary, and tertiary structure of proteins.
- Be able to explain the difference between α helix and β sheet peptide and protein structures.
- Understand the distinction between starch and cellulose structures.
- Classify molecules as saccharides or lipids based on their structures.
- Understand the difference between *cis* and *trans*, and saturated and unsaturated fatty acids.
- Understand the structure of nucleic acids.

VISUALIZING CONCEPTS

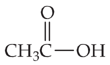
25.1 Which of the following molecules is unsaturated? [Section 25.2]

$CH_3CH_2CH_2CH_3$

(a)



(b)



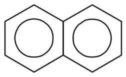
$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

(c)

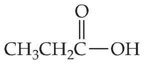
$CH_3CH{=}CHCH_3$

(d)

25.2 Which of the following molecules will most readily undergo an addition reaction? [Section 25.3]

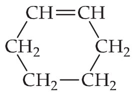


(a)

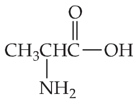


$$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

(b)



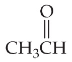
(c)



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

(d)

25.3 Which of the following compounds would you expect to have the highest boiling point? Explain. [Section 25.4]



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

(a)

CH_3CH_2OH

(b)

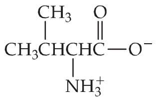
$CH_3C{\equiv}CH$

(c)

$H\overset{O}{\overset{\|}{C}}OCH_3$

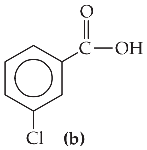
(d)

25.4 Which of the following compounds is capable of possessing isomerism? In each case where isomerism is possible, identify the type or types of isomerism. [Sections 25.3 and 25.4]



$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{NH_3^+}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}{-}O^-$

(a)



(b)

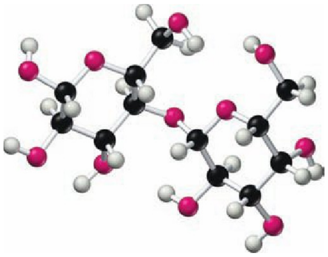
$CH_3CH_2CH{=}CHCH_3$

(c)

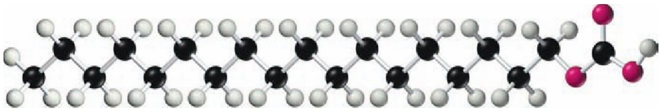
$CH_3CH_2CH_3$

(d)

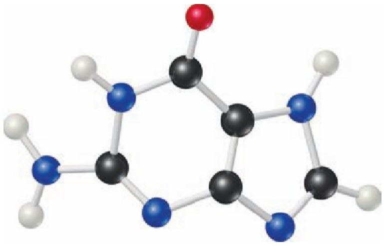
25.5 From examination of the following ball-and-stick molecular models, choose the substance that **(a)** can be hydrolyzed to form a solution containing glucose, **(b)** is capable of forming a zwitterion, **(c)** is one of the four bases present in DNA, **(d)** reacts with an acid to form an ester, **(e)** is a lipid. [Sections 25.6–25.10]



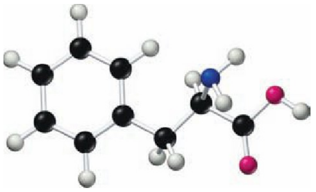
(i)



(ii)



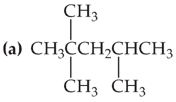
(iii)



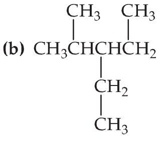
(iv)

(v)

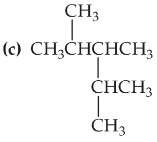
25.6 All the structures that follow have the same molecular formula, C_8H_{18}. Which structures are the same molecule? (*Hint:* One way to do this is to determine the chemical name for each.) [Section 25.3]



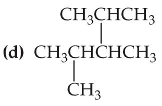
(a) $CH_3\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CH_2\underset{CH_3}{\underset{|}{C}}HCH_3$



(b) $CH_3\overset{CH_3}{\overset{|}{C}}H\underset{\underset{CH_3}{\underset{|}{CH_2}}}{\underset{|}{C}}H\overset{CH_3}{\overset{|}{C}}H_2$



(c) $CH_3\overset{CH_3}{\overset{|}{C}}H\underset{\underset{CH_3}{\underset{|}{CHCH_3}}}{\underset{|}{C}}HCH_3$



(d) $CH_3\underset{CH_3}{\underset{|}{C}}H\overset{CH_3CHCH_3}{\overset{|}{C}}HCH_3$

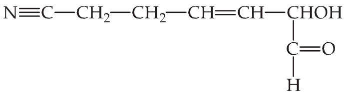
EXERCISES

Introduction to Organic Compounds; Hydrocarbons

25.7 Predict the ideal values for the bond angles about each carbon atom in the following molecule. Indicate the hybridization of orbitals for each carbon.

CH_3CCCH_2COOH

25.8 Identify the carbon atom(s) in the structure shown that has (have) each of the following hybridizations: **(a)** sp^3, **(b)** sp, **(c)** sp^2.



$N{\equiv}C{-}CH_2{-}CH_2{-}CH{=}CH{-}\underset{\underset{H}{\underset{|}{C{=}O}}}{\underset{|}{C}}HOH$

25.9 Are carbon monoxide or ammonia considered organic molecules? Why or why not?

25.10 Organic compounds containing $\mathrm{C{-}O}$ and $\mathrm{C{-}Cl}$ bonds are more reactive than simple alkane hydrocarbons. Considering the comparative values of $\mathrm{C{-}H}$, $\mathrm{C{-}C}$, $\mathrm{C{-}O}$, and $\mathrm{C{-}Cl}$ bond energies (Table 8.4), why is this so?

25.11 **(a)** What is the difference between a straight-chain and branched-chain alkane? **(b)** What is the difference between an alkane and an alkyl group? **(c)** Why are alkanes said to be saturated? **(d)** Give an example of an unsaturated molecule.

25.12 What structural features help us identify a compound as **(a)** an alkane, **(b)** a cycloalkane, **(c)** an alkene, **(d)** an alkyne, **(e)** a saturated hydrocarbon, **(f)** an aromatic hydrocarbon?

25.13 Give the molecular formula of a hydrocarbon containing five carbon atoms that is **(a)** an alkane, **(b)** a cycloalkane, **(c)** an alkene, **(d)** an alkyne. Which are saturated and which are unsaturated hydrocarbons?

25.14 Give the molecular formula of a cyclic alkane, a cyclic alkene, a linear alkyne, and an aromatic hydrocarbon that in each case contains six carbon atoms. Which are saturated and which are unsaturated hydrocarbons?

25.15 Enediynes are a class of compounds that include some antibiotic drugs. Draw the structure of an "enediyne" fragment that contains six carbons in a row. (*Hint:* "di" means "two".)

25.16 Give the general formula for any cyclic alkene, that is, a cyclic hydrocarbon with one double bond.

25.17 Write the condensed structural formulas for as many alkenes and alkynes as you can think of that have the molecular formula C_6H_{10}.

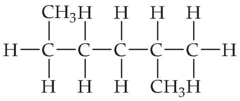
25.18 Draw all the possible noncyclic structural isomers of C_5H_{10}. Name each compound.

25.19 What are the characteristic hybrid orbitals employed by **(a)** carbon in an alkane, **(b)** carbon in a double bond in an alkene, **(c)** carbon in the benzene ring, **(d)** carbon in a triple bond in an alkyne?

25.20 What are the approximate bond angles **(a)** about carbon in an alkane, **(b)** about a doubly bonded carbon atom in an alkene, **(c)** about a triply bonded carbon atom in an alkyne?

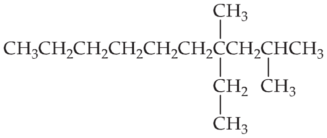
25.21 Draw the structural formula or give the name, as appropriate, for the following:

(a)



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

(b)

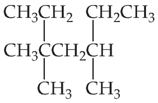


$$\begin{array}{rcccl} & \mathrm{CH_3} & & & \\ & | & & & \\ \mathrm{CH_3CH_2CH_2CH_2CH_2CH_2} & \mathrm{C} & \mathrm{CH_2} & \mathrm{CH} & \mathrm{CH_3} \\ & | & & | & \\ & \mathrm{CH_2} & & \mathrm{CH_3} & \\ & | & & & \\ & \mathrm{CH_3} & & & \end{array}$$

(c) 2-methylheptane
(d) 4-ethyl-2,3-dimethyloctane
(e) 1,2-dimethylcyclohexane

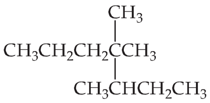
25.22 Draw the structural formula or give the name, as appropriate, for the following:

(a)



$$\begin{array}{cccc} & \mathrm{CH_3CH_2} & & \mathrm{CH_2CH_3} \\ & | & & | \\ \mathrm{CH_3} & \mathrm{C} & \mathrm{CH_2} & \mathrm{CH} \\ & | & & | \\ & \mathrm{CH_3} & & \mathrm{CH_3} \end{array}$$

(b)

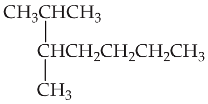


$$\begin{array}{rcl} & \mathrm{CH_3} & \\ & | & \\ \mathrm{CH_3CH_2CH_2} & \mathrm{C} & \mathrm{CH_3} \\ & | & \\ \mathrm{CH_3} & \mathrm{CH} & \mathrm{CH_2CH_3} \end{array}$$

(c) 2,5,6-trimethylnonane
(d) 3-propyl-4,5-methyldecane
(e) 1-ethyl-3-methylcyclohexane

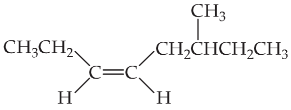
25.23 Name the following compounds:

(a)



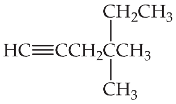
$$\begin{array}{ccl} \mathrm{CH_3} & \mathrm{CH} & \mathrm{CH_3} \\ & | & \\ & \mathrm{CH} & \mathrm{CH_2CH_2CH_2CH_3} \\ & | & \\ & \mathrm{CH_3} & \end{array}$$

(b)



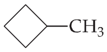
(c)

(d)



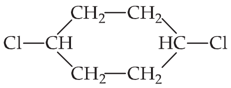
$$\begin{array}{rcl} & \mathrm{CH_2CH_3} & \\ & | & \\ \mathrm{HC{\equiv}CCH_2} & \mathrm{C} & \mathrm{CH_3} \\ & | & \\ & \mathrm{CH_3} & \end{array}$$

(e)



25.24 Name the following compounds:

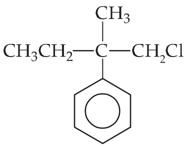
(a)



(b) $\mathrm{HC{\equiv}C{-}CH_2{-}Cl}$

(c) *trans*-$\mathrm{CH_3CH{=}CHCH_2CH_2CH_3}$

(d)



(e) *cis*-$\mathrm{CH_2{=}CH{-}CH{=}CH{-}CH_2Cl}$

25.25 Why is geometric isomerism possible for alkenes, but not for alkanes and alkynes?

25.26 Draw all structural and geometric isomers of butene and name them.

25.27 Indicate whether each of the following molecules is capable of geometrical (cis-trans) isomerism. For those that are, draw the structures: **(a)** 1,1-dichloro-1-butene, **(b)** 2,4-dichloro-2-butene, **(c)** 1,4-dichlorobenzene, **(d)** 4,5-dimethyl-2-pentyne.

25.28 Draw all the distinct geometric isomers of 2,4-hexadiene.

25.29 What is the octane number of a mixture of 35% heptane and 65% isooctane?

25.30 Describe two ways in which the octane number of a gasoline consisting of alkanes can be increased.

Reactions of Hydrocarbons

25.31 **(a)** What is the difference between a substitution reaction and an addition reaction? Which one is commonly observed with alkenes, and which one with aromatic hydrocarbons? **(b)** Using condensed structural formulas, write the balanced equation for the addition reaction of 2-pentene with Br_2 and name the resulting compound. **(c)** Write a balanced chemical equation for the substitution reaction of Cl_2 with benzene to make *para*-dichlorobenzene in the presence of $FeCl_3$ as a catalyst.

25.32 Using condensed structural formulas, write a balanced chemical equation for each of the following reactions: **(a)** hydrogenation of cyclohexene; **(b)** addition of H_2O to *trans*-2-pentene using H_2SO_4 as a catalyst (two products); **(c)** reaction of 2-chloropropane with benzene in the presence of $AlCl_3$.

25.33 **(a)** When cyclopropane is treated with HI, 1-iodopropane is formed. A similar type of reaction does not occur with cyclopentane or cyclohexane. How do you account for the reactivity of cyclopropane? **(b)** Suggest a method of preparing ethylbenzene, starting with benzene and ethylene as the only organic reagents.

25.34 **(a)** One test for the presence of an alkene is to add a small amount of bromine, a red-brown liquid, and look for the disappearance of the red-brown color. This test does not work for detecting the presence of an aromatic hydrocarbon. Explain. **(b)** Write a series of reactions leading to *para*-bromoethylbenzene, beginning with benzene and using other reagents as needed. What isomeric side products might also be formed?

25.35 The rate law for addition of Br_2 to an alkene is first order in Br_2 and first order in the alkene. Does this fact prove that the mechanism of addition of Br_2 to an alkene proceeds in the same manner as for addition of HBr? Explain.

25.36 Describe the intermediate that is thought to form in the addition of a hydrogen halide to an alkene, using cyclohexene as the alkene in your description.

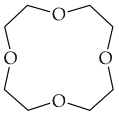
25.37 The molar heat of combustion of gaseous cyclopropane is −2089 kJ/mol; that for gaseous cyclopentane is −3317 kJ/mol. Calculate the heat of combustion per CH_2 group in the two cases, and account for the difference.

25.38 The heat of combustion of decahydronaphthalene ($C_{10}H_{18}$) is −6286 kJ/mol. The heat of combustion of naphthalene ($C_{10}H_8$) is −5157 kJ/mol. (In both cases $CO_2(g)$ and $H_2O(l)$ are the products.) Using these data and data in Appendix C, calculate the heat of hydrogenation of naphthalene. Does this value provide any evidence for aromatic character in naphthalene?

Functional Groups and Chirality

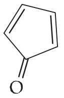
25.39 Identify the functional groups in each of the following compounds:

(a) H_3C-CH_2-OH

(b)


(c)

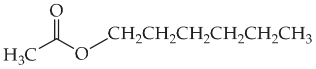
$H_3C-\overset{H}{N}-CH_2CH=CH_2$

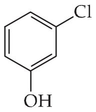
(d)


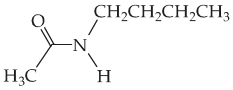
(e) $CH_3CH_2CH_2CH_2CHO$

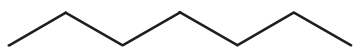
(f) CH_3CCH_2COOH

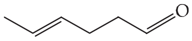
25.40 Identify the functional groups in each of the following compounds:

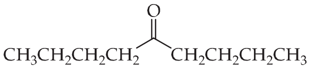
(a)


(b)


(c)


(d)


(e)


(f)


25.41 Give the structural formula for **(a)** an aldehyde that is an isomer of acetone, **(b)** an ether that is an isomer of 1-propanol.

25.42 **(a)** Give the empirical formula and structural formula for a cyclic ether containing four carbon atoms in the ring. **(b)** Write the structural formula for a straight-chain compound that is a structural isomer of your answer to part (a).

25.43 The IUPAC name for a carboxylic acid is based on the name of the hydrocarbon with the same number of carbon atoms. The ending *-oic* is appended, as in ethanoic acid, which is the IUPAC name for acetic acid. Draw the structure of the following acids: **(a)** methanoic acid, **(b)** pentanoic acid, and **(c)** 2-chloro-3-methyldecanoic acid.

25.44 Aldehydes and ketones can be named in a systematic way by counting the number of carbon atoms (including the carbonyl carbon) that they contain. The name of the aldehyde or ketone is based on the hydrocarbon with the same number of carbon atoms. The ending *-al* for aldehyde or *-one* for ketone is added as appropriate. Draw the structural formulas for the following aldehydes or ketones: **(a)** propanal, **(b)** 2-pentanone, **(c)** 3-methyl-2-butanone, **(d)** 2-methylbutanal.

25.45 Draw the condensed structure of the compounds formed by condensation reactions between **(a)** benzoic acid and ethanol, **(b)** ethanoic acid and methylamine, **(c)** acetic acid and phenol. Name the compound in each case.

25.46 Draw the condensed structures of the compounds formed from **(a)** butanoic acid and methanol, **(b)** benzoic acid and 2-propanol, **(c)** propanoic acid and dimethylamine. Name the compound in each case.

25.47 Write a balanced chemical equation using condensed structural formulas for the saponification (base hydrolysis) of **(a)** methyl propionate, **(b)** phenyl acetate.

25.48 Write a balanced chemical equation using condensed structural formulas for **(a)** the formation of butyl propionate from the appropriate acid and alcohol, **(b)** the saponification (base hydrolysis) of methyl benzoate.

25.49 Would you expect pure acetic acid to be a strongly hydrogen-bonded substance? How do the melting and boiling points of the substance (see the "Chemistry Put to Work" box on p. 1076 for data) support your answer?

25.50 Acetic anhydride is formed from acetic acid in a condensation reaction that involves the removal of a molecule of water from between two acetic acid molecules. Write the chemical equation for this process, and show the structure of acetic anhydride.

25.51 Write the condensed structural formula for each of the following compounds: **(a)** 2-pentanol, **(b)** 1,2-propanediol, **(c)** ethyl acetate, **(d)** diphenyl ketone, **(e)** methyl ethyl ether.

25.52 Write the condensed structural formula for each of the following compounds: **(a)** 3,3-dichlorobutyraldehyde, **(b)** methyl phenyl ketone, **(c)** *para*-bromobenzoic acid, **(d)** methyl-*trans*-2-butenyl ether, **(e)** *N*, *N*-dimethylbenzamide.

25.53 Draw the structure for 2-bromo-2-chloro-3-methylpentane, and indicate any chiral carbons in the molecule.

25.54 Does 3-chloro-3-methylhexane have optical isomers? Why or why not?

Proteins

25.55 **(a)** What is an α-amino acid? **(b)** How do amino acids react to form proteins? **(c)** Draw the bond that links amino acids together in proteins. What is this called?

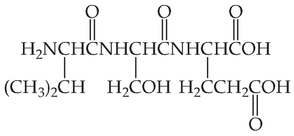
25.56 What properties of the side chains (R groups) of amino acids are important in affecting the amino acid's overall biochemical behavior? Give examples to illustrate your reply.

25.57 Draw the two possible dipeptides formed by condensation reactions between leucine and tryptophan.

25.58 Write a chemical equation for the formation of methionyl glycine from the constituent amino acids.

25.59 **(a)** Draw the condensed structure of the tripeptide Gly-Gly-His. **(b)** How many different tripeptides can be made from the amino acids glycine and histidine? Give the abbreviations for each of these tripeptides, using the three-letter and one-letter codes for the amino acids.

25.60 **(a)** What amino acids would be obtained by hydrolysis of the following tripeptide?



$$\mathrm{H_2N\underset{(CH_3)_2CH}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}NH\underset{H_2COH}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}NH\underset{H_2CCH_2\underset{O}{\underset{\|}{C}}OH}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}OH}$$

(b) How many different tripeptides can be made from the amino acids glycine, serine, and glutamic acid? Give the abbreviation for each of these tripeptides, using the three-letter codes and one-letter codes for the amino acids.

[25.61] **(a)** Describe the primary, secondary, and tertiary structures of proteins. **(b)** *Quaternary structures* of proteins arise if two or more smaller polypeptides or proteins associate with each other to make an overall much larger protein structure. The association is due to the same hydrogen bonding, electrostatic, and dispersion forces we have seen before. Hemoglobin, the protein used to transport oxygen molecules in our blood, is an example of a protein that has quaternary structure. Hemoglobin is a tetramer; it is made of four smaller polypeptides, two "alphas" and two "betas." (These names do not imply anything about the number of alpha helices or beta sheets in the individual polypeptides.) What kind of experiments would provide sound evidence that hemoglobin exists as a tetramer and not as one enormous polypeptide chain? You may need to look into the chemical literature to discover techniques that chemists and biochemists use to make these decisions.

25.62 What is the difference between the α helix and β sheet secondary structures in proteins?

Carbohydrates and Lipids

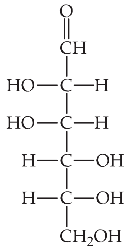
25.63 In your own words, define the following terms: **(a)** carbohydrate, **(b)** monosaccharide, **(c)** disaccharide, **(d)** polysaccharide.

25.64 What is the difference between α-glucose and β-glucose? Show the condensation of two glucose molecules to form a disaccharide with an α linkage; with a β linkage.

25.65 What is the empirical formula of cellulose? What is the unit that forms the basis of the cellulose polymer? What form of linkage joins these monomeric units?

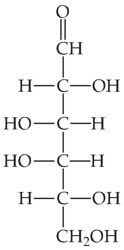
25.66 What is the empirical formula of glycogen? What is the unit that forms the basis of the glycogen polymer? What form of linkage joins these monomeric units?

25.67 The structural formula for the linear form of D-mannose is:



(a) How many chiral carbons are present in the molecule? **(b)** Draw the structure of the six-member-ring form of this sugar.

25.68 The structural formula for the linear form of galactose is:



(a) How many chiral carbons are present in the molecule? **(b)** Draw the structure of the six-member-ring form of this sugar.

25.69 Describe the chemical structures of lipids and phospholipids. Why can phospholipids form a bilayer in water?

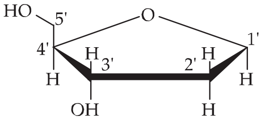
25.70 Using data from Table 8.4 on bond energies, show that the more C—H bonds a molecule has compared to C—O and O—H bonds, the more energy it can store.

Nucleic Acids

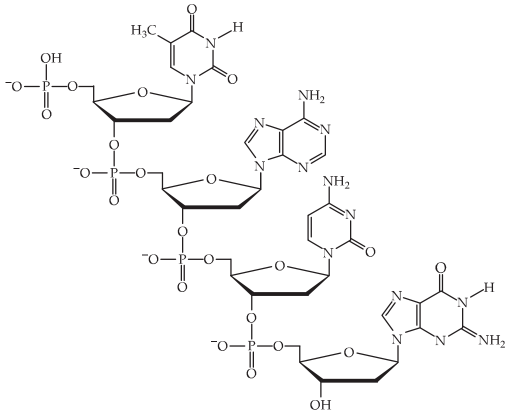
25.71 Adenine and guanine are members of a class of molecules known as *purines*; they have two rings in their structure. Thymine and cytosine, on the other hand, are *pyrimidines*, and have only one ring in their structure. Predict which have larger dispersion forces in aqueous solution, the purines or the pyrimidines.

25.72 A nucleoside consists of an organic base of the kind shown in Section 25.10, bound to ribose or deoxyribose. Draw the structure for deoxyguanosine, formed from guanine and deoxyribose.

25.73 Just as the amino acids in a protein are listed in the order from the amine end to the carboxylic acid end (the *protein sequence*), the bases in nucleic acids are listed in the order 5′ to 3′, where the numbers refer to the position of the carbons in the sugars (shown here for deoxyribose):



The base is attached to the sugar at the 1′ carbon. The 5′ end of a DNA sequence is a phosphate of an OH group, and the 3′ end of a DNA sequence is the OH group. What is the DNA sequence for the molecule shown here?



25.74 When samples of double-stranded DNA are analyzed, the quantity of adenine present equals that of thymine. Similarly, the quantity of guanine equals that of cytosine. Explain the significance of these observations.

25.75 Imagine a single DNA strand containing a section with the following base sequence: 5′-GCATTGGC-3′. What is the base sequence of the complementary strand? (The two strands of DNA will come together in an *antiparallel* fashion: that is, 5′-TAG-3′ will bind to 3′-ATC-5′.)

25.76 Explain the chemical differences between DNA and RNA.

ADDITIONAL EXERCISES

25.77 Draw the condensed structural formulas for two different molecules with the formula C_3H_4O.

25.78 How many structural isomers are there for a five-member straight carbon chain with one double bond? For a six-member straight carbon chain with two double bonds?

25.79 There are no known stable cyclic compounds with ring sizes of seven or less that have an alkyne linkage in the ring. Why is this? Could a ring with a larger number of carbon atoms accommodate an alkyne linkage? Explain.

25.80 Draw the condensed structural formulas for the cis and trans isomers of 2-pentene. Can cyclopentene exhibit cis-trans isomerism? Explain.

25.81 Although there are silicon analogs of alkanes, silicon analogs of alkenes or alkynes are virtually unknown. Suggest an explanation.

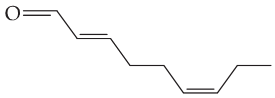
25.82 If a molecule is an "ene-one," what functional groups must it have?

25.83 Write the structural formulas for as many alcohols as you can think of that have empirical formula C_3H_6O.

[25.84] Dinitromethane, $CH_2(NO_2)_2$, is a dangerously reactive substance that decomposes readily on warming. On the other hand, dichloromethane is relatively unreactive. Why is the nitro compound so reactive compared to the chloro compound? (*Hint:* Consider the oxidation numbers of the atoms involved and the possible products of decomposition.)

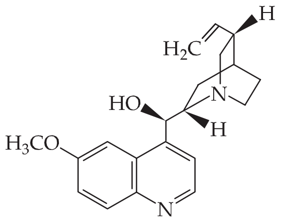
25.85 Identify each of the functional groups in the following molecules:

(a)



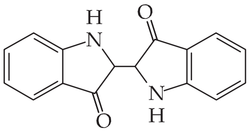
(Responsible for the odor of cucumbers)

(b)



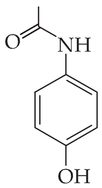
(Quinine – an antimalarial drug)

(c)



(Indigo – a blue dye)

(d)

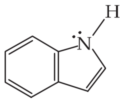


(Acetaminophen – aka Tylenol)

25.86 Write a condensed structural formula for each of the following: **(a)** an acid with the formula $C_4H_8O_2$, **(b)** a cyclic ketone with the formula C_5H_8O, **(c)** a dihydroxy compound with formula $C_3H_8O_2$, **(d)** a cyclic ester with formula $C_5H_8O_2$.

25.87 Although carboxylic acids and alcohols both contain an —OH group, one is acidic in water and the other is not. Explain the difference.

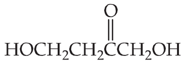
[25.88] Indole smells rather terrible in high concentrations but has a pleasant floral-like odor when highly diluted. It has the following structure:



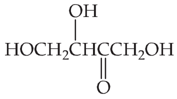
Indole is a planar molecule. The nitrogen is a very weak base, with a K_b of 2×10^{-12}. Explain how this information indicates that the indole molecule is aromatic in character.

25.89 Locate the chiral carbon atoms, if any, in each of the following substances:

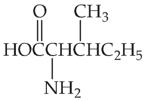
(a)


$\mathrm{HOCH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2OH}$

(b)


$\mathrm{HOCH_2}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{H}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{CH_2OH}$

(c)


$\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\underset{\mathrm{NH_2}}{\underset{|}{\mathrm{C}}}\mathrm{H}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{HC_2H_5}$

25.90 Which of the following peptides have a net positive charge at pH 7? **(a)** Gly-Ser-Lys, **(b)** Pro-Leu-Ile, **(c)** Phe-Tyr-Asp.

25.91 Glutathione is a tripeptide found in most living cells. Partial hydrolysis yields Cys-Gly and Glu-Cys. What structures are possible for glutathione?

25.92 Starch, glycogen, and cellulose are all polymers of glucose. What are the structural differences among them?

25.93 Monosaccharides can be categorized in terms of the number of carbon atoms (pentoses have five carbons and hexoses have six carbons) and according to whether they contain an aldehyde (*aldo-* prefix, as in aldopentose) or ketone group (*keto-* prefix, as in ketopentose). Classify glucose and fructose in this way.

25.94 Can a DNA strand bind to a complementary RNA strand? Explain.

INTEGRATIVE EXERCISES

25.95 Explain why the boiling point of ethanol (78 °C) is much higher than that of its isomer, dimethyl ether (−25 °C) and why the boiling point of CH_2F_2 (−52 °C) is far above that of CH_4 (−128 °C).

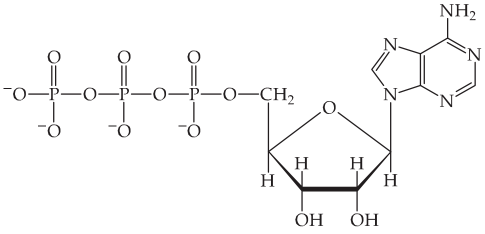
[25.96] An unknown organic compound is found on elemental analysis to contain 68.1% carbon, 13.7% hydrogen, and 18.2% oxygen by mass. It is slightly soluble in water. Upon careful oxidation it is converted into a compound that behaves chemically like a ketone and contains 69.7% carbon, 11.7% hydrogen, and 18.6% oxygen by mass. Indicate two or more reasonable structures for the unknown.

25.97 An organic compound is analyzed and found to contain 66.7% carbon, 11.2% hydrogen, and 22.1% oxygen by mass. The compound boils at 79.6 °C. At 100 °C and 0.970 atm, the vapor has a density of 2.28 g/L. The compound has a carbonyl group and cannot be oxidized to a carboxylic acid. Suggest a structure for the compound.

[25.98] An unknown substance is found to contain only carbon and hydrogen. It is a liquid that boils at 49 °C at 1 atm pressure. Upon analysis it is found to contain 85.7% carbon and 14.3% hydrogen by mass. At 100 °C and 735 torr, the vapor of this unknown has a density of 2.21 g/L. When it is dissolved in hexane solution and bromine water is added, no reaction occurs. What is the identity of the unknown compound?

25.99 The standard free energy of formation of solid glycine is −369 kJ/mol, whereas that of solid glycylglycine is −488 kJ/mol. What is $\Delta G°$ for the condensation of glycine to form glycylglycine?

25.100 One of the most important molecules in biochemical systems is adenosine triphosphate (ATP), for which the structure is

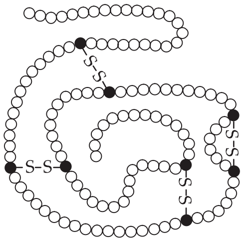


ATP

ATP is the principal carrier of biochemical energy. It is considered an energy-rich compound because the hydrolysis of ATP to yield adenosine diphosphate (ADP) and inorganic phosphate is spontaneous under aqueous biochemical conditions. **(a)** Write a balanced equation for the reaction of ATP with water to yield ADP and inorganic phosphate ion. [*Hint:* Hydrolysis reactions are just the reverse of condensation reactions (Section 22.8).] **(b)** What would you expect for the sign of the free-energy change for this reaction? **(c)** ADP can undergo further hydrolysis. What would you expect for the product of that reaction?

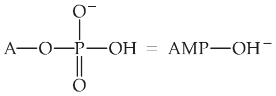
25.101 A typical amino acid with one amino group and one carboxylic acid group, such as serine (Figure 25.23), can exist in water in several ionic forms. **(a)** Suggest the forms of the amino acid at low pH and at high pH. **(b)** Amino acids generally have two pK_a values, one in the range of 2 to 3 and the other in the range of 9 to 10. Serine, for example, has pK_a values of 2.19 and 9.21. Using species such as acetic acid and ammonia as models, suggest the origin of the two pK_a values. **(c)** Glutamic acid is an amino acid that has three pK_a's: 2.10, 4.07, and 9.47. Draw the structure of glutamic acid, and assign each pK_a to the appropriate part of the molecule.

[25.102] The protein ribonuclease A in its native, or most stable, form is folded into a compact globular shape. **(a)** Does the native form have a lower or higher free energy than the denatured form, in which the protein is an extended chain? **(b)** What is the sign of the entropy change in going from the denatured to the folded form? **(c)** In the folded form the ribonuclease A has four —S—S— bonds that bridge between parts of the chain, as shown in the accompanying figure. What effect do you predict that these four linkages have on the free energy and entropy of the folded form as compared with a hypothetical folded structure that does not possess the four —S—S— linkages? Explain. **(d)** A gentle reducing agent converts the four —S—S— linkages to eight —S—H bonds. What effect do you predict this would have on the tertiary structure and entropy of the protein? **(e)** Which amino acid must be present for —SH bonds to exist in ribonuclease A?



Native ribonuclease A

25.103 The monoanion of adenosine monophosphate (AMP) is an intermediate in phosphate metabolism:



$$\text{A—O—}\overset{\displaystyle O^-}{\underset{\displaystyle \overset{\|}{O}}{\overset{|}{P}}}\text{—OH} = \text{AMP—OH}^-$$

where A = adenosine. If the pK_a for this anion is 7.21, what is the ratio of [AMP—OH$^-$] to [AMP—O^{2-}] in blood at pH 7.4?