

22 Organic and Biological Molecules

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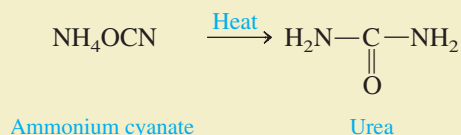
Polarized light micrograph of crystals of phenylalanine, one of the essential amino acids that the body cannot synthesize.



Two Group 4A elements, carbon and silicon, form the basis of most natural substances. Silicon, with its great affinity for oxygen, forms chains and rings containing Si—O—Si bridges to produce the silica and silicates that form the basis for most rocks, sands, and soils. What silicon is to the geological world, carbon is to the biological world. Carbon has the unusual ability of bonding strongly to itself to form long chains or rings of carbon atoms. In addition, carbon forms strong bonds to other nonmetals such as hydrogen, nitrogen, oxygen, sulfur, and the halogens. Because of these bonding properties, there are a myriad of carbon compounds; several million are now known, and the number continues to grow rapidly. Among these many compounds are the **biomolecules**, those responsible for maintaining and reproducing life.

The study of carbon-containing compounds and their properties is called **organic chemistry**. Although a few compounds involving carbon, such as its oxides and carbonates, are considered to be inorganic substances, the vast majority are organic compounds that typically contain chains or rings of carbon atoms.

Originally, the distinction between inorganic and organic substances was based on whether a compound was produced by living systems. For example, until the early nineteenth century it was believed that organic compounds had some sort of “life force” and could be synthesized only by living organisms. This view was dispelled in 1828 when the German chemist Friedrich Wöhler (1800–1882) prepared urea from the inorganic salt ammonium cyanate by simple heating:



Urea is a component of urine, so it is clearly an organic material; yet here was clear evidence that it could be produced in the laboratory as well as by living things.

Organic chemistry plays a vital role in our quest to understand living systems. Beyond that, the synthetic fibers, plastics, artificial sweeteners, and drugs that are such an accepted part of modern life are products of industrial organic chemistry. In addition, the energy on which we rely so heavily to power our civilization is based mostly on the organic materials found in coal and petroleum.

Because organic chemistry is such a vast subject, we can provide only a brief introduction to it in this book. We will begin with the simplest class of organic compounds, the hydrocarbons, and then show how most other organic compounds can be considered to be derivatives of hydrocarbons.

22.1 Alkanes: Saturated Hydrocarbons

As the name indicates, **hydrocarbons** are compounds composed of carbon and hydrogen. Those compounds whose carbon–carbon bonds are all single bonds are said to be **saturated**, because each carbon is bound to four atoms, the maximum number. Hydrocarbons containing carbon–carbon multiple bonds are described as being **unsaturated**,

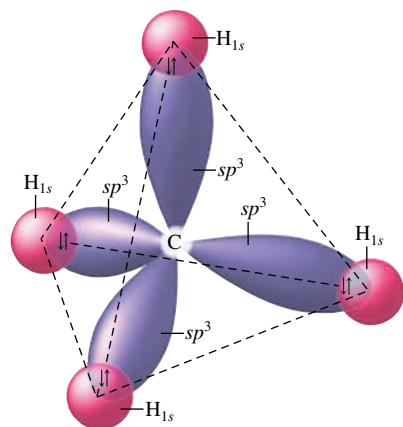
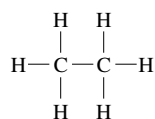
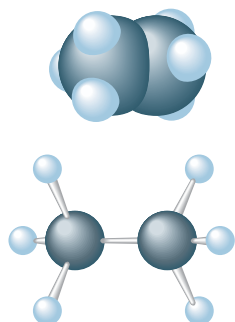


FIGURE 22.1
The C—H bonds in methane.



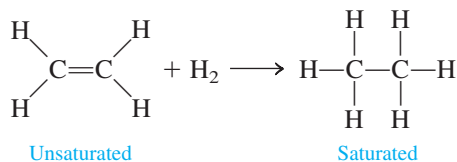
(a)



(b)

FIGURE 22.2
(a) The Lewis structure of ethane (C_2H_6).
(b) The molecular structure of ethane represented by space-filling and ball-and-stick models.

since the carbon atoms involved in a multiple bond can react with additional atoms, as shown by the *addition* of hydrogen to ethylene:

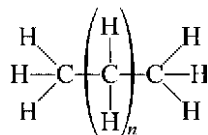


Note that each carbon in ethylene is bonded to three atoms (one carbon and two hydrogens) but that each can bond to one additional atom if one bond of the carbon–carbon double bond is broken.

The simplest member of the saturated hydrocarbons, which are also called the **alkanes**, is *methane* (CH_4). As discussed in Section 9.1, methane has a tetrahedral structure and can be described in terms of a carbon atom using an sp^3 hybrid set of orbitals to bond to the four hydrogen atoms (see Fig. 22.1). The next alkane, the one containing two carbon atoms, is *ethane* (C_2H_6), as shown in Fig. 22.2. Each carbon in ethane is surrounded by four atoms and thus adopts a tetrahedral arrangement and sp^3 hybridization, as predicted by the localized electron model.

The next two members of the series are *propane* (C_3H_8) and *butane* (C_4H_{10}), shown in Fig. 22.3. Again, each carbon is bonded to four atoms and is described as sp^3 hybridized.

Alkanes in which the carbon atoms form long “strings” or chains are called **normal, straight-chain, or unbranched hydrocarbons**. As can be seen from Fig. 22.3, the chains in normal alkanes are not really straight but zig-zag, since the tetrahedral C—C—C angle is 109.5° . The normal alkanes can be represented by the structure



where n is an integer. Note that each member is obtained from the previous one by inserting a *methylene* (CH_2) group. We can condense the structural formulas by omitting some of the C—H bonds. For example, the general formula for normal alkanes shown above can be condensed to



The first ten normal alkanes and some of their properties are listed in Table 22.1. Note that all alkanes can be represented by the general formula $\text{C}_n\text{H}_{2n+2}$. For example, nonane, which has nine carbon atoms, is represented by $\text{C}_9\text{H}_{(2 \times 9) + 2}$, or C_9H_{20} . Also note from Table 22.1 that the melting points and boiling points increase as the molar masses increase, as we would expect.

Isomerism in Alkanes

Butane and all succeeding members of the alkanes exhibit **structural isomerism**. Recall from Section 21.4 that structural isomerism occurs when two molecules have the same atoms

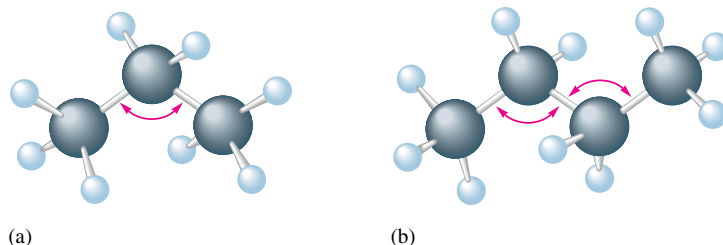


FIGURE 22.3
The structures of (a) propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) and (b) butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$). Each angle shown in red is 109.5° .

TABLE 22.1 Selected Properties of the First Ten Normal Alkanes

Name	Formula	Molar Mass	Melting Point (°C)	Boiling Point (°C)	Number of Structural Isomers
Methane	CH ₄	16	-182	-162	1
Ethane	C ₂ H ₆	30	-183	-89	1
Propane	C ₃ H ₈	44	-187	-42	1
Butane	C ₄ H ₁₀	58	-138	0	2
Pentane	C ₅ H ₁₂	72	-130	36	3
Hexane	C ₆ H ₁₄	86	-95	68	5
Heptane	C ₇ H ₁₆	100	-91	98	9
Octane	C ₈ H ₁₈	114	-57	126	18
Nonane	C ₉ H ₂₀	128	-54	151	35
Decane	C ₁₀ H ₂₂	142	-30	174	75

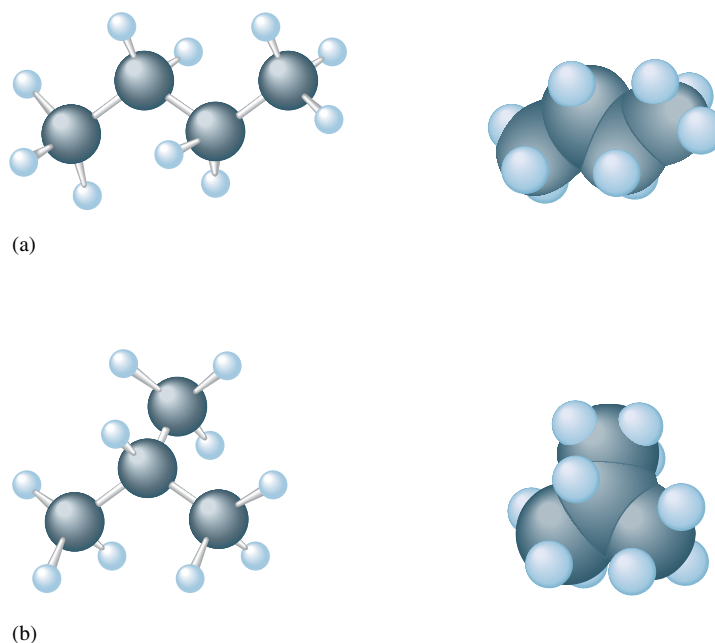


FIGURE 22.4

(a) Normal butane (abbreviated *n*-butane).
 (b) The branched isomer of butane (called isobutane).

but different bonds. For example, butane can exist as a straight-chain molecule (normal butane, or *n*-butane) or with a branched-chain structure (called isobutane), as shown in Fig. 22.4. Because of their different structures, these molecules exhibit different properties. For example, the boiling point of *n*-butane is -0.5°C , whereas that of isobutane is -12°C .

Sample Exercise 22.1

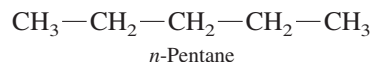
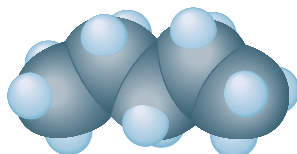
Structural Isomerism

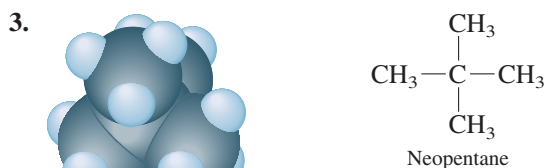
Draw the isomers of pentane.

Solution

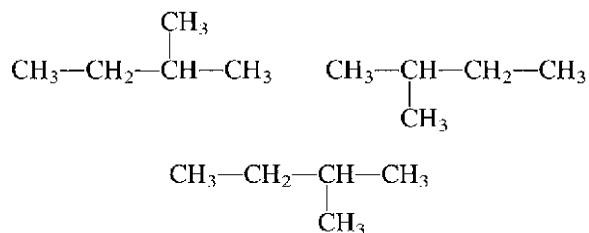
Pentane (C₅H₁₂) has the following isomeric structures:

1.





Note that the structures



which might appear to be other isomers, are actually identical to structure 2.

See Exercise 22.13.

TABLE 22.2 The Most Common Alkyl Substituents and Their Names

Structure*	Name†
$-\text{CH}_3$	Methyl
$-\text{CH}_2\text{CH}_3$	Ethyl
$-\text{CH}_2\text{CH}_2\text{CH}_3$	Propyl
$\begin{array}{c} \\ \text{CH}_3\text{CHCH}_3 \end{array}$	Isopropyl
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Butyl
$\begin{array}{c} \\ \text{CH}_3\text{CHCH}_2\text{CH}_3 \end{array}$	<i>sec</i> -Butyl
$\begin{array}{c} \text{H} \\ \\ -\text{CH}_2-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	Isobutyl
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butyl

*The bond with one end open shows the point of attachment of the substituent to the carbon chain.

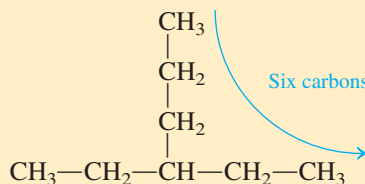
†For the butyl groups, *sec*- indicates attachment to the chain through a secondary carbon, a carbon atom attached to *two* other carbon atoms. The designation *tert*- signifies attachment through a tertiary carbon, a carbon attached to *three* other carbon atoms.

Nomenclature

Because there are literally millions of organic compounds, it would be impossible to remember common names for all of them. We must have a systematic method for naming them. The following rules are used in naming alkanes.

Rules for Naming Alkanes

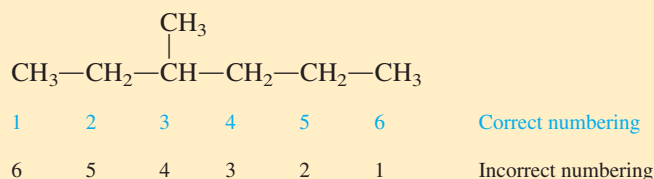
- The names of the alkanes beyond butane are obtained by adding the suffix *-ane* to the Greek root for the number of carbon atoms (*pent*- for five, *hex*- for six, and so on). For a branched hydrocarbon, the longest continuous chain of carbon atoms determines the root name for the hydrocarbon. For example, in the alkane



the longest chain contains six carbon atoms, and this compound is named as a hexane.

- When alkane groups appear as substituents, they are named by dropping the *-ane* and adding *-yl*. For example, $-\text{CH}_3$ is obtained by removing a hydrogen from methane and is called *methyl*, $-\text{C}_2\text{H}_5$ is called *ethyl*, $-\text{C}_3\text{H}_7$ is called *propyl*, and so on. The compound above is therefore an ethylhexane. (See Table 22.2.)

3. The positions of substituent groups are specified by numbering the longest chain of carbon atoms sequentially, starting at the end closest to the branching. For example, the compound



is called 3-methylhexane. Note that the top set of numbers is correct since the left end of the molecule is closest to the branching, and this gives the smallest number for the position of the substituent. Also, note that a hyphen is written between the number and the substituent name.

4. The location and name of each substituent are followed by the root alkane name. The substituents are listed in alphabetical order, and the prefixes *di-*, *tri-*, and so on, are used to indicate multiple, identical substituents.

Sample Exercise 22.2

Isomerism and Nomenclature

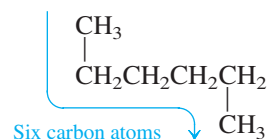
Draw the structural isomers for the alkane C_6H_{14} and give the systematic name for each one.

Solution

We will proceed systematically, starting with the longest chain and then rearranging the carbons to form the shorter, branched chains.

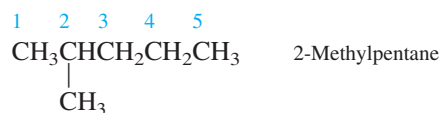
1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ Hexane

Note that although a structure such as



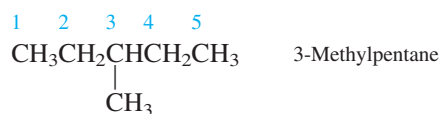
may look different it is still hexane, since the longest carbon chain has six atoms.

2. We now take one carbon out of the chain and make it a methyl substituent.



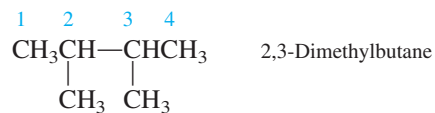
Since the longest chain consists of five carbons, this is a substituted pentane: 2-methylpentane. The 2 indicates the position of the methyl group on the chain. Note that if we numbered the chain from the right end, the methyl group would be on carbon 4. Because we want the smallest possible number, the numbering shown is correct.

3. The methyl substituent can also be on carbon 3 to give



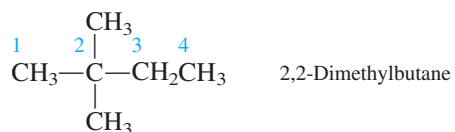
Note that we have now exhausted all possibilities for placing a single methyl group on pentane.

4. Next, we can take two carbons out of the original six-member chain:

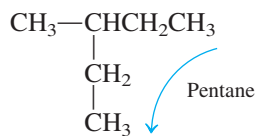


Since the longest chain now has four carbons, the root name is butane. Since there are two methyl groups, we use the prefix *di-*. The numbers denote that the two methyl groups are positioned on the second and third carbons in the butane chain. Note that when two or more numbers are used, they are separated by a comma.

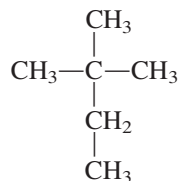
5. The two methyl groups can also be attached to the same carbon atom as shown here:



We might also try ethyl-substituted butanes, such as



However, note that this is instead a pentane (3-methylpentane), since the longest chain has five carbon atoms. Thus it is not a new isomer. Trying to reduce the chain to three atoms provides no further isomers either. For example, the structure



is actually 2,2-dimethylbutane.

Thus there are only five distinct structural isomers of C_6H_{14} : hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane.

See Exercises 22.15 and 22.16.

Sample Exercise 22.3

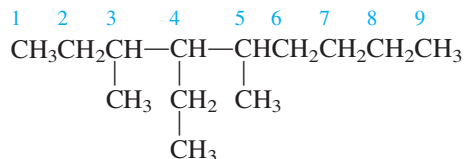
Structures from Names

Determine the structure for each of the following compounds.

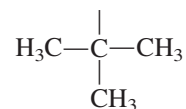
- a. 4-ethyl-3,5-dimethylnonane b. 4-*tert*-butylheptane

Solution

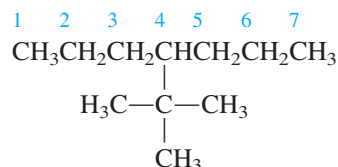
- a. The root name *nonane* signifies a nine-carbon chain. Thus we have



b. Heptane signifies a seven-carbon chain, and the *tert*-butyl group is



Thus we have

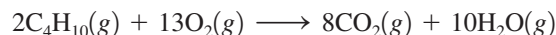


See Exercises 22.19 and 22.20.

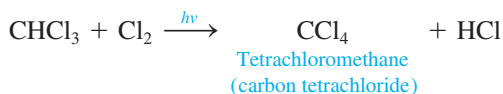
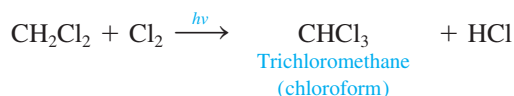
Reactions of Alkanes

Because they are saturated compounds and because the C—C and C—H bonds are relatively strong, the alkanes are fairly unreactive. For example, at 25°C they do not react with acids, bases, or strong oxidizing agents. This chemical inertness makes them valuable as lubricating materials and as the backbone for structural materials such as plastics.

At a sufficiently high temperature alkanes do react vigorously and exothermically with oxygen, and these **combustion reactions** are the basis for their widespread use as fuels. For example, the reaction of butane with oxygen is



The alkanes can also undergo **substitution reactions**, primarily where halogen atoms replace hydrogen atoms. For example, methane can be successively chlorinated as follows:



Note that the products of the last two reactions have two names; the systematic name is given first, followed by the common name in parentheses. (This format will be used throughout this chapter for compounds that have common names.) Also, note that ultraviolet light ($h\nu$) furnishes the energy to break the Cl—Cl bond to produce chlorine atoms:



A chlorine atom has an unpaired electron, as indicated by the dot, which makes it very reactive and able to attack the C—H bond.

Substituted methanes with the general formula $\text{CF}_x\text{Cl}_{4-x}$ containing both chlorine and fluorine as substituents are called chlorofluorocarbons (CFCs) and are also known as *Freons*. These substances are very unreactive and have been extensively used as coolant fluids in refrigerators and air conditioners. Unfortunately, their chemical inertness allows

The $h\nu$ above the arrow represents ultraviolet light.



A butane lighter used for camping.

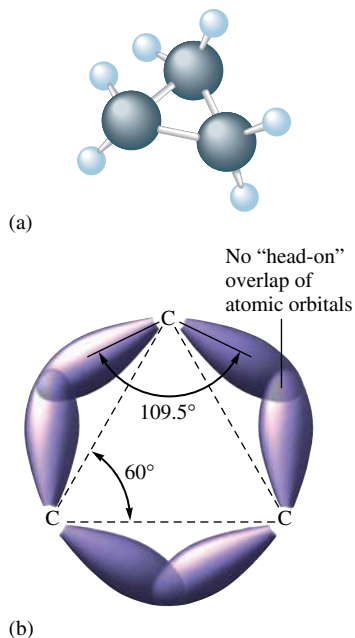
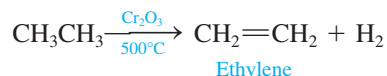


FIGURE 22.5
 (a) The molecular structure of cyclopropane (C_3H_6). (b) The overlap of the sp^3 orbitals that form the C—C bonds in cyclopropane.

Freons to remain in the atmosphere so long that they eventually reach altitudes where they are a threat to the protective ozone layer (see Section 12.8), and the use of these compounds is being rapidly phased out.

Alkanes can also undergo **dehydrogenation reactions** in which hydrogen atoms are removed and the product is an unsaturated hydrocarbon. For example, in the presence of chromium(III) oxide at high temperatures, ethane can be dehydrogenated, yielding ethylene:



Cyclic Alkanes

Besides forming chains, carbon atoms also form rings. The simplest of the **cyclic alkanes** (general formula C_nH_{2n}) is cyclopropane (C_3H_6), shown in Fig. 22.5(a). Since the carbon atoms in cyclopropane form an equilateral triangle with 60° bond angles, their sp^3 hybrid orbitals do not overlap head-on as in normal alkanes [Fig. 22.5(b)]. This results in unusually weak, or *strained*, C—C bonds; thus the cyclopropane molecule is much more reactive than straight-chain propane. The carbon atoms in cyclobutane (C_4H_8) form a square with 88° bond angles, and cyclobutane is also quite reactive.

The next two members of the series, cyclopentane (C_5H_{10}) and cyclohexane (C_6H_{12}), are quite stable, because their rings have bond angles very close to the tetrahedral angles, which allows the sp^3 hybrid orbitals on adjacent carbon atoms to overlap head-on and form normal C—C bonds, which are quite strong. To attain the tetrahedral angles, the cyclohexane ring must “pucker”—that is, become nonplanar. Cyclohexane can exist in two forms, the *chair* and the *boat* forms, as shown in Fig. 22.6. The two hydrogen atoms above the ring in the boat form are quite close to each other, and the resulting repulsion between these atoms causes the chair form to be preferred. At $25^\circ C$ more than 99% of cyclohexane exists in the chair form.

For simplicity, the cyclic alkanes are often represented by the following structures:



Thus the structure



represents methylcyclopropane.

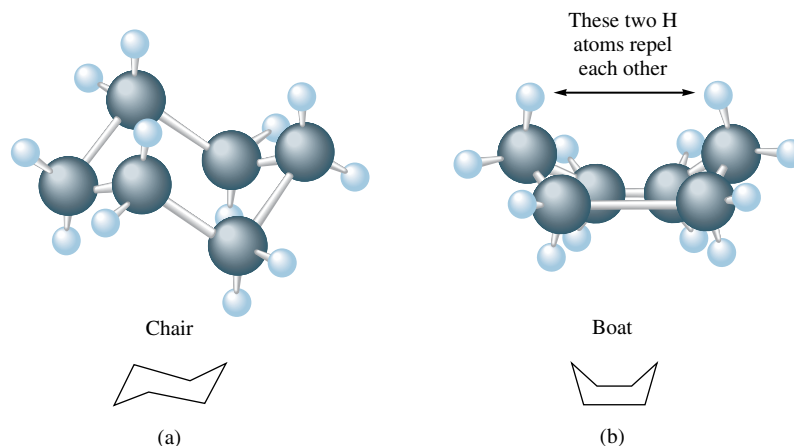


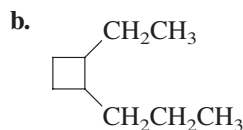
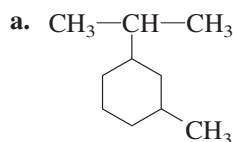
FIGURE 22.6
 The (a) chair and (b) boat forms of cyclohexane.

The nomenclature for cycloalkanes follows the same rules as for the other alkanes except that the root name is preceded by the prefix *cyclo-*. The ring is numbered to yield the smallest substituent numbers possible.

Sample Exercise 22.4

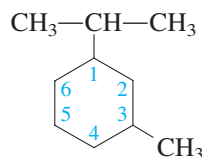
Naming Cyclic Alkanes

Name each of the following cyclic alkanes.



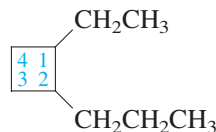
Solution

a. The six-carbon cyclohexane ring is numbered as follows:



There is an isopropyl group at carbon 1 and a methyl group at carbon 3. The name is 1-isopropyl-3-methylcyclohexane, since the alkyl groups are named in alphabetical order.

b. This is a cyclobutane ring, which is numbered as follows:

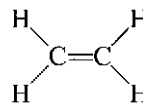


The name is 1-ethyl-2-propylcyclobutane.

See Exercise 22.22.

22.2 Alkenes and Alkynes

Multiple carbon–carbon bonds result when hydrogen atoms are removed from alkanes. Hydrocarbons that contain at least one carbon–carbon double bond are called **alkenes** and have the general formula C_nH_{2n} . The simplest alkene (C_2H_4), commonly known as *ethylene*, has the Lewis structure



As discussed in Section 9.1, each carbon in ethylene can be described as sp^2 hybridized. The C–C σ bond is formed by sharing an electron pair between sp^2 orbitals, and the π bond is formed by sharing a pair of electrons between p orbitals (Fig. 22.7).

The systematic nomenclature for alkenes is quite similar to that for alkanes.

1. The root hydrocarbon name ends in *-ene* rather than *-ane*. Thus the systematic name for C_2H_4 is *ethene* and the name for C_3H_6 is *propene*.
2. In alkenes containing more than three carbon atoms, the location of the double bond is indicated by the lowest-numbered carbon atom involved in the bond. Thus $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ is called 1-butene, and $\text{CH}_3\text{CH}=\text{CHCH}_3$ is called 2-butene.

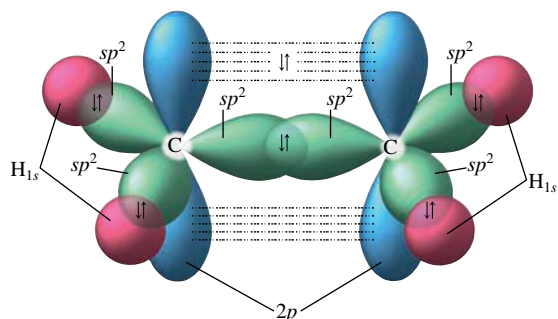


FIGURE 22.7
The bonding in ethylene.

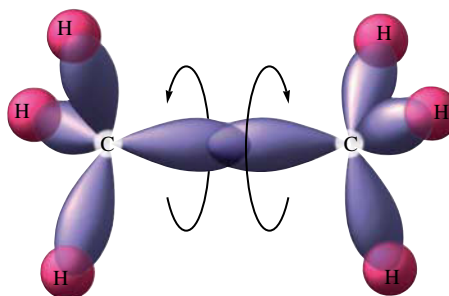


FIGURE 22.8
The bonding in ethane.

Note from Fig. 22.7 that the p orbitals on the two carbon atoms in ethylene must be lined up (parallel) to allow formation of the π bond. This prevents rotation of the two CH_2 groups relative to each other at ordinary temperatures, in contrast to alkanes, where free rotation is possible (see Fig. 22.8). The restricted rotation around doubly bonded carbon atoms means that alkenes exhibit ***cis-trans* isomerism**. For example, there are two stereoisomers of 2-butene (Fig. 22.9). Identical substituents on the same side of the double bond are designated *cis* and those on opposite sides are labeled *trans*.

Alkynes are unsaturated hydrocarbons containing at least one triple carbon-carbon bond. The simplest alkyne is C_2H_2 (commonly called *acetylene*), which has the systematic name *ethyne*. As discussed in Section 9.1, the triple bond in acetylene can be described as one σ bond between two sp hybrid orbitals on the two carbon atoms and two π bonds involving two $2p$ orbitals on each carbon atom (Fig. 22.10).

The nomenclature for alkynes involves the use of *-yne* as a suffix to replace the *-ane* of the parent alkane. Thus the molecule $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_3$ has the name 2-pentyne.

Like alkanes, unsaturated hydrocarbons can exist as ringed structures, for example,

For cyclic alkenes, number through the double bond toward the substituent.

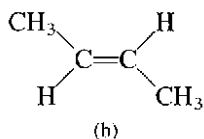
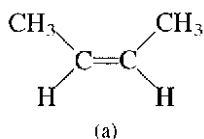


FIGURE 22.9
The two stereoisomers of 2-butene: (a) *cis*-2-butene and (b) *trans*-2-butene.

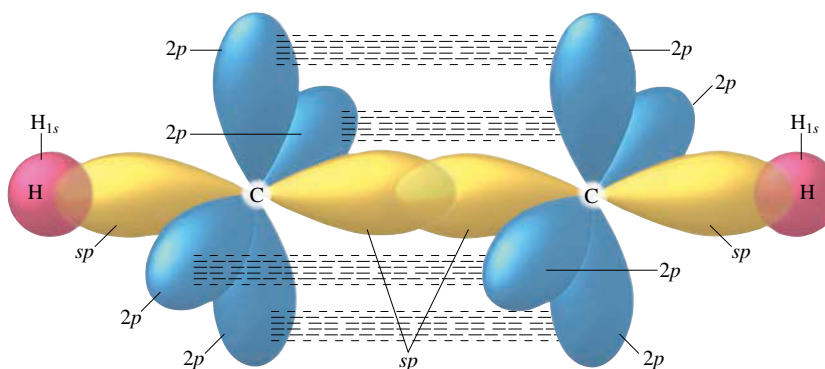
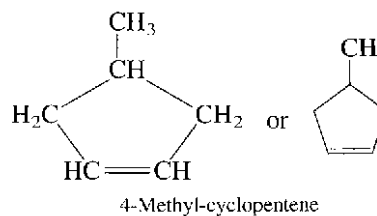
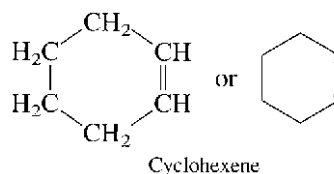
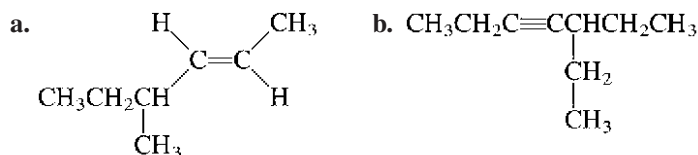


FIGURE 22.10
The bonding in acetylene.

Sample Exercise 22.5

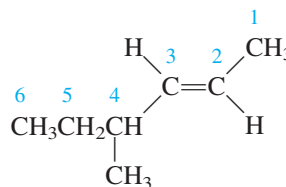
Naming Alkenes and Alkynes

Name each of the following molecules.



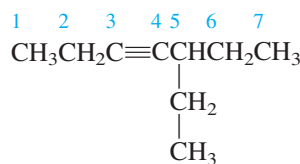
Solution

a. The longest chain, which contains six carbon atoms, is numbered as follows:



Thus the hydrocarbon is a 2-hexene. Since the hydrogen atoms are located on opposite sides of the double bond, this molecule corresponds to the *trans* isomer. The name is 4-methyl-*trans*-2-hexene.

b. The longest chain, consisting of seven carbon atoms, is numbered as shown (giving the triple bond the lowest possible number):

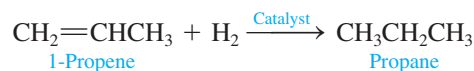


The hydrocarbon is a 3-heptyne. The full name is 5-ethyl-3-heptyne, where the position of the triple bond is indicated by the lower-numbered carbon atom involved in this bond.

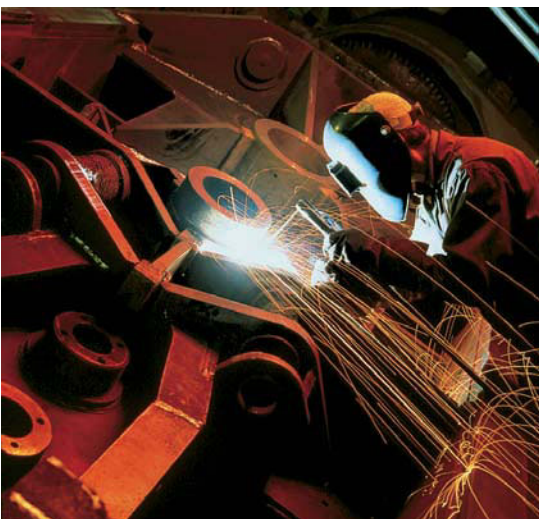
See Exercises 22.25 through 22.28 and 22.44.

Reactions of Alkenes and Alkynes

Because alkenes and alkynes are unsaturated, their most important reactions are **addition reactions**. In these reactions π bonds, which are weaker than the C—C σ bonds, are broken, and new σ bonds are formed to the atoms being added. For example, **hydrogenation reactions** involve the addition of hydrogen atoms:

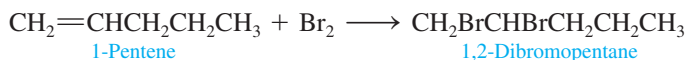


For this reaction to proceed rapidly at normal temperatures, a catalyst of platinum, palladium, or nickel is used. The catalyst serves to help break the relatively strong H—H bond, as was discussed in Section 12.8. Hydrogenation of alkenes is an important industrial process, particularly in the manufacture of solid shortenings where unsaturated fats (fats containing double bonds), which are generally liquid, are converted to solid saturated fats.



A worker using an oxyacetylene torch.

Halogenation of unsaturated hydrocarbons involves addition of halogen atoms. For example,

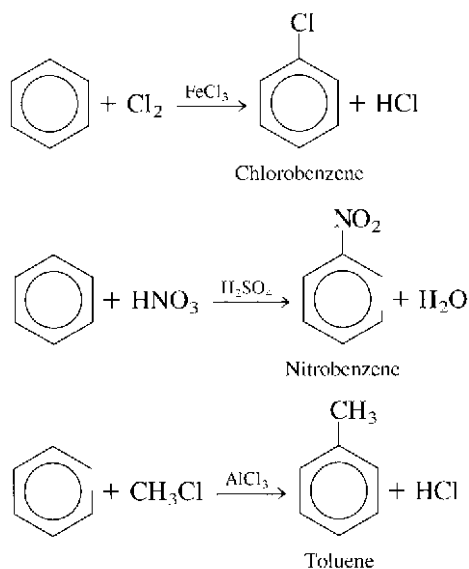


Another important reaction involving certain unsaturated hydrocarbons is **polymerization**, a process in which many small molecules are joined together to form a large molecule. Polymerization will be discussed in Section 22.5.

22.3 Aromatic Hydrocarbons

A special class of cyclic unsaturated hydrocarbons is known as the **aromatic hydrocarbons**. The simplest of these is benzene (C_6H_6), which has a planar ring structure, as shown in Fig. 22.11(a). In the localized electron model of the bonding in benzene, resonance structures of the type shown in Fig. 22.11(b) are used to account for the known equivalence of all the carbon-carbon bonds. But as we discussed in Section 9.5, the best description of the benzene molecule assumes that sp^2 hybrid orbitals on each carbon are used to form the C—C and C—H σ bonds, while the remaining $2p$ orbital on each carbon is used to form π molecular orbitals. The delocalization of these π electrons is usually indicated by a circle inside the ring [Fig. 22.11(c)].

The delocalization of the π electrons makes the benzene ring behave quite differently from a typical unsaturated hydrocarbon. As we have seen previously, unsaturated hydrocarbons generally undergo rapid addition reactions. However, benzene does not. Instead, it undergoes substitution reactions in which *hydrogen atoms are replaced by other atoms*. For example,

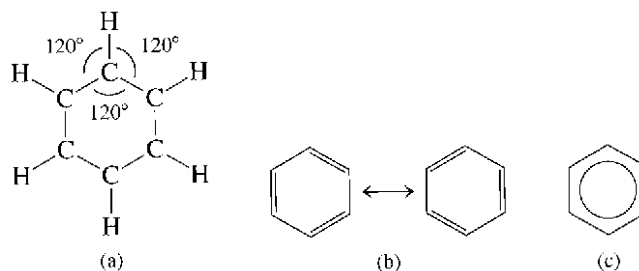


In each case the substance shown over the arrow is needed to catalyze these substitution reactions.

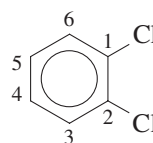
Substitution reactions are characteristic of saturated hydrocarbons, and addition reactions are characteristic of unsaturated ones. The fact that benzene reacts more like a saturated hydrocarbon indicates the great stability of the delocalized π electron system.

FIGURE 22.11

(a) The structure of benzene, a planar ring system in which all bond angles are 120° .
 (b) Two of the resonance structures of benzene.
 (c) The usual representation of benzene. The circle represents the electrons in the delocalized π system. All C—C bonds in benzene are equivalent.



The nomenclature of benzene derivatives is similar to the nomenclature for saturated ring systems. If there is more than one substituent present, numbers are used to indicate substituent positions. For example, the compound



is named 1,2-dichlorobenzene. Another nomenclature system uses the prefix *ortho-* (*o-*) for two adjacent substituents, *meta-* (*m-*) for two substituents with one carbon between them, and *para-* (*p-*) for two substituents opposite each other. When benzene is used as a substituent, it is called the **phenyl group**. Examples of some aromatic compounds are shown in Fig. 22.12.

Benzene is the simplest aromatic molecule. More complex aromatic systems can be viewed as consisting of a number of “fused” benzene rings. Some examples are given in Table 22.3.

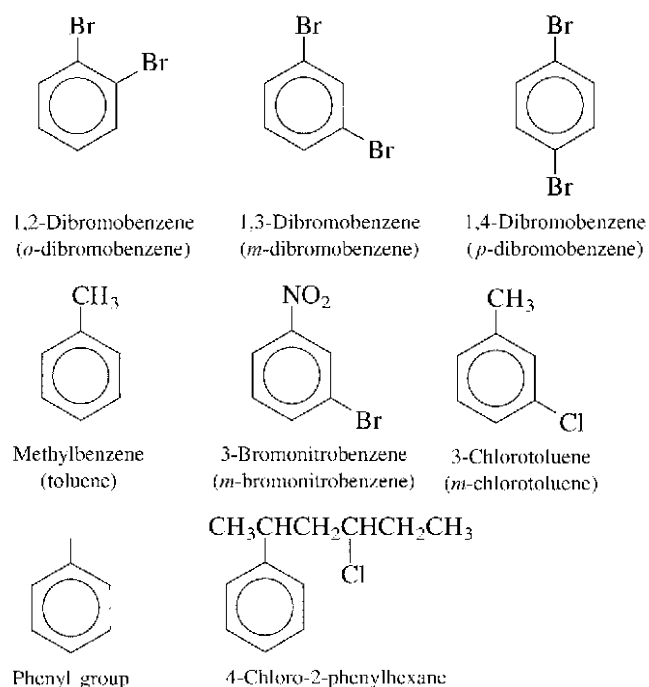
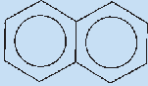

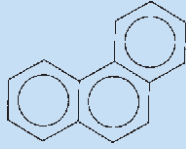
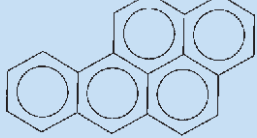


FIGURE 22.12

Some selected substituted benzenes and their names. Common names are given in parentheses.

TABLE 22.3 More Complex Aromatic Systems

Structural Formula	Name	Use of Effect
	Naphthalene	Formerly used in mothballs
	Anthracene	Dyes
	Phenanthrene	Dyes, explosives, and synthesis of drugs
	3,4-Benzpyrene	Active carcinogen found in smoke and smog

22.4 Hydrocarbon Derivatives

The vast majority of organic molecules contain elements in addition to carbon and hydrogen. However, most of these substances can be viewed as **hydrocarbon derivatives**, molecules that are fundamentally hydrocarbons but that have additional atoms or groups of atoms called **functional groups**. The common functional groups are listed in Table 22.4. Because each functional group exhibits characteristic chemistry, we will consider the groups separately.

Alcohols

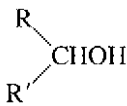
Alcohols are characterized by the presence of the hydroxyl group (—OH). Some common alcohols are shown in Table 22.5. The systematic name for an alcohol is obtained by replacing the final *-e* of the parent hydrocarbon with *-ol*. The position of the —OH group is specified by a number (where necessary) chosen so that it is the smallest of the substituent numbers. Alcohols are classified according to the number of hydrocarbon fragments bonded to the carbon where the —OH group is attached (see margin), where R, R', and R'' (which may be the same or different) represent hydrocarbon fragments.

Alcohols usually have much higher boiling points than might be expected from their molar masses. For example, both methanol and ethane have a molar mass of 30, but the boiling point for methanol is 65°C while that for ethane is -89°C . This difference can be understood if we consider the types of intermolecular attractions that occur in these liquids. Ethane molecules are nonpolar and exhibit only weak London dispersion interactions. However, the polar —OH group of methanol produces extensive hydrogen bonding similar to that found in water (see Section 10.1), which results in the relatively high boiling point.

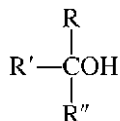
Although there are many important alcohols, the simplest ones, methanol and ethanol, have the greatest commercial value. Methanol, also known as *wood alcohol* because it was formerly obtained by heating wood in the absence of air, is prepared industrially



Primary alcohol
(one R group)



Secondary alcohol
(two R groups)



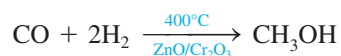
Tertiary alcohol
(three R groups)

TABLE 22.4 The Common Functional Groups

Class	Functional Group	General Formula*	Example
Halohydrocarbons	—X (F, Cl, Br, I)	R—X	CH ₃ I Iodomethane (methyl iodide)
Alcohols	—OH	R—OH	CH ₃ OH Methanol (methyl alcohol)
Ethers	—O—	R—O—R'	CH ₃ OCH ₃ Dimethyl ether
Aldehydes	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	CH ₂ O Methanal (formaldehyde)
Ketones	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}$	CH ₃ COCH ₃ Propanone (dimethyl ketone or acetone)
Carboxylic acids	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$	CH ₃ COOH Ethanoic acid (acetic acid)
Esters	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}- \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}$	CH ₃ COOCH ₂ CH ₃ Ethyl acetate
Amines	—NH ₂	R—NH ₂	CH ₃ NH ₂ Aminomethane (methylamine)

*R and R' represent hydrocarbon fragments.

(approximately 4 million tons annually in the United States) by the hydrogenation of carbon monoxide:



Methanol is used as a starting material for the synthesis of acetic acid and for many types of adhesives, fibers, and plastics. It is also used (and such use may increase) as a motor fuel. Methanol is highly toxic to humans and can lead to blindness and death if ingested.

Ethanol is the alcohol found in beverages such as beer, wine, and whiskey; it is produced by the fermentation of glucose in corn, barley, grapes, and so on:



A winemaker drawing off a glass of wine in a modern wine cellar.

TABLE 22.5 Some Common Alcohols

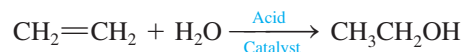
Formula	Systematic Name	Common Name
CH ₃ OH	Methanol	Methyl alcohol
CH ₃ CH ₂ OH	Ethanol	Ethyl alcohol
CH ₃ CH ₂ CH ₂ OH	1-Propanol	<i>n</i> -Propyl alcohol
$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ \\ \text{OH} \end{array}$	2-Propanol	Isopropyl alcohol



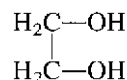
Ethanol is being tested in selected areas as a fuel for automobiles.

The reaction is catalyzed by the enzymes found in yeast. This reaction can proceed only until the alcohol content reaches about 13% (the percentage found in most wines), at which point the yeast can no longer survive. Beverages with higher alcohol content are made by distilling the fermentation mixture.

Ethanol, like methanol, can be burned in the internal combustion engines of automobiles and is now commonly added to gasoline to form gasohol (see Section 6.6). It is also used in industry as a solvent and for the preparation of acetic acid. The commercial production of ethanol (500,000 tons per year in the United States) is carried out by reaction of water with ethylene:

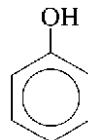


Many polyhydroxyl (more than one —OH group) alcohols are known, the most important being 1,2-ethanediol (ethylene glycol),



a toxic substance that is the major constituent of most automobile antifreeze solutions.

The simplest aromatic alcohol is

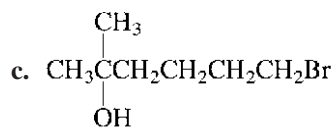
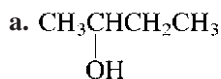


which is commonly called **phenol**. Most of the 1 million tons of phenol produced annually in the United States is used to make polymers for adhesives and plastics.

Sample Exercise 22.6

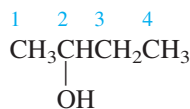
Naming and Classifying Alcohols

For each of the following alcohols, give the systematic name and specify whether the alcohol is primary, secondary, or tertiary.

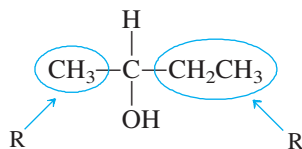


Solution

a. The chain is numbered as follows:

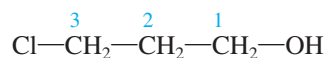


The compound is called 2-butanol, since the —OH group is located at the number 2 position of a four-carbon chain. Note that the carbon to which the —OH is attached also has —CH₃ and —CH₂CH₃ groups attached:

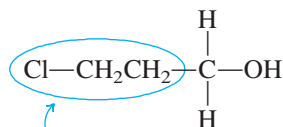


Therefore, this is a *secondary* alcohol.

b. The chain is numbered as follows:

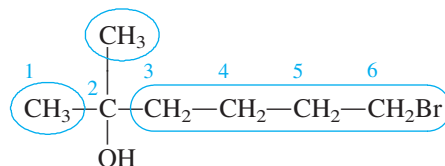


The name is 3-chloro-1-propanol. This is a *primary* alcohol:



One R group attached to the carbon with the —OH group

c. The chain is numbered as follows:



The name is 6-bromo-2-methyl-2-hexanol. This is a *tertiary* alcohol since the carbon where the —OH is attached also has three other R groups attached.

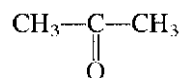
See Exercises 22.51 and 22.52.

Aldehydes and Ketones

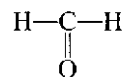
Aldehydes and ketones contain the **carbonyl group**,



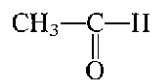
In **ketones** this group is bonded to two carbon atoms, as in acetone,



In **aldehydes** the carbonyl group is bonded to at least one hydrogen atom, as in formaldehyde,



or acetaldehyde,



Cinnamaldehyde produces the characteristic odor of cinnamon.

The systematic name for an aldehyde is obtained from the parent alkane by removing the final *-e* and adding *-al*. For ketones the final *-e* is replaced by *-one*, and a number indicates the position of the carbonyl group where necessary. Examples of common aldehydes and ketones are shown in Fig. 22.13. Note that since the aldehyde functional group always occurs at the end of the carbon chain, the aldehyde carbon is assigned the number 1 when substituent positions are listed in the name.

Ketones often have useful solvent properties (acetone is found in nail polish remover, for example) and are frequently used in industry for this purpose. Aldehydes typically have strong odors. Vanillin is responsible for the pleasant odor in vanilla beans; cinnamaldehyde

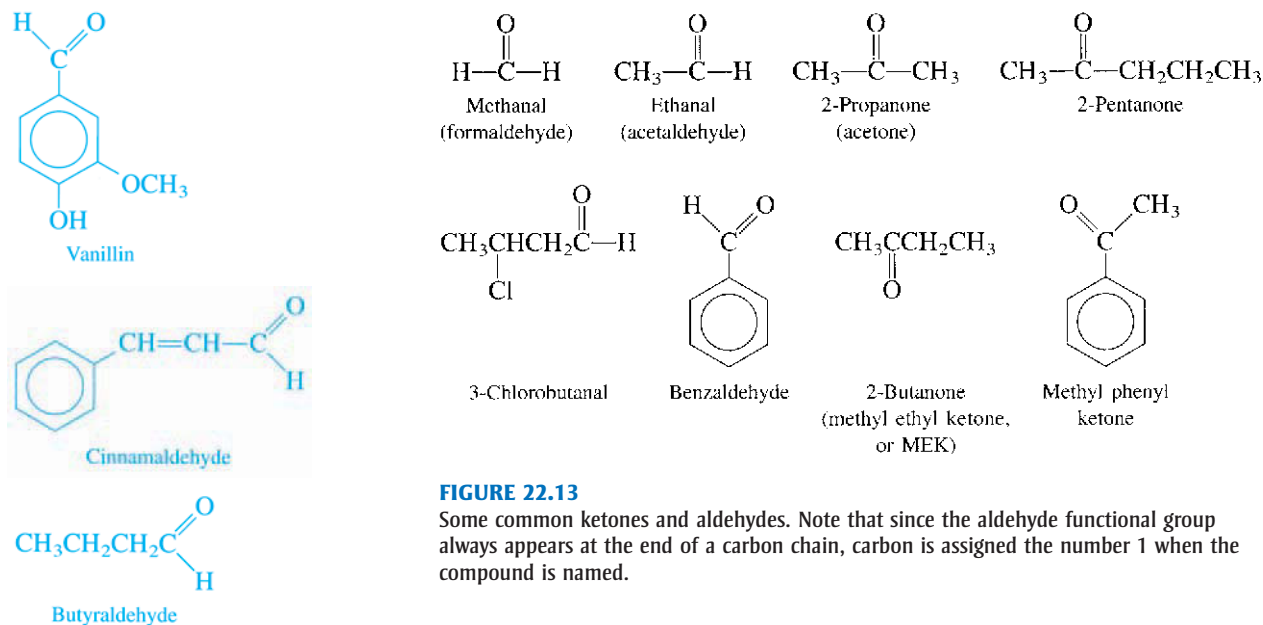


FIGURE 22.13

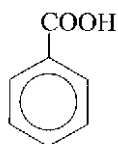
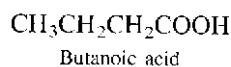
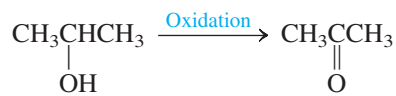
Some common ketones and aldehydes. Note that since the aldehyde functional group always appears at the end of a carbon chain, carbon is assigned the number 1 when the compound is named.

produces the characteristic odor of cinnamon. On the other hand, the unpleasant odor in rancid butter arises from the presence of butyraldehyde.

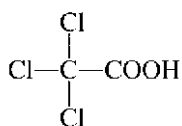
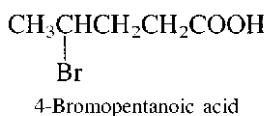
Aldehydes and ketones are most often produced commercially by the oxidation of alcohols. For example, oxidation of a *primary* alcohol yields the corresponding aldehyde:



Oxidation of a *secondary* alcohol results in a ketone:



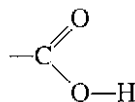
Benzoic acid



Trichloroethanoic acid (trichloroacetic acid)

Carboxylic Acids and Esters

Carboxylic acids are characterized by the presence of the **carboxyl group**



that gives an acid of the general formula RCOOH . Typically, these molecules are weak acids in aqueous solution (see Section 14.5). Organic acids are named from the parent alkane by dropping the final *-e* and adding *-oic*. Thus CH_3COOH , commonly called acetic acid, has the systematic name ethanoic acid, since the parent alkane is ethane. Other examples of carboxylic acids are shown in Fig. 22.14.

Many carboxylic acids are synthesized by oxidizing primary alcohols with a strong oxidizing agent. For example, ethanol can be oxidized to acetic acid by using potassium permanganate:

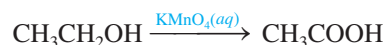
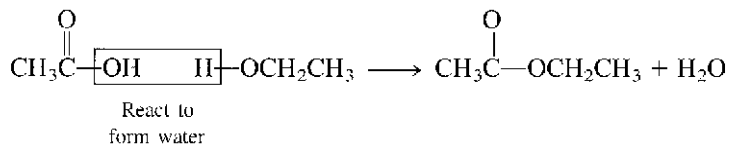


FIGURE 22.14
Some carboxylic acids.

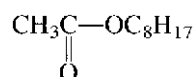
A carboxylic acid reacts with an alcohol to form an **ester** and a water molecule. For example, the reaction of acetic acid with ethanol produces ethyl acetate and water:



Esters often have a sweet, fruity odor that is in contrast to the often pungent odors of the parent carboxylic acids. For example, the odor of bananas is caused by *n*-amyl acetate,

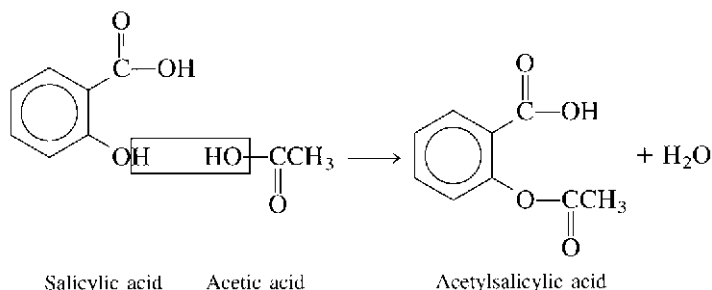


and that of oranges is caused by *n*-octyl acetate,



The systematic name for an ester is formed by changing the *-oic* ending of the parent acid to *-oate*. The parent alcohol chain is named first with a *-yl* ending. For example, the systematic name for *n*-octyl acetate is *n*-octylethanoate (from ethanoic acid).

A very important ester is formed from the reaction of salicylic acid and acetic acid:

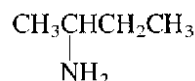


The product is acetylsalicylic acid, commonly known as *aspirin*, which is used in huge quantities as an analgesic (painkiller).

Amines

Amines are probably best viewed as derivatives of ammonia in which one or more N—H bonds are replaced by N—C bonds. The resulting amines are classified as *primary* if one N—C bond is present, *secondary* if two N—C bonds are present, and *tertiary* if all three N—H bonds in NH_3 have been replaced by N—C bonds (Fig. 22.15). Examples of some common amines are given in Table 22.6.

Common names are often used for simple amines; the systematic nomenclature for more complex molecules uses the name *amino-* for the —NH_2 functional group. For example, the molecule



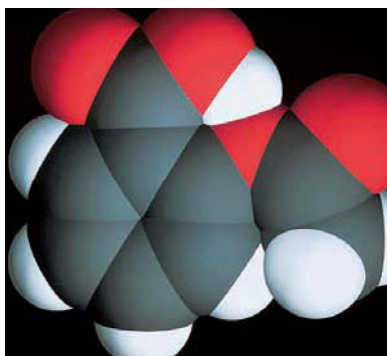
is named 2-aminobutane.

Many amines have unpleasant “fishlike” odors. For example, the odors associated with decaying animal and human tissues are caused by amines such as putrescine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) and cadaverine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$).

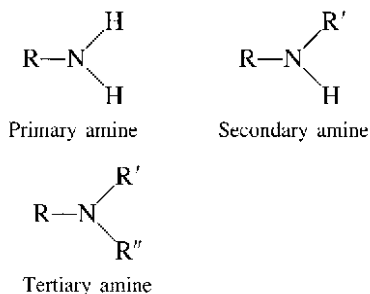
Aromatic amines are primarily used to make dyes. Since many of them are carcinogenic, they must be handled with great care.



Aspirin tablets.

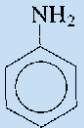
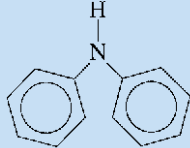


Computer-generated space-filling model of acetylsalicylic acid (aspirin).

**FIGURE 22.15**

The general formulas for primary, secondary, and tertiary amines. R, R', and R'' represent carbon-containing substituents.

TABLE 22.6 Some Common Amines

Formula	Common Name	Type
CH_3NH_2	Methylamine	Primary
$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethylamine	Primary
$(\text{CH}_3)_2\text{NH}$	Dimethylamine	Secondary
$(\text{CH}_3)_3\text{N}$	Trimethylamine	Tertiary
	Aniline	Primary
	Diphenylamine	Secondary

22.5 Polymers

Polymers are large, usually chainlike molecules that are built from small molecules called *monomers*. Polymers form the basis for synthetic fibers, rubbers, and plastics and have played a leading role in the revolution that has been brought about in daily life by chemistry. It has been estimated that about 50% of the industrial chemists in the United States work in some area of polymer chemistry, a fact that illustrates just how important polymers are to our economy and standard of living.

The Development and Properties of Polymers

The development of the polymer industry provides a striking example of the importance of serendipity in the progress of science. Many discoveries in polymer chemistry arose from accidental observations that scientists followed up.

The age of plastics might be traced to a day in 1846 when Christian Schoenbein, a chemistry professor at the University of Basel in Switzerland, spilled a flask containing nitric and sulfuric acids. In his hurry to clean up the spill, he grabbed his wife's cotton apron, which he then rinsed out and hung up in front of a hot stove to dry. Instead of drying, the apron flared and burned.

Very interested in this event, Schoenbein repeated the reaction under more controlled conditions and found that the new material, which he correctly concluded to be nitrated cellulose, had some surprising properties. As he had experienced, the nitrated cellulose is extremely flammable and, under certain circumstances, highly explosive. In addition, he found that it could be molded at moderate temperatures to give objects that were, upon cooling, tough but elastic. Predictably, the explosive nature of the substance was initially of more interest than its other properties, and cellulose nitrate rapidly became the basis for smokeless gun powder. Although Schoenbein's discovery cannot be described as a truly synthetic polymer (because he simply found a way to modify the natural polymer cellulose), it formed the basis for a large number of industries that grew up to produce photographic films, artificial fibers, and molded objects of all types.

The first synthetic polymers were produced as by-products of various organic reactions and were regarded as unwanted contaminants. Thus the first preparations of many of the polymers now regarded as essential to our modern lifestyle were thrown away in



The soybeans on the left are coated with a red acrylic polymer to delay soybean emergence. This allows farmers to plant their crops more efficiently.

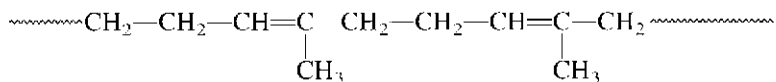
disgust. One chemist who refused to be defeated by the “tarry” products obtained when he reacted phenol with formaldehyde was the Belgian-American chemist Leo H. Baekeland (1863–1944). Baekeland’s work resulted in the first completely synthetic plastic (called Bakelite), a substance that when molded to a certain shape under high pressure and temperature cannot be softened again or dissolved. Bakelite is a **thermoset polymer**. In contrast, cellulose nitrate is a **thermoplastic polymer**; that is, it can be remelted after it has been molded.

The discovery of Bakelite in 1907 spawned a large plastics industry, producing telephones, billiard balls, and insulators for electrical devices. During the early days of polymer chemistry, there was a great deal of controversy over the nature of these materials. Although the German chemist Hermann Staudinger speculated in 1920 that polymers were very large molecules held together by strong chemical bonds, most chemists of the time assumed that these materials were much like colloids, in which small molecules are aggregated into large units by forces weaker than chemical bonds.

One chemist who contributed greatly to the understanding of polymers as giant molecules was Wallace H. Carothers of the DuPont Chemical Company. Among his accomplishments was the preparation of nylon. The nylon story further illustrates the importance of serendipity in scientific research. When nylon is first prepared, the resulting product is a sticky material with little structural integrity. Because of this, it was initially put aside as having no apparently useful characteristics. However, Julian Hill, a chemist in the Carothers research group, one day put a small ball of this nylon on the end of a stirring rod and drew it away from the remaining sticky mass, forming a string. He noticed the silky appearance and strength of this thread and realized that nylon could be drawn into useful fibers.

The reason for this behavior of nylon is now understood. When nylon is first formed, the individual polymer chains are oriented randomly, like cooked spaghetti, and the substance is highly amorphous. However, when drawn out into a thread, the chains tend to line up (the nylon becomes more crystalline), which leads to increased hydrogen bonding between adjacent chains. This increase in crystallinity, along with the resulting increase in hydrogen-bonding interactions, leads to strong fibers and thus to a highly useful material. Commercially, nylon is produced by forcing the raw material through a *spinneret*, a plate containing small holes, which forces the polymer chains to line up.

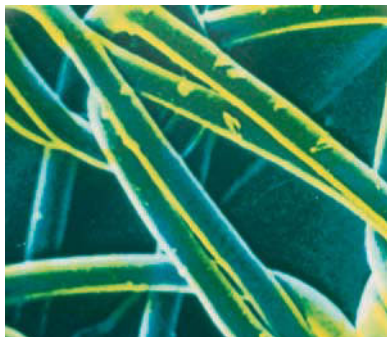
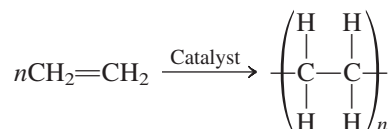
Another property that adds strength to polymers is **crosslinking**, the existence of covalent bonds between adjacent chains. The structure of Bakelite is highly crosslinked, which accounts for the strength and toughness of this polymer. Another example of crosslinking occurs in the manufacture of rubber. Raw natural rubber consists of chains of the type



and is a soft, sticky material unsuitable for tires. However, in 1839 Charles Goodyear (1800–1860), an American chemist, accidentally found that if sulfur is added to rubber and the resulting mixture is heated (a process called **vulcanization**), the resulting rubber is still elastic (reversibly stretchable) but is much stronger. This change in character occurs because sulfur atoms become bonded between carbon atoms on different chains. These sulfur atoms form bridges between the polymer chains, thus linking the chains together.

Types of Polymers

The simplest and one of the best-known polymers is *polyethylene*, which is constructed from ethylene monomers:



Nylon netting magnified 62 times.

Charles Goodyear tried for many years to change natural rubber into a useful product. In 1839 he accidentally dropped some rubber containing sulfur on a hot stove. Noting that the rubber did not melt as expected, Goodyear pursued this lead and developed vulcanization.

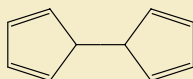


CHEMICAL IMPACT

Heal Thyself

One major problem with structural materials is that they crack and weaken as they age. The human body has mechanisms for healing itself if the skin is cut or a bone is broken. However, inanimate materials have had no such mechanisms—until now. Scientists at the University of Illinois at Urbana–Champaign (UIUC) have invented a plastic that automatically heals microscopic cracks before they can develop into large cracks that would degrade the usefulness of the material. This accomplishment was achieved by an interdisciplinary team of scientists including aeronautical engineering professors Scott White and Philippe Geubelle, applied mechanics professor Nancy Sottos, and chemistry professor Jeffrey Moore.

The self-healing system is based on microcapsules containing liquid dicyclopentadiene



Dicyclopentadiene

that are blended into the plastic. When a microscopic crack develops, it encounters and breaks a microcapsule. The dicyclopentadiene then leaks out, where it encounters a catalyst (blended into the plastic when it was formulated) that mediates a repair polymerization process. This process involves opening the cyclopentadiene rings, which leads to a highly cross-linked repair of the crack.

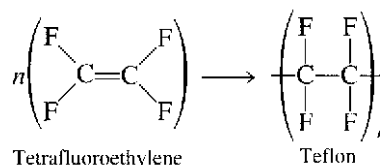
The trickiest part of the repair mechanism is to get the microcapsules to be the correct size and to have the appropriate wall strength. They must be small enough not to degrade the strength of the plastic. The walls must also be thick enough to survive the molding of the plastic but thin enough to burst as the lengthening crack reaches them.

Self-healing materials should have many applications. The U.S. Air Force, which partially funded the research at UIUC, is interested in using the materials in tanks that hold gases and liquids under pressure. The current materials used for these tanks are subject to microcracks that eventually grow, causing the tanks to leak. Self-healing materials would



Cross-linking gives the rubber in these tires strength and toughness.

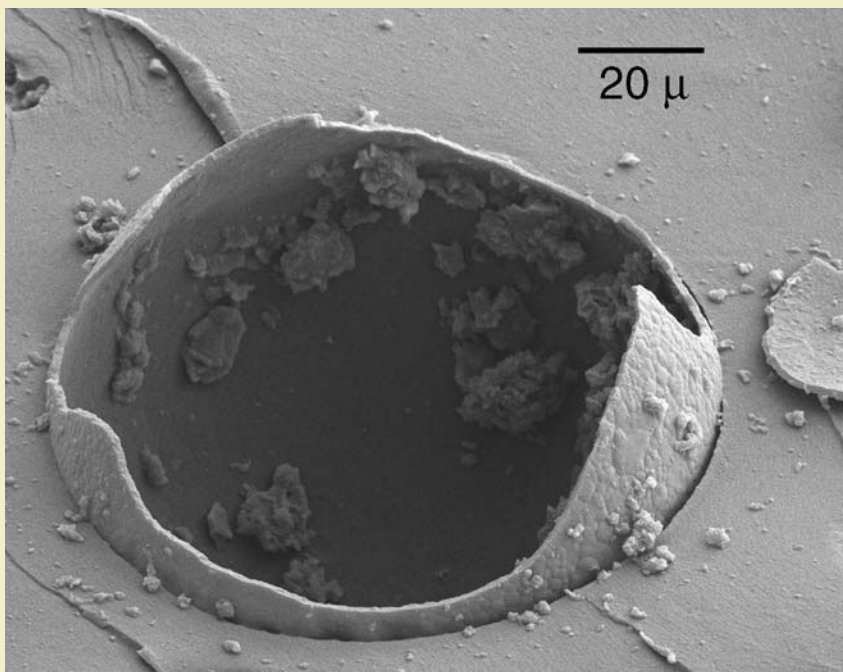
where n represents a large number (usually several thousand). Polyethylene is a tough, flexible plastic used for piping, bottles, electrical insulation, packaging films, garbage bags, and many other purposes. Its properties can be varied by using substituted ethylene monomers. For example, when tetrafluoroethylene is the monomer, the polymer Teflon is obtained:



The discovery of Teflon, a very important substituted polyethylene, is another illustration of the role of chance in chemical research. In 1938 a DuPont chemist named Roy Plunkett was studying the chemistry of gaseous tetrafluoroethylene. He synthesized about 100 pounds of the chemical and stored it in steel cylinders. When one of the cylinders failed to produce perfluoroethylene gas when the valve was opened, the cylinder was cut open to reveal a white powder. This powder turned out to be a polymer of perfluoroethylene, which was eventually developed into Teflon. Because of the resistance of the strong C—F bonds to chemical attack, Teflon is an inert, tough, and nonflammable material widely used for electrical insulation, nonstick coatings on cooking utensils, and bearings for low-temperature applications.

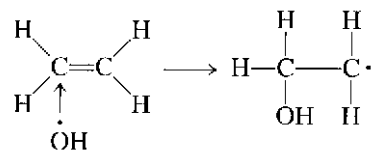
Other polyethylene-type polymers are made from monomers containing chloro, methyl, cyano, and phenyl substituents, as summarized in Table 22.7 on page 1020. In each case the double carbon–carbon bond in the substituted ethylene monomer becomes a single bond in the polymer. The different substituents lead to a wide variety of properties.

also be valuable in situations where repair is impossible or impractical, such as electronic circuit boards, components of deep space probes, and implanted medical devices.

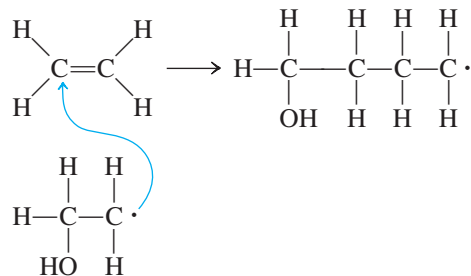


A scanning electron microscope image showing the fractured plane of a self-healing material with a ruptured microcapsule in a thermosetting matrix.

The polyethylene polymers illustrate one of the major types of polymerization reactions, called **addition polymerization**, in which the monomers simply “add together” to produce the polymer. No other products are formed. The polymerization process is initiated by a **free radical** (a species with an unpaired electron) such as the hydroxyl radical ($\text{HO}\cdot$). The free radical attacks and breaks the π bond of an ethylene molecule to form a new free radical,




which is then available to attack another ethylene molecule:



Repetition of this process thousands of times creates a long-chain polymer. Termination of the growth of the chain occurs when *two radicals* react to form a bond, a process that consumes two radicals without producing any others.

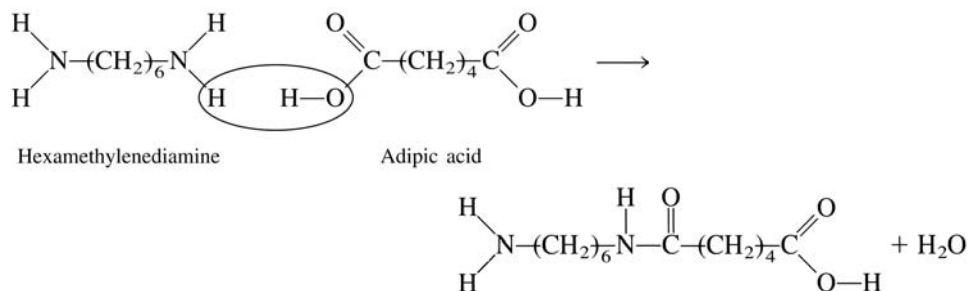
TABLE 22.7 Some Common Synthetic Polymers, Their Monomers and Applications

Monomer		Polymer		
Name	Formula	Name	Formula	Uses
Ethylene	$\text{H}_2\text{C}=\text{CH}_2$	Polyethylene	$-(\text{CH}_2-\text{CH}_2)_n-$	Plastic piping, bottles, electrical insulation, toys
Propylene	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{CH}_3 \end{array}$	Polypropylene	$\begin{array}{c} -(\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2)_n- \\ \qquad \qquad \\ \text{CH}_3 \qquad \qquad \text{CH}_3 \end{array}$	Film for packaging, carpets, lab wares, toys
Vinyl chloride	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{Cl} \end{array}$	Polyvinyl chloride (PVC)	$(\text{CH}_2-\text{CH})_n-$ Cl	Piping, siding, floor tile, clothing, toys
Acrylonitrile	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{CN} \end{array}$	Polyacrylonitrile (PAN)	$-(\text{CH}_2-\text{CH})_n-$ CN	Carpets, fabrics
Tetrafluoroethylene	$\text{F}_2\text{C}=\text{CF}_2$	Teflon	$-(\text{CF}_2-\text{CF}_2)_n-$	Cooking utensils, electrical insulation, bearings
Styrene	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{C}_6\text{H}_5 \end{array}$	Polystyrene	$-(\text{CH}_2\text{CH})_n-$ 	Containers, thermal insulation, toys
Butadiene	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}_2\text{C}=\text{C}-\text{C}=\text{CH}_2 \end{array}$	Polybutadiene	$-(\text{CH}_2\text{CH}=\text{CHCH}_2)_n-$	Tire tread, coating resin
Butadiene and styrene	(See above.)	Styrene-butadiene rubber	$\begin{array}{c} -(\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n- \\ \\ \text{C}_6\text{H}_5 \end{array}$	Synthetic rubber



Visualization: Synthesis of Nylon

Another common type of polymerization is **condensation polymerization**, in which a small molecule, such as water, is formed for each extension of the polymer chain. The most familiar polymer produced by condensation is *nylon*. Nylon is a **copolymer**, since two different types of monomers combine to form the chain; a **homopolymer** is the result of polymerizing a single type of monomer. One common form of nylon is produced when hexamethylenediamine and adipic acid react by splitting out a water molecule to form a C—N bond:



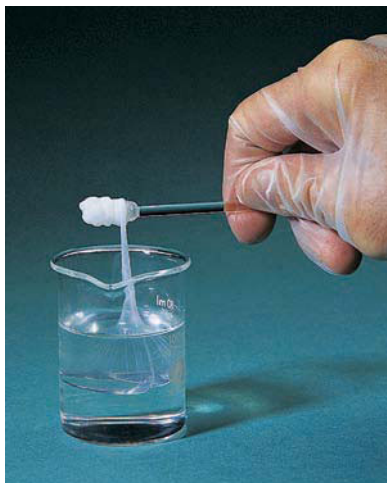
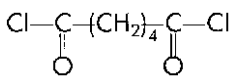


FIGURE 22.16

The reaction to form nylon can be carried out at the interface of two immiscible liquid layers in a beaker. The bottom layer contains adipoyl chloride,

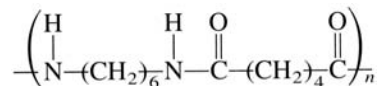


dissolved in CCl_4 , and the top layer contains hexamethylenediamine,



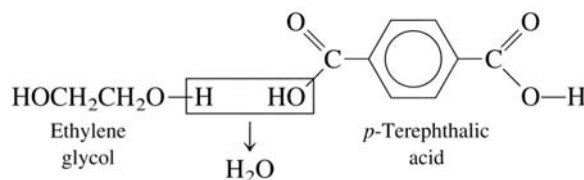
dissolved in water. A molecule of HCl is formed as each $\text{C}-\text{N}$ bond forms.

The molecule formed, called a **dimer** (two monomers joined), can undergo further condensation reactions since it has an amino group at one end and a carboxyl group at the other. Thus both ends are free to react with another monomer. Repetition of this process leads to a long chain of the type

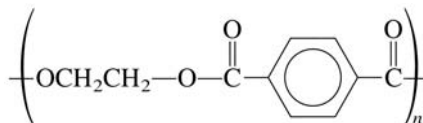


which is the basic structure of nylon. The reaction to form nylon occurs quite readily and is often used as a lecture demonstration (see Fig. 22.16). The properties of nylon can be varied by changing the number of carbon atoms in the chain of the acid or amine monomer.

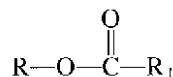
More than 1 million tons of nylon is produced annually in the United States for use in clothing, carpets, rope, and so on. Many other types of condensation polymers are also produced. For example, Dacron is a copolymer formed from the condensation reaction of ethylene glycol (a dialcohol) and *p*-terephthalic acid (a dicarboxylic acid):



The repeating unit of Dacron is



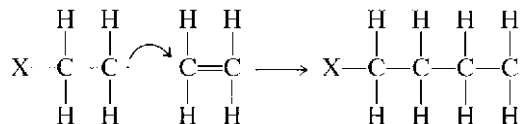
Note that this polymerization involves a carboxylic acid and an alcohol forming an ester group:



Thus Dacron is called a **polyester**. By itself or blended with cotton, Dacron is widely used in fibers for the manufacture of clothing.

Polymers Based on Ethylene

A large section of the polymer industry involves the production of macromolecules from ethylene or substituted ethylenes. As discussed previously, ethylene molecules polymerize by addition after the double bond has been broken by some initiator:



This process continues by adding new ethylene molecules to eventually give polyethylene, a thermoplastic material.

There are two forms of polyethylene: low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The chains in LDPE contain many branches and thus do not pack as tightly as those in HDPE, which consist of mostly straight-chain molecules.

Traditionally, LDPE has been manufactured under conditions of high pressure ($\approx 20,000$ psi) and high temperature (500°C). These severe reaction conditions require specially designed equipment, and for safety reasons the reaction usually has been run behind a reinforced concrete barrier. More recently, lower reaction pressures and

psi is the abbreviation for pounds per square inch: $15 \text{ psi} \approx 1 \text{ atm}$.



CHEMICAL IMPACT

Wallace Hume Carothers

Wallace H. Carothers, a brilliant organic chemist who was principally responsible for the development of nylon and the first synthetic rubber (Neoprene), was born in 1896 in Burlington, Iowa. As a youth, Carothers was fascinated by tools and mechanical devices and spent many hours experimenting. In 1915 he entered Tarkio College in Missouri. Carothers so excelled in chemistry that even before his graduation, he was made a chemistry instructor.

Carothers eventually moved to the University of Illinois at Urbana–Champaign, where he was appointed to the faculty when he completed his Ph.D. in organic chemistry in 1924. He moved to Harvard University in 1926, and then to DuPont in 1928 to participate in a new program in fundamental research. At DuPont, Carothers headed the organic chemistry division, and during his ten years there played a prominent role in laying the foundations of polymer chemistry.

By the age of 33, Carothers had become a world-famous chemist whose advice was sought by almost everyone working in polymers. He was the first industrial chemist to be elected to the prestigious National Academy of Sciences.

Carothers was an avid reader of poetry and a lover of classical music. Unfortunately, he also suffered from severe bouts of depression that finally led to his suicide in 1937 in a Philadelphia hotel room, where he drank a cyanide



Wallace H. Carothers.

solution. He was 41 years old. Despite the brevity of his career, Carothers was truly one of the finest American chemists of all time. His great intellect, his love of chemistry, and his insistence on perfection produced his special genius.

temperatures have become possible through the use of catalysts. One catalytic system using triethylaluminum, $\text{Al}(\text{C}_2\text{H}_5)_3$, and titanium(IV) chloride was developed by Karl Ziegler in Germany and Giulio Natta in Italy. Although this catalyst is very efficient, it catches fire on contact with air and must be handled very carefully. A safer catalytic system was developed at Phillips Petroleum Company. It uses a chromium(III) oxide (Cr_2O_3) and aluminosilicate catalyst and has mainly taken over in the United States. The product of the catalyzed reaction is highly linear (unbranched) and is often called *linear low-density polyethylene*. It is very similar to HDPE.

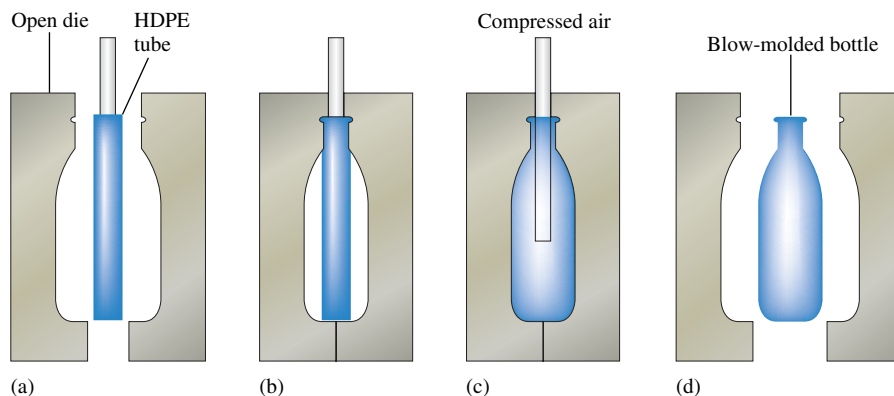
The major use of LDPE is in the manufacture of the tough transparent film that is used in packaging so many consumer goods. Two-thirds of the approximately 10 billion pounds of LDPE produced annually in the United States are used for this purpose. The major use of HDPE is for blow-molded products, such as bottles for consumer products (see Fig. 22.17).

The useful properties of polyethylene are due primarily to its high molecular weight (molar mass). Although the strengths of the interactions between specific points on the nonpolar chains are quite small, the chains are so long that these small attractions accumulate to a very significant value, so that the chains stick together very tenaciously. There is also a great deal of physical tangling of the lengthy chains. The combination of these interactions gives the polymer strength and toughness. However, a material like polyethylene can be melted and formed into a new shape (thermoplastic behavior), because in the melted state the molecules can readily flow past one another.

Molecular weight (not molar mass) is the common terminology in the polymer industry.

FIGURE 22.17

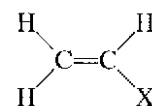
A major use of HDPE is for blow-molded objects such as bottles for soft drinks, shampoos, bleaches, and so on. (a) A tube composed of HDPE is inserted into the mold (die). (b) The die closes, sealing the bottom of the tube. (c) Compressed air is forced into the warm HDPE tube, which then expands to take the shape of the die. (d) The molded bottle is removed from the die.



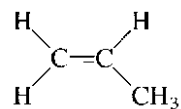
Since a high molecular weight gives a polymer useful properties, one might think that the goal would be to produce polymers with chains as long as possible. However, this is not the case—polymers become much more difficult to process as the molecular weights increase. Most industrial operations require that the polymer flow through pipes as it is processed. But as the chain lengths increase, viscosity also increases. In practice, the upper limit of a polymer's molecular weight is set by the flow requirements of the manufacturing process. Thus the final product often reflects a compromise between the optimal properties for the application and those needed for ease of processing.

Although many polymer properties are greatly influenced by molecular weight, some other important properties are not. For example, chain length does not affect a polymer's resistance to chemical attack. Physical properties such as color, refractive index, hardness, density, and electrical conductivity are also not greatly influenced by molecular weight.

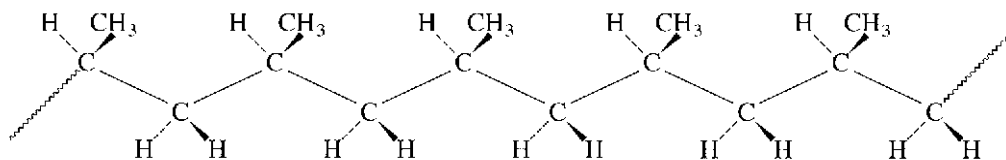
We have already seen that one way of altering the strength of a polymeric materials is to vary the chain length. Another method for modifying polymer behavior involves varying the substituents. For example, if we use a monomer of the type



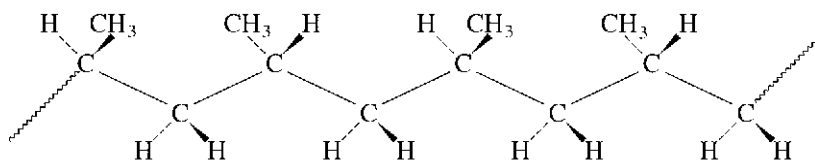
the properties of the resulting polymer depend on the identity of X. The simplest example is polypropylene, whose monomer is



and that has the form



The CH_3 groups can be arranged on the same side of the chain (called an **isotactic chain**) as shown above, can alternate (called a **syndiotactic chain**) as shown below,



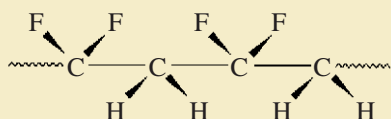
or can be randomly distributed (called an **atactic chain**).



CHEMICAL IMPACT

Plastic That Talks and Listens

Imagine a plastic so “smart” that it can be used to sense a baby’s breath, measure the force of a karate punch, sense the presence of a person 100 feet away, or make a balloon that sings. There is a plastic film capable of doing all these things. It’s called polyvinylidene difluoride (PVDF), which has the structure



When this polymer is processed in a particular way, it becomes piezoelectric and pyroelectric. A piezoelectric substance produces an electric current when it is physically deformed or alternatively undergoes a deformation caused by the application of a current. A pyroelectric material is one that develops an electrical potential in response to a change in its temperature.

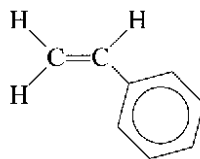
Because PVDF is piezoelectric, it can be used to construct a paper-thin microphone; it responds to sound by producing a current proportional to the deformation caused by the sound waves. A ribbon of PVDF plastic one-quarter of

an inch wide could be strung along a hallway and used to listen to all the conversations going on as people walk through. On the other hand, electric pulses can be applied to the PVDF film to produce a speaker. A strip of PVDF film glued to the inside of a balloon can play any song stored on a microchip attached to the film—hence a balloon that can sing “Happy Birthday” at a party. The PVDF film can also be used to construct a sleep apnea monitor, which, when placed beside the mouth of a sleeping infant, will set off an alarm if the breathing stops, thus helping to prevent sudden infant death syndrome (SIDS). The same type of film is used by the U.S. Olympic karate team to measure the force of kicks and punches as the team trains. Also, gluing two strips of film together gives a material that curls in response to a current, creating an artificial muscle. In addition, because the PVDF film is pyroelectric, it responds to the infrared (heat) radiation emitted by a human as far away as 100 feet, making it useful for burglar alarm systems.

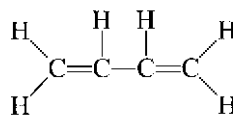
Making the PVDF polymer piezoelectric and pyroelectric requires some very special processing, which makes it costly (\$10 per square foot). This expense seems a small price to pay for its near-magical properties.

The chain arrangement has a significant effect on the polymer’s properties. Most polypropylene is made using the Ziegler-Natta catalyst, $\text{Al}(\text{C}_2\text{H}_5)_3 \cdot \text{TiCl}_4$, which produces highly isotactic chains that pack together quite closely. As a result, polypropylene is more crystalline, and therefore stronger and harder, than polyethylene. The major uses of polypropylene are for molded parts (40%), fibers (35%), and packaging films (10%). Polypropylene fibers are especially useful for athletic wear because they do not absorb water from perspiration, as cotton does. Rather, the moisture is drawn away from the skin to the surface of the polypropylene garment, where it can evaporate. The annual U.S. production of polypropylene is about 7 billion pounds.

Another related polymer, **polystyrene**, is constructed from the monomer styrene,

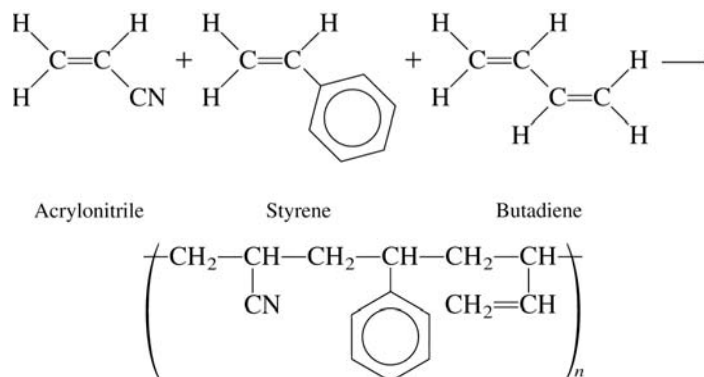


Pure polystyrene is too brittle for many uses, so most polystyrene-based polymers are actually *copolymers* of styrene and butadiene,



thus incorporating bits of butadiene rubber into the polystyrene matrix. The resulting polymer is very tough and is often used as a substitute for wood in furniture.

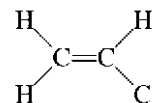
Another polystyrene-based product is acrylonitrile-butadiene-styrene (ABS), a tough, hard, and chemically resistant plastic used for pipes and for items such as radio housings, telephone cases, and golf club heads, for which shock resistance is an essential property. Originally, ABS was produced by copolymerization of the three monomers:



PVC pipe is widely used in industry.

It is now prepared by a special process called *grafting*, in which butadiene is polymerized first, and then the cyanide and phenyl substituents are added chemically.

Another high-volume polymer, **polyvinyl chloride (PVC)**, is constructed from the monomer vinyl chloride,



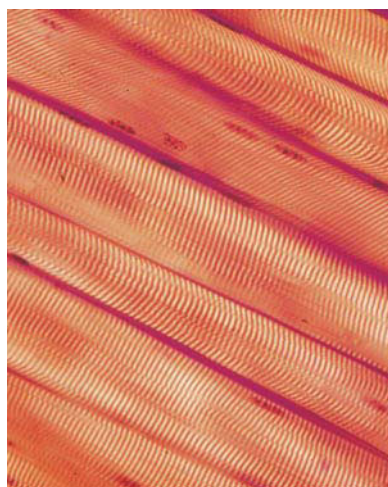
22.6 Natural Polymers

Proteins

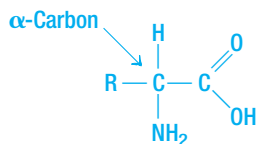
We have seen that many useful synthetic materials are polymers. Thus it should not be surprising that a great many natural materials are also polymers: starch, hair, silicate chains in soil and rocks, silk and cotton fibers, and the cellulose in woody plants, to name only a few.

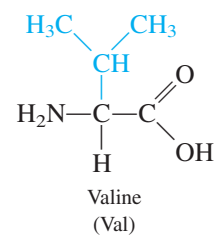
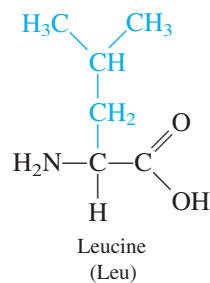
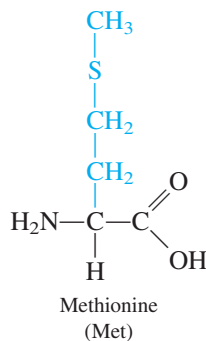
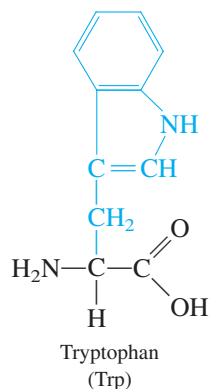
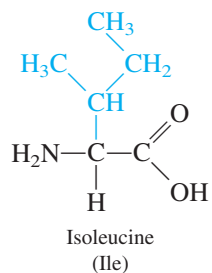
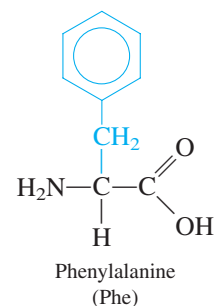
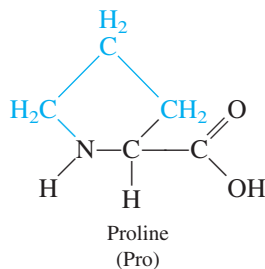
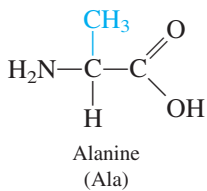
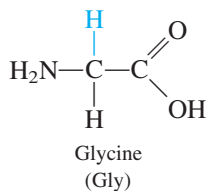
In this section we consider a class of natural polymers, the **proteins**, which make up about 15% of our bodies and have molecular weights (molar masses) that range from about 6000 to over 1,000,000 grams per mole. Proteins perform many functions in the human body. **Fibrous proteins** provide structural integrity and strength for many types of tissue and are the main components of muscle, hair, and cartilage. Other proteins, usually called **globular proteins** because of their roughly spherical shape, are the “worker” molecules of the body. These proteins transport and store oxygen and nutrients, act as catalysts for the thousands of reactions that make life possible, fight invasion by foreign objects, participate in the body’s many regulatory systems, and transport electrons in the complex process of metabolizing nutrients.

The building blocks of all proteins are the **α -amino acids**, where R may represent H, CH₃, or a more complex substituent. These molecules are called α -amino acids because the amino group (—NH₂) is always attached to the α -carbon, the one next to the carboxyl group (—CO₂H). The 20 amino acids most commonly found in proteins are shown in Fig. 22.18.



The protein in muscles enables them to contract.



Nonpolar
R groups

Polar R groups

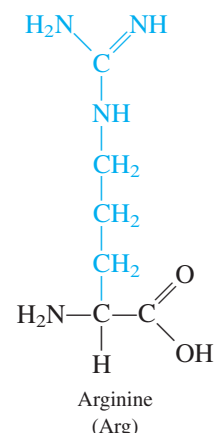
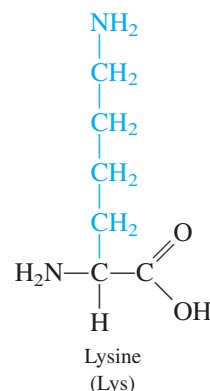
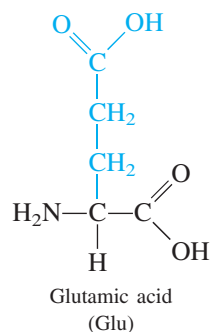
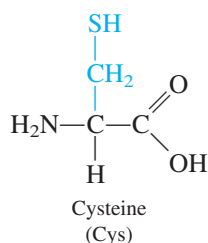
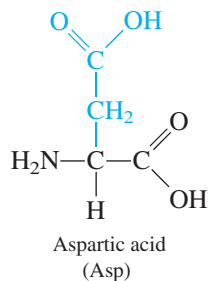
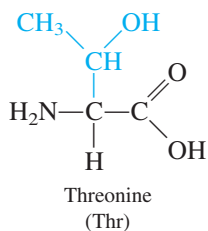
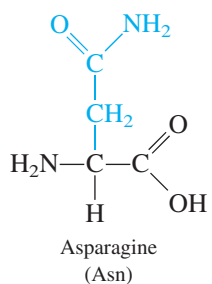
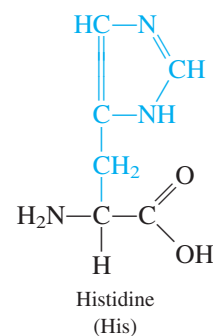
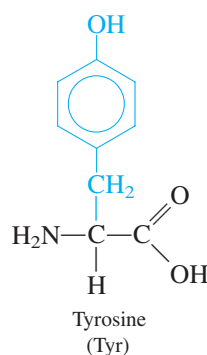
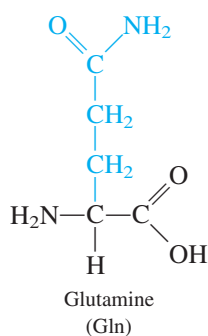
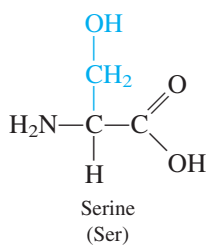


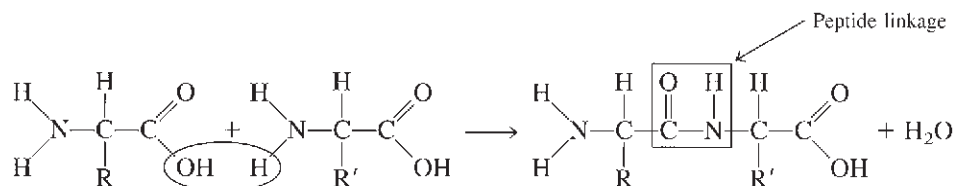
FIGURE 22.18

The 20 α -amino acids found in most proteins. The R group is shown in color.

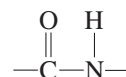
At the pH in biological fluids, the amino acids shown in Fig. 22.18 exist in a different form, with the proton of the —COOH group transferred to the —NH₂ group. For example, glycine would be in the form H₃⁺NCH₂COO⁻.

Note from Fig. 22.18 that the amino acids are grouped into polar and nonpolar classes, determined by the R groups, or **side chains**. Nonpolar side chains contain mostly carbon and hydrogen atoms, whereas polar side chains contain large numbers of nitrogen and oxygen atoms. This difference is important, because polar side chains are *hydrophilic* (water-loving), but nonpolar side chains are *hydrophobic* (water-fearing), and this characteristic greatly affects the three-dimensional structure of the resulting protein.

The protein polymer is built by condensation reactions between amino acids. For example,



The product shown above is called a **dipeptide**. This name is used because the structure



The peptide linkage is also found in nylon (see Section 22.5).

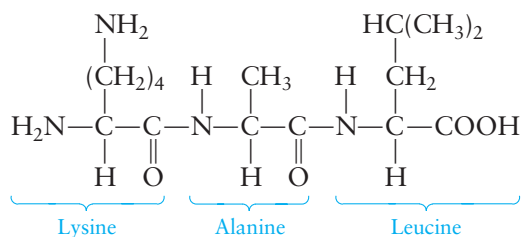
is called a **peptide linkage** by biochemists. (The same grouping is called an amide by organic chemists.) Additional condensation reactions lengthen the chain to produce a **polypeptide**, eventually yielding a protein.

You can imagine that with 20 amino acids, which can be assembled in any order, there is essentially an infinite variety possible in the construction of proteins. This flexibility allows an organism to tailor proteins for the many types of functions that must be carried out.

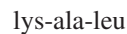
The order, or sequence, of amino acids in the protein chain is called the **primary structure**, conveniently indicated by using three-letter codes for the amino acids (see Fig. 22.18), where it is understood that the terminal carboxyl group is on the right and the terminal amino group is on the left. For example, one possible sequence for a tripeptide containing the amino acids lysine, alanine, and leucine is



A tripeptide containing glycine, cysteine, and alanine.



which is represented in the shorthand notation by



Note from Sample Exercise 22.7 that there are six sequences possible for a polypeptide with three given amino acids. There are three possibilities for the first amino acid (any one of the three given amino acids), there are two possibilities for the second amino acid (one has already been accounted for), but there is only one possibility left for the third amino acid. Thus the number of sequences is $3 \times 2 \times 1 = 6$. The product $3 \times 2 \times 1$ is often written $3!$ (and is called 3 factorial). Similar reasoning shows that for a polypeptide with four amino acids, there are $4!$, or $4 \times 3 \times 2 \times 1 = 24$, possible sequences.

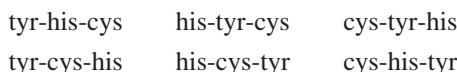
Sample Exercise 22.7

Tripeptide Sequences

Write the sequences of all possible tripeptides composed of the amino acids tyrosine, histidine, and cysteine.

Solution

There are six possible sequences:



See Exercise 22.89.

Sample Exercise 22.8

Polypeptide Sequences

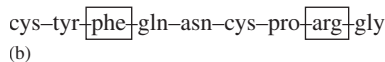
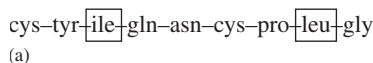


FIGURE 22.19

The amino acid sequences in (a) oxytocin and (b) vasopressin. The differing amino acids are boxed.

What number of possible sequences exists for a polypeptide composed of 20 different amino acids?

Solution

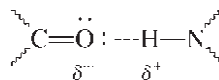
The answer is $20!$, or

$$20 \times 19 \times 18 \times 17 \times 16 \times \cdots \times 5 \times 4 \times 3 \times 2 \times 1 = 2.43 \times 10^{18}$$

See Exercise 22.90.

A striking example of the importance of the primary structure of polypeptides can be seen in the differences between *oxytocin* and *vasopressin*. Both of these molecules are nine-unit polypeptides that differ by only two amino acids (Fig. 22.19), yet they perform completely different functions in the human body. Oxytocin is a hormone that triggers contraction of the uterus and milk secretion. Vasopressin raises blood pressure levels and regulates kidney function.

A second level of structure in proteins, beyond the sequence of amino acids, is the arrangement of the chain of the long molecule. The **secondary structure** is determined to a large extent by hydrogen bonding between lone pairs on an oxygen atom in the carbonyl group of an amino acid and a hydrogen atom attached to a nitrogen of another amino acid:



Such interactions can occur *within* the chain coils to form a spiral structure called an **α -helix**, as shown in Fig. 22.20 and Fig. 22.21. This type of secondary structure gives the protein elasticity (springiness) and is found in the fibrous proteins in wool, hair, and tendons. Hydrogen bonding can also occur *between different* protein chains, joining them together in an arrangement called a **pleated sheet**, as shown in Fig. 22.22. Silk contains this arrangement of proteins, making its fibers flexible yet very strong and resistant to stretching. The pleated sheet is also found in muscle fibers. The hydrogen bonds in the α -helical protein are called *intrachain* (within a given protein chain), and those in the pleated sheet are said to be *interchain* (between protein chains).

As you might imagine, a molecule as large as a protein has a great deal of flexibility and can assume a variety of overall shapes. The specific shape that a protein assumes depends on its function. For long, thin structures, such as hair, wool and silk fibers, and tendons, an elongated shape is required. This may involve an α -helical secondary structure, as found in the protein α -keratin in hair and wool or in the collagen found in tendons [Fig. 22.23(a)], or it may involve a pleated-sheet secondary structure, as found in

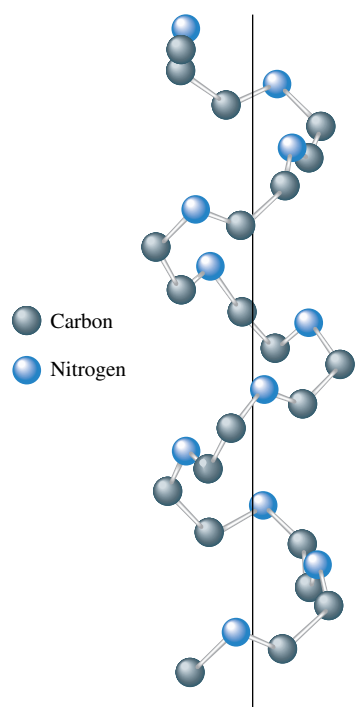
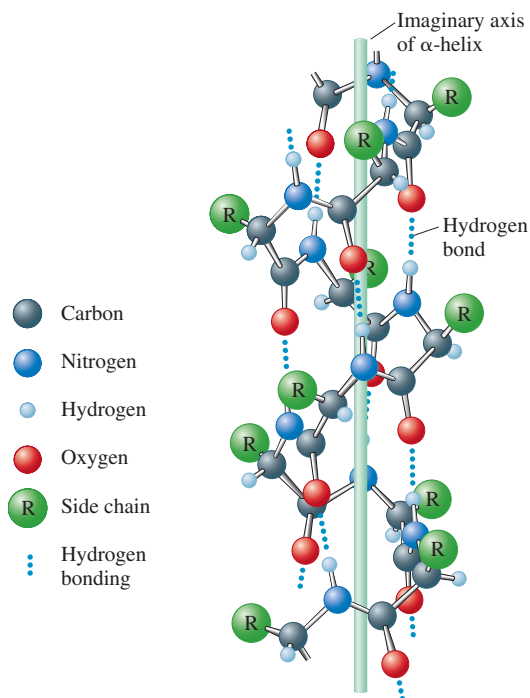


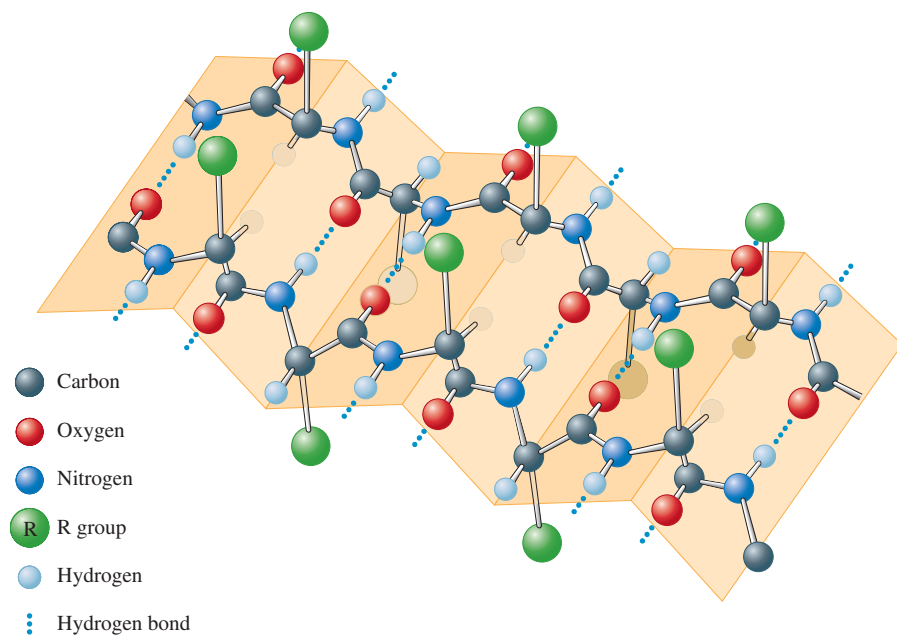
FIGURE 22.20

Hydrogen bonding within a protein chain causes it to form a stable helical structure called the α -helix. Only the main atoms in the helical backbone are shown here. The hydrogen bonds are not shown.

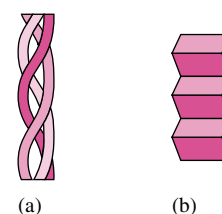
**FIGURE 22.21**

Ball-and-stick model of a portion of a protein chain in the α -helical arrangement, showing the hydrogen-bonding interactions.

silk [Fig. 22.23(b)]. Many of the proteins in the body having nonstructural functions are globular, such as myoglobin (see Fig. 21.31). Note that the secondary structure of myoglobin is basically α -helical. However, in the areas where the chain bends to give the protein its compact globular structure, the α -helix breaks down to give a secondary configuration known as the **random-coil arrangement**.

**FIGURE 22.22**

When hydrogen bonding occurs between protein chains rather than within them, a stable structure (the pleated sheet) results. This structure contains many protein chains and is found in natural fibers, such as silk, and in muscles.

**FIGURE 22.23**

(a) Collagen, a protein found in tendons, consists of three protein chains (each with a helical structure) twisted together to form a superhelix. The result is a long, relatively narrow protein. (b) The pleated-sheet arrangement of many proteins bound together to form the elongated protein found in silk fibers.

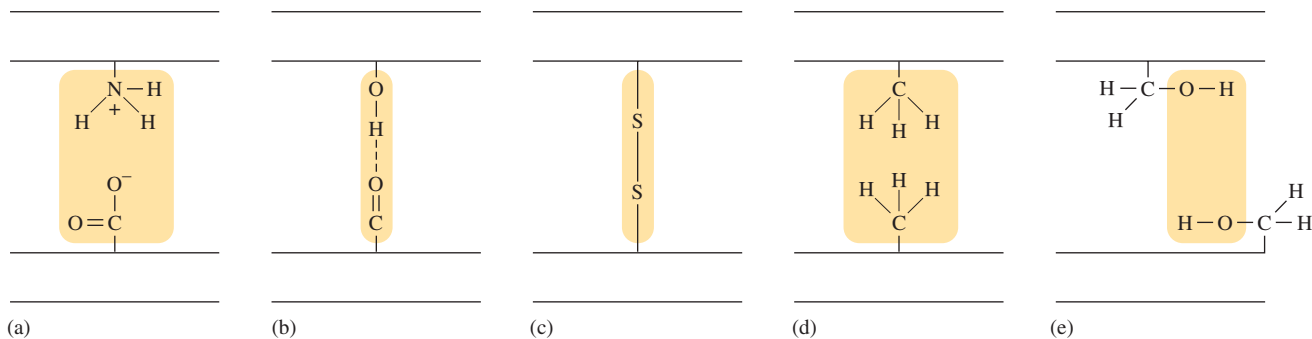


FIGURE 22.24 Summary of the various types of interactions that stabilize the tertiary structure of a protein: (a) ionic, (b) hydrogen bonding, (c) covalent, (d) London dispersion, and (e) dipole–dipole.

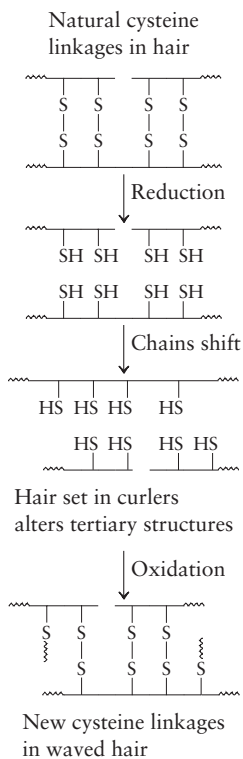
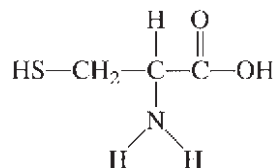


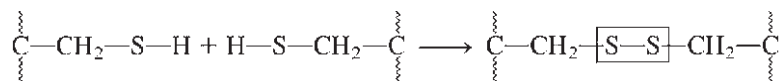
FIGURE 22.25 The permanent waving of hair.

The overall shape of the protein, long and narrow or globular, is called its **tertiary structure** and is maintained by several different types of interactions: hydrogen bonding, dipole–dipole interactions, ionic bonds, covalent bonds, and London dispersion forces between nonpolar groups. These bonds, which represent all the bonding types discussed in this text, are summarized in Fig. 22.24.

The amino acid *cysteine*



plays a special role in stabilizing the tertiary structure of many proteins because the —SH groups on two cysteines can react in the presence of an oxidizing agent to form a S—S bond called a **disulfide linkage**:



A practical application of the chemistry of disulfide bonds is permanent waving of hair, as summarized in Fig. 22.25. The S—S linkages in the protein of hair are broken by treatment with a reducing agent. The hair is then set in curlers to change the tertiary protein structure to the desired shape. Then treatment with an oxidizing agent causes new S—S bonds to form, which allow the hair protein to retain the new structure.

The three-dimensional structure of a protein is crucial to its function. The process of breaking down this structure is called **denaturation** (Fig. 22.26). For example, the denaturation of egg proteins occurs when an egg is cooked. Any source of energy can cause denaturation of proteins and is thus potentially dangerous to living organisms. For example, ultraviolet and X-ray radiation or nuclear radioactivity can disrupt protein structure, which may lead to cancer or genetic damage. Protein damage is also caused by chemicals like benzene, trichloroethane, and 1,2-dibromoethane. The metals lead and mercury, which have a very high affinity for sulfur, cause protein denaturation by disrupting disulfide bonds between protein chains.

The tremendous flexibility in the various levels of protein structure allows the tailoring of proteins for a wide range of specific functions. Proteins are the “workhorse” molecules of living organisms.

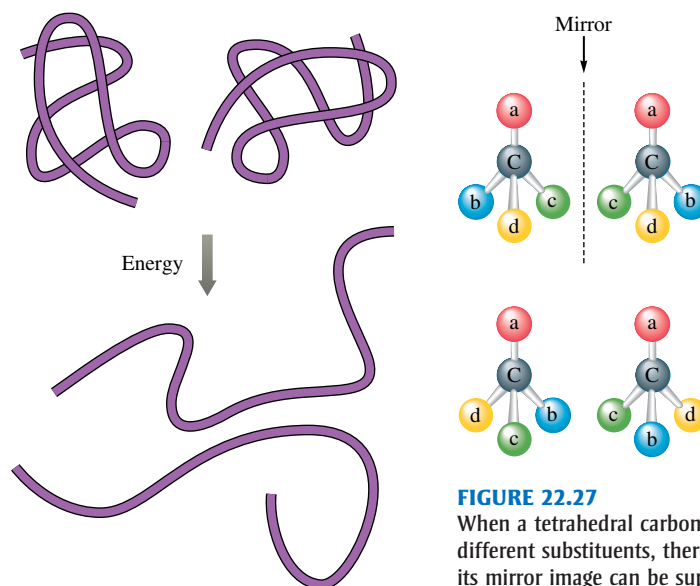


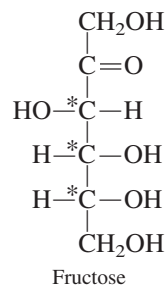
FIGURE 22.26
A schematic representation of the thermal denaturation of a protein.

FIGURE 22.27
When a tetrahedral carbon atom has four different substituents, there is no way that its mirror image can be superimposed. The lower two forms show other possible orientations of the molecule. Compare these with the mirror image and note that they cannot be superimposed.

Carbohydrates

Carbohydrates form another class of biologically important molecules. They serve as a food source for most organisms and as a structural material for plants. Because many carbohydrates have the empirical formula CH_2O , it was originally believed that these substances were hydrates of carbon, thus accounting for the name.

Most important carbohydrates, such as starch and cellulose, are polymers composed of monomers called **monosaccharides**, or **simple sugars**. The monosaccharides are polyhydroxy ketones and aldehydes. The most important contain five carbon atoms (**pentoses**) or six carbon atoms (**hexoses**). One important hexose is *fructose*, a sugar found in honey and fruit. Its structure is



where the asterisks indicate chiral carbon atoms. In Section 21.4 we saw that molecules with nonsuperimposable mirror images exhibit optical isomerism. A carbon atom with four *different* groups bonded to it in a tetrahedral arrangement *always* has a nonsuperimposable mirror image (see Fig. 22.27), which gives rise to a pair of optical isomers. For example, the simplest sugar, glyceraldehyde,

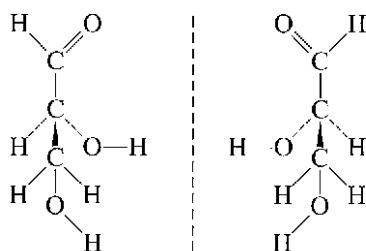
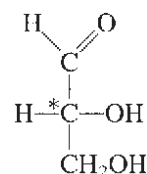


FIGURE 22.28
The mirror image optical isomers of glyceraldehyde. Note that these mirror images cannot be superimposed.



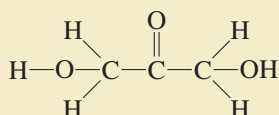
which has one chiral carbon, has two optical isomers, as shown in Fig. 22.28.



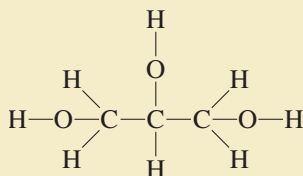
CHEMICAL IMPACT

Tanning in the Shade

Among today's best-selling cosmetics are self-tanning lotions. Many light-skinned people want to look like they have just spent a vacation in the Caribbean, but they recognize the dangers of too much sun—it causes premature aging and may lead to skin cancer. Chemistry has come to the rescue in the form of lotions that produce an authentic-looking tan. All of these lotions have the same active ingredient: dihydroxyacetone (DHA). DHA, which has the structure



is a nontoxic, simple sugar that occurs as an intermediate in carbohydrate metabolism in higher-order plants and animals. The DHA used in self-tanners is prepared by bacterial fermentation of glycerine,



The tanning effects of DHA were discovered by accident in the 1950s at Children's Hospital at the University of Cincinnati, where DHA was being used to treat children with glycogen storage disease. When the DHA was accidentally spilled on the skin, it produced brown spots.

The mechanism of the browning process involves the Maillard reaction, which was discovered by Louis-Camille Maillard in 1912. In this process amino acids react with sugars to create brown or golden brown products. The same reaction is responsible for much of the browning that occurs during the manufacture and storage of foods. It is also the reason that beer is golden brown.

The browning of skin occurs in the stratum corneum—the outermost, dead layer—where the DHA reacts with free amino ($-\text{NH}_2$) groups of the proteins found there.

DHA is present in most tanning lotions at concentrations between 2% and 5%, although some products designed to give a deeper tan are more concentrated. Because the lotions themselves turn brown above pH 7, the tanning lotions are buffered at pH 5.

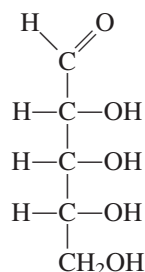
Thanks to these new products, tanning is now both safe and easy.

In fructose each of the three chiral carbon atoms satisfies the requirement of being surrounded by four different groups. This leads to a total of 2^3 , or 8, isomers that differ in their ability to rotate polarized light. The particular isomer whose structure is shown in Table 22.8 is called D-fructose. Generally, monosaccharides have one isomer that is more common in nature than the others. The most important pentoses and hexoses are shown in Table 22.8.

Sample Exercise 22.9

Chiral Carbons in Carbohydrates

Determine the number of chiral carbon atoms in the following pentose:



Solution

We must look for carbon atoms that have four different substituents. The top carbon has only three substituents and thus cannot be chiral. The three carbon atoms shown in blue



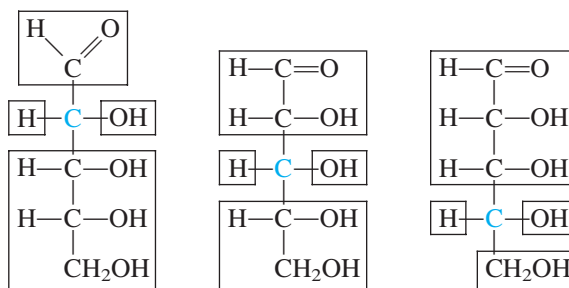
Self-tanning products and a close-up of a label showing the contents.

General Name of Sugar	Number of Carbon Atoms
Triose	3
Tetrose	4
Pentose	5
Hexose	6
Heptose	7
Octose	8
Nonose	9

TABLE 22.8 Some Important Monosaccharides

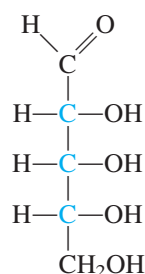
Pentoses			
D-Ribose	D-Arabinose	D-Ribulose	
$\begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	
Hexoses			
D-Glucose	D-Mannose	D-Galactose	D-Fructose
$\begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$

each have four different groups attached to them:



Since the fifth carbon atom has only three types of substituents (it has two hydrogen atoms), it is not chiral.

Thus the three chiral carbon atoms in this pentose are those shown in blue:



Note that D-ribose and D-arabinose, shown in Table 22.8, are two of the eight isomers of this pentose.

See Exercises 22.108 and 22.113 through 22.116.

Although we have so far represented the monosaccharides as straight-chain molecules, they usually cyclize, or form a ring structure, in aqueous solution. Figure 22.29 shows this reaction for fructose. Note that a new bond is formed between the oxygen of the terminal hydroxyl group and the carbon of the ketone group. In the cyclic form fructose is a five-membered ring containing a C—O—C bond. The same type of reaction can occur between a hydroxyl group and an aldehyde group, as shown for D-glucose in Fig. 22.30. In this case a six-membered ring is formed.

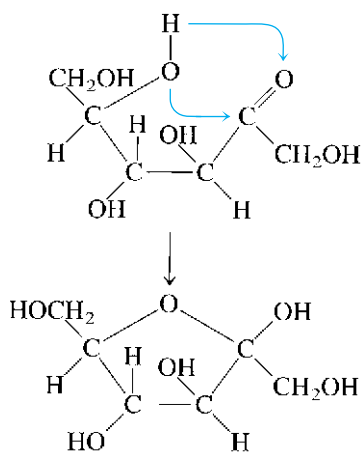


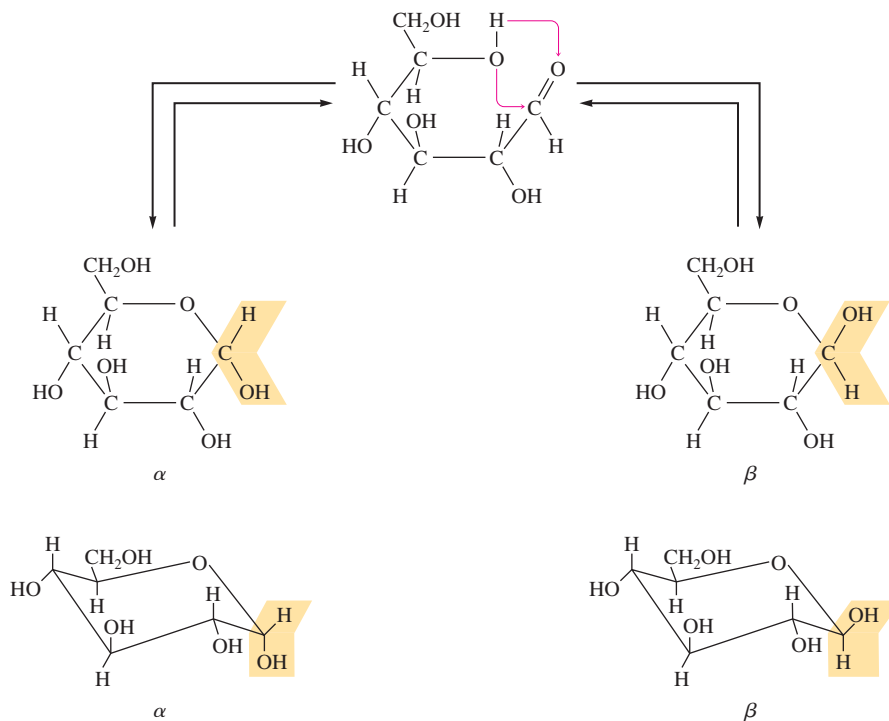
FIGURE 22.29
The cyclization of D-fructose.

More complex carbohydrates are formed by combining monosaccharides. For example, **sucrose**, common table sugar, is a **disaccharide** formed from glucose and fructose by elimination of water to form a C—O—C bond between the rings, which is called a **glycoside linkage** (Fig. 22.31). When sucrose is consumed in food, the above reaction is reversed. An enzyme in saliva catalyzes the breakdown of this disaccharide.

Large polymers consisting of many monosaccharide units, called polysaccharides, can form when each ring forms two glycoside linkages, as shown in Fig. 22.32. Three of the most important of these polymers are starch, cellulose, and glycogen. All these substances are polymers of α -D-glucose, differing from each other in the nature of the glycoside linkage, the amount of branching, and molecular weight (molar mass).

Starch, a polymer of α -D-glucose, consists of two parts: *amylose*, a straight-chain polymer of α -glucose [see Fig. 22.32(a)], and *amylopectin*, a highly branched polymer of α -glucose with a molecular weight that is 10 to 20 times that of amylose. Branching occurs when a third glycoside linkage attaches a branch to the main polymer chain.

Starch, the carbohydrate reservoir in plants, is the form in which glucose is stored by the plant for later use as cellular fuel. Glucose is stored in this high-molecular-weight form because it results in less stress on the plant's internal structure by osmotic pressure. Recall

**FIGURE 22.30**

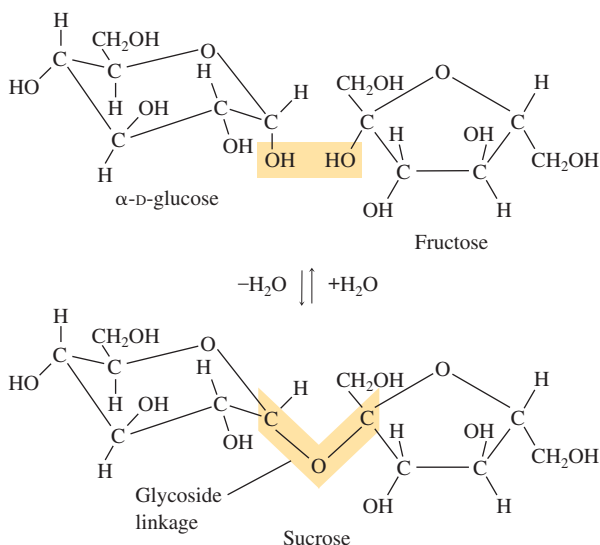
The cyclization of glucose. Two different rings are possible; they differ in the orientation of the hydroxy group and hydrogen on one carbon, as indicated. The two forms are designated α and β and are shown here in two representations.



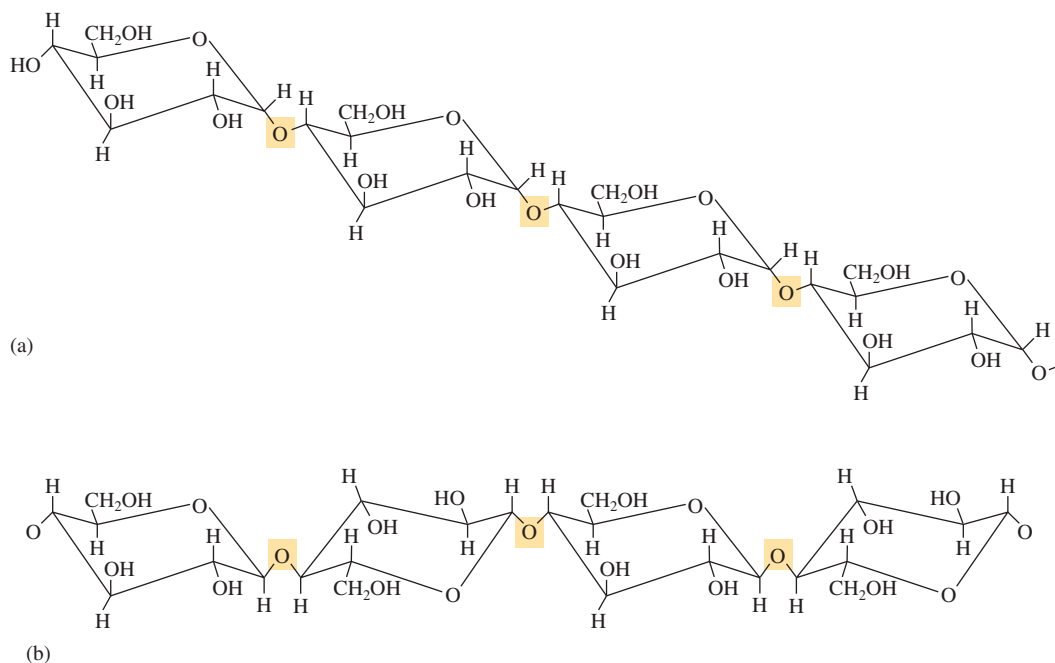
Bowl of sugar cubes.

from Section 11.6 that it is the concentration of solute molecules (or ions) that determines the osmotic pressure. Combining the individual glucose molecules into one large chain keeps the concentration of solute molecules relatively low, minimizing the osmotic pressure.

Cellulose, the major structural component of woody plants and natural fibers (such as cotton), is a polymer of β -D-glucose and has the structure shown in Fig. 22.32(b). Note that the β -glycoside linkages in cellulose give the glucose rings a different relative orientation than is found in starch. Although this difference may seem minor, it has very important consequences. The human digestive system contains α -glycosidases, enzymes that can catalyze breakage of the α -glycoside bonds in starch. These enzymes are not effective on the β -glycoside bonds of cellulose, presumably because the different structure

**FIGURE 22.31**

Sucrose is a disaccharide formed from α -D-glucose and fructose.

**FIGURE 22.32**

(a) The polymer amylose is a major component of starch and is made up of α -D-glucose monomers. (b) The polymer cellulose, which consists of β -D-glucose monomers.

results in a poor fit between the enzyme's active site and the carbohydrate. The enzymes necessary to cleave β -glycoside linkages, the β -glycosidases, are found in bacteria that exist in the digestive tracts of termites, cows, deer, and many other animals. Thus, unlike humans, these animals can derive nutrition from cellulose.

Glycogen, the main carbohydrate reservoir in animals, has a structure similar to that of amylopectin but with more branching. It is this branching that is thought to facilitate the rapid breakdown of glycogen into glucose when energy is required.

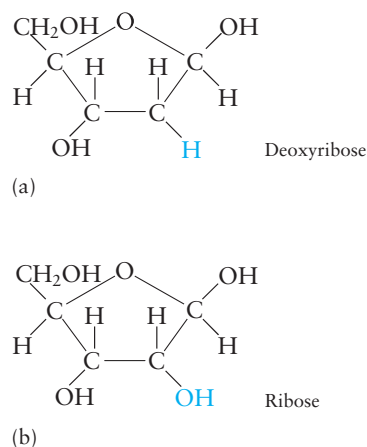
Nucleic Acids

Life is possible only because each cell, when it divides, can transmit the vital information about how it works to the next generation. It has been known for a long time that this process involves the chromosomes in the nucleus of the cell. Only since 1953, however, have scientists understood the molecular basis of this intriguing cellular "talent."

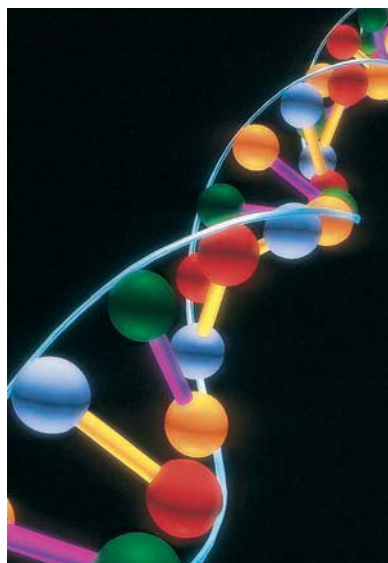
The substance that stores and transmits the genetic information is a polymer called **deoxyribonucleic acid (DNA)**, a huge molecule with a molecular weight as high as several billion grams per mole. Together with other similar nucleic acids called the **ribonucleic acids (RNA)**, DNA is also responsible for the synthesis of the various proteins needed by the cell to carry out its life functions. The RNA molecules, which are found in the cytoplasm outside the nucleus, are much smaller than DNA polymers, with molecular weights of only 20,000 to 40,000 grams per mole.

The monomers of the nucleic acids, called **nucleotides**, are composed of three distinct parts:

1. A *five-carbon sugar*, deoxyribose in DNA and ribose in RNA (Fig. 22.33)
2. A *nitrogen-containing organic base* of the type shown in Fig. 22.34
3. A *phosphoric acid molecule* (H_3PO_4)

**FIGURE 22.33**

The structure of the pentoses (a) deoxyribose and (b) ribose. Deoxyribose is the sugar molecule present in DNA; ribose is found in RNA.



A computer image of the base pairs of DNA. The blue lines represent the sugar-phosphate backbone and the colored bars represent the hydrogen bonding between the base pairs.

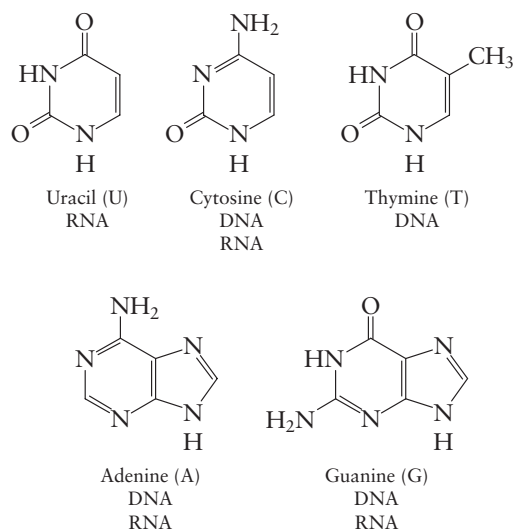


FIGURE 22.34

The organic bases found in DNA and RNA.

The base and the sugar combine as shown in Fig. 22.35(a) to form a unit that in turn reacts with phosphoric acid to create the nucleotide, which is an ester [see Fig. 22.35(b)]. The nucleotides become connected through condensation reactions that eliminate water to give a polymer of the type represented in Fig. 22.36; such a polymer can contain a *billion* units.

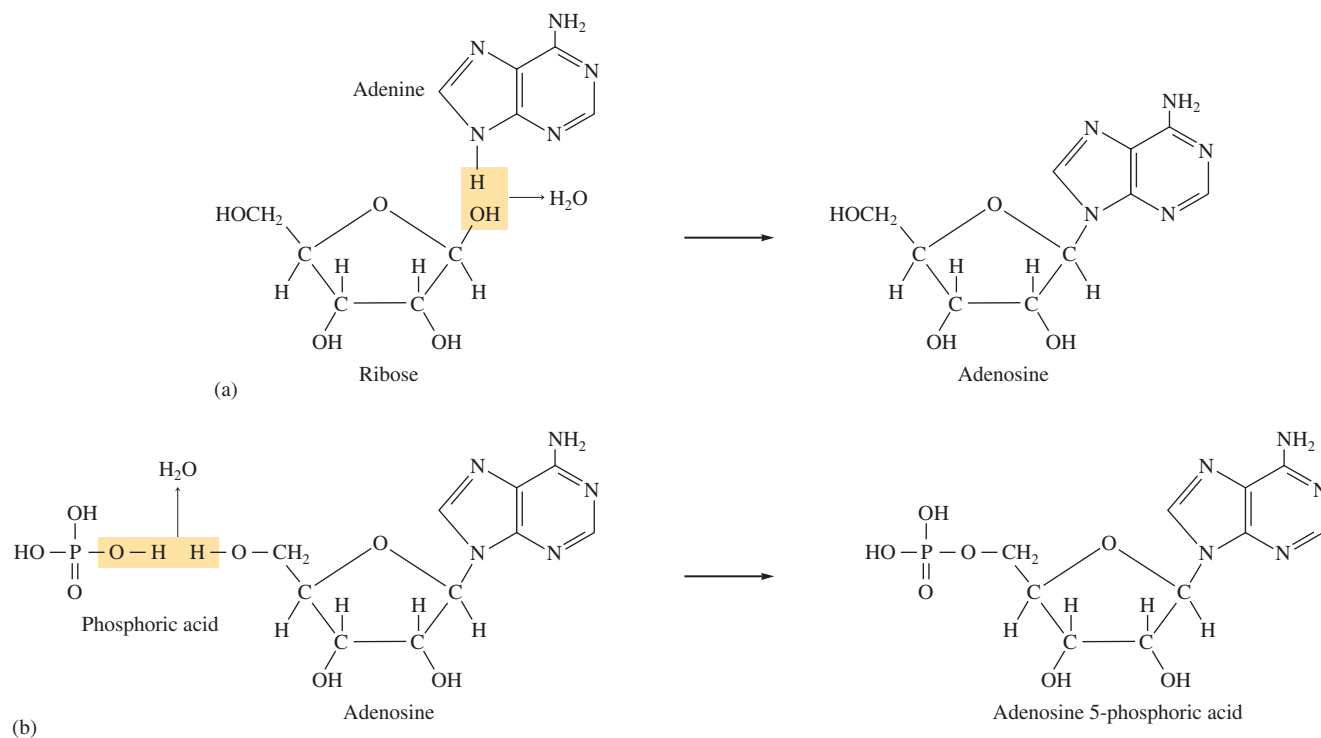


FIGURE 22.35

(a) Adenosine is formed by the reaction of adenine with ribose. (b) The reaction of phosphoric acid with adenosine to form the ester adenosine 5-phosphoric acid, a nucleotide. (At biological pH, the phosphoric acid would not be fully protonated as is shown here.)

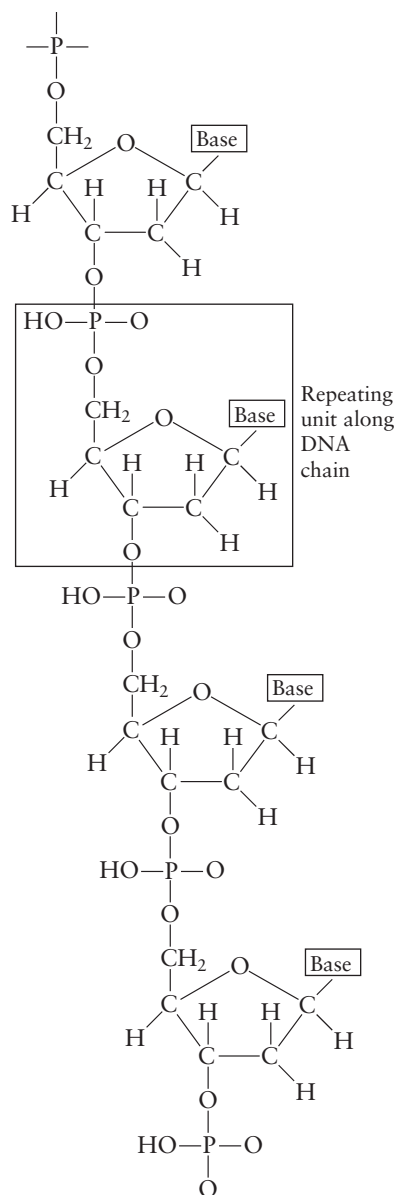


FIGURE 22.36
A portion of a typical nucleic acid chain. Note that the backbone consists of sugar–phosphate esters.

The key to DNA’s functioning is its *double-helical structure with complementary bases on the two strands*. The bases form hydrogen bonds to each other, as shown in Fig. 22.37. Note that the structures of cytosine and guanine make them perfect partners for hydrogen bonding, and they are *always* found as pairs on the two strands of DNA. Thymine and adenine form similar hydrogen-bonding pairs.

There is much evidence to suggest that the two strands of DNA unwind during cell division and that new complementary strands are constructed on the unraveled strands (Fig. 22.38). Because the bases on the strands always pair in the same way—cytosine with guanine and thymine with adenine—each unraveled strand serves as a template for attaching the complementary bases (along with the rest of the nucleotide). This process results in two double-helix DNA structures that are identical to the original one. Each new double strand contains one strand from the original DNA double helix and one newly synthesized strand. This replication of DNA allows for the transmission of genetic information as the cells divide.

The other major function of DNA is **protein synthesis**. A given segment of the DNA, called a **gene**, contains the code for a specific protein. These codes transmit the primary structure of the protein (the sequence of amino acids) to the construction “machinery” of the cell. There is a specific code for each amino acid in the protein, which ensures that the correct amino acid will be inserted as the protein chain grows. A code consists of a set of three bases called a **codon**.

DNA stores the genetic information, while RNA molecules are responsible for transmitting this information to the ribosomes, where protein synthesis actually occurs. This complex process involves, first, the construction of a special RNA molecule called **messenger RNA (mRNA)**. The mRNA is built in the cell nucleus on the appropriate section of DNA (the gene); the double helix is “unzipped,” and the complementarity of the bases

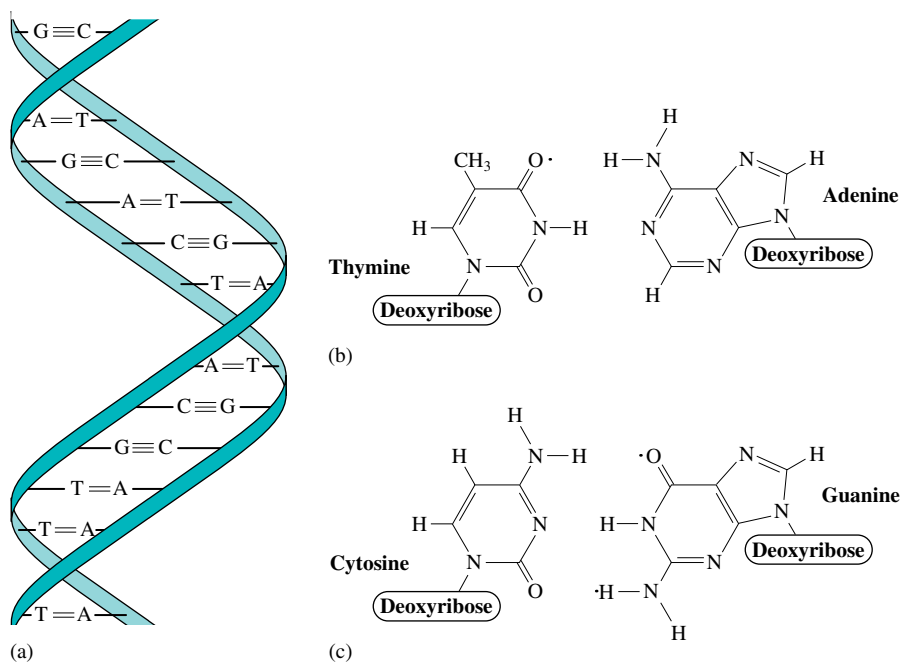


FIGURE 22.37
(a) The DNA double helix contains two sugar–phosphate backbones, with the bases from the two strands hydrogen-bonded to each other. The complementarity of the (b) thymine-adenine and (c) cytosine-guanine pairs.

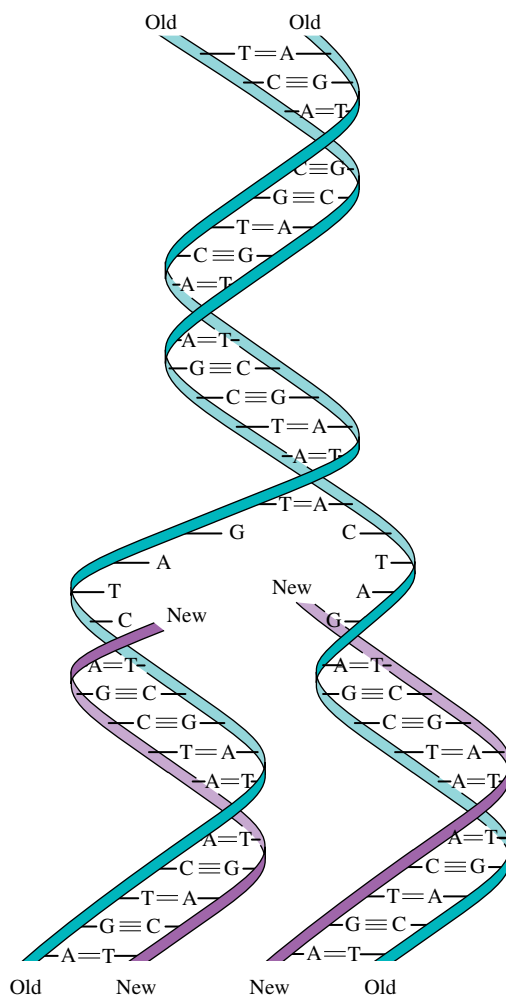


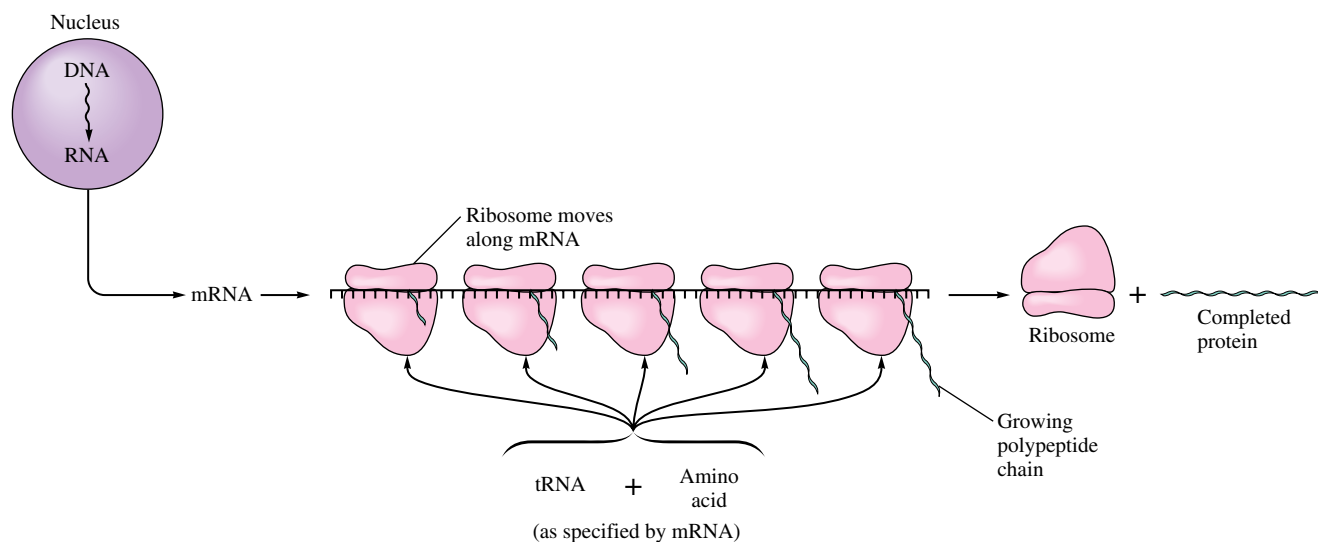
FIGURE 22.38

During cell division the original DNA double helix unwinds and new complementary strands are constructed on each original strand.

is used in a process similar to that used in DNA replication. The mRNA then migrates into the cytoplasm of the cell where, with the assistance of the ribosomes, the protein is synthesized.

Small RNA fragments, called **transfer RNA (tRNA)**, are tailored to find specific amino acids and then to attach them to the growing protein chain as dictated by the codons in the mRNA. Transfer RNA has a lower molecular weight than messenger RNA. It consists of a chain of 75 to 80 nucleotides, including the bases adenine, cytosine, guanine, and uracil, among others. The chain folds back onto itself in various places as the complementary bases along the chain form hydrogen bonds. The tRNA decodes the genetic message from the mRNA, using a complementary triplet of bases called an **anticodon**. The nature of the anticodon governs which amino acid will be brought to the protein under construction.

The protein is built in several steps. First, a tRNA molecule brings an amino acid to the mRNA [the anticodon of the tRNA must complement the codon of the mRNA (see Fig. 22.39)]. Once this amino acid is in place, another tRNA moves to the second codon site of the mRNA with its specific amino acid. The two amino acids link via a peptide bond, and the tRNA on the first codon breaks away. The process is repeated down the chain, always matching the tRNA anticodon with the mRNA codon.

**FIGURE 22.39**

The mRNA molecule, constructed from a specific gene on the DNA, is used as the pattern to construct a given protein with the assistance of ribosomes. The tRNA molecules attach to specific amino acids and put them in place as called for by the codons on the mRNA.

Key Terms

biomolecule
organic chemistry

Section 22.1

hydrocarbons
saturated
unsaturated
alkanes
normal (straight-chain or unbranched)
hydrocarbons

structural isomerism
combustion reaction
substitution reaction
dehydrogenation reaction
cyclic alkanes

Section 22.2

alkenes
cis-trans isomerism
alkynes
addition reaction
hydrogenation reaction
halogenation
polymerization

Section 22.3

aromatic hydrocarbons
phenyl group

Section 22.4

hydrocarbon derivatives
functional group
alcohols
phenol
carbonyl group

For Review

Hydrocarbons

- Compounds composed of mostly carbon and hydrogen atoms that typically contain chains or rings of carbon atoms
- Alkanes
 - Contain compounds with only C—C single bonds
 - Can be represented by the formula C_nH_{2n+2}
 - Are said to be saturated because each carbon present is bonded to the maximum number of atoms (4)
 - The carbon atoms are described as being sp^3 hybridized
 - Their structural isomerism involves the formation of branched chains
 - React with O_2 to form CO_2 and H_2O (called a combustion reaction)
 - Undergo substitution reactions
- Alkenes
 - Contain one or more C=C double bonds
 - Simplest alkene is C_2H_4 (ethylene) which is described as containing sp^2 hybridized carbon atoms
 - Restricted rotation about the C=C bonds in alkenes can lead to *cis-trans* isomerism
 - Undergo addition reactions
- Alkynes
 - Contain one or more C≡C triple bonds
 - Simplest example is C_2H_2 (acetylene), described as containing sp -hybridized carbon atoms
 - Undergo addition reactions
- Aromatic hydrocarbons
 - Contain rings of carbon atoms with delocalized π electrons
 - Undergo substitution reactions rather than addition reactions

ketones
aldehydes
carboxylic acids
carboxyl group
ester
amines

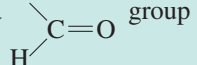
Section 22.5

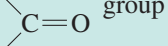
polymers
thermoset polymer
thermoplastic polymer
crosslinking
vulcanization
addition polymerization
free radical
condensation polymerization
copolymer
homopolymer
dimer
polyester
isotactic chain
syndiotactic chain
atactic chain
polystyrene
polyvinyl chloride (PVC)

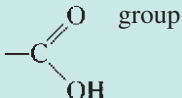
Section 22.6

proteins
fibrous proteins
globular proteins
 α -amino acids
side chains
dipeptide
peptide linkage
polypeptide
primary structure
secondary structure
 α -helix
pleated sheet
random-coil arrangement
tertiary structure
disulfide linkage
denaturation
carbohydrates
monosaccharides (simple sugars)
pentoses
hexoses
sucrose
disaccharide
glycoside linkage
starch
cellulose
glycogen
deoxyribonucleic acid (DNA)
ribonucleic acid (RNA)
nucleotides
protein synthesis
gene
codon

Hydrocarbon derivatives

- Contain one or more functional groups
- Alcohols: contain the —OH group
- Aldehydes: contain a  group

- Ketones: contain the  group

- Carboxylic acids: contain the  group

Polymers

- Large molecules formed from many small molecules (called monomers)
 - Addition polymerization: monomers add together by a free radical mechanism
 - Condensation polymerization: monomers connect by splitting out a small molecule, such as water

Proteins

- A class of natural polymers with molar masses ranging from 600 to 1,000,000
- Fibrous proteins form the structural basis of muscle, hair, and cartilage
- Globular proteins perform many biologic functions, including transport and storage of oxygen, catalysis of biologic reactions, and regulation of biologic systems
- Building blocks of proteins (monomers) are α -amino acids, which connect by a condensation reaction to form a peptide linkage
- Protein structure
 - Primary: the order of amino acids in the chain
 - Secondary: the arrangement of the protein chain
 - α -helix
 - pleated sheet
 - Tertiary structure: the overall shape of the protein

Carbohydrates

- Contain carbon, hydrogen, and oxygen
- Serve as food sources for most organisms
- Monosaccharides are most commonly five-carbon and six-carbon polyhydroxy ketones and aldehydes
 - Monosaccharides combine to form more complex carbohydrates, such as sucrose, starch, and cellulose

Genetic processes

- When a cell divides, the genetic information is transmitted via deoxyribonucleic acid (DNA), which has a double helical structure
 - During cell division, the double helix unravels and a new polymer forms along each strand of the original DNA
 - The genetic code is carried by organic bases that hydrogen-bond to each other in specific pairs in the interior of the DNA double helix

REVIEW QUESTIONS

1. What is a hydrocarbon? What is the difference between a saturated hydrocarbon and an unsaturated hydrocarbon? Distinguish between normal and branched hydrocarbons. What is an alkane? What is a cyclic alkane? What are the two general formulas for alkanes? What is the hybridization of carbon atoms in alkanes? What are the bond angles in alkanes? Why are cyclopropane and cyclobutane so reactive?

messenger RNA (mRNA)
transfer RNA (tRNA)
anticodon

- The normal (unbranched) hydrocarbons are often referred to as *straight-chain hydrocarbons*. What does this name refer to? Does it mean that the carbon atoms in a straight-chain hydrocarbon really have a linear arrangement? Explain. In the shorthand notation for cyclic alkanes, the hydrogens are usually omitted. How do you determine the number of hydrogens bonded to each carbon in a ring structure?
2. What is an alkene? What is an alkyne? What are the general formulas for alkenes and alkynes, assuming one multiple bond in each? What are the bond angles in alkenes and alkynes? Describe the bonding in alkenes and alkynes using C_2H_4 and C_2H_2 as your examples. Why is there restricted rotation in alkenes and alkynes? Is the general formula for a cyclic alkene C_nH_{2n} ? If not, what is the general formula, assuming one multiple bond?
 3. What are aromatic hydrocarbons? Benzene exhibits resonance. Explain. What are the bond angles in benzene? Give a detailed description of the bonding in benzene. The π electrons in benzene are delocalized, while the π electrons in alkenes and alkynes are localized. Explain the difference.
 4. Summarize the nomenclature rules for alkanes, alkenes, alkynes, and aromatic compounds. Correct the following false statements regarding nomenclature of hydrocarbons.
 - a. The root name for a hydrocarbon is based on the shortest continuous chain of carbon atoms.
 - b. The suffix used to name all hydrocarbons is *-ane*.
 - c. Substituent groups are numbered so as to give the largest numbers possible.
 - d. No number is required to indicate the positions of double or triple bonds in alkenes and alkynes.
 - e. Substituent groups get the lowest number possible in alkenes and alkynes.
 - f. The *ortho-* term in aromatic hydrocarbons indicates the presence of two substituent groups bonded to carbon-1 and carbon-3 in benzene.
 5. What functional group distinguishes each of the following hydrocarbon derivatives?
 - a. halohydrocarbons
 - b. alcohols
 - c. ethers
 - d. aldehydes
 - e. ketones
 - f. carboxylic acids
 - g. esters
 - h. amines

Give examples of each functional group. What prefix or suffix is used to name each functional group? What are the bond angles in each? Describe the bonding in each functional group. What is the difference between a primary, secondary, and tertiary alcohol? For the functional groups in a–h, when is a number required to indicate the position of the functional group? Carboxylic acids are often written as $RCOOH$. What does $—COOH$ indicate and what does R indicate? Aldehydes are sometimes written as $RCHO$. What does $—CHO$ indicate?

6. Distinguish between isomerism and resonance. Distinguish between structural and geometric isomerism. When writing the various structural isomers, the most difficult task is identifying which are different isomers and which are identical to a previously written structure—that is, which are compounds that differ only by the rotation of a carbon single bond. How do you distinguish between structural isomers and those that are identical?

Alkenes and cycloalkanes are structural isomers of each other. Give an example of each using C_4H_{10} . Another common feature of alkenes and cycloalkanes

is that both have restricted rotation about one or more bonds in the compound, so both can exhibit *cis-trans* isomerism. What is required for an alkene or cycloalkane to exhibit *cis-trans* isomerism? Explain the difference between *cis* and *trans* isomers.

Alcohols and ethers are structural isomers of each other, as are aldehydes and ketones. Give an example of each to illustrate. Which functional group in Table 22.4 can be structural isomers of carboxylic acids?

What is optical isomerism? What do you look for to determine whether an organic compound exhibits optical isomerism? 1-Bromo-1-chloroethane is optically active whereas 1-bromo-2-chloroethane is not optically active. Explain.

7. What type of intermolecular forces do hydrocarbons exhibit? Explain why the boiling point of *n*-heptane is greater than that of *n*-butane. A general rule for a group of hydrocarbon isomers is that as the amount of branching increases, the boiling point decreases. Explain why this would be true.

The functional groups listed in Table 22.4 all exhibit London dispersion forces, but they also usually exhibit additional dipole-dipole forces. Explain why this is the case for each functional group. Although alcohols and ethers are structural isomers of each other, alcohols always boil at significantly higher temperatures than similar-size ethers. Explain. What would you expect when comparing the boiling points of similar-size carboxylic acids to esters? $\text{CH}_3\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2\text{OH}$, CH_3CHO , and HCOOH all have about the same molar mass, but they boil at very different temperatures. Why? Place these compounds in order by increasing boiling point.

8. Distinguish between substitution and addition reactions. Give an example of each type of reaction. Alkanes and aromatics are fairly stable compounds. To make them react, a special catalyst must be present. What catalyst must be present when reacting Cl_2 with an alkane or with benzene? Adding Cl_2 to an alkene or alkyne does not require a special catalyst. Why are alkenes and alkynes more reactive than alkanes and aromatic compounds? All organic compounds can be combusted. What is the other reactant in a combustion reaction, and what are the products, assuming the organic compound contains only C, H, and perhaps O?

The following are some other organic reactions covered in Section 22.4. Give an example to illustrate each type of reaction.

- Adding H_2O to an alkene (in the presence of H^+) yields an alcohol.
 - Primary alcohols are oxidized to aldehydes, which can be further oxidized to carboxylic acids.
 - Secondary alcohols are oxidized to ketones.
 - Reacting an alcohol with a carboxylic acid (in the presence of H^+) produces an ester.
9. Define and give an example of each of the following.
- addition polymer
 - condensation polymer
 - copolymer
 - homopolymer
 - polyester
 - polyamide

Distinguish between a thermoset polymer and a thermoplastic polymer. How do the physical properties of polymers depend on chain length and extent of chain branching? Explain how crosslinking agents are used to change the physical properties of polymers. Isotactic polypropylene makes stronger fibers than atactic polypropylene. Explain. In which polymer, polyethylene or polyvinyl chloride, would you expect to find the stronger intermolecular forces (assuming the average chain lengths are equal)?

10. Give the general formula for an amino acid. Some amino acids are labeled hydrophilic and some are labeled hydrophobic. What do these terms refer to? Aqueous solutions of amino acids are buffered solutions. Explain. Most of the amino acids in Fig. 22.18 are optically active. Explain. What is a peptide bond? Show how glycine, serine, and alanine react to form a tripeptide. What is a protein, and what are the monomers in proteins? Distinguish between the primary, secondary, and tertiary structures of a protein. Give examples of the types of forces that maintain each type of structure. Describe how denaturation affects the function of a protein.

What are carbohydrates, and what are the monomers in carbohydrates? The monosaccharides in Table 22.8 are all optically active. Explain. What is a *disaccharide*? Which monosaccharide units make up the disaccharide sucrose? What do you call the bond that forms between the monosaccharide units? What forces are responsible for the solubility of starch in water? What is the difference between starch, cellulose, and glycogen?

Describe the structural differences between DNA and RNA. The monomers in nucleic acids are called nucleotides. What are the three parts of a nucleotide? The compounds adenine, guanine, cytosine, and thymine are called the nucleic acid bases. What structural features in these compounds make them bases? DNA exhibits a double-helical structure. Explain. Describe how the complementary base pairing between the two individual strands of DNA forms the overall double-helical structure. How is complementary base pairing involved in the replication of DNA molecule during cell division? Describe how protein synthesis occurs. What is a codon, and what is a gene? The deletion of a single base from a DNA molecule can constitute a fatal mutation, whereas substitution of one base for another is often not as serious a mutation. Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

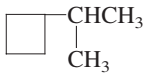
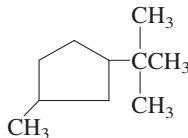
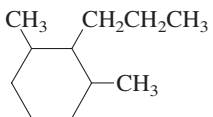
- A confused student was doing an isomer problem and listed the following six names as different structural isomers of C_7H_{16} .
 - 1-sec-butylpropane
 - 4-methylhexane
 - 2-ethylpentane
 - 1-ethyl-1-methylbutane
 - 3-methylhexane
 - 4-ethylpentane
 How many different structural isomers are actually present in these six names?
- For the following formulas, what types of isomerism could be exhibited? For each formula, give an example that illustrates the specific type of isomerism. The types of isomerism are structural, geometric, and optical.
 - C_6H_{12}
 - $C_5H_{12}O$
 - $C_6H_4Br_2$
- What is wrong with the following names? Give the correct name for each compound.
 - 2-ethylpropane
 - 5-iodo-5, 6-dimethylhexane
 - cis*-4-methyl-3-pentene
 - 2-bromo-3-butanol
- The following organic compounds cannot exist. Why?
 - 2-chloro-2-butyne
 - 2-methyl-2-propanone
 - 1,1-dimethylbenzene
 - 2-pentanal
 - 3-hexanoic acid
 - 5,5-dibromo-1-cyclobutanol
- If you had a group of hydrocarbons, what structural features would you look at to rank the hydrocarbons in order of increasing boiling point?
- Which of the functional groups in Table 22.4 can exhibit hydrogen bonding intermolecular forces? Can CH_2CF_2 exhibit hydrogen bonding? Explain.
- A polypeptide is also called a polyamide. What is a polyamide? Consider a polyhydrocarbon, a polyester, and a polyamide. Assuming average chain lengths are equal, which polymer would you expect to make the strongest fibers and which polymer would you expect to make the weakest fibers? Explain.
- Give an example reaction that would yield the following products. Name the organic reactant and product in each reaction.
 - alkane
 - monohalogenated alkane

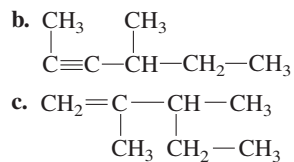
- c. dihalogenated alkane
 d. tetrahalogenated alkane
 e. monohalogenated benzene
 f. alkene
9. Give an example reaction that would yield the following products as major organic products. See Exercises 22.62 and 22.65 for some hints. For oxidation reactions, just write oxidation over the arrow and don't worry about the actual reagent.
- primary alcohol
 - secondary alcohol
 - tertiary alcohol
 - aldehyde
 - ketone
 - carboxylic acid
 - ester
10. What is polystyrene? The following processes result in a stronger polystyrene polymer. Explain why in each case.
- addition of catalyst to form syndiotactic polystyrene
 - addition of 1,3-butadiene and sulfur
 - producing long chains of polystyrene
 - addition of a catalyst to make linear polystyrene
11. Answer the following questions regarding the formation of polymers.
- What structural features must be present in a monomer in order to form a homopolymer polyester?
 - What structural features must be present in the monomers in order to form a copolymer polyamide?
 - What structural features must be present in a monomer that can form both an addition polymer and a condensation polymer?
12. In Section 22.6, three important classes of biologically important natural polymers are discussed. What are the three classes, what are the monomers used to form the polymers, and why are they biologically important?

Exercises

In this section similar exercises are paired.

Hydrocarbons

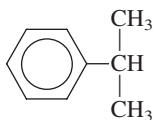
13. Draw the five structural isomers of hexane (C_6H_{14}).
14. Name the structural isomers in Exercise 13.
15. Draw all the structural isomers for C_8H_{18} that have the following root name (longest carbon chain). Name the structural isomers.
- heptane
 - butane
16. Draw all the structural isomers for C_8H_{18} that have the following root name (longest carbon chain). Name the structural isomers.
- hexane
 - pentane
17. Draw a structural formula for each of the following compounds.
- 2-methylpropane
 - 2-methylbutane
 - 2-methylpentane
 - 2-methylhexane
18. Draw a structural formula for each of the following compounds.
- 2,2-dimethylheptane
 - 2,3-dimethylheptane
 - 3,3-dimethylheptane
 - 2,4-dimethylheptane
19. Draw the structural formula for each of the following.
- 3-isobutylhexane
 - 2,2,4-trimethylpentane, also called *isooctane*. This substance is the reference (100 level) for octane ratings.
 - 2-*tert*-butylpentane
 - The names given in parts a and c are incorrect. Give the correct names for these hydrocarbons.
20. Draw the structure for 4-ethyl-2,3-diisopropylpentane. This name is incorrect. Give the correct systematic name.
21. Name each of the following:
- $$\begin{array}{ccccccc} & & \text{CH}_3 & & & & \\ & & | & & & & \\ \text{CH}_3 & - & \text{C} & - & \text{CH}_2 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_3 \\ & & | & & & & | & & & & \\ & & \text{CH}_3 & & & & \text{CH}_3 & & & & \end{array}$$
 - $$\begin{array}{ccccccccccc} & & & & & & & & & & & & \\ & & & & & & & & & & & & \\ \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_2 \\ & & & & & & | & & & & & & | \\ & & & & & & \text{CH}_3 & & & & & & \text{CH}_3 \end{array}$$
 - $$\begin{array}{ccccccc} & & \text{CH}_3 & & & & \text{CH}_3 \\ & & | & & & & | \\ \text{CH}_3 & - & \text{C} & - & \text{CH}_2 & - & \text{C} & - & \text{CH}_3 \\ & & | & & & & | \\ & & \text{CH}_3 & & & & \text{CH}_3 \end{array}$$
 - $$\begin{array}{ccccccccccc} & & & & & & & & & & & & \\ & & & & & & & & & & & & \\ \text{CH}_3 & - & \text{C} & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_2 & - & \text{CH}_3 \\ & & | & & & & & & & & & & \\ & & \text{CH}_2 & - & \text{CH}_3 & & & & & & & & \end{array}$$
22. Name each of the following cyclic alkanes, and indicate the formula of the compound.
- 
 - 
 - 
23. Give two examples of saturated hydrocarbons. How many other atoms are bonded to each carbon in a saturated hydrocarbon?
24. Draw the structures for two examples of *unsaturated* hydrocarbons. What structural feature makes a hydrocarbon unsaturated?
25. Name each of the following alkenes.
- $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$
 - $$\begin{array}{ccccccc} & & & & & & \text{CH}_2\text{CH}_3 \\ & & & & & & | \\ \text{CH}_3 & - & \text{CH} & = & \text{CH} & - & \text{CHCH}_3 \\ & & & & & & | \\ & & & & & & \text{CH}_3 \end{array}$$
 - $$\begin{array}{ccccccccccc} & & & & & & & & & & & & \\ & & & & & & & & & & & & \\ \text{CH}_3 & \text{CH}_2 & \text{CH} & - & \text{CH} & = & \text{CH} & - & \text{CHCH}_3 \\ & & | & & & & & & | \\ & & \text{CH}_3 & & & & & & \text{CH}_3 \end{array}$$
26. Name each of the following alkenes or alkynes.
- $$\begin{array}{ccccccc} & & & & & & \\ & & & & & & \\ \text{CH}_3 & - & \text{C} & = & \text{C} & - & \text{CH}_3 \\ & & | & & | \\ & & \text{CH}_3 & & \text{CH}_3 \end{array}$$



27. Give the structure for each of the following.
 a. 3-hexene b. 2,4-heptadiene c. 2-methyl-3-octene
28. Give the structure for each of the following.
 a. 4-methyl-1-pentyne
 b. 2,3,3-trimethyl-1-hexene
 c. 3-ethyl-4-decene

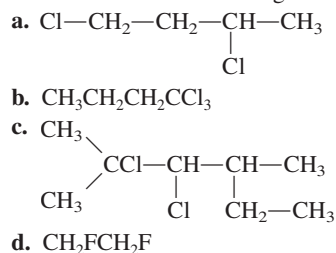
29. Give the structure of each of the following aromatic hydrocarbons.
 a. *o*-ethyltoluene
 b. *p*-di-*tert*-butylbenzene
 c. *m*-diethylbenzene
 d. 1-phenyl-2-butene

30. Cumene is the starting material for the industrial production of acetone and phenol. The structure of cumene is

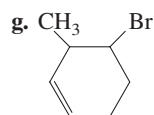
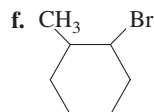
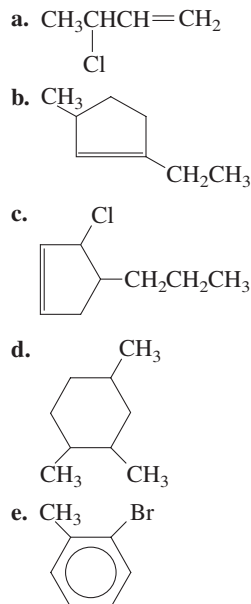


Give the systematic name for cumene.

31. Name each of the following.

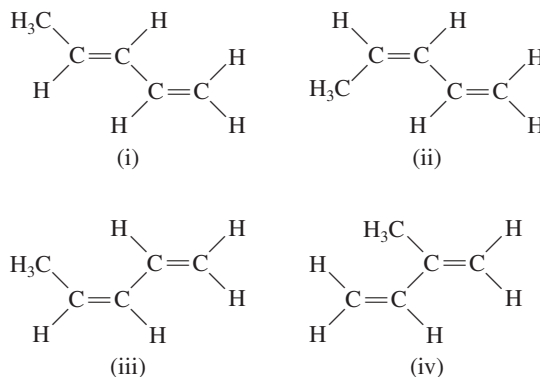


32. Name each of the following compounds.



Isomerism

33. There is only one compound that is named 1,2-dichloroethane, but there are two distinct compounds that can be named 1,2-dichloroethene. Why?
34. Consider the following four structures:



- a. Which of these compounds would have the same physical properties (melting point, boiling point, density, and so on)?
 b. Which of these compounds is (are) *trans* isomers?
 c. Which of these compounds do not exhibit *cis-trans* isomerism?

35. Which of the compounds in Exercises 25 and 27 exhibit *cis-trans* isomerism?
36. Which of the compounds in Exercises 26 and 28 exhibit *cis-trans* isomerism?

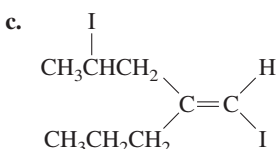
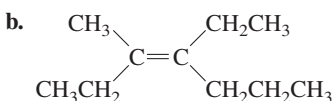
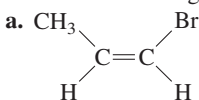
37. Draw all the structural isomers of C_5H_{10} . Ignore any cyclic isomers.
38. Which of the structural isomers in Exercise 37 exhibit *cis-trans* isomerism?

39. Draw all the structural and geometrical (*cis-trans*) isomers of $\text{C}_3\text{H}_5\text{Cl}$.
40. Draw all the structural and geometrical (*cis-trans*) isomers of bromochloropropene.

41. Draw all structural and geometrical (*cis-trans*) isomers of $\text{C}_4\text{H}_7\text{F}$. Ignore any cyclic isomers.
42. *Cis-trans* isomerism is also possible in molecules with rings. Draw the *cis* and *trans* isomers of 1,2-dimethylcyclohexane. In Exercise 41, you drew all of the noncyclic structural and geometric isomers of $\text{C}_4\text{H}_7\text{F}$. Now draw the cyclic structural and geometric isomers of $\text{C}_4\text{H}_7\text{F}$.

43. Draw the following.
 a. *cis*-2-hexene
 b. *trans*-2-butene
 c. *cis*-2,3-dichloro-2-pentene

44. Name the following compounds.



45. If one hydrogen in a hydrocarbon is replaced by a halogen atom, the number of isomers that exist for the substituted compound depends on the number of types of hydrogen in the original hydrocarbon. Thus there is only one form of chloroethane (all hydrogens in ethane are equivalent), but there are two isomers of propane that arise from the substitution of a methyl hydrogen or a methylene hydrogen. How many isomers can be obtained when one hydrogen in each of the compounds named below is replaced by a chlorine atom?

- a. *n*-pentane c. 2,4-dimethylpentane
b. 2-methylbutane d. methylcyclobutane

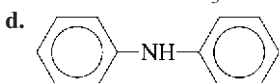
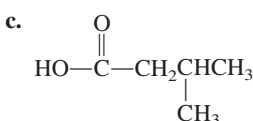
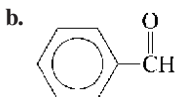
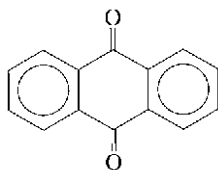
46. There are three isomers of dichlorobenzene, one of which has now replaced naphthalene as the main constituent of mothballs.

- a. Identify the *ortho*, the *meta*, and the *para* isomers of dichlorobenzene.
b. Predict the number of isomers for trichlorobenzene.
c. It turns out that the presence of one chlorine atom on a benzene ring will cause the next substituent to add *ortho* or *para* to the first chlorine atom on the benzene ring. What does this tell you about the synthesis of *m*-dichlorobenzene?
d. Which of the isomers of trichlorobenzene will be the hardest to prepare?

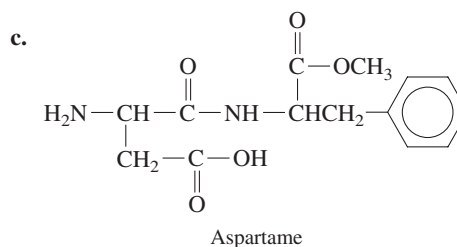
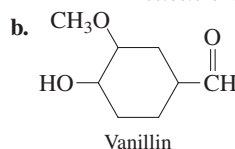
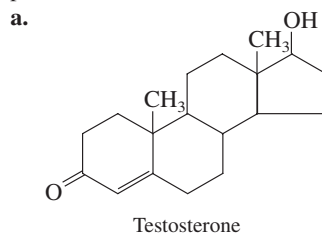
Functional Groups

47. Identify each of the following compounds as a carboxylic acid, ester, ketone, aldehyde, or amine.

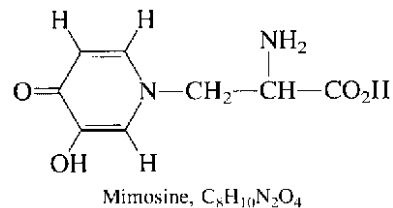
- a. Anthraquinone, an important starting material in the manufacture of dyes:



48. Identify the functional groups present in the following compounds.

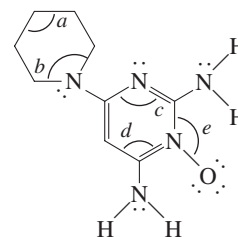


49. Mimosine is a natural product found in large quantities in the seeds and foliage of some legume plants and has been shown to cause inhibition of hair growth and hair loss in mice.



- a. What functional groups are present in mimosine?
b. Give the hybridization of the eight carbon atoms in mimosine.
c. How many σ and π bonds are found in mimosine?

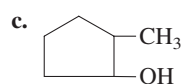
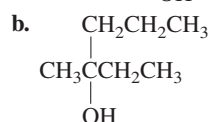
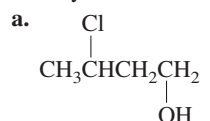
50. Minoxidil ($C_9H_{15}N_5O$) is a compound produced by Pharmacia Company that has been approved as a treatment of some types of male pattern baldness.



- a. Would minoxidil be more soluble in acidic or basic aqueous solution? Explain.
b. Give the hybridization of the five nitrogen atoms in minoxidil.
c. Give the hybridization of each of the nine carbon atoms in minoxidil.
d. Give approximate values of the bond angles marked *a*, *b*, *c*, *d*, and *e*.

- e. Including all the hydrogen atoms, how many σ bonds exist in minoxidil?
 f. How many π bonds exist in minoxidil?

51. For each of the following alcohols, give the systematic name and specify whether the alcohol is primary, secondary, or tertiary.



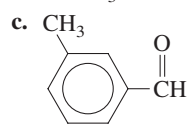
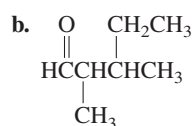
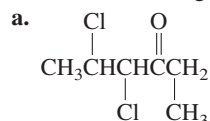
52. Draw structural formulas for each of the following alcohols. Indicate whether the alcohol is primary, secondary, or tertiary.

- a. 1-butanol c. 2-methyl-1-butanol
 b. 2-butanol d. 2-methyl-2-butanol

53. Name all the alcohols that have the formula $C_5H_{12}O$. How many ethers have the formula $C_5H_{12}O$?

54. Name all the aldehydes and ketones that have the formula $C_5H_{10}O$.

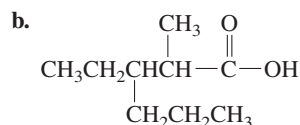
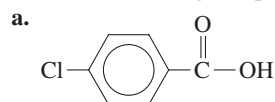
55. Name the following compounds.



56. Draw the structural formula for each of the following.

- a. formaldehyde (methanal)
 b. 4-heptanone
 c. 3-chlorobutanal
 d. 5,5-dimethyl-2-hexanone

57. Name the following compounds.



- c. $HCOOH$

58. Draw a structural formula for each of the following.

- a. 3-methylpentanoic acid
 b. ethyl methanoate
 c. methyl benzoate
 d. 3-chloro-2,4-dimethylhexanoic acid

59. Which of the following statements is (are) false? Explain why the statement(s) is (are) false.

- a. is a structural isomer of pentanoic acid.
 b. is a structural isomer of 2-methyl-3-pentanone.
 c. $CH_3CH_2OCH_2CH_2CH_3$ is a structural isomer of 2-pentanol.
 d. is a structural isomer of 2-butanal.

- e. Trimethylamine is a structural isomer of $CH_3CH_2CH_2NH_2$.

60. Draw the isomer(s) specified. There may be more than one possible isomer for each part.

- a. a cyclic compound that is an isomer of *trans*-2-butene
 b. an ester that is an isomer of propanoic acid
 c. a ketone that is an isomer of butanal
 d. a secondary amine that is an isomer of butylamine
 e. a tertiary amine that is an isomer of butylamine
 f. an ether that is an isomer of 2-methyl-2-propanol
 g. a secondary alcohol that is an isomer of 2-methyl-2-propanol

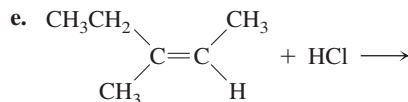
Reactions of Organic Compounds

61. Complete the following reactions.

- a. $CH_3CH=CHCH_3 + H_2 \xrightarrow{Pt}$
 b.
 c.
 d. $CH_3C(CH_3)=CH_2 + O_2 \xrightarrow{\text{Spark}}$

62. Reagents such as HCl, HBr, and HOH (H_2O) can add across carbon-carbon double and triple bonds, with H forming a bond to one of the carbon atoms in the multiple bond and Cl, Br, or OH forming a bond to the other carbon atom in the multiple bond. In some cases, two products are possible. For the major organic product, the addition occurs so that the hydrogen atom in the reagent attaches to the carbon atom in the multiple bond that already has the greater number of hydrogen atoms bonded to it. With this rule in mind, draw the structure of the major product in each of the following reactions.

- a. $CH_3CH_2CH=CH_2 + H_2O \longrightarrow$
 b. $CH_3CH_2CH=CH_2 + HBr \longrightarrow$
 c. $CH_3CH_2C\equiv CH + 2HBr \longrightarrow$
 d.

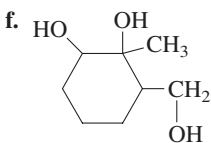
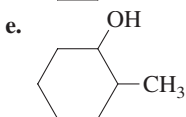
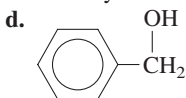


63. When toluene ($\text{C}_6\text{H}_5\text{CH}_3$) reacts with chlorine gas in the presence of iron(III) catalyst, the product is a mixture of the *ortho* and *para* isomers of $\text{C}_6\text{H}_4\text{ClCH}_3$. However, when the reaction is light-catalyzed with no Fe^{3+} catalyst present, the product is $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$. Explain.

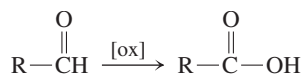
64. Why is it preferable to produce chloroethane by the reaction of $\text{HCl}(g)$ with ethene than by the reaction of $\text{Cl}_2(g)$ with ethane? (See Exercise 62.)

65. Using appropriate reactants, alcohols can be oxidized into aldehydes, ketones, and/or carboxylic acids. Primary alcohols can be oxidized into aldehydes, which can then be oxidized into carboxylic acids. Secondary alcohols can be oxidized into ketones, while tertiary alcohols do not undergo this type of oxidation. Give the structure of the product(s) resulting from the oxidation of each of the following alcohols.

- a. 3-methyl-1-butanol
b. 3-methyl-2-butanol
c. 2-methyl-2-butanol



66. Oxidation of an aldehyde yields a carboxylic acid:



Draw the structures for the products of the following oxidation reactions.

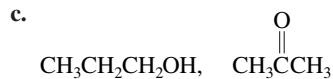
- a. propanal $\xrightarrow{[\text{ox}]}$
b. 2,3-dimethylpentanal $\xrightarrow{[\text{ox}]}$
c. 3-ethylbenzaldehyde $\xrightarrow{[\text{ox}]}$

67. How would you synthesize each of the following?

- a. 1,2-dibromopropane from propene
b. acetone (2-propanone) from an alcohol
c. *tert*-butyl alcohol (2-methyl-2-propanol) from an alkene (See Exercise 62.)
d. propanoic acid from an alcohol

68. What tests could you perform to distinguish between the following pairs of compounds?

- a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_2=\text{CHCH}_2\text{CH}_3$
b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_3$

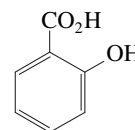


69. How would you synthesize the following esters?

a. *n*-octylacetate



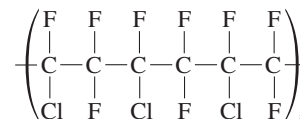
70. Salicylic acid has the following structure:



Since salicylic acid has both an alcohol functional group and a carboxylic acid functional group, it can undergo two different esterification reactions depending on which functional group reacts. For example, when treated with ethanoic acid (acetic acid), salicylic acid behaves as an alcohol and the ester produced is acetylsalicylic acid (aspirin). On the other hand, when reacted with methanol, salicylic acid behaves as an acid and the ester methyl salicylate (oil of wintergreen) is produced. Methyl salicylate is also an analgesic and part of the formulation of many liniments for sore muscles. What are the structures of acetylsalicylic acid and methyl salicylate?

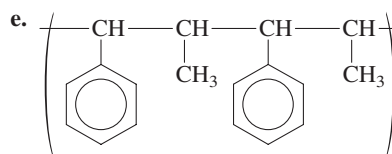
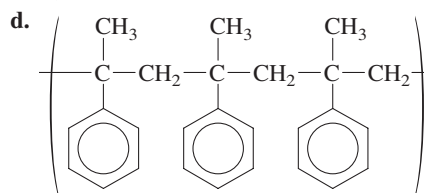
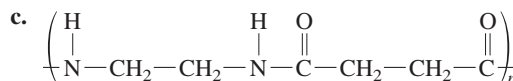
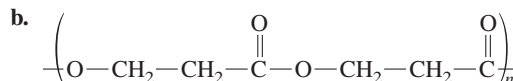
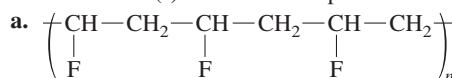
Polymers

71. Kel-F is a polymer with the structure



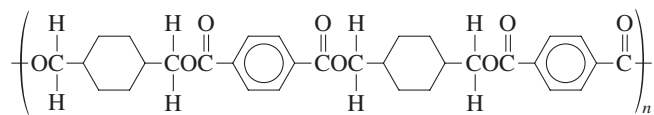
What is the monomer for Kel-F?

72. What monomer(s) must be used to produce the following polymers?





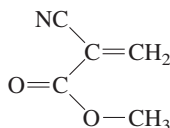
g.



(This polymer is Kodel, used to make fibers of stain-resistant carpeting.)

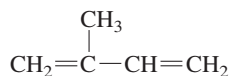
Classify these polymers as condensation or addition polymers. Which are copolymers?

73. "Super glue" contains methyl cyanoacrylate,

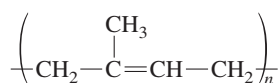


which readily polymerizes upon exposure to traces of water or alcohols on the surfaces to be bonded together. The polymer provides a strong bond between the two surfaces. Draw the structure of the polymer formed by methyl cyanoacrylate.

74. Isoprene is the repeating unit in natural rubber. The structure of isoprene is

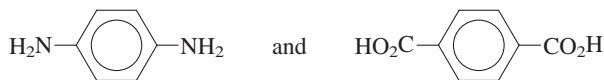


- a. Give a systematic name for isoprene.
b. When isoprene is polymerized, two polymers of the form



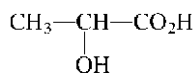
are possible. In natural rubber, the *cis* configuration is found. The polymer with the *trans* configuration about the double bond is called gutta percha and was once used in the manufacture of golf balls. Draw the structure of natural rubber and gutta percha showing three repeating units and the configuration about the carbon-carbon double bonds.

75. Kevlar, used in bulletproof vests, is made by the condensation copolymerization of the monomers



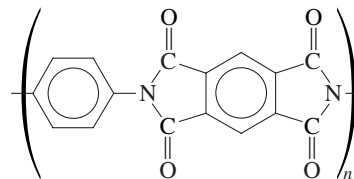
Draw the structure of a portion of the Kevlar chain.

76. The polyester formed from lactic acid,

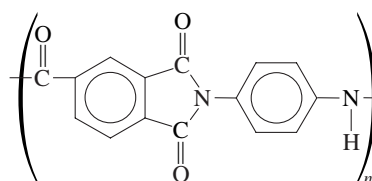


is used for tissue implants and surgical sutures that will dissolve in the body. Draw the structure of a portion of this polymer.

77. Polyimides are polymers that are tough and stable at temperatures of up to 400°C. They are used as a protective coating on the quartz fibers used in fiber optics. What monomers were used to make the following polyimide?

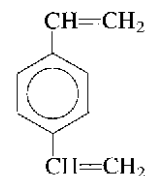


78. The Amoco Chemical Company has successfully raced a car with a plastic engine. Many of the engine parts, including piston skirts, connecting rods, and valve-train components, were made of a polymer called
- Torlon*
- :



What monomers are used to make this polymer?

79. Polystyrene can be made more rigid by copolymerizing styrene with divinylbenzene:



How does the divinylbenzene make the copolymer more rigid?

80. Polyesters containing double bonds are often crosslinked by reacting the polymer with styrene.

- a. Draw the structure of the copolymer of

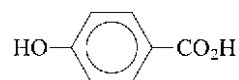


- b. Draw the structure of the crosslinked polymer (after the polyester has been reacted with styrene).

81. Which of the following polymers would be stronger or more rigid? Explain your choices.

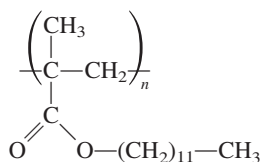
- a. The copolymer of ethylene glycol and terephthalic acid or the copolymer of 1,2-diaminoethane and terephthalic acid (1,2-diaminoethane = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)

- b. The polymer of
- $\text{HO-(CH}_2\text{)}_6\text{-CO}_2\text{H}$
- or that of



- c. Polyacetylene or polyethylene (The monomer in polyacetylene is ethyne.)

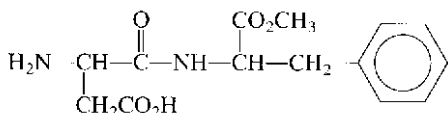
82. Poly(lauryl methacrylate) is used as an additive in motor oils to counter the loss of viscosity at high temperature. The structure is



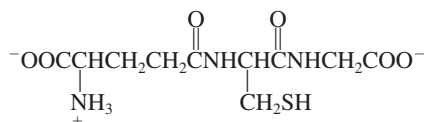
The long hydrocarbon chain of poly(lauryl methacrylate) makes the polymer soluble in oil (a mixture of hydrocarbons with mostly 12 or more carbon atoms). At low temperatures the polymer is coiled into balls. At higher temperatures the balls uncoil and the polymer exists as long chains. Explain how this helps control the viscosity of oil.

Natural Polymers

83. Which of the amino acids in Fig. 22.18 contain the following functional groups in their R group?
 a. alcohol c. amine
 b. carboxylic acid d. amide
84. When pure crystalline amino acids are heated, decomposition generally occurs before the solid melts. Account for this observation. (Hint: Crystalline amino acids exist as $\text{H}_3\text{N}^+\text{NCRHCOO}^-$, called *zwitterions*.)
85. Aspartame, the artificial sweetener marketed under the name Nutra-Sweet, is a methyl ester of a dipeptide:



- a. What two amino acids are used to prepare aspartame?
 b. There is concern that methanol may be produced by the decomposition of aspartame. From what portion of the molecule can methanol be produced? Write an equation for this reaction.
86. Glutathione, a tripeptide found in virtually all cells, functions as a reducing agent. The structure of glutathione is



What amino acids make up glutathione?

87. Draw the structures of the two dipeptides that can be formed from serine and alanine.
88. Draw the structures of the tripeptides gly–ala–ser and ser–ala–gly. How many other tripeptides are possible using these three amino acids?
89. Write the sequence of all possible tetrapeptides composed of the following amino acids.
 a. two phenylalanines and two glycines
 b. two phenylalanines, glycine, and alanine
90. How many different pentapeptides can be formed using five different amino acids?

91. Give an example of amino acids that could give rise to the interactions pictured in Fig. 22.24 that maintain the tertiary structures of proteins.

92. What types of interactions can occur between the side chains of the following amino acids that would help maintain the tertiary structure of a protein?

- a. cysteine and cysteine c. glutamic acid and lysine
 b. glutamine and serine d. proline and leucine

93. Oxygen is carried from the lungs to tissues by the protein hemoglobin in red blood cells. Sick cell anemia is a disease resulting from abnormal hemoglobin molecules in which a valine is substituted for a single glutamic acid in normal hemoglobin. How might this substitution affect the structure of hemoglobin?

94. Over 100 different kinds of mutant hemoglobin molecules have been detected in humans. Unlike sickle cell anemia (see Exercise 93), not all of these mutations are as serious. In one nonlethal mutation, glutamine substitutes for a single glutamic acid in normal hemoglobin. Rationalize why this substitution is nonlethal.

95. Draw cyclic structures for D-ribose and D-mannose.

96. Indicate the chiral carbon atoms found in the monosaccharides D-ribose and D-mannose.

97. In addition to using *numerical* prefixes in the general names of sugars to indicate how many carbon atoms are present, we often use the prefixes *keto-* and *aldo-* to indicate whether the sugar is a ketone or an aldehyde. For example, the monosaccharide fructose is frequently called a *ketohexose* to emphasize that it contains six carbons as well as the ketone functional group. For each of the monosaccharides shown in Table 22.8 classify the sugars as aldohexoses, aldopentoses, ketohexoses, or ketopentoses.

98. Glucose can occur in three forms: two cyclic forms and one open-chain structure. In aqueous solution, only a tiny fraction of the glucose is in the open-chain form. Yet tests for the presence of glucose depend on reaction with the aldehyde group, which is found only in the open-chain form. Explain why these tests work.

99. What are the structural differences between α - and β -glucose? These two cyclic forms of glucose are the building blocks to form two different polymers. Explain.

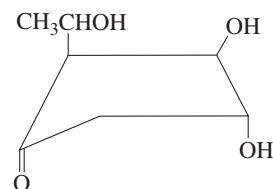
100. Cows can digest cellulose, but humans can't. Why not?

101. Which of the amino acids in Fig. 22.18 contain more than one chiral carbon atom? Draw the structures of these amino acids and indicate all chiral carbon atoms.

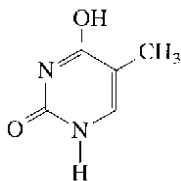
102. Why is glycine not optically active?

103. Which of the noncyclic isomers of bromochloropropene are optically active?

104. How many chiral carbon atoms does the following structure have?



105. Part of a certain DNA sequence is G–G–T–C–T–A–T–A–C. What is the complementary sequence?
106. The codons (words) in DNA (that specify which amino acid should be at a particular point in a protein) are three bases long. How many such three-letter words can be made from the four bases adenine, cytosine, guanine, and thymine?
107. Which base will hydrogen-bond with uracil within an RNA molecule? Draw the structure of this base pair.
108. Tautomers are molecules that differ in the position of a hydrogen atom. A tautomeric form of thymine has the structure



If the tautomer above, rather than the stable form of thymine were present in a strand of DNA during replication, what would be the result?

109. The base sequences in mRNA that code for certain amino acids are

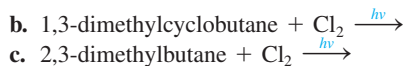
Glu: GAA, GAG
 Val: GUU, GUC, GUA, GUG
 Met: AUG
 Trp: UGG
 Phe: UUU, UUC
 Asp: GAU, GAC

These sequences are complementary to the sequences in DNA.

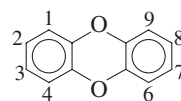
- Give the corresponding sequences in DNA for the amino acids listed above.
 - Give a DNA sequence that would code for the peptide trp–glu–phe–met.
 - How many different DNA sequences can code for the butapeptide in part b?
 - What is the peptide that is produced from the DNA sequence T–A–C–C–T–G–A–A–G?
 - What other DNA sequences would yield the same tripeptide as in part d?
110. The change of a single base in the DNA sequence for normal hemoglobin can encode for the abnormal hemoglobin giving rise to sickle cell anemia. Which base in the codon for glu in DNA is replaced to give the codon(s) for val? (See Exercises 93 and 109.)

Additional Exercises

111. Draw the following incorrectly named compounds and name them correctly.
- 2-ethyl-3-methyl-5-isopropylhexane
 - 2-ethyl-4-*tert*-butylpentane
 - 3-methyl-4-isopropylpentane
 - 2-ethyl-3-butyne
112. In the presence of light, chlorine can substitute for one (or more) of the hydrogens in an alkane. For the following reactions, draw the possible monochlorination products.
- 2,2-dimethylpropane + Cl₂ $\xrightarrow{h\nu}$

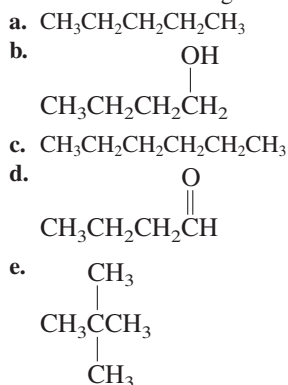


113. Polychlorinated dibenzo-*p*-dioxins (PCDDs) are highly toxic substances that are present in trace amounts as by-products of some chemical manufacturing processes. They have been implicated in a number of environmental incidents—for example, the chemical contamination at Love Canal and the herbicide spraying in Vietnam. The structure of dibenzo-*p*-dioxin, along with the customary numbering convention, is



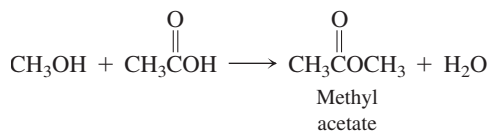
The most toxic PCDD is 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin. Draw the structure of this compound. Also draw the structures of two other isomers containing four chlorine atoms.

114. Consider the following five compounds.



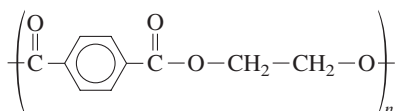
The boiling points of these five compounds are 9.5°C, 36°C, 69°C, 76°C, and 117°C. Which compound boils at 36°C? Explain.

115. The two isomers having the formula C₂H₆O boil at –23°C and 78.5°C. Draw the structure of the isomer that boils at –23°C and of the isomer that boils at 78.5°C.
116. Ignoring ring compounds, which isomer of C₂H₄O₂ should boil at the lowest temperature?
117. Explain why methyl alcohol is soluble in water in all proportions, while stearyl alcohol [CH₃(CH₂)₁₆OH] is a waxy solid that is not soluble in water.
118. Is octanoic acid more soluble in 1 *M* HCl, 1 *M* NaOH, or pure water? Explain. Drugs such as morphine (C₁₇H₁₉NO₃) are often treated with strong acids. The most commonly used form of morphine is morphine hydrochloride (C₁₇H₂₀ClNO₃). Why is morphine treated in this way? (*Hint*: Morphine is an amine.)
119. Consider the compounds butanoic acid, pentanal, *n*-hexane, and 1-pentanol. The boiling points of these compounds (in no specific order) are 69°C, 103°C, 137°C, and 164°C. Match the boiling points to the correct compound.
120. Consider the reaction to produce the ester methyl acetate:



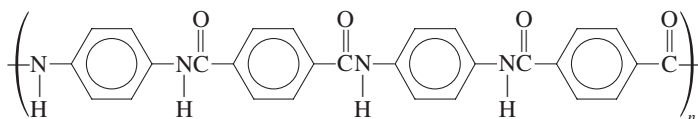
When this reaction is carried out with CH_3OH containing radioactive oxygen-18, the water produced does not contain oxygen-18. Explain the results of this radioisotope tracer experiment.

121. A compound containing only carbon and hydrogen is 85.63% C by mass. Reaction of this compound with H_2O produces a secondary alcohol as the major product and a primary alcohol as the minor product (see Exercise 62). If the molar mass of the hydrocarbon is between 50 and 60 g/mol, name the compound.
122. Diborane, B_2H_6 , is a highly unstable compound that reacts explosively with oxygen. Ethane, C_2H_6 , combines with oxygen only at elevated temperatures. Explain the differences in these two compounds.
123. Three different organic compounds have the formula $\text{C}_3\text{H}_8\text{O}$. Only two of these isomers react with KMnO_4 (a strong oxidizing agent). What are the names of the products when these isomers react with excess KMnO_4 ?
124. Consider the following polymer:



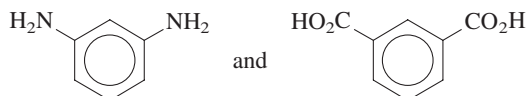
Is this polymer a homopolymer or a copolymer, and is it formed by addition polymerization or condensation polymerization? What is (are) the monomer(s) for this polymer?

125. Nylon is named according to the number of C atoms between the N atoms in the chain. Nylon-46 has 4 C atoms then 6 C atoms, and this pattern repeats. Nylon-6 always has 6 atoms in a row. Speculate as to why nylon-46 is stronger than nylon-6. (*Hint*: Consider the strengths of interchain forces.)
126. The polymer nitrile is a copolymer made from acrylonitrile and butadiene; it is used to make automotive hoses and gaskets. Draw the structure of nitrile. (*Hint*: See Table 22.7.)
127. *Polyaramid* is a term applied to polyamides containing aromatic groups. These polymers were originally made for use as tire cords but have since found many other uses.
- a. Kevlar is used in bulletproof vests and many high-strength



composites. The structure of Kevlar is
Which monomers are used to make Kevlar?

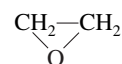
- b. Nomex is a polyaramid used in fire-resistant clothing. It is a copolymer of



Draw the structure of the Nomex polymer. How do Kevlar and Nomex differ in their structures?

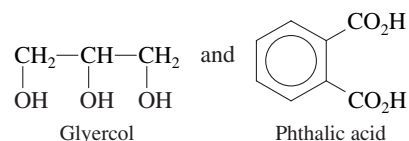
128. When acrylic polymers are burned, toxic fumes are produced. For example, in many airplane fires, more passenger deaths have been caused by breathing toxic fumes than by the fire itself. Using polyacrylonitrile as an example, what would you expect to be one of the most toxic, gaseous combustion products created in the reaction?

129. Ethylene oxide,



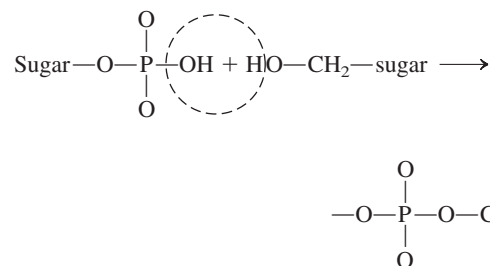
is an important industrial chemical. Although most ethers are unreactive, ethylene oxide is quite reactive. It resembles C_2H_4 in its reactions in that addition reactions occur across the C—O bond in ethylene oxide.

- a. Why is ethylene oxide so reactive? (*Hint*: Consider the bond angles in ethylene oxide as compared with those predicted by the VSEPR model.)
- b. Ethylene oxide undergoes addition polymerization, forming a polymer used in many applications requiring a nonionic surfactant. Draw the structure of this polymer.
130. Another way of producing highly crosslinked polyesters is to use glycerol. Alkyd resins are a polymer of this type. The polymer forms very tough coatings when baked onto a surface and is used in paints for automobiles and large appliances. Draw the structure of the polymer formed from the condensation of



Explain how crosslinking occurs in this polymer.

131. Monosodium glutamate (MSG) is commonly used as a flavoring in foods. Draw the structure of MSG.
132. a. Use bond energies (Table 8.4) to estimate ΔH for the reaction of two molecules of glycine to form a peptide linkage.
b. Would you predict ΔS to favor the formation of peptide linkages between two molecules of glycine?
c. Would you predict the formation of proteins to be a spontaneous process?
133. The reaction to form a phosphate ester linkage between two nucleotides can be approximated as follows:



Would you predict the formation of a dinucleotide from two nucleotides to be a spontaneous process?

134. Considering your answers to Exercises 132 and 133, how can you justify the existence of proteins and nucleic acids in light of the second law of thermodynamics?
135. All amino acids have at least two functional groups with acidic or basic properties. In alanine, the carboxylic acid group has $K_a = 4.5 \times 10^{-3}$ and the amino group has $K_b = 7.4 \times 10^{-5}$. Three ions of alanine are possible when alanine is dissolved in

water. Which of these ions would predominate in a solution with $[H^+] = 1.0 M$? In a solution with $[OH^-] = 1.0 M$?

136. The average molar mass of one base pair of nucleotides in DNA is approximately 600 g/mol. The spacing between successive base pairs is about 0.34 nm, and a complete turn in the helical structure of DNA occurs about every 3.4 nm. If a DNA molecule has a molar mass of 4.5×10^9 g/mol, approximately how many complete turns exist in the DNA α -helix structure?
137. When heat is added to proteins, the hydrogen bonding in the secondary structure is disrupted. What are the algebraic signs of ΔH and ΔS for the denaturation process?
138. In glycine, the carboxylic acid group has $K_a = 4.3 \times 10^{-3}$ and the amino group has $K_b = 6.0 \times 10^{-5}$. Use these equilibrium constant values to calculate the equilibrium constants for the following.
- $^+H_3NCH_2CO_2^- + H_2O \rightleftharpoons H_2NCH_2CO_2^- + H_3O^+$
 - $H_2NCH_2CO_2^- + H_2O \rightleftharpoons H_2NCH_2CO_2H + OH^-$
 - $^+H_3NCH_2CO_2H \rightleftharpoons 2H^+ + H_2NCH_2CO_2^-$

Challenge Problems

139. The isoelectric point of an amino acid is the pH at which the molecule has no net charge. For glycine, that point would be the pH at which virtually all glycine molecules are in the form $^+H_3NCH_2CO_2^-$. This form of glycine is amphoteric since it can act as both an acid and a base. If we assume that the principal equilibrium at the isoelectric point has the best acid reacting with the best base present, then the reaction is

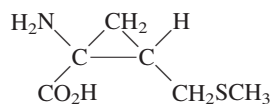


Assuming this reaction is the principal equilibrium, then the following relationship must hold true:

$$[H_2NCH_2CO_2^-] = [^+H_3NCH_2CO_2H] \quad (ii)$$

Use this result and your answer to part c of Exercise 138 to calculate the pH at which equation (ii) is true. It will be the isoelectric point of glycine.

140. In 1994 chemists at Texas A & M University reported the synthesis of a non-naturally occurring amino acid (*C & E News*, April 18, 1994, pp. 26–27):

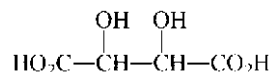


- To which naturally occurring amino acid is this compound most similar?
- A tetrapeptide, phe–met–arg–phe–NH₂, is synthesized in the brains of rats addicted to morphine and heroin. (The

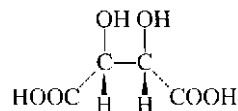
—NH₂ indicates that the peptide ends in $-\overset{O}{\parallel}C-NH_2$ instead of $-CO_2H$.) The TAMU scientists synthesized a similar tetrapeptide, with the synthetic amino acid above replacing one of the original amino acids. Draw a structure for the tetrapeptide containing the synthetic amino acid.

- Indicate the chiral carbon atoms in the synthetic amino acid.

141. The structure of tartaric acid is



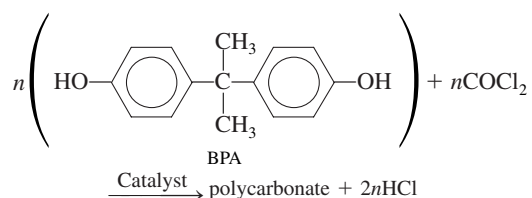
- Is the form of tartaric acid pictured below optically active? Explain.



Note: The dashed lines show groups behind the plane of the page. The wedges show groups in front of the plane.

- Draw the optically active forms of tartaric acid.
142. Using one of the Lewis structures for benzene (C_6H_6), estimate ΔH_f° for $C_6H_6(g)$ using bond energies and given the standard enthalpy of formation of $C(g)$ is 717 kJ/mol. The experimental ΔH_f° value for $C_6H_6(g)$ is 83 kJ/mol. Explain the discrepancy between the experimental value and the calculated ΔH_f° value for $C_6H_6(g)$.
143. Mycomycin, a naturally occurring antibiotic produced by the fungus *Nocardia acidophilus*, has the molecular formula $C_{13}H_{10}O_2$ and the systematic name 3,5,7,8-tridecatetraene-10,12-dienoic acid. Draw the structure of mycomycin.
144. Sorbic acid is used to prevent mold and fungus growth in some food products, especially cheeses. The systematic name for sorbic acid is 2,4-hexadienoic acid. Draw structures for the four geometrical isomers of sorbic acid.
145. Consider the following reactions. For parts b–d, see Exercise 62.
- When C_5H_{12} is reacted with $Cl_2(g)$ in the presence of ultraviolet light, four different monochlorination products form. What is the structure of C_5H_{12} in this reaction?
 - When C_4H_8 is reacted with H_2O , a tertiary alcohol is produced as the major product. What is the structure of C_4H_8 in this reaction?
 - When C_7H_{12} is reacted with HCl , 1-chloro-1-methylcyclohexane is produced as the major product. What are the two possible structures for C_7H_{12} in this reaction?
 - When a hydrocarbon is reacted with H_2O and the major product of this reaction is then oxidized, acetone (2-propanone) is produced. What is the structure of the hydrocarbon in this reaction?
 - When $C_5H_{12}O$ is oxidized, a carboxylic acid is produced. What are the possible structures for $C_5H_{12}O$ in this reaction?

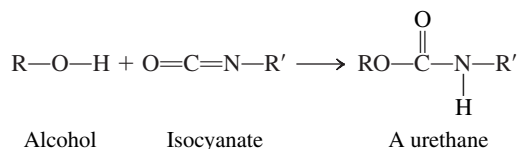
146. Polycarbonates are a class of thermoplastic polymers that are used in the plastic lenses of eyeglasses and in the shells of bicycle helmets. A polycarbonate is made from the reaction of bisphenol A (BPA) with phosgene ($COCl_2$):



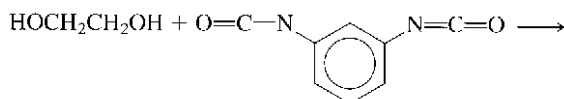
Phenol (C_6H_5OH) is used to terminate the polymer (stop its growth).

- Draw the structure of the polycarbonate chain formed from the above reaction.
- Is this reaction a condensation or addition polymerization?

147. A urethane linkage occurs when an alcohol adds across the carbon–nitrogen double bond in an isocyanate:

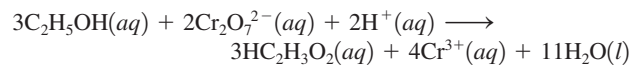


Polyurethanes (formed from the copolymerization of a diol with a diisocyanate) are used in foamed insulation and a variety of other construction materials. What is the structure of the polyurethane formed by the following reaction?



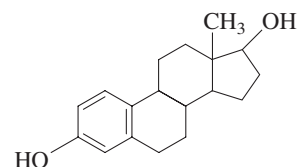
148. ABS plastic is a tough, hard plastic used in applications requiring shock resistance. The polymer consists of three monomer units: acrylonitrile (C_3H_3N), butadiene (C_4H_6), and styrene (C_8H_8).
- Draw two repeating units of ABS plastic assuming that the three monomer units react in a 1:1:1 mole ratio and react in the same order as the monomers listed above.
 - A sample of ABS plastic contains 8.80% N by mass. It took 0.605 g of Br_2 to react completely with a 1.20-g sample of ABS plastic. What is the percent by mass of acrylonitrile, butadiene, and styrene in this polymer sample?
 - ABS plastic does not react in a 1:1:1 mole ratio among the three monomer units. Using the results from part b, determine the relative numbers of the monomer units in this sample of ABS plastic.
149. Stretch a rubber band while holding it gently to your lips. Then slowly let it relax while still in contact with your lips.
- What happens to the temperature of the rubber band on stretching?
 - Is the stretching an exothermic or endothermic process?
 - Explain the above result in terms of intermolecular forces.
 - What is the sign of ΔS and ΔG for stretching the rubber band?
 - Give the molecular explanation for the sign of ΔS for stretching.
150. Alcohols are very useful starting materials for the production of many different compounds. The following conversions, starting with 1-butanol, can be carried out in two or more steps. Show the steps (reactants/catalysts) you would follow to carry out the conversions, drawing the formula for the organic product in each step. For each step, a major product must be produced. See Exercise 62. *Hint:* in the presence of H^+ , an alcohol is converted into an alkene and water. This is the exact reverse of the reaction of adding water to an alkene to form an alcohol.
- 1-butanol \longrightarrow butane
 - 1-butanol \longrightarrow 2-butanone

151. A chemical “breathalyzer” test works because ethyl alcohol in the breath is oxidized by the dichromate ion (orange) to form acetic acid and chromium(III) ion (green). The balanced reaction is



You analyze a breathalyzer test in which 4.2 mg of $K_2Cr_2O_7$ was reduced. Assuming the volume of the breath was 0.500 L at 30.°C and 750. mm Hg, what was the mole percent alcohol of the breath?

152. Consider a sample of a hydrocarbon at 0.959 atm and 298 K. Upon combusting the entire sample in oxygen, you collect a mixture of gaseous carbon dioxide and water vapor at 1.51 atm and 375 K. This mixture has a density of 1.391 g/L and occupies a volume four times as large as that of the pure hydrocarbon. Determine the molecular formula of the hydrocarbon and name it.
153. Estradiol is a female hormone with the following structure:



How many chiral carbon atoms are in estradiol?

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

154. Helicenes are extended fused polyaromatic hydrocarbons that have a helical or screw-shaped structure.
- A 0.1450-g sample of solid helicene is combusted in air to give 0.5063 g of CO_2 . What is the empirical formula of this helicene?
 - If a 0.0938-g sample of this helicene is dissolved in 12.5 g of solvent to give a 0.0175 *m* solution, what is the molecular formula of this helicene?
 - What is the balanced reaction for the combustion of this helicene?
155. An organometallic compound is one containing at least one metal–carbon bond. An example of an organometallic species is $(CH_3CH_2)MBr$, which contains a metal–ethyl bond.
- If M^{2+} has the electron configuration $[Ar]3d^{10}$, what is the percent by mass of M in $(CH_3CH_2)MBr$?
 - One of the reactions in which $(CH_3CH_2)MBr$ becomes involved is the conversion of a ketone to an alcohol as illustrated here:



How does the hybridization of the starred carbon atom change, if at all, in going from reactants to products?

- What is the systematic name of the product?

Hint: In this shorthand notation, all the C–H bonds have been eliminated and the lines represent C–C bonds, unless shown differently. As is typical of most organic compounds, each carbon atom has four bonds to it and the oxygen atoms have only two bonds.

Marathon Problems

These problems are designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

156. For each of the following, fill in the blank with the correct response. All of these fill-in-the-blank problems pertain to material covered in the sections on alkanes, alkenes and alkynes, aromatic hydrocarbons, and hydrocarbon derivatives.
- The first “organic” compound to be synthesized in the laboratory, rather than being isolated from nature, was _____, which was prepared from _____.
 - An organic compound whose carbon–carbon bonds are all single bonds is said to be _____.
 - The general orientation of the four pairs of electrons around the carbon atoms in alkanes is _____.
 - Alkanes in which the carbon atoms form a single unbranched chain are said to be _____ alkanes.
 - Structural isomerism occurs when two molecules have the same number of each type of atom but exhibit different arrangements of the _____ between those atoms.
 - The systematic names of all saturated hydrocarbons have the ending _____ added to a root name that indicates the number of carbon atoms in the molecule.
 - For a branched hydrocarbon, the root name for the hydrocarbon comes from the number of carbon atoms in the _____ continuous chain in the molecule.
 - The positions of substituents along the hydrocarbon framework of a molecule are indicated by the _____ of the carbon atom to which the substituents are attached.
 - The major use of alkanes has been in _____ reactions, as a source of heat and light.
 - With very reactive agents, such as, the halogen elements, alkanes undergo _____ reactions, whereby a new atom replaces one or more hydrogen atoms of the alkane.
 - Alkenes and alkynes are characterized by their ability to undergo rapid, complete _____ reactions, by which other atoms attach themselves to the carbon atoms of the double or triple bond.
 - Unsaturated fats may be converted to saturated fats by the process of _____.
 - Benzene is the parent member of the group of hydrocarbons called _____ hydrocarbons.
 - An atom or group of atoms that imparts new and characteristic properties to an organic molecule is called a _____ group.
 - A _____ alcohol is one in which there is only one hydrocarbon group attached to the carbon atom holding the hydroxyl group.
 - The simplest alcohol, methanol, is prepared industrially by the hydrogenation of _____.
 - Ethanol is commonly prepared by the _____ of certain sugars by yeast.
 - Both aldehydes and ketones contain the _____ group, but they differ in where this group occurs along the hydrocarbon chain.
 - Aldehydes and ketones can be prepared by _____ of the corresponding alcohol.
 - Organic acids, which contain the _____ group, are typically weak acids.
- u. The typically sweet-smelling compounds called _____ result from the condensation reaction of an organic acid with an _____.
157. Choose one of the following terms to match the description given in statements (1)–(17). All of the following pertain to proteins or carbohydrates.
- | | | |
|----------------------|----------------------|----------------------|
| a. aldohexose | g. disaccharides | m. ketohexoses |
| b. saliva | h. disulfide | n. oxytocin |
| c. cellulose | i. globular | o. pleated sheet |
| d. CH ₂ O | j. glycogen | p. polypeptide |
| e. cysteine | k. glycoside linkage | q. primary structure |
| f. denaturation | l. hydrophobic | |
- polymer consisting of many amino acids
 - linkage that forms between two cysteine species
 - peptide hormone that triggers milk secretion
 - proteins with roughly spherical shape
 - sequence of amino acids in a protein
 - silk protein secondary structure
 - water-repelling amino acid side chain
 - amino acid responsible for permanent wave in hair
 - breakdown of a protein’s tertiary and/or secondary structure
 - animal polymer of glucose
 - C—O—C— bond between rings in disaccharide sugars
 - empirical formula leading to the name carbohydrate
 - where enzymes catalyzing the breakdown of glycoside linkages are found
 - six-carbon ketone sugars
 - structural component of plants, polymer of glucose
 - sugars consisting of two monomer units
 - six-carbon aldehyde sugars
158. For each of the following, fill in the blank with the correct response(s). All of the following pertain to nucleic acids.
- The substance in the nucleus of the cell that stores and transmits genetic information is DNA, which stands for _____.
 - The basic repeating monomer units of DNA and RNA are called _____.
 - The pentose deoxyribose is found in DNA, whereas _____ is found in RNA.
 - The basic linkage in DNA or RNA between the sugar molecule and phosphoric acid is a phosphate _____ linkage.
 - The bases on opposite strands of DNA are said to be _____ to each other, which means the bases fit together specifically by hydrogen bonding to one another.
 - In a strand of normal DNA, the base _____ is always found paired with the base adenine, whereas _____ is always found paired with cytosine.
 - A given segment of the DNA molecule, which contains the molecular coding for a specific protein to be synthesized, is referred to as a _____.
 - During protein synthesis, _____ RNA molecules attach to and transport specific amino acids to the appropriate position on the pattern provided by _____ RNA molecules.
 - The codes specified by _____ are responsible for assembling the correct primary structure of proteins.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl7e.