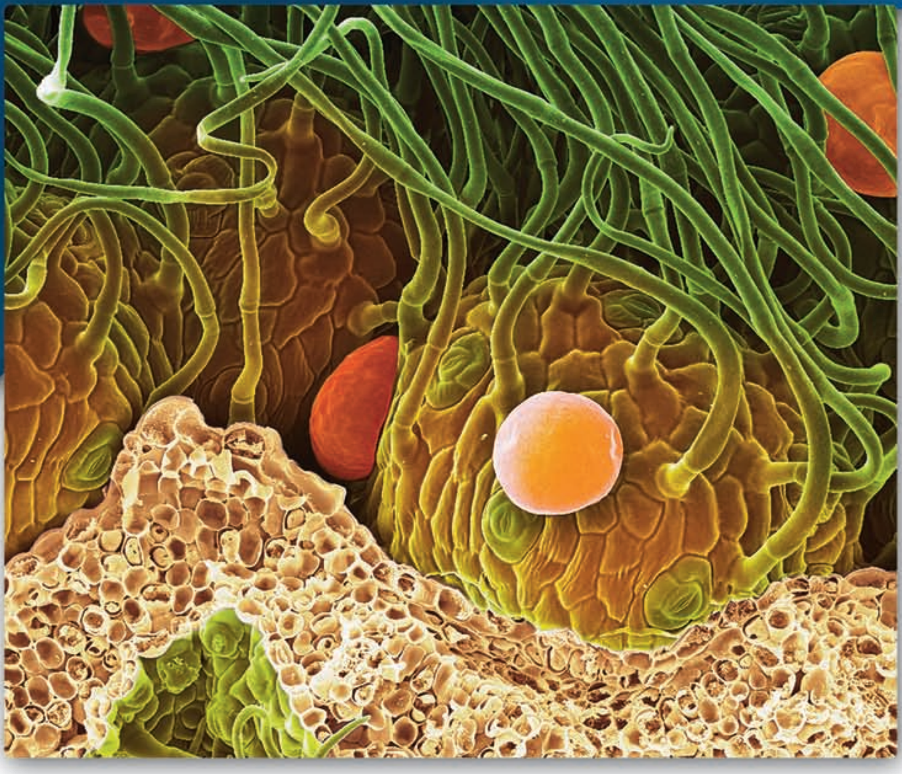
15



Herbal Essence This colored scanning electron micrograph of a freeze-fractured sage leaf reveals the round, reddish oil glands that secrete the numerous organic compounds responsible for the herb's taste and odor. Ultimately, the behavior of a living system is derived from that of its organic chemicals, which, as you'll see in this chapter, emerges from the behavior of the carbon atom.

Organic Compounds and the Atomic Properties of Carbon

Concepts & Skills to Review
before you study this chapter

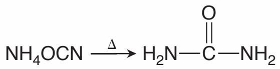
- naming simple organic compounds; the functional-group concept (Section 2.8)
- constitutional isomerism (Section 3.2)
- ΔEN and bond polarity (Section 9.5)
- resonance structures (Section 10.1)
- VSEPR theory (Section 10.2)
- orbital hybridization (Section 11.1)
- σ and π bonding (Section 11.2)
- types of intermolecular forces and the shapes of biological macromolecules (Sections 12.3, 12.7, and 13.2)
- properties of the Period 2 elements (Section 14.2)
- properties of the Group 4A(14) elements (Section 14.6)

The most remarkable chemical system known is a living cell. Through delicately controlled mechanisms, it oxidizes food for energy, maintains the concentrations of thousands of aqueous components, interacts continuously with its environment, synthesizes both simple and complex molecules, and even reproduces itself! For all our technological prowess, no human-made system even approaches the cell in its complexity and sheer elegance of function.

This amazing chemical machine consumes, creates, and consists largely of *organic compounds.* Except for a few inorganic salts and ever-present water, nearly everything you put into or on your body—food, medicine, cosmetics, and clothing—consists of organic compounds. Organic fuels warm our homes, cook our meals, and power our society. Major industries are devoted to producing organic compounds, such as polymers, pharmaceuticals, and insecticides.

What *is* an organic compound? Dictionaries define it as "a compound of carbon," but that definition is too general because it includes carbonates, cyanides, carbides, cyanates, and other carbon-containing ionic compounds that most chemists classify as inorganic. Here is a more specific definition: all **organic compounds** contain carbon, nearly always bonded to other carbons and hydrogen, and often to other elements.

The word *organic* has a biological connotation arising from a major misconception that stifled research into the chemistry of living systems for many decades. In the early 19th century, many prominent thinkers believed that an unobservable spiritual energy, a "vital force," existed *within* the compounds of living things, making them impossible to synthesize and fundamentally different from compounds of the mineral world. This idea of *vitalism* was challenged in 1828, when the young German chemist Friedrich Wöhler heated ammonium cyanate, a "mineral-world" compound, and produced urea, a "living-world" compound:



$$NH_4OCN \xrightarrow{\Delta} H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

Although Wöhler did not appreciate the significance of this reaction—he was more interested in the fact that two compounds can have the same molecular formula—his experiment is considered a key event in the origin of organic chemistry. Chemists soon synthesized methane, acetic acid, acetylene, and many other organic compounds from inorganic sources. ● Today, we know that *the same chemical principles govern organic and inorganic systems* because the behavior of a compound arises from the properties of its elements, no matter how marvelous that behavior may be.

● **Organic Chemistry Is Enough to Drive One Mad** The vitalists did not change their beliefs overnight. Indeed, organic compounds *do* seem different from inorganic compounds because of their complex structures and compositions. Imagine the consternation of the 19th-century chemist who was accustomed to studying compounds with formulas such as $CaCO_3$, $Ba(NO_3)_2$, and $CuSO_4{\cdot}5H_2O$ and then isolated white crystals from a gallstone and found their empirical formula to be $C_{27}H_{46}O$ (cholesterol). Even Wöhler later said, "Organic chemistry . . . is enough to drive one mad. It gives me the impression of a primeval tropical forest, full of the most remarkable things, a monstrous and boundless thicket, with no way of escape, into which one may well dread to enter."

IN THIS CHAPTER . . . We apply the text's central theme to the enormous field of organic chemistry to see how the structure and reactivity of organic molecules emerge naturally from the properties of their component atoms. First, we review the special atomic properties of carbon and see how they lead to the complex structure and reactivity of organic molecules. Next, we focus on writing and naming hydrocarbons as a prelude to naming other types of organic compounds. We classify the main types of organic reactions and apply them to various families of organic compounds. Finally, we extend these ideas to the giant molecules of commerce and life—synthetic and natural polymers.

15.1 THE SPECIAL NATURE OF CARBON AND THE CHARACTERISTICS OF ORGANIC MOLECULES

Although there is nothing mystical about organic molecules, their indispensable role in biology and industry leads us to ask if carbon has some extraordinary attributes that give it a special chemical "personality." Of course, each element has its own specific properties, and carbon is no more unique than sodium, hafnium, or any other element. But the atomic properties of carbon do give it bonding capabilities beyond those of any other element, which in turn lead to the two obvious characteristics of organic molecules—structural complexity and chemical diversity.

The Structural Complexity of Organic Molecules

Most organic molecules have much more complex structures than most inorganic molecules, and a quick review of carbon's atomic properties and bonding behavior shows why:

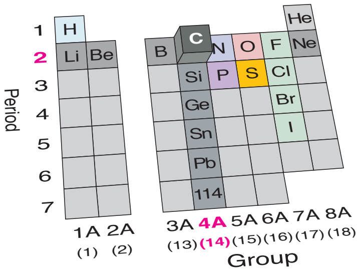


Figure 15.1 The position of carbon in the periodic table. Lying at the center of Period 2, carbon has an intermediate electronegativity (EN), and its position at the top of Group 4A(14) means it is relatively small. Other elements common in organic compounds are H, N, O, P, S, and the halogens.

1. *Electron configuration, electronegativity, and covalent bonding.* Carbon's ground-state electron configuration of [He] $2s^22p^2$—four electrons more than He and four fewer than Ne—means that the formation of carbon ions is energetically impossible under ordinary conditions: to form a C^{4+} cation requires energy equal to the sum of IE_1 through IE_4, and to form a C^{4-} anion requires the sum of EA_1 through EA_4, the last three steps of which are endothermic. Carbon's position in the periodic table (Figure 15.1) and its electronegativity are midway between the most metallic and the most nonmetallic elements of Period 2: Li = 1.0, C = 2.5, F = 4.0. Therefore, *carbon shares electrons to attain a filled outer (valence) level,* bonding covalently in all its elemental forms and compounds.

2. *Bond properties, catenation, and molecular shape.* The *number* and *strength* of carbon's bonds lead to its outstanding ability to *catenate* (form chains of atoms), which allows it to form a multitude of chemically and thermally stable chain, ring, and branched compounds. Through the process of orbital hybridization (Section 11.1), *carbon forms four bonds in virtually all its compounds,* and they point in as many as four different directions. The small size of carbon allows close approach to another atom and thus greater orbital overlap, meaning that *carbon forms relatively short, strong bonds.* The C—C bond is short enough to allow side-to-side overlap of half-filled, unhybridized *p* orbitals and the formation of *multiple bonds,* which restrict rotation of attached groups (see Figure 11.13, p. 421). These features add more possibilities for the molecular shapes of carbon compounds.

3. *Molecular stability.* Although silicon and several other elements also catenate, none can compete with carbon. Atomic and bonding properties confer three crucial differences between C and Si chains that explain why C chains are so stable and, therefore, so common:

- *Atomic size and bond strength.* As atomic size increases down Group 4A(14), bonds between identical atoms become longer and weaker. Thus, a C—C bond (347 kJ/mol) is much stronger than an Si—Si bond (226 kJ/mol).
- *Relative heats of reaction.* A C—C bond (347 kJ/mol) and a C—O bond (358 kJ/mol) have nearly the same energy, so relatively little heat is released when a C chain reacts and one bond replaces the other. In contrast, an Si—O bond (368 kJ/mol) is much stronger than an Si—Si bond (226 kJ/mol), so a large quantity of heat is released when an Si chain reacts.
- *Orbitals available for reaction.* Unlike C, Si has low-energy *d* orbitals that can be attacked (occupied) by the lone pairs of incoming reactants. Thus, for example, ethane (CH_3—CH_3) is stable in water and does not react in air unless sparked, whereas disilane (SiH_3—SiH_3) breaks down in water and ignites spontaneously in air.

The Chemical Diversity of Organic Molecules

In addition to their elaborate geometries, organic compounds are noted for their sheer number and diverse chemical behavior. Look, for example, at the *CRC Handbook of Chemistry and Physics,* and you'll find that the number of organic compounds of carbon dwarfs the number of inorganic compounds of all the elements combined! Several million organic compounds are known, and thousands more are discovered or synthesized each year.

This incredible diversity is also founded on atomic and bonding behavior and is due to three interrelated factors:

1. *Bonding to heteroatoms.* Many organic compounds contain **heteroatoms,** atoms other than C or H. The most common heteroatoms are N and O, but S, P, and the halogens often occur, and organic compounds with other elements are known as well. Figure 15.2 shows that 23 different molecular structures are possible from various arrangements of four C atoms singly bonded to each other, the necessary number of H atoms, and just one O atom (either singly or doubly bonded).

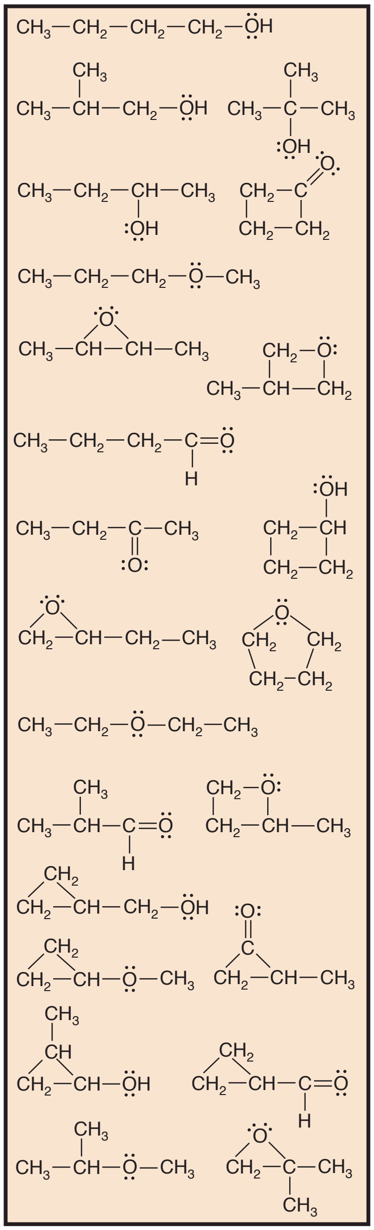


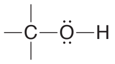
Figure 15.2 The chemical diversity of organic compounds. Different arrangements of chains, branches, rings, and heteroatoms give rise to many structures. There are 23 different compounds possible from just four C atoms joined by single bonds, one O atom, and the necessary H atoms.

2. *Electron density and reactivity.* Most reactions start—that is, a new bond begins to form—*when a region of high electron density on one molecule meets a region of low electron density on another.* These regions may be due to the presence of a multiple bond or to the partial charges that occur in carbon-heteroatom bonds. For example, consider four bonds commonly found in organic molecules:

- *The C—C bond.* When C is singly bonded to another C, as occurs in portions of nearly every organic molecule, the EN values are equal and the bond is nonpolar. Therefore, in general, *C—C bonds are unreactive.*
- *The C—H bond.* This bond, which also occurs in nearly every organic molecule, is very nearly nonpolar because it is short (109 pm) and the EN values of H (2.1) and C (2.5) are close. Thus, *C—H bonds are largely unreactive* as well.

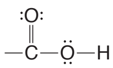
- *The C—O bond.* This bond, which occurs in many types of organic molecules, is highly polar (ΔEN = 1.0), with the O end of the bond electron rich and the C end electron poor. As a result of this imbalance in electron density, *the C—O bond is reactive* and, given appropriate conditions, a reaction will occur there.
- *Bonds to other heteroatoms.* Even when a carbon-heteroatom bond has a small ΔEN, such as that for C—Br (ΔEN = 0.3), or none at all, as for C—S (ΔEN = 0), heteroatoms like these are large, and so their bonds to carbon are long, weak, and thus reactive.

3. *Nature of functional groups.* One of the most important ideas in organic chemistry is that of the **functional group,** a specific combination of bonded atoms that reacts in a *characteristic* way, no matter what molecule it occurs in (we mentioned this idea briefly in Section 2.8). In nearly every case, *the reaction of an organic compound takes place at the functional group.* In fact, as you'll see, we often substitute a general symbol for the remainder of the molecule because it usually stays the same while the functional group reacts. Functional groups vary from carbon-carbon multiple bonds to several combinations of carbon-heteroatom bonds, and each has its own pattern of reactivity. A particular bond may be a functional group itself or *part* of one or more functional groups. For example, the C—O bond occurs in four functional groups. We will discuss the reactivity of three of these groups in this chapter:



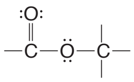
$-\underset{|}{\overset{|}{C}}-\ddot{\underset{..}{O}}-H$

alcohol group



$-\overset{:O:}{\overset{\|}{C}}-\ddot{\underset{..}{O}}-H$

carboxylic acid group



$-\overset{:O:}{\overset{\|}{C}}-\ddot{\underset{..}{O}}-\underset{|}{\overset{|}{C}}-$

ester group

Section Summary

The structural complexity of organic compounds arises from carbon's small size, intermediate EN, four valence electrons, ability to form multiple bonds, and absence of *d* orbitals in the valence level. These factors lead to chains, branches, and rings of C atoms joined by strong, chemically resistant bonds that point in as many as four directions from each C. • The chemical diversity of organic compounds arises from carbon's ability to bond to many other elements, including O and N, which creates polar bonds and greater reactivity. These factors lead to compounds that contain functional groups, specific portions of molecules that react in characteristic ways.

15.2 THE STRUCTURES AND CLASSES OF HYDROCARBONS

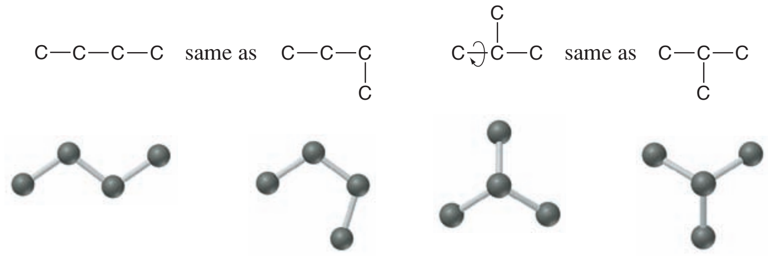
A fanciful, anatomical analogy can be made between an organic molecule and an animal. The carbon-carbon bonds form the skeleton: the longest continual chain is the backbone, and any branches are the limbs. Covering the skeleton is a skin of hydrogen atoms, with functional groups protruding at specific locations, like chemical fingers ready to grab an incoming reactant.

In this section, we "dissect" one group of compounds down to their skeletons and see how to name and draw them. **Hydrocarbons,** the simplest type of organic compound, are a large group of substances containing only H and C atoms. Some common fuels, such as natural gas and gasoline, are hydrocarbon mixtures. Hydrocarbons are also important *feedstocks,* precursor reactants used to make other compounds. Ethylene, acetylene, and benzene, for example, are feedstocks for hundreds of other substances.

Carbon Skeletons and Hydrogen Skins

Let's begin by examining the possible bonding arrangements of C atoms only (we'll leave off the H atoms at first) in simple skeletons without multiple bonds or rings. To distinguish different skeletons, focus on the *arrangement* of C atoms (that is, the successive linkages of one to another) and keep in mind that *groups joined by single (sigma) bonds are relatively free to rotate* (Section 11.2).

Structures with one, two, or three carbons can be arranged in only one way. Whether you draw three C atoms in a line or with a bend, the arrangement is the same. Four C atoms, however, have two possible arrangements—a four-C chain or a three-C chain with a one-C branch at the central C:



Even when we show the chain more realistically, with the bends due to the tetrahedral shape around the C atoms (as in the ball-and-stick models), the situation is the same. Notice that if the branch is added to either end of the three-C chain, it is simply a bend in a four-C chain, *not* a different arrangement. Similarly, if the branch points down instead of up, it represents the same arrangement because groups joined by single bonds rotate.

As the total number of C atoms increases, the number of different arrangements increases as well. Five C atoms have 3 possible arrangements; 6 C atoms can be arranged in 5 ways, 7 C atoms in 9 ways, 10 C atoms in 75 ways, and

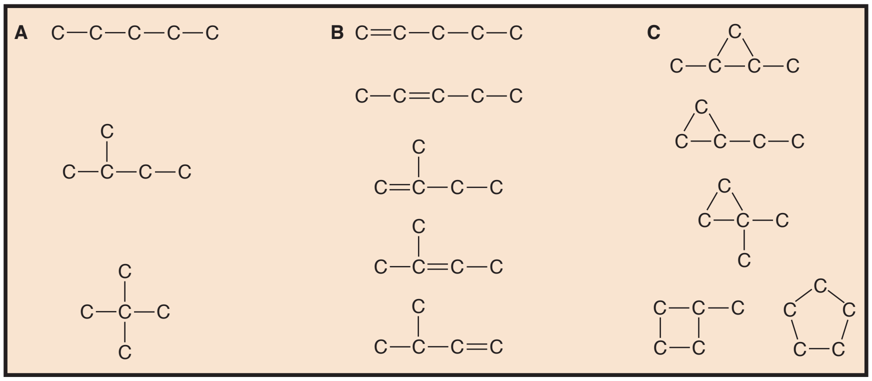


Figure 15.3 Some five-carbon skeletons. **A,** Three five-C skeletons are possible with only single bonds. **B,** Five more skeletons are possible with one C=C bond present. **C,** Five more skeletons are possible with one ring present. Even more would be possible with a ring *and* a double bond.

20 C atoms in more than 300,000 ways! If we include multiple bonds and rings, the number of arrangements increases further. For example, including one C=C bond in the five-C skeletons creates 5 more arrangements, and including one ring creates 5 more (Figure 15.3).

When determining the number of different skeletons for a given number of C atoms, remember that

- Each C atom can form a *maximum* of four single bonds, or two single and one double bond, or one single and one triple bond.
- The *arrangement* of C atoms determines the skeleton, so a straight chain and a bent chain represent the same skeleton.
- Groups joined by single bonds can *rotate,* so a branch pointing down is the same as one pointing up. (Recall that a double bond restricts rotation.)

If we put a hydrogen "skin" on a carbon skeleton, we obtain a hydrocarbon. Figure 15.4 shows that the skeleton has the correct number of H atoms when each C has four bonds. Sample Problem 15.1 provides practice drawing hydrocarbons.

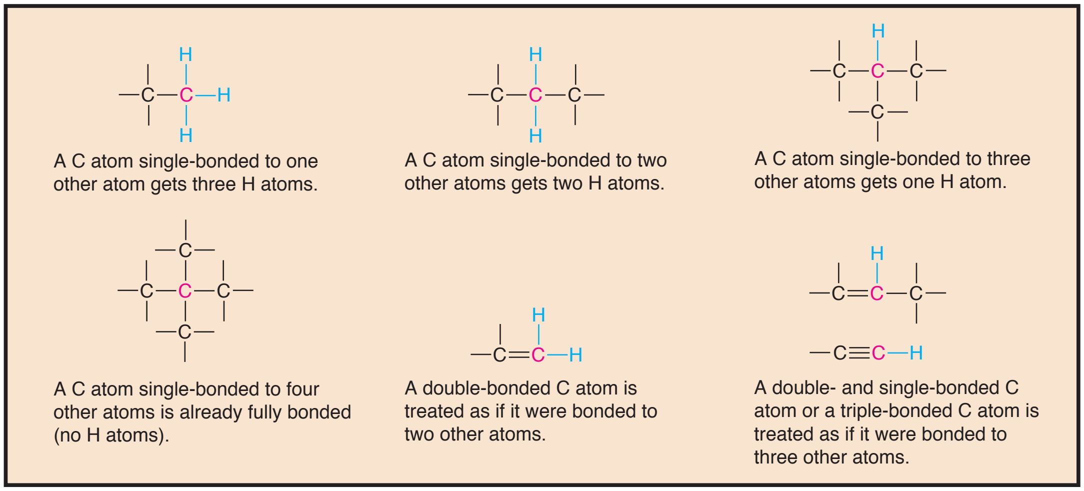


Figure 15.4 Adding the H-atom skin to the C-atom skeleton. In a hydrocarbon molecule, each carbon atom bonds to as many hydrogen atoms as needed to give the carbon a total of four bonds.

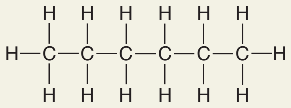
SAMPLE PROBLEM 15.1 Drawing Hydrocarbons

PROBLEM Draw structures that have different atom arrangements for hydrocarbons with:
(a) Six C atoms, no multiple bonds, and no rings
(b) Four C atoms, one double bond, and no rings
(c) Four C atoms, no multiple bonds, and one ring

PLAN In each case, we draw the longest carbon chain first and then work down to smaller chains with branches at different points along them. The process typically involves trial and error. Then, we add H atoms to give each C a total of four bonds.

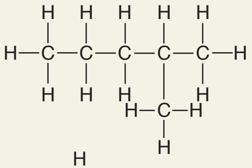
SOLUTION **(a)** Compounds with six C atoms:

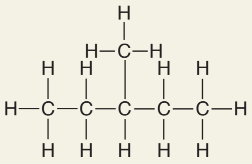
6-C chain:



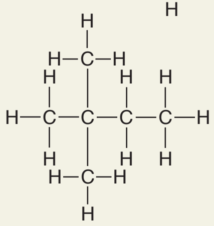
$$\begin{array}{ccccccccccccccc}
 & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\
 & & | & & | & & | & & | & & | & & | & & \\
\mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H}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

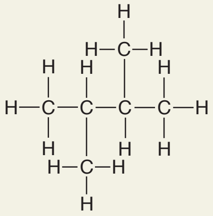
5-C chains:





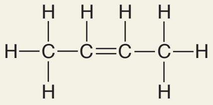
4-C chains:



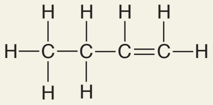


(b) Compounds with four C atoms and one double bond:

4-C chains:

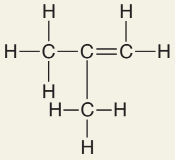


$$\begin{array}{ccccccccccc}
 & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\
 & & | & & | & & | & & | & & \\
\mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & = & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\
 & & | & & & & & & | & & \\
 & & \mathrm{H} & & & & & & \mathrm{H} & &
\end{array}$$



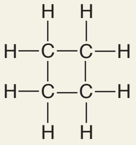
$$\begin{array}{ccccccccccc}
 & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\
 & & | & & | & & | & & | & & \\
\mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & = & \mathrm{C} & - & \mathrm{H} \\
 & & | & & | & & & & & & \\
 & & \mathrm{H} & & \mathrm{H} & & & & & &
\end{array}$$

3-C chain:

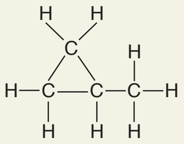


(c) Compounds with four C atoms and one ring:

4-C ring:



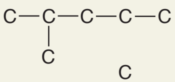
3-C ring:



CHECK Be sure each skeleton has the correct number of C atoms, multiple bonds, and/or rings, and no arrangements are repeated or omitted; remember a double bond counts as two bonds.

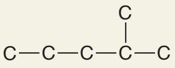
COMMENT Avoid some *common mistakes:*

In (a):

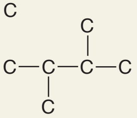


$$\begin{array}{ccccccccc}
\mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} \\
 & & | & & & & & & \\
 & & \mathrm{C} & & & & & &
\end{array}$$

is the same skeleton as

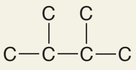


$$\begin{array}{ccccccccc}
 & & & & & & \mathrm{C} & & \\
 & & & & & & | & & \\
\mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C}
\end{array}$$



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

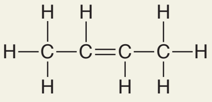
is the same skeleton as



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

In (b): C—C—C=C is the same skeleton as C=C—C—C

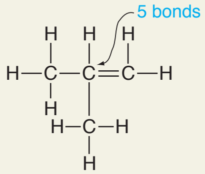
The double bond restricts rotation, so, in addition to the *cis* form shown in part (b), another possibility is the *trans* form:



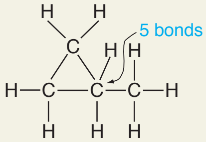
$$\begin{array}{ccccccccccc}
 & & \mathrm{H} & & \mathrm{H} & & & & \mathrm{H} & & \\
 & & | & & | & & & & | & & \\
\mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & = & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\
 & & | & & & & | & & | & & \\
 & & \mathrm{H} & & & & \mathrm{H} & & \mathrm{H} & &
\end{array}$$

(We discuss *cis-trans* isomers fully later in this section.)

Also, there are too many bonds to one C in



In (c): Too many bonds to one C in



FOLLOW-UP PROBLEM 15.1 Draw all hydrocarbons that have different atom arrangements with:
(a) Seven C atoms, no multiple bonds, and no rings (nine arrangements)
(b) Five C atoms, one triple bond, and no rings (three arrangements)

Hydrocarbons can be classified into four main groups. In the remainder of this section, we examine the names and some structural features and physical properties of each group. Later, we discuss the chemical behavior of the hydrocarbons.

Alkanes: Hydrocarbons with Only Single Bonds

A hydrocarbon that contains only single bonds is an **alkane** (general formula $\mathbf{C_nH_{2n+2}}$, where n is a positive integer). For example, if $n = 5$, the formula is $C_5H_{[(2\times5)+2]}$, or C_5H_{12}. The alkanes comprise a **homologous series,** one in which each member differs from the next by a $-CH_2-$ (methylene) group. In an alkane, each C is sp^3 hybridized. Because each C is bonded to the *maximum number of other atoms* (C or H), alkanes are referred to as **saturated hydrocarbons.**

Naming Alkanes You learned how to name simple alkanes in Section 2.8. Here we discuss general rules for naming any alkane and, by extension, other organic compounds as well. The key point is that *each chain, branch, or ring has a name based on the* ***number*** *of C atoms.* The name of a compound has three portions:

PREFIX + ROOT + SUFFIX

- *Root:* The root tells the number of C atoms in the longest *continuous* chain in the molecule. The roots for the ten smallest alkanes are shown in Table 15.1. As you can see, there are special roots for compounds of one to four C atoms; roots of longer chains are based on Greek numbers.
- *Suffix:* The suffix tells the *type of organic compound* the molecule represents; that is, it identifies the key functional group the molecule possesses. The suffix is placed *after* the root.
- *Prefix:* Each prefix identifies a *group attached to the main chain* and the number of the carbon to which it is attached. Prefixes identifying hydrocarbon branches are the same as root names (Table 15.1) but have *-yl* as their ending. Each prefix is placed *before* the root.

For example, in the name 2-methylbutane, *2-methyl-* is the prefix (a one-carbon branch is attached to C-2 of the main chain), *-but-* is the root (the main chain has four C atoms), and *-ane* is the suffix (the compound is an alkane).

To obtain the systematic name of a compound,

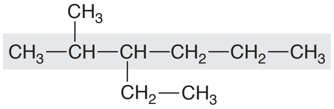
1. Name the longest chain (root).
2. Add the compound type (suffix).
3. Name any branches (prefix).

Table 15.1 Numerical Roots for Carbon Chains and Branches

Roots	Number of C Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Table 15.2 Rules for Naming an Organic Compound

1. Naming the longest chain (root)
   (a) Find the longest *continuous* chain of C atoms.
   (b) Select the root that corresponds to the number of C atoms in this chain.



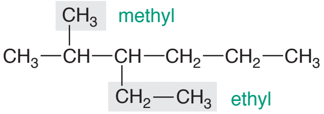
$CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_2-CH_2-CH_3$

6 carbons ⟹ hex-

2. Naming the compound type (suffix)
   (a) For alkanes, add the suffix *-ane* to the chain root. (Other suffixes appear in Table 15.5 with their functional group and compound type.)
   (b) If the chain forms a ring, the name is preceded by *cyclo-*.

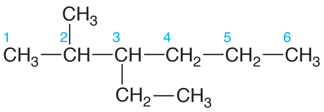
hex- + -ane ⟹ hexane

3. Naming the branches (prefixes) (If the compound has no branches, the name consists of the root and suffix.)
   (a) Each branch name consists of a subroot (number of C atoms) and the ending *-yl* to signify that it is not part of the main chain.
   (b) Branch names precede the chain name. When two or more branches are present, their names appear in *alphabetical* order.
   (c) To specify where the branch occurs along the chain, number the main-chain C atoms consecutively, starting at the end *closer* to a branch, to achieve the *lowest* numbers for the branches. Precede each branch name with the number of the main-chain C to which that branch is attached.



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

ethylmethylhexane



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

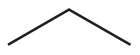
3-ethyl-2-methylhexane

Table 15.2 presents the rules for naming any organic compound and applies them to an alkane component of gasoline. Other organic compounds are named with a variety of other prefixes and suffixes (see Table 15.5, p. 651). In addition to these *systematic* names, we'll also note important *common* names still in use.

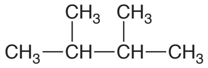
Depicting Alkanes with Formulas and Models Chemists have several ways to depict organic compounds. Expanded, condensed, and carbon-skeleton formulas are easy to draw; ball-and-stick and space-filling models show the actual shapes.

The *expanded formula* shows each atom and bond. One type of *condensed formula* groups each C atom with its H atoms. *Carbon-skeleton formulas* show only carbon-carbon bonds and appear as zig-zag lines, often with branches. *Each end or bend of a zig-zag line or branch represents a C atom attached to the number of H atoms that gives it a total of four bonds:*

propane $CH_3-CH_2-CH_3$



2,3-dimethylbutane



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

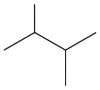
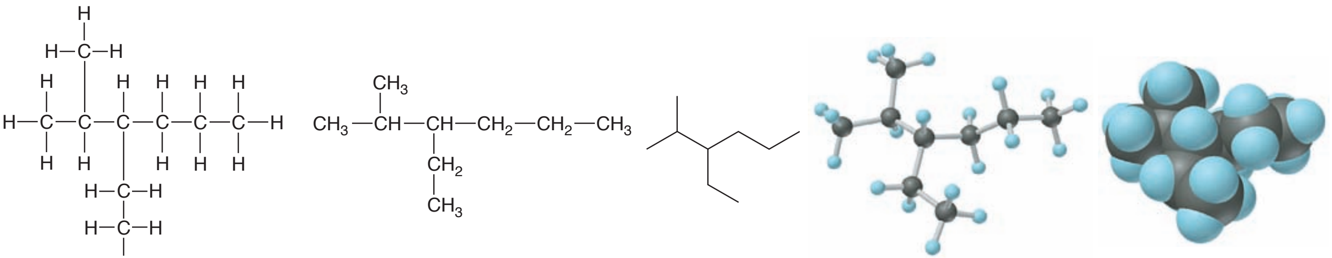


Figure 15.5 shows these types of formulas, together with ball-and-stick and space-filling models, of the compound named in Table 15.2.

Figure 15.5 Ways of depicting an alkane.



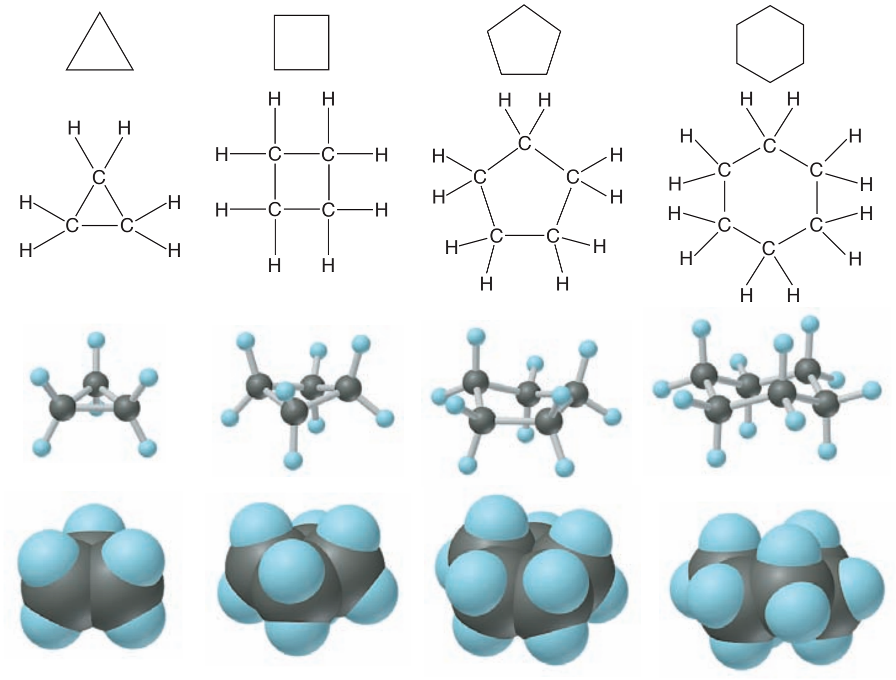
Expanded formula

Condensed formula

Carbon-skeleton formula

Ball-and-stick model

Space-filling model



A Cyclopropane **B Cyclobutane** **C Cyclopentane** **D Cyclohexane**

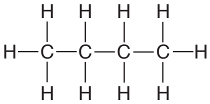
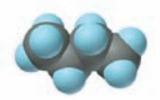
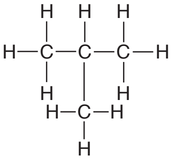
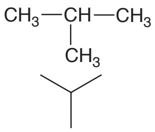
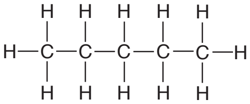
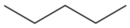
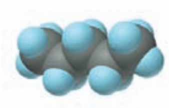
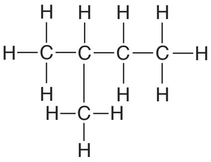
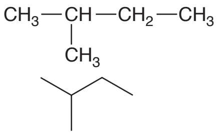
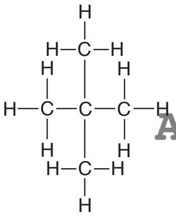
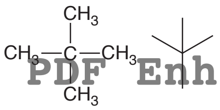
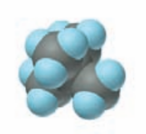
Figure 15.6 Depicting cycloalkanes. Cycloalkanes are usually drawn as regular polygons. Each side is a C—C bond, and each corner represents a C atom with its required number of H atoms. The expanded formulas show each bond in the molecule. The ball-and-stick and space-filling models show that, except for cyclopropane, the rings are not planar. These conformations minimize electron repulsions between adjacent H atoms. Cyclohexane **(D)** is shown in its more stable chair conformation.

Cyclic Hydrocarbons A **cyclic hydrocarbon** contains one or more rings in its structure. When a straight-chain alkane (C_nH_{2n+2}) forms a ring, two H atoms are lost as the C—C bond forms to join the two ends of the chain. Thus, *cycloalkanes* have the general formula C_nH_{2n}. Cyclic hydrocarbons are often drawn with carbon-skeleton formulas, as shown at the top of Figure 15.6. Except for three-carbon rings, *cycloalkanes are nonplanar.* This structural feature arises from the tetrahedral shape around each C atom and the need to minimize electron repulsions between adjacent H atoms. As a result, orbital overlap of adjacent C atoms is maximized. The most stable form of cyclohexane, called the *chair conformation,* is shown in Figure 15.6D.

Constitutional Isomerism and the Physical Properties of Alkanes

Recall from Section 3.2 that two or more compounds with the same molecular formula but different properties are called **isomers.** Those with *different arrangements of bonded atoms* are **constitutional** (or **structural**) **isomers;** alkanes with the same number of C atoms but different skeletons are examples. The smallest alkane to exhibit constitutional isomerism has four C atoms: two different compounds have the formula C_4H_{10}, as shown in Table 15.3, on page 638. The unbranched one is butane (common name, *n*-butane; *n*- stands for "normal," or having a straight chain), and the other is 2-methylpropane (common name, *iso*butane). Similarly, three compounds have the formula C_5H_{12} (shown in Table 15.3). The unbranched isomer is pentane (common name, *n*-pentane); the one with a

Table 15.3 **The Constitutional Isomers of C_4H_{10} and C_5H_{12}**

Systematic Name (Common Name)	Expanded Formula	Condensed and Skeleton Formulas	Space-Filling Model	Density (g/mL)	Boiling Point (°C)
Butane (*n*-butane)		$CH_3-CH_2-CH_2-CH_3$ 		0.579	−0.5
2-Methylpropane (isobutane)		 $CH_3-\underset{\underset{\textstyle CH_3}{\vert}}{CH}-CH_3$		0.549	−11.6
Pentane (*n*-pentane)		$CH_3-CH_2-CH_2-CH_2-CH_3$ 		0.626	36.1
2-Methylbutane (isopentane)		 $CH_3-\underset{\underset{\textstyle CH_3}{\vert}}{CH}-CH_2-CH_3$		0.620	27.8
2,2-Dimethylpropane (neopentane)		 $CH_3-\overset{\overset{\textstyle CH_3}{\vert}}{\underset{\underset{\textstyle CH_3}{\vert}}{C}}-CH_3$		0.614	9.5

methyl group at C-2 of a four-C chain is 2-methylbutane (common name, *iso*pentane). The third isomer has two methyl branches on C-2 of a three-C chain, so its name is 2,2-dimethylpropane (common name, *neo*pentane).

Because alkanes are nearly nonpolar, we expect their physical properties to be determined by dispersion forces, and the boiling points in Table 15.3 certainly bear this out. The four-C alkanes boil lower than the five-C compounds. Moreover, within each group of isomers, the more spherical member (isobutane or neopentane) boils lower than the more elongated one (*n*-butane or *n*-pentane). As you saw in Chapter 12, this trend occurs because a spherical shape leads to less intermolecular contact, and thus lower total dispersion forces, than does an elongated shape.

A particularly clear example of the effect of dispersion forces on physical properties occurs among the unbranched alkanes (*n*-alkanes). Among these compounds, boiling points increase steadily with chain length: the longer the chain, the greater the intermolecular contact, the stronger the dispersion forces, and the higher the boiling point (Figure 15.7). Pentane (five C atoms) is the smallest *n*-alkane that exists as a liquid at room temperature. The solubility of alkanes, and of all hydrocarbons, is easy to predict from the like-dissolves-like rule (Section 13.1). Alkanes are miscible in each other and in other nonpolar solvents, such as benzene, but are nearly insoluble in water. The solubility of pentane in water, for example, is only 0.36 g/L at room temperature.

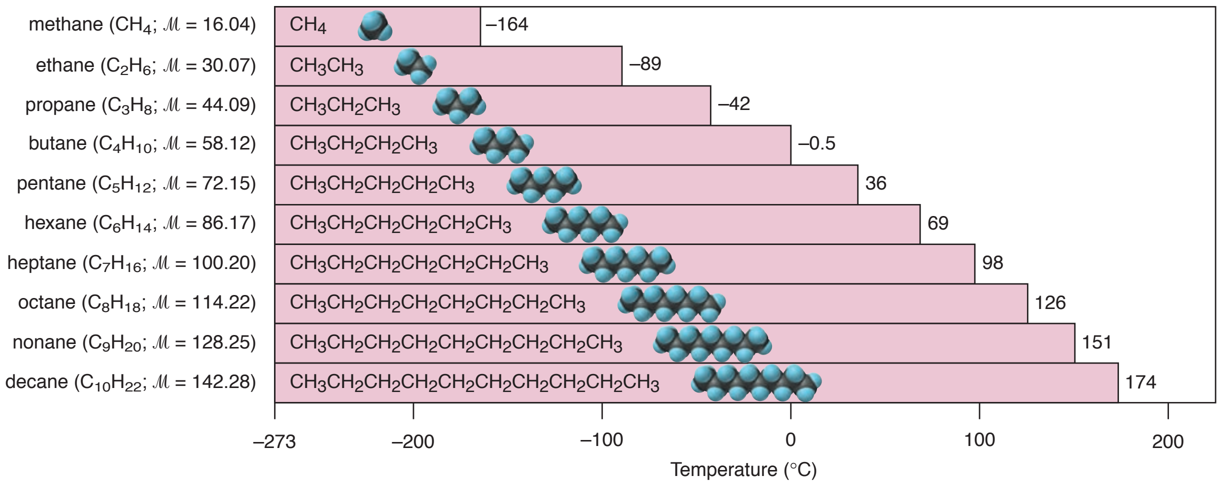


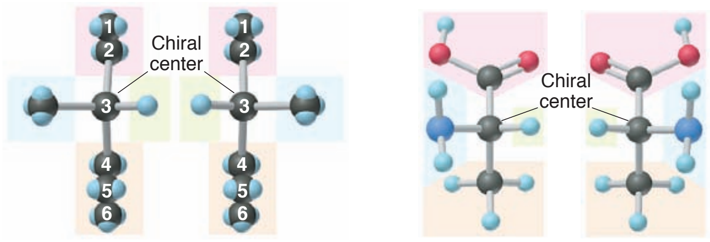
Figure 15.7 **Boiling points of the first 10 unbranched alkanes.** Boiling point increases smoothly with chain length because dispersion forces increase. Each entry includes the name, molecular formula, molar mass (ℳ, in g/mol), condensed formula, space-filling model, and boiling point at 1 atm pressure.

Chiral Molecules and Optical Isomerism

Another type of isomerism exhibited by some alkanes and many other organic (as well as some inorganic) compounds is called *stereoisomerism.* **Stereoisomers** are molecules with the same arrangement of atoms *but different orientations of groups in space. Optical isomerism* is one type of stereoisomerism: *when two objects are mirror images of each other and cannot be superimposed, they are* **optical isomers,** also called *enantiomers.* To use a familiar example, your right hand is an optical isomer of your left. Look at your right hand in a mirror, and you will see that the *image* is identical to your left hand (Figure 15.8). No matter how you twist your arms around, however, your hands cannot lie on top of each other with all parts superimposed. They are not superimposable because each is *asymmetric:* there is no plane of symmetry that divides your hand into two identical parts.

Figure 15.8 **An analogy for optical isomers.** The reflection of your right hand looks like your left hand. Each hand is asymmetric, so you cannot superimpose them with your palms facing in the same direction.

An asymmetric molecule is called **chiral** (Greek *cheir,* "hand"). Typically, an organic molecule *is chiral if it contains a carbon atom that is bonded to four* ***different*** *groups.* This C atom is called a *chiral center* or an asymmetric carbon. In 3-methylhexane, for example, C-3 is a chiral center because it is bonded to four different groups: H—, CH_3—, $CH_3—CH_2$—, and $CH_3—CH_2—CH_2$— (Figure 15.9A). Like your two hands, the two forms are mirror images and cannot be superimposed on each other: when two of the groups are superimposed, the other two are opposite each other. Thus, the two forms are optical isomers. The central C atom in the amino acid alanine is also a chiral center (Figure 15.9B).



A **Optical isomers of 3-methylhexane**

B **Optical isomers of alanine**

Figure 15.9 **Two chiral molecules. A,** 3-Methylhexane is chiral because C-3 is bonded to four different groups. These two models are optical isomers (enantiomers). **B,** The central C in the amino acid alanine is also bonded to four different groups.

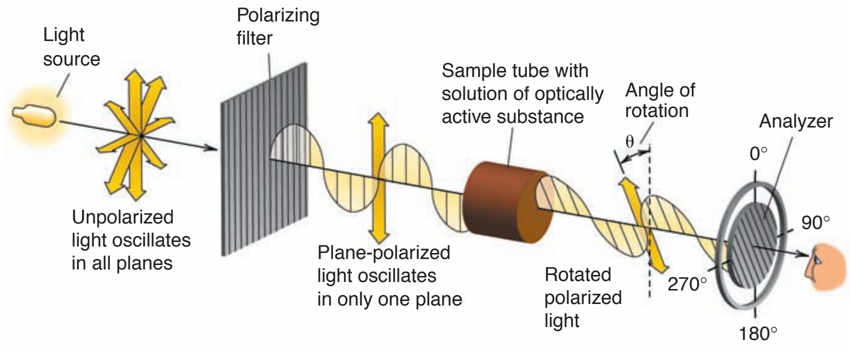


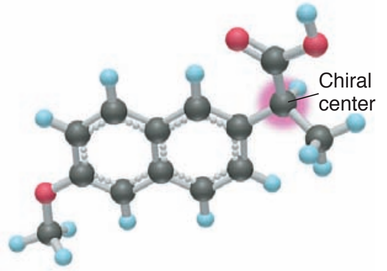
Figure 15.10 The rotation of plane-polarized light by an optically active substance. The source emits light oscillating in all planes. When the light passes through the first polarizing filter, light oscillating in only one plane emerges. The plane-polarized light enters the sample compartment, which contains a known concentration of an optical isomer, and the plane rotates as the light passes through the solution. For the experimenter to see the light, it must pass through a second polarizing filter (called the *analyzer*), which is attached to a movable ring that is calibrated in degrees and measures the angle of rotation.

Unlike constitutional isomers, optical isomers are identical in all but two respects:

1. In their physical properties, *optical isomers differ only in the direction that each isomer rotates the plane of polarized light.* A **polarimeter** is used to measure the angle that the plane is rotated (Figure 15.10). A beam of light consists of waves that oscillate in all planes. A polarizing filter blocks all waves except those in one plane, so the light emerging through the filter is *plane-polarized.* An optical isomer is **optically active** because it rotates the plane of this polarized light. (Liquid crystal displays incorporate polarizing filters and optically active compounds; see Figure 12.45, p. 481.) The *dextrorotatory* isomer (designated *d* or +) rotates the plane of light clockwise; the *levorotatory* isomer (designated *l* or −) is the mirror image of the *d* isomer and rotates the plane counterclockwise. An equimolar mixture of the two isomers (called a *racemic mixture*) does not rotate the plane at all because the dextrorotation cancels the levorotation. The *specific rotation* is a characteristic, measurable property of the isomer at a certain temperature, concentration, and wavelength of light.

2. In their chemical properties, *optical isomers differ only in a chiral (asymmetric) chemical environment,* one that distinguishes "right-handed" from "left-handed" molecules. As an analogy, your right hand fits well in your right glove but not in your left glove. Typically, one isomer of an optically active reactant is added to a mixture of optical isomers of another compound. The products of the reaction have different properties and can be separated. For example, when the anion *d*-lactate is added to a mixture of the cationic forms *d*-alanine and *l*-alanine, the *d* isomer of alanine crystallizes as the *d*-lactate/*d*-alanine salt, but the *d*-lactate/*l*-alanine salt is more soluble and remains in solution.

Optical isomerism plays a vital role in living cells. Nearly all carbohydrates and amino acids are optically active, but only one of the isomers is biologically usable. For example, *d*-glucose is metabolized for energy, but *l*-glucose is excreted unused. Similarly, *l*-alanine is incorporated naturally into proteins, but *d*-alanine is not. The organism distinguishes one optical isomer from the other through its enzymes, large molecules that speed virtually every reaction in the cell by binding to the reactants. A specific portion of the enzyme provides the asymmetric environment, so only one of the isomers can bind there and undergo reaction (Figure 15.11).



Chiral Medicines Many drugs are chiral molecules of which one optical isomer is biologically active and the other has either a different type of activity or none at all. Naproxen, the pain reliever and anti-inflammatory agent, is an example; one isomer (see the model) is active as an anti-arthritic agent, and the other is a potent liver toxin that must be removed from the mixture during synthesis. The notorious drug thalidomide is another example. One optical isomer is active against depression, whereas the other causes fetal mutations and deaths. Tragically, the drug was sold in the 1950s as the racemic mixture and caused limb malformations in many children whose mothers had it prescribed to relieve "morning sickness" during pregnancy.

Alkenes: Hydrocarbons with Double Bonds

A hydrocarbon that contains at least one C═C bond is called an **alkene.** With two H atoms removed to make the double bond, alkenes have the general formula $\mathbf{C_nH_{2n}}$. The double-bonded C atoms are sp^2 hybridized. Because their carbon atoms are bonded to fewer than the maximum of four atoms each, alkenes are considered **unsaturated hydrocarbons.**

Alkene names differ from those of alkanes in two respects:

1. The main chain (root) *must* contain both C atoms of the double bond, even if it is not the longest chain. The chain is numbered from the end *closer* to the C═C bond, and the position of the bond is indicated by the number of the *first* C atom in it.
2. The suffix for alkenes is *-ene*.

For example, there are three four-C alkenes (C_4H_8), two unbranched and one branched (see Sample Problem 15.1b). The branched isomer is 2-methylpropene; the unbranched isomer with the C═C bond between C-1 and C-2 is 1-butene; the unbranched isomer with the C═C bond between C-2 and C-3 is 2-butene. As you'll see next, there are two isomers of 2-butene, but they are of a different sort (discussed briefly in Sections 10.3 and 11.2).

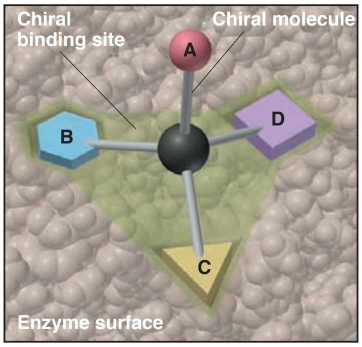
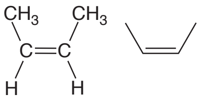
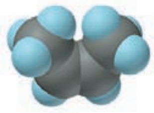
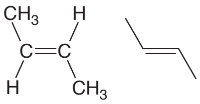


Figure 15.11 The binding site of an enzyme. Organisms can utilize only one of a pair of optical isomers because their enzymes have binding sites with shapes that are chiral (asymmetric). The shape of the mirror image of this molecule does not allow it to bind at this site.

The C═C Bond and Geometric (*cis-trans*) Isomerism There are two major structural differences between alkenes and alkanes. First, alkanes have a *tetrahedral* geometry (bond angles of ~109.5°) around each C atom, whereas the double-bonded C atoms in alkenes are *trigonal planar* (~120°). Second, the C—C bond *allows* rotation of bonded groups, so the atoms in an alkane continually change their relative positions. In contrast, the π bond of the C═C bond *restricts* rotation, which fixes the relative positions of the atoms bonded to it.

This rotational restriction leads to another type of stereoisomerism. **Geometric isomers** (also called ***cis-trans*** **isomers**) have different orientations of groups around a double bond (or similar structural feature). Table 15.4 shows the two geometric isomers of 2-butene (also see Comment, Sample Problem 15.1). One isomer, *cis*-2-butene, has the CH_3 groups on the *same* side of the C═C bond, whereas the other isomer, *trans*-2-butene, has them on *opposite* sides of the C═C bond. In general, the *cis* isomer has the *larger portions of the main chain* (in this case, two CH_3 groups) *on the same side* of the double bond, and the *trans* isomer has them on opposite sides. (*Cis-trans* isomerism also occurs in many transition metal compounds, which have a different structural feature that restricts rotation, as we discuss in Chapter 23.) For a molecule to have geometric isomers, *each C atom in the C═C bond must be bonded to two different groups.* Like other isomers, geometric isomers have different properties. Note in Table 15.4 that the two 2-butenes differ in molecular shape *and* physical properties. The *cis* isomer has a bend in the chain that the *trans* isomer lacks. In Chapters 10 and 12, you saw how such a difference affects molecular polarity and physical properties, which arise from differing strengths of intermolecular attractions. The upcoming Chemical Connections essay shows how this simple difference in geometry has profound effects in biological systems as well.

Table 15.4 The Geometric Isomers of 2-Butene

Systematic Name	Condensed and Skeleton Formulas	Space-Filling Model	Density (g/mL)	Boiling Point (°C)
cis-2-Butene			0.621	3.7
trans-2-Butene			0.604	0.9

Chemical Connections to Sensory Physiology

Geometric Isomers and the Chemistry of Vision

Of all our senses, sight provides the most information about the external world. Light bouncing off objects enters the lens of the eye and is focused on the retina. From there, molecular signals are converted to mechanical signals and then to electrical signals that are transmitted to the brain. This remarkable sequence is one of the few physiological processes that we understand thoroughly at the molecular level. The first step relies on the different shapes of geometric isomers.

The molecule responsible for receiving the light energy is *retinal.* It is derived from retinol (vitamin A), which we obtain mostly from β-carotene in yellow and green vegetables. Retinal is a 20-C compound consisting of a 15-C chain and five 1-C branches. As you can see from the ball-and-stick model in Figure B15.1, the chain includes five C=C bonds, a six-C ring at one end, and a C=O bond at the other. There are two biologically occurring isomers of retinal. The all-*trans* isomer, shown on the right, has a *trans* orientation around all five double bonds. The 11-*cis* isomer, shown on the left, has a *cis* orientation around the C=C bond between C-11 and C-12. Note the significant difference in shape between the two isomers.

Certain cells of the retina are densely packed with *rhodopsin,* which consists of the relatively small 11-*cis*-retinal covalently bonded to a large protein. The initial chemical event in vision occurs when rhodopsin absorbs a photon of visible light. The energy of visible photons (between 165 and 293 kJ/mol) lies in the range needed to break a C=C π bond (~250 kJ/mol). Retinal is bonded to the protein in such a way that the 11-*cis* π bond is the most susceptible to breakage. The photon is absorbed in a few trillionths of a second, the *cis* π bond breaks, the groups attached to the intact σ bond rotate, and a π bond re-forms to produce all-*trans*-retinal in another few millionths of a second. In effect, light energy is converted into the mechanical energy of the moving molecular chain.

This rapid and relatively large change in the shape of retinal causes the protein portion of rhodopsin to change shape as well—a process that breaks the bond between the protein portion and retinal. The change in protein shape triggers a flow of ions into the retina cells, initiating electrical impulses to the optic nerve, which conducts them to the brain. Meanwhile, the free all-*trans*-retinal diffuses away and is changed back to the *cis* form, which then binds to the protein portion again.

Retinal must be ideally suited to its function because it has been selected through evolution as a photon absorber in organisms as different as purple bacteria, mollusks, insects, and vertebrates. The features that make it the perfect choice are its strong absorption in the visible region, the efficiency with which light converts the *cis* to the *trans* form, and the large structural change it undergoes when this takes place.

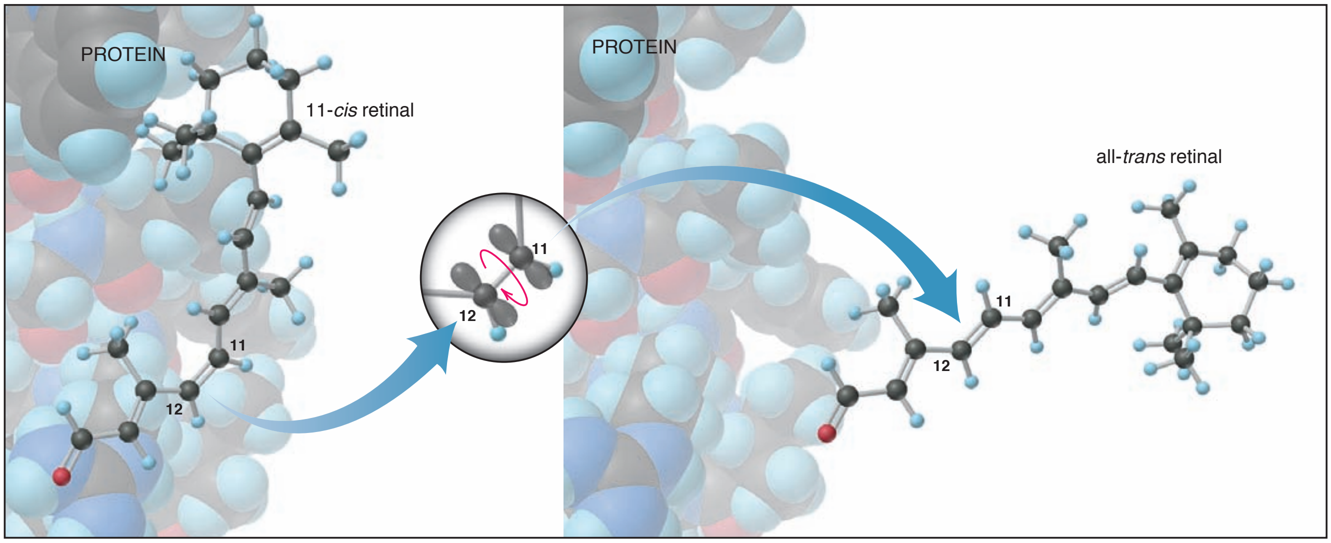


Figure B15.1 The initial chemical event in vision. In rhodopsin, the geometric isomer 11-*cis*-retinal is bonded to (*shown here as lying on*) a large protein. A photon absorbed by the retinal breaks the 11-*cis* π bond. The two parts of the retinal chain rotate around the σ bond (*shown in circle*), and the π bond forms again but with a *trans* orientation. This change in the shape of retinal changes the shape of the protein, causing it to release the all-*trans*-retinal.

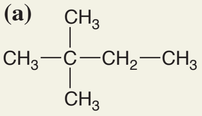
Alkynes: Hydrocarbons with Triple Bonds

Hydrocarbons that contain at least one C≡C bond are called **alkynes.** Their general formula is $\mathbf{C_nH_{2n-2}}$ because they have two H atoms fewer than alkenes with the same number of carbons. Because a carbon in a C≡C bond can bond to only one other atom, the geometry around each C atom is linear (180°): each C is *sp* hybridized. Alkynes are named in the same way as alkenes, except that the suffix is *-yne*. Because of their localized π electrons, C=C and C≡C bonds are electron rich and act as functional groups. Thus, alkenes and alkynes are much more reactive than alkanes, as we'll discuss in Section 15.4.

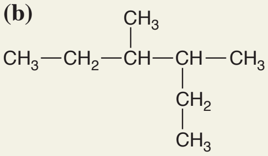
SAMPLE PROBLEM 15.2 Naming Alkanes, Alkenes, and Alkynes

PROBLEM Give the systematic name for each of the following, indicate the chiral center in part (d), and draw two geometric isomers for part (e):

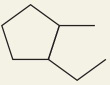
(a)


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

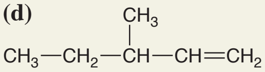
(b)


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

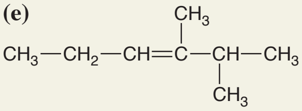
(c)



(d)


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

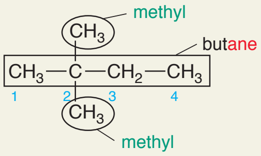
(e)


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

PLAN For (a) to (c), we refer to Table 15.2, p. 636. We first name the longest chain (*root-* + *-ane*). Then we find the *lowest* branch numbers by counting C atoms from the end *closer* to a branch. Finally, we name each branch (*root-* + *-yl*) and put the names alphabetically before the chain name. For (d) and (e), the longest chain that *includes* the multiple bond is numbered from the end closer to it. For (d), the chiral center is the C atom bonded to four different groups. In (e), the *cis* isomer has larger groups on the same side of the double bond, and the *trans* isomer has them on opposite sides.

SOLUTION

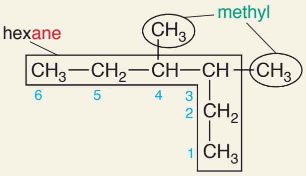
(a)



2,2-dimethylbutane

When a type of branch appears more than once, we group the chain numbers and indicate the number of branches with a numerical prefix, such as 2,2-*di*methyl.

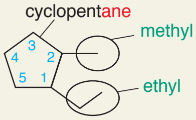
(b)



3,4-dimethylhexane

In this case, we can number the chain from either end because the branches are the same and are attached to the two central C atoms.

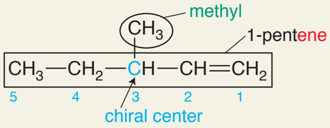
(c)



1-ethyl-2-methylcyclopentane

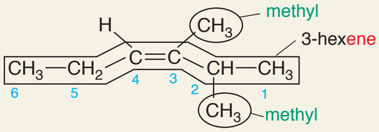
We number the ring C atoms so that a branch is attached to C-1.

(d)

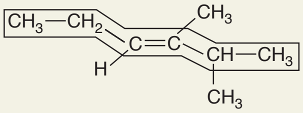


3-methyl-1-pentene

(e)



cis-2,3-dimethyl-3-hexene



trans-2,3-dimethyl-3-hexene

CHECK A good check (and excellent practice) is to reverse the process by drawing structures for the names to see if you come up with the structures given in the problem.

COMMENT In part (b), C-3 and C-4 are chiral centers, as are C-1 and C-2 in part (c). However, in (b) the molecule is not chiral: it has a plane of symmetry between C-3 and C-4, so half of the molecule rotates light opposite to the other half. Avoid these common mistakes: In (b), 2-ethyl-3-methylpentane is wrong: the longest chain is *hexane.* In (c), 1-methyl-2-ethylcyclopentane is wrong: the branch names appear *alphabetically.*

FOLLOW-UP PROBLEM 15.2 Draw condensed formulas for the following compounds: **(a)** 3-ethyl-3-methyloctane; **(b)** 1-ethyl-3-propylcyclohexane (also draw a carbon-skeleton formula for this compound); **(c)** 3,3-diethyl-1-hexyne; **(d)** *trans*-3-methyl-3-heptene.

Aromatic Hydrocarbons: Cyclic Molecules with Delocalized π Electrons

Unlike the cycloalkanes, **aromatic hydrocarbons** are planar molecules, usually with one or more rings of six C atoms, and are often drawn with alternating single and double bonds. As you learned for benzene (Section 10.1), however, all the ring bonds are identical, with values of length and strength *between* those of a C—C and a C═C bond. To indicate this, benzene is also shown as a resonance hybrid, with a circle (or dashed circle) representing the delocalized character of the π electrons (Figure 15.12A). An orbital picture shows the two lobes of the delocalized π cloud above and below the hexagonal plane of the σ-bonded C atoms (Figure 15.12B).

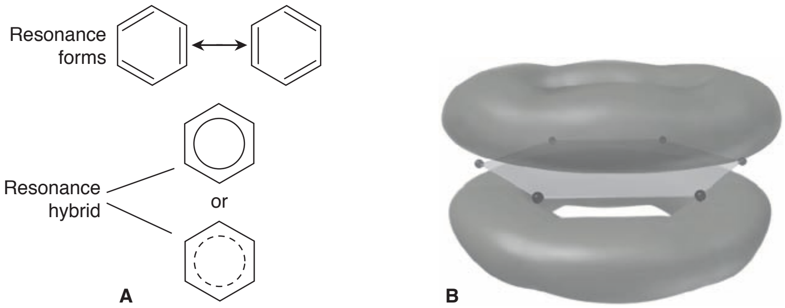
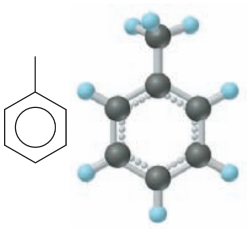
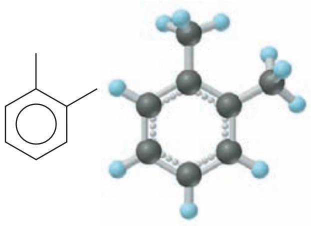


Figure 15.12 Representations of benzene. A, Benzene is often drawn with two resonance forms, showing alternating single and double bonds in different positions. The molecule is more correctly depicted as the resonance hybrid, with the delocalized electrons shown as an unbroken or dashed circle. **B,** The delocalized π cloud and the σ-bond plane of the benzene ring.

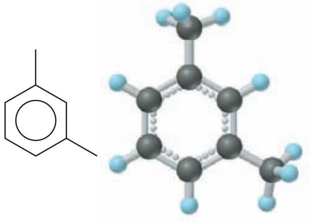
The systematic naming of simple aromatic compounds is quite straightforward. Usually, benzene is the parent compound, and attached groups, or *substituents,* are named as prefixes. However, many common names are still in use. For example, benzene with one methyl group attached is systematically named *methylbenzene* but is better known by its common name, *toluene.* With only one substituent present in toluene, we do not number the ring C atoms; when two or more groups are attached, however, we number in such a way that one of the groups is attached to ring C-1. Thus, toluene and the three structural isomers with two methyl groups attached are



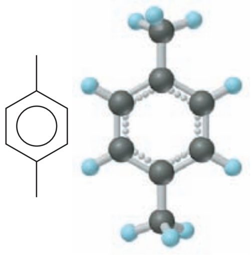
methylbenzene
(toluene)
bp = 110.6°C



1,2-dimethylbenzene
(*o*-xylene)
bp = 144.4°C



1,3-dimethylbenzene
(*m*-xylene)
bp = 139.1°C

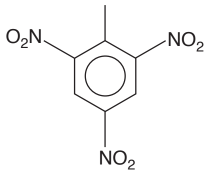


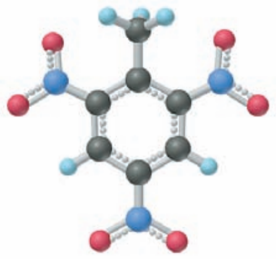
1,4-dimethylbenzene
(*p*-xylene)
bp = 138.3°C

In common names, the positions of two groups are indicated by *o-* (ortho) for groups on adjacent ring C atoms, *m-* (meta) for groups separated by one ring C atom, and *p-* (para) for groups on opposite ring C atoms. The dimethylbenzenes (commonly known as *xylenes*) are important solvents and feedstocks for polyester fibers and dyes. (See the margin note on page 645.) ●

The number of isomers increases with more than two attached groups. For example, there are six isomers for a compound with one methyl and three nitro

(—NO_2) groups attached to a benzene ring; the explosive TNT, shown below, is only one:





2,4,6-trinitromethylbenzene
(**t**ri**n**itro**t**oluene, TNT)

One of the most important methods for determining the structures of organic molecules is discussed in the upcoming Tools of the Laboratory essay.

Variations on a Theme: Catenated Inorganic Hydrides

In short discussions called *Variations on a Theme* found throughout this chapter, we examine similarities between organic and inorganic compounds. From this perspective, you'll see that the behavior of carbon is remarkable, but not unique, in the chemistry of the elements.

Although no element approaches carbon in the variety and complexity of its hydrides, catenation occurs frequently in the periodic table, and many ring, chain, and cage structures are known. Some of the most fascinating belong to the boron hydrides, or boranes (Section 14.5). Although their shapes rival even those of the hydrocarbons, the weakness of their unusual bridge bonds renders most of them thermally and chemically unstable.

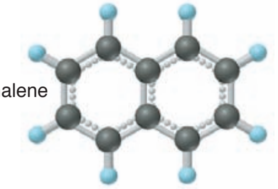
An obvious structural similarity exists between alkanes and the silicon hydrides, or silanes (Section 14.6). Silanes even have an analogous general formula (Si_nH_{2n+2}). Branched silanes are also known, but no cyclic or unsaturated (containing an Si═Si bond) compounds had been prepared until very recently. Unlike alkanes, silanes are unstable thermally and ignite spontaneously in air.

Sulfur's ability to catenate is second only to carbon's, and many chains and rings occur among its allotropes (Section 14.8). A large series of sulfur hydrides, or polysulfanes, is known. However, these molecules are unbranched chains with H atoms at the ends only (H—S_n—H). Like the silanes, the polysulfanes are oxidized easily and decompose readily to sulfur's only stable hydride, H_2S, and its most stable allotrope, cyclo-S_8.

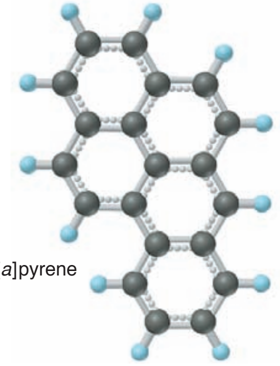
Section Summary

Hydrocarbons contain only C and H atoms, so their physical properties depend on the strength of their dispersion forces. • Names of organic compounds have a root for the longest chain, a prefix for any attached group, and a suffix for the type of compound. • Alkanes (C_nH_{2n+2}) have only single bonds. Cycloalkanes (C_nH_{2n}) have ring structures that are typically nonplanar. Alkenes (C_nH_{2n}) have at least one C═C bond. Alkynes (C_nH_{2n-2}) have at least one C≡C bond. Aromatic hydrocarbons have at least one planar ring with delocalized π electrons.

Isomers are compounds with the same molecular formula but different properties. • Structural isomers have different atom arrangements. • Stereoisomers (optical and geometric) have the same arrangement of atoms, but their atoms are oriented differently in space. Optical isomers cannot be superimposed on each other because they are asymmetric, with four different groups bonded to the C that is the chiral center. They have identical physical and chemical properties except in their rotation of plane-polarized light and their reaction with chiral reactants. Geometric (*cis-trans*) isomers have groups oriented differently around a C═C bond, which restricts rotation. • Light converts a *cis* isomer of retinal to the all-*trans* form, which initiates the visual response. • ^{1}H-NMR spectroscopy indicates the relative numbers of H atoms in the various environments within an organic molecule.



Naphthalene



Benzo[*a*]pyrene

● **Aromatic Carcinogens** *Polycyclic aromatic compounds* have "fused" ring systems, in which two or more rings share one or more sides. The simplest is naphthalene, a feedstock for dyes. Many of these compounds (and benzene itself) have been shown to have carcinogenic (cancer-causing) activity. One of the most potent, benzo[*a*]pyrene, is found in soot, cigarette smoke, car exhaust, and even the smoke from barbecue grills!

Tools of the Laboratory

Nuclear Magnetic Resonance (NMR) Spectroscopy

Chemists rely on a battery of instrumental methods to determine the complex structures of organic molecules. We discussed the methods of mass spectrometry in Chapter 2 and infrared (IR) spectroscopy in Chapter 9. One of the most useful tools for analyzing organic and biochemical structures is **nuclear magnetic resonance (NMR) spectroscopy,** which measures environments of certain nuclei in a molecule to elucidate its structure.

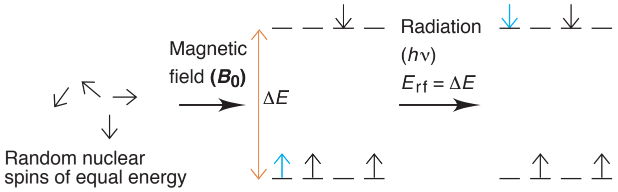


Figure B15.2 The basis of proton spin resonance. The randomly oriented magnetic fields of protons in a sample become aligned in a strong external field (B_0), with slightly more protons in the lower spin state. In a process called *resonance,* the spin flips when the proton absorbs a photon with energy equal to ΔE (radio-frequency region).

In Chapter 8, we saw that an electron can spin in either of two directions, each of which creates a tiny magnetic field. Several types of nuclei behave in a similar way. The most important of these are ^{1}H, ^{13}C, ^{19}F, and ^{31}P. In this discussion we focus primarily on the proton, ^{1}H, the nucleus of the most common isotope of hydrogen, and therefore refer to ^{1}H-NMR spectroscopy. Generally, the magnetic fields of all the protons in a sample of compound are oriented randomly. When placed in a strong external magnetic field ($\boldsymbol{B}_0$), however, the proton fields become aligned with it (parallel) or against it (antiparallel). The parallel orientation is slightly lower in energy, with the energy difference (ΔE) between the two energy states (spin states) lying in the radio-frequency (rf) region of the spectrum.

The protons in the sample oscillate rapidly between the two spin states, and in a process known as *resonance,* the rf value is varied until it matches the frequency of this oscillation. At this point, the protons are "in resonance" with the rf radiation and they absorb and re-emit the energy, which is detected by the rf receiver of the ^{1}H-NMR spectrometer (Figure B15.2). If all the protons in a sample required the same ΔE for resonance, a ^{1}H-NMR spectrum would have only one peak and be useless. However, the ΔE between the two states depends on the *actual* magnetic field felt by each proton, which is affected by the tiny magnetic fields of the *electrons* of atoms adjacent to that proton. Thus, the ΔE of each proton depends on the electrons in the adjacent atoms—C atoms, electronegative atoms, multiple bonds, and aromatic rings—in other words, on the specific molecular environment. Therefore, the ^{1}H-NMR spectrum is *unique* to that compound.

The ^{1}H-NMR spectrum of a compound is a series of peaks that represents the resonance of each proton as a function of the changing magnetic field. The *chemical shift* of the protons in a given environment is where a peak appears; it represents the ratio of the frequency at which resonance occurs for that proton to the magnitude of the external magnetic field. The chemical shifts are shown relative to that of an added standard, tetramethylsilane [$(CH_3)_4Si$, TMS], which has 12 protons bonded to four C atoms that are bonded to one Si atom. Because the shape of TMS is tetrahedral around Si, all 12 protons are in identical environments and so produce one peak. Figure B15.3 shows the ^{1}H-NMR spectrum of acetone. The six protons of acetone also have identical environments—bonded to two C atoms that are each bonded to the C atom in a C═O bond—so they, too, produce one peak, but at a different position from that for TMS. (The axes need not concern us.) The spectrum of dimethoxymethane in Figure B15.4 shows *two* peaks in addition to the TMS peak. The taller one is due

15.3 SOME IMPORTANT CLASSES OF ORGANIC REACTIONS

In Chapter 4, we classified chemical reactions based on the chemical process involved (precipitation, acid-base, or redox) and then briefly included a classification based on the number of reactants and products (combination, decomposition, or displacement). We take a similar approach here with organic reactions.

From here on, we use the notation of an uppercase R with a single bond, R—, to signify a general organic group attached to one of the atoms shown; you can usually picture R— as an **alkyl group,** a saturated hydrocarbon chain with one bond available to link to another atom. Thus, $R—CH_2—Br$ has an alkyl group attached to a CH_2 group bearing a Br atom; $R—CH═CH_2$ is an alkene with an alkyl group attached to one of the carbons in the double bond; and so forth. (Often, when more than one R group is present, we write R, R′, R″, and so forth, to indicate that these groups may be different.)

Types of Organic Reactions

Most organic reactions are examples of three broad types that can be identified by comparing the *number of bonds to C* in reactants and products:

to the six CH_3 protons, and the shorter is due to the two CH_2 protons. The area under each peak (given here in units of chart-paper spaces) is proportional to *the number of protons in a given environment*. Note that the area ratio is $20.3/6.8 \approx 3/1$, the same as the ratio of six CH_3 protons to two CH_2 protons. Thus, by analyzing the chemical shifts and peak areas, the chemist learns the type and number of hydrogens in the compound.

Newer NMR methods measure the resonance of protons and other nuclei and have many applications in biochemistry and medicine. In fact, Kurt Wüthrich shared the 2002 Nobel Prize in chemistry for developing NMR methods to study biopolymer structures in solution. ^{13}C-NMR is used to monitor changes in protein and nucleic acid shape and function, and ^{31}P-NMR can determine the health of various organs. For example, the extent of damage from a heart attack can be learned by using ^{31}P-NMR to measure the concentrations of specific phosphate-containing molecules involved in energy utilization by cardiac muscle tissue.

Computer-aided magnetic resonance imaging (MRI) has allowed visualization of damage to organs and greatly assists physicians in medical diagnosis. For example, an MRI scan of the head (Figure B15.5) can show various levels of metabolic activity in different regions of the brain. The 2003 Nobel Prize in physiology or medicine was awarded to Paul C. Lauterbur and Peter Mansfield for their discoveries applying magnetic resonance to imaging of organs and other body parts.

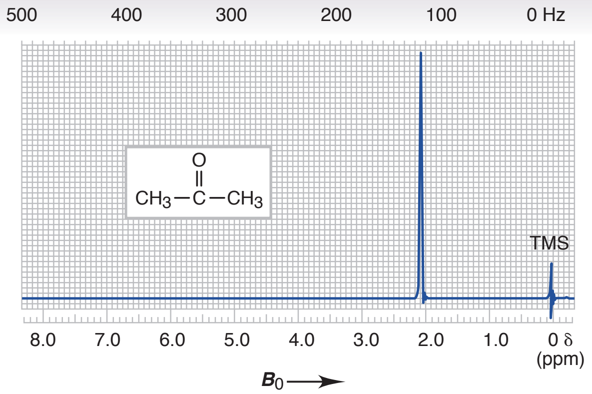


Figure B15.3 **The ^1H-NMR spectrum of acetone.** The six CH_3 protons are in identical environments, so they produce one peak; it has a different chemical shift from that for the 12 protons of the TMS standard.

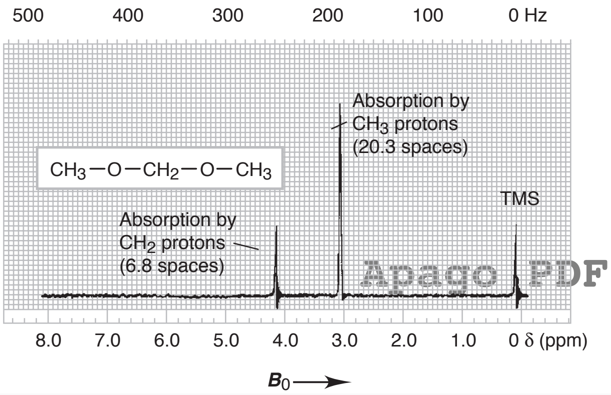


Figure B15.4 **The ^1H-NMR spectrum of dimethoxymethane.** The two peaks show chemical shifts of protons in two different environments. The area under each peak is proportional to the number of protons.

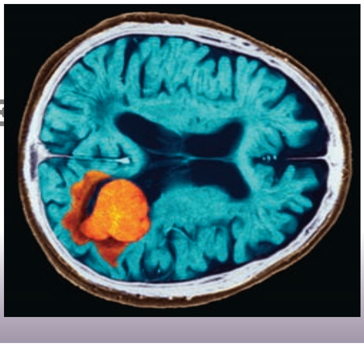
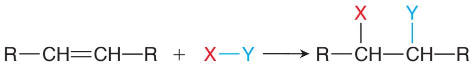


Figure B15.5 **Magnetic resonance imaging (MRI) of a brain tumor**

1. An **addition reaction** occurs when an unsaturated reactant becomes a saturated product:



$$\text{R—CH=CH—R} + \text{X—Y} \longrightarrow \text{R—}\underset{}{\overset{\text{X}}{\overset{|}{\text{CH}}}}\text{—}\overset{\text{Y}}{\overset{|}{\text{CH}}}\text{—R}$$

Note the C atoms are bonded to *more* atoms in the product than in the reactant.

The C═C and C≡C bonds and the C═O bond commonly undergo addition reactions. In each case, the π bond breaks, leaving the σ bond intact. In the product, the two C atoms (or C and O) form two additional σ bonds. Let's examine the standard heat of reaction (ΔH°_{rxn}) for a typical addition reaction to see why these reactions occur. Consider the reaction between ethene (common name, ethylene) and HCl:

$$CH_2{=}CH_2 + H{-}Cl \longrightarrow H{-}CH_2{-}CH_2{-}Cl$$

Reactants (bonds broken)	Product (bonds formed)
1 C═C = 614 kJ	1 C—C = −347 kJ
4 C—H = 1652 kJ	5 C—H = −2065 kJ
1 H—Cl = 427 kJ	1 C—Cl = −339 kJ
Total = 2693 kJ	Total = −2751 kJ

$$\Delta H^\circ_{rxn} = \Sigma\Delta H^\circ_{\text{bonds broken}} + \Sigma\Delta H^\circ_{\text{bonds formed}} = 2693\text{ kJ} + (-2751\text{ kJ}) = -58\text{ kJ}$$

The reaction is exothermic. By looking at the *net* change in bonds, we see that the driving force for many additions is the formation of two σ bonds (in this case, C—H and C—Cl) from one σ bond (in this case, H—Cl) and one relatively weak π bond. An addition reaction is the basis of a color test for the presence of C═C bonds (Figure 15.13).

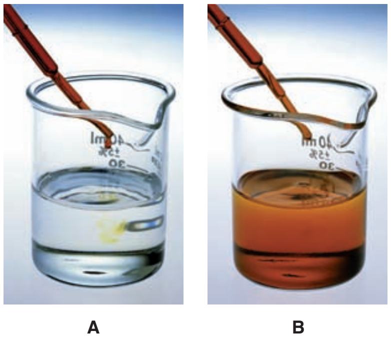
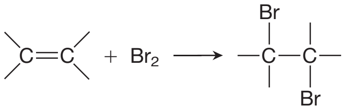
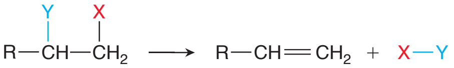


Figure 15.13 A color test for C═C bonds. A, Br_2 (in pipet) reacts with a compound that has a C═C bond (in beaker), and its orange-brown color disappears:



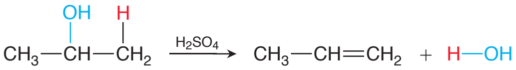
B, The compound in this beaker has no C═C bond, so the Br_2 does not react, and the orange-brown color remains.

2. **Elimination reactions** are the opposite of addition reactions. They occur when a saturated reactant becomes an unsaturated product:



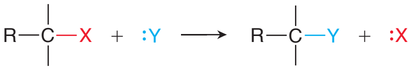
$$\mathrm{R{-}\overset{\overset{Y}{|}}{C}H{-}\overset{\overset{X}{|}}{C}H_2 \longrightarrow R{-}CH{=}CH_2 + X{-}Y}$$

Note that the C atoms are bonded to *fewer* atoms in the product than in the reactant. A pair of halogen atoms, an H atom and a halogen atom, or an H atom and an —OH group are typically eliminated, but C atoms are not. Thus, the driving force for many elimination reactions is the formation of a small, stable molecule, such as HCl(*g*) or H_2O, which increases the entropy of the system (Section 13.3):



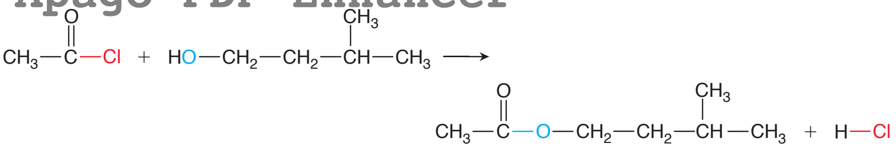
$$\mathrm{CH_3{-}\overset{\overset{OH}{|}}{C}H{-}\overset{\overset{H}{|}}{C}H_2 \xrightarrow{H_2SO_4} CH_3{-}CH{=}CH_2 + H{-}OH}$$

3. A **substitution reaction** occurs when an atom (or group) from an added reagent substitutes for one in the organic reactant:



$$\mathrm{R{-}\overset{|}{\underset{|}{C}}{-}X + {:}Y \longrightarrow R{-}\overset{|}{\underset{|}{C}}{-}Y + {:}X}$$

Note that the C atom is bonded to the *same number* of atoms in the product as in the reactant. The C atom may be saturated or unsaturated, and X and Y can be many different atoms, but generally *not* C. The main flavor ingredient in banana oil, for instance, forms through a substitution reaction; note that the O substitutes for the Cl:



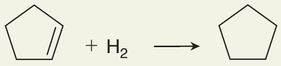
$$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}Cl + HO{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3 \longrightarrow CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3 + H{-}Cl}$$

SAMPLE PROBLEM 15.3 Recognizing the Type of Organic Reaction

PROBLEM State whether each reaction is an addition, elimination, or substitution:

(a) $CH_3{-}CH_2{-}CH_2{-}Br \longrightarrow CH_3{-}CH{=}CH_2 + HBr$

(b)



(c)

$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}{-}Br + CH_3CH_2OH \longrightarrow CH_3\overset{\overset{O}{\|}}{C}{-}OCH_2CH_3 + HBr}$$

PLAN We determine the type of reaction by looking for any change in the number of atoms bonded to C:

- More atoms bonded to C is an *addition.*
- Fewer atoms bonded to C is an *elimination.*
- Same number of atoms bonded to C is a *substitution.*

SOLUTION

(a) Elimination: two bonds in the reactant, C—H and C—Br, are absent in the product, so fewer atoms are bonded to C.

(b) Addition: two more C—H bonds have formed in the product, so more atoms are bonded to C.

(c) Substitution: the reactant C—Br bond becomes a C—O bond in the product, so the same number of atoms are bonded to C.

FOLLOW-UP PROBLEM 15.3 Write a balanced equation for each of the following:
(a) An addition reaction between 2-butene and Cl_2
(b) A substitution reaction between $CH_3—CH_2—CH_2—Br$ and OH^-
(c) The elimination of H_2O from $(CH_3)_3C—OH$

The Redox Process in Organic Reactions

An important process in many organic reactions is *oxidation-reduction.* But chemists do not usually monitor the change in oxidation numbers of the various C atoms in a reaction. Rather, they note the movement of electron density around a C atom by counting the number of bonds to more electronegative atoms (usually O) or to less electronegative atoms (usually H). A more electronegative atom takes some electron density from the C, whereas a less electronegative atom gives some electron density to the C. Moreover, even though a redox reaction always involves both an oxidation and a reduction, organic chemists typically *focus on the organic reactant only.* Therefore,

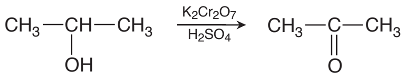
- When a C atom in the organic reactant forms more bonds to O or fewer bonds to H, the reactant is oxidized and the reaction is called an *oxidation.*
- When a C atom in the organic reactant forms fewer bonds to O or more bonds to H, the reactant is reduced and the reaction is called a *reduction.*

The most dramatic redox reactions are combustion reactions. All organic compounds contain C and H atoms and burn in excess O_2 to form CO_2 and H_2O. For ethane, the reaction is

$$2CH_3—CH_3 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$$

Obviously, when ethane is converted to CO_2 and H_2O, each of its C atoms has more bonds to O and fewer bonds to H. Thus, ethane is oxidized, and this reaction is referred to as an *oxidation,* even though O_2 is reduced as well.

Most oxidations do not involve such a total breaking apart of the molecule, however. When 2-propanol reacts with potassium dichromate in acidic solution (a common oxidizing agent in organic reactions), the organic compound that forms is 2-propanone:



$$CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3—\underset{\displaystyle O}{\underset{\|}{C}}—CH_3$$

2-propanol 2-propanone

Note that C-2 has one fewer bond to H and one more bond to O in 2-propanone than it does in 2-propanol. Thus, 2-propanol is oxidized, so this is an *oxidation.* Don't forget, however, that the dichromate ion is reduced at the same time:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

The addition of H_2 to an alkene is referred to as a *reduction:*

$$CH_2{=}CH_2 + H_2 \xrightarrow{Pd} CH_3—CH_3$$

Note that each C has more bonds to H in ethane than it has in ethene, so the ethene is reduced. (The H_2 is oxidized in the process, and the palladium shown over the arrow acts as a catalyst to speed up the reaction.)

Section Summary

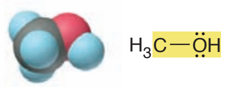
In an addition reaction, a π bond breaks and the two C atoms bond to more atoms. • In an elimination, a π bond forms and the two C atoms bond to fewer atoms. • In a substitution, one atom replaces another, but the total number of atoms bonded to C does not change. • In an organic redox process, the organic reactant is oxidized if a C atom in the compound forms more bonds to O atoms (or fewer bonds to H atoms), and it is reduced if a C atom forms more bonds to H (or fewer bonds to O).

15.4 PROPERTIES AND REACTIVITIES OF COMMON FUNCTIONAL GROUPS

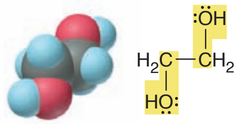
The central organizing principle of organic reaction chemistry is the *functional group*. To predict how an organic compound might react, we narrow our focus there because *the distribution of electron density in a functional group affects the reactivity*. The electron density can be high, as in the C=C and C≡C bonds, or it can be low at one end of a bond and high at the other, as in the C—Cl and C—O bonds. Such bond sites enhance a dipole in the other reactant. As a result, the reactants attract each other and begin a sequence of bond-forming and bond-breaking steps that lead to product. Thus, *the intermolecular forces that affect physical properties and solubility also affect reactivity*. Table 15.5 lists some of the important functional groups in organic compounds.

When we classify functional groups by bond order (single, double, and so forth), they tend to follow certain patterns of reactivity:

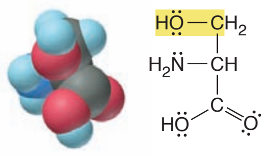
- Functional groups with only single bonds undergo substitution or elimination.
- Functional groups with double or triple bonds undergo addition.
- Functional groups with both single and double bonds undergo substitution.



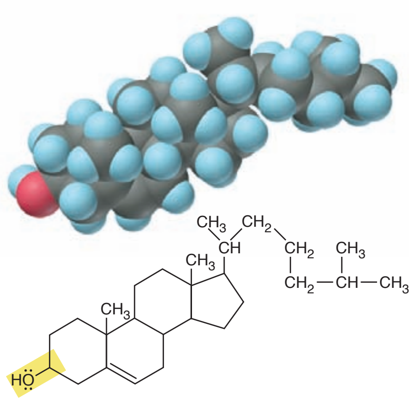
Methanol (methyl alcohol)
Byproduct in coal gasification; de-icing agent; gasoline substitute; precursor of organic compounds



1,2-Ethanediol (ethylene glycol)
Main component of auto antifreeze



Serine
Amino acid found in most proteins

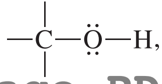


Cholesterol
Major sterol in animals; essential for cell membranes; precursor of steroid hormones

Figure 15.14 Some molecules with the alcohol functional group.

Functional Groups with Only Single Bonds

The most common functional groups with only single bonds are alcohols, haloalkanes, and amines.

Alcohols The **alcohol** functional group consists of carbon bonded to an —OH group,  $-\overset{|}{\underset{|}{C}}-\ddot{\underset{..}{O}}-H$, and the general formula of an alcohol is R—OH. Alcohols are named by dropping the final *-e* from the parent hydrocarbon name and adding the suffix *-ol*. Thus, the two-carbon alcohol is ethanol (ethan- + -ol). The common name is the hydrocarbon *root-* + *-yl,* followed by "alcohol"; thus, the common name of ethanol is ethyl alcohol. (This substance, obtained from fermented grain, has been consumed by people as an intoxicant in beverages since ancient times; today, it is recognized as the most abused drug in the world.) Alcohols are important laboratory reagents, and the functional group occurs in many biomolecules, including carbohydrates, sterols, and some amino acids. Figure 15.14 shows the names, structures, and uses of some important compounds that contain the alcohol group.

You can think of an alcohol as a water molecule with an R group in place of one of the H atoms. In fact, alcohols react with very active metals, such as the alkali metals [Group 1A(1)], in a manner similar to water:

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

$$2Na + 2CH_3—CH_2—OH \longrightarrow 2CH_3—CH_2—ONa + H_2$$

Water forms a solution of the strongly basic hydroxide ion (HO^-), and an alcohol forms a solution of the strongly basic *alkoxide ion* (RO^-): ethanol forms the ethoxide ion ($CH_3—CH_2—O^-$). The physical properties of the smaller alcohols are also similar to those of water. They have high melting and boiling points as a result of hydrogen bonding, and they dissolve polar molecules and some salts. (Substitution of R groups for both H atoms of water gives *ethers,* R—O—R.)

Alcohols undergo elimination and substitution reactions. Dehydration, the elimination of H and OH, requires acid and forms alkenes:

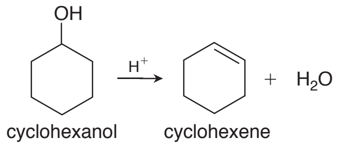
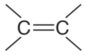
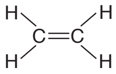
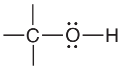
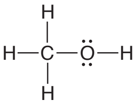
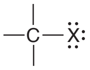
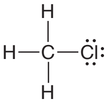
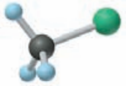
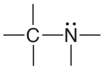
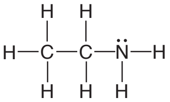
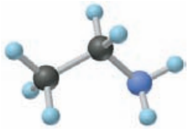
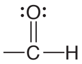
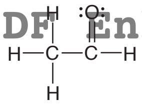
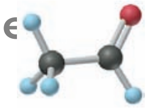
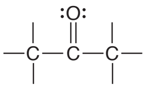
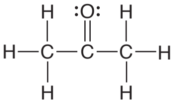
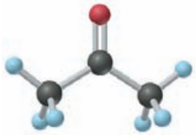
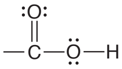
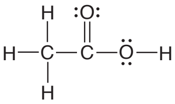
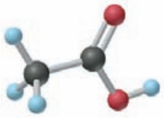
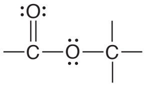
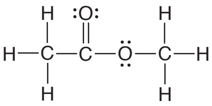
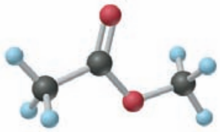
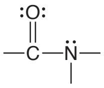
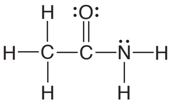
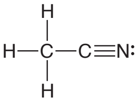
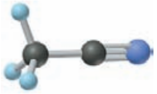
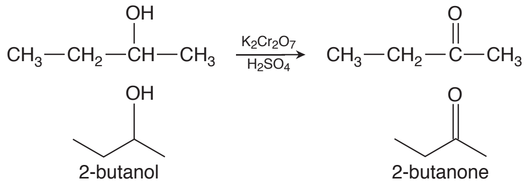


Table 15.5 Important Functional Groups in Organic Compounds

Functional Group	Compound Type	Prefix or Suffix of Name	Example		
			Lewis Structure	Ball-and-Stick Model	Systematic Name (Common Name)
	alkene	-ene			ethene (ethylene)
$-C\equiv C-$	alkyne	-yne	$H-C\equiv C-H$		ethyne (acetylene)
	alcohol	-ol			methanol (methyl alcohol)
 (X = halogen)	haloalkane	halo-			chloromethane (methyl chloride)
	amine	-amine			ethanamine (ethylamine)
	aldehyde	-al			ethanal (acetaldehyde)
	ketone	-one			2-propanone (acetone)
	carboxylic acid	-oic acid			ethanoic acid (acetic acid)
	ester	-oate			methyl ethanoate (methyl acetate)
	amide	-amide			ethanamide (acetamide)
$-C\equiv N\colon$	nitrile	-nitrile			ethanenitrile (acetonitrile, methyl cyanide)

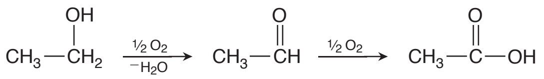
Elimination of two H atoms requires inorganic oxidizing agents, such as $K_2Cr_2O_7$ in aqueous H_2SO_4. As we saw in Section 15.3, the reaction is an oxidation and produces the C=O group (shown with condensed and carbon-skeleton formulas):



$$CH_3-CH_2-\overset{\overset{OH}{|}}{C}H-CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

2-butanol 2-butanone

For alcohols with an OH group at the end of the chain ($R-CH_2-OH$), another oxidation occurs. Wine turns sour, for example, when the ethanol in contact with air is oxidized to acetic acid:



$$CH_3-\overset{\overset{OH}{|}}{C}H_2 \xrightarrow[-H_2O]{\frac{1}{2}O_2} CH_3-\overset{\overset{O}{\|}}{C}H \xrightarrow{\frac{1}{2}O_2} CH_3-\overset{\overset{O}{\|}}{C}-OH$$

Substitution yields products with other single-bonded functional groups. With hydrohalic acids, many alcohols give haloalkanes:

$$R_2CH-OH + HBr \longrightarrow R_2CH-Br + HOH$$

As you'll see below, *the C atom undergoing the change in a substitution is bonded to a more electronegative element,* which makes it partially positive and, thus, a target for a negatively charged or electron-rich group of an incoming reactant.

Haloalkanes A *halogen* atom (X) bonded to C gives the **haloalkane** functional group, $-\overset{|}{\underset{|}{C}}-\ddot{\underset{..}{X}}\colon$, and compounds with the general formula R—X. Haloalkanes (common name, **alkyl halides**) are named by adding the halogen as a prefix to the hydrocarbon name and numbering the C atom to which the halogen is attached, as in bromomethane, 2-chloropropane, or 1,3-diiodohexane.

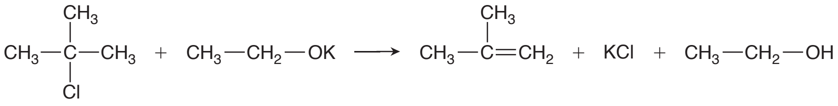
Just as many alcohols undergo substitution to alkyl halides when treated with halide ions in acid, many halides undergo substitution to alcohols in base. For example, OH^- attacks the positive C end of the C—X bond and displaces X^-:

$$CH_3-CH_2-CH_2-CH_2-Br + OH^- \longrightarrow CH_3-CH_2-CH_2-CH_2-OH + Br^-$$

1-bromobutane 1-butanol

Substitution by groups such as —CN, —SH, —OR, and $-NH_2$ allows chemists to convert alkyl halides to a host of other compounds.

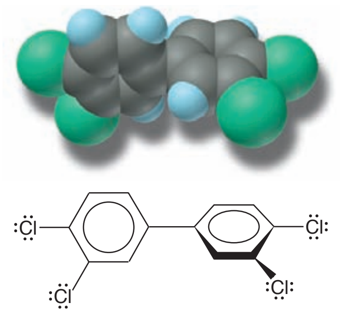
Just as addition of HX *to* an alkene produces haloalkanes, elimination of HX *from* a haloalkane by reaction with a strong base, such as potassium ethoxide, produces an alkene:



$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + CH_3-CH_2-OK \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + KCl + CH_3-CH_2-OH$$

2-chloro-2-methylpropane potassium ethoxide 2-methylpropene

Haloalkanes have many important uses, but many are carcinogenic in mammals, have severe neurological effects in humans, and, to make matters worse, are very stable and accumulate in the environment. ●



● **Pollutants in the Food Chain** Until recently, halogenated aromatic hydrocarbons, such as the *polychlorinated biphenyls* (*PCBs;* one of 209 different compounds is shown above), were used as insulating fluids in electrical transformers and then discharged in wastewater. Because of their low solubility and high stability, they accumulate for decades in river and lake sediment and are eaten by microbes and invertebrates. Fish eat the invertebrates, and birds and mammals, including humans, eat the fish. PCBs become increasingly concentrated in body fat at each stage. As a result of their health risks, PCBs in natural waters present an enormous cleanup problem.

Amines The **amine** functional group is $-\overset{|}{\underset{|}{C}}-\underset{|}{\ddot{N}}-$. Chemists classify amines as derivatives of ammonia, with R groups in place of one or more H atoms. *Primary* (1°) amines are RNH_2, *secondary* (2°) amines are R_2NH, and *tertiary* (3°) amines are R_3N. Like ammonia, amines have trigonal pyramidal shapes and a lone pair

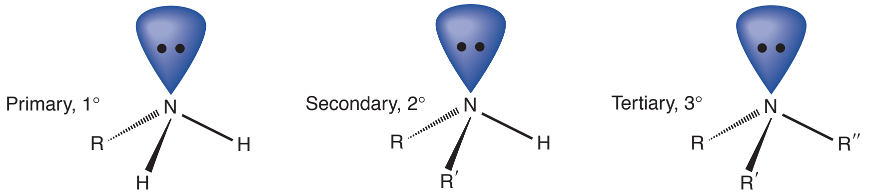


Figure 15.15 General structures of amines. Amines have a trigonal pyramidal shape and are classified by the number of R groups bonded to N. The lone pair on the nitrogen atom is the key to amine reactivity.

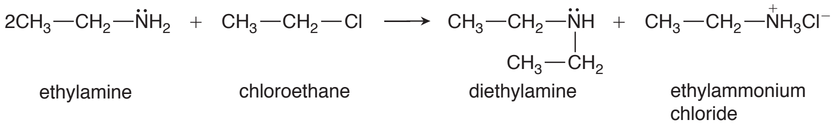
of electrons on a partially negative N atom (Figure 15.15). Systematic names drop the final *-e* of the alkane and add the suffix *-amine,* as in ethanamine. However, there is still wide usage of common names, in which the suffix *-amine* follows the name of the alkyl group; thus, methylamine has one methyl group attached to N, diethylamine has two ethyl groups attached, and so forth. Figure 15.16 shows that the amine functional group occurs in many biomolecules.

Primary and secondary amines can form H bonds, so they have higher melting and boiling points than hydrocarbons and alkyl halides of similar molar mass. For example, dimethylamine ($\mathcal{M}$ = 45.09 g/mol) boils 45°C higher than ethyl fluoride ($\mathcal{M}$ = 48.06 g/mol). Trimethylamine has a greater molar mass than dimethylamine, but it melts more than 20°C *lower* because trimethylamine molecules are not H bonded.

Amines of low molar mass are fishy smelling, water soluble, and weakly basic. The reaction with water proceeds only slightly to the right to reach equilibrium:

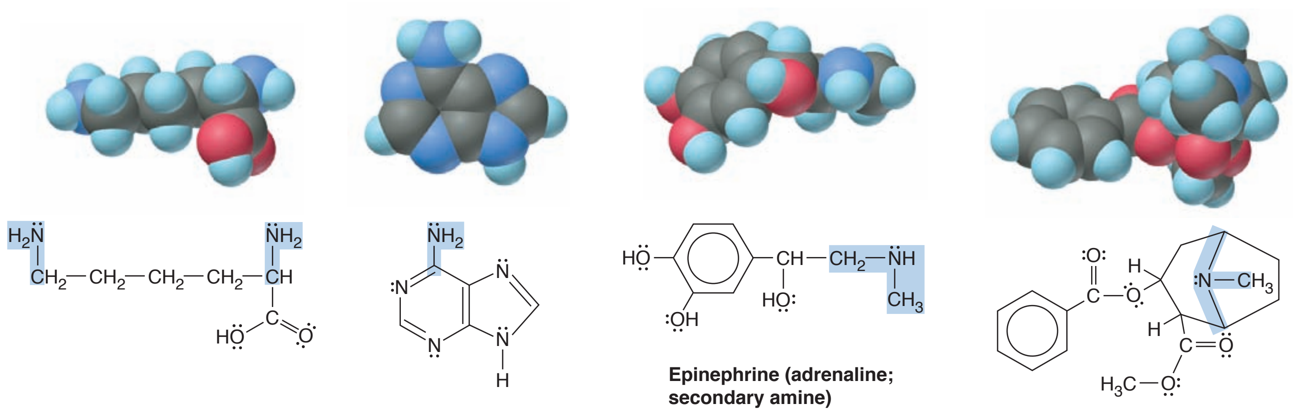
$$CH_3{-}\ddot{N}H_2 + H_2O \rightleftharpoons CH_3{-}\overset{+}{N}H_3 + OH^-$$

Amines undergo substitution reactions in which the lone pair on N attacks the partially positive C in alkyl halides to displace X^- and form a larger amine:



$$2CH_3{-}CH_2{-}\ddot{N}H_2 + CH_3{-}CH_2{-}Cl \longrightarrow \underset{\displaystyle |\atop \displaystyle CH_3{-}CH_2}{CH_3{-}CH_2{-}\ddot{N}H} + CH_3{-}CH_2{-}\overset{+}{N}H_3Cl^-$$

(Two molecules of ethylamine are needed: while one attacks the chloroethane, the other binds the released H^+ to prevent it from remaining on the diethylamine.)



Lysine (primary amine)
Amino acid found in most proteins

Adenine (primary amine)
Component of nucleic acids

Epinephrine (adrenaline; secondary amine)
Neurotransmitter in brain; hormone released during stress

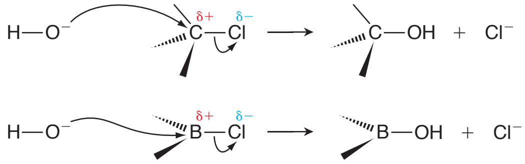
Cocaine (tertiary amine)
Brain stimulant; widely abused drug

Figure 15.16 Some biomolecules with the amine functional group.

Variations on a Theme: Inorganic Compounds with Single Bonds to O, X, and N

The —OH group occurs frequently in inorganic compounds. All oxoacids contain at least one —OH, usually bonded to a relatively electronegative nonmetal atom, which in most cases is bonded to other O atoms. Oxoacids are acidic in water because these additional O atoms pull electron density from the central nonmetal, which pulls electron density from the O—H bond, releasing an H^+ ion and stabilizing the oxoanion through resonance. Alcohols are *not* acidic in water because they lack the additional O atoms and the electronegative nonmetal.

Halides of nearly every nonmetal are known, and many undergo substitution reactions in base. As in the case of an alkyl halide, the process involves an attack on the partially positive central atom by OH^-:



Thus, alkyl halides undergo the same general reaction as other nonmetal halides, such as BCl_3, SiF_4, and PCl_5.

The bonds between nitrogen and larger nonmetals, such as Si, P, and S, have significant double-bond character, which affects structure and reactivity. For example, trisilylamine, the Si analog of trimethylamine (see Figure 14.16, p. 590), is planar, rather than trigonal pyramidal, partially as a result of *p*,*d*–π bonding. The lone pair on N is delocalized in this π bond, so trisilylamine is not basic.

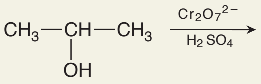
SAMPLE PROBLEM 15.4 Predicting the Reactions of Alcohols, Alkyl Halides, and Amines

PROBLEM Determine the reaction type and predict the product(s) for each reaction:

(a) $CH_3—CH_2—CH_2—I + NaOH \longrightarrow$

(b) $CH_3—CH_2—Br + 2CH_3—CH_2—CH_2—NH_2 \longrightarrow$

(c)

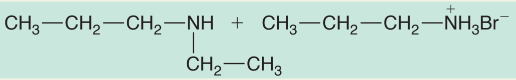


$CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3 \xrightarrow[H_2SO_4]{Cr_2O_7^{2-}}$

PLAN We first determine the functional group(s) of the reactant(s) and then examine any inorganic reagent(s) to decide on the reaction type, keeping in mind that, in general, these functional groups undergo substitution or elimination. In (a), the reactant is an alkyl halide, so the OH^- of the inorganic reagent substitutes for the I. In (b), the reactants are an amine and an alkyl halide, so the N of the amine substitutes for the Br. In (c), the reactant is an alcohol, the inorganic reagents form a strong oxidizing agent, and the alcohol undergoes elimination to a carbonyl compound.

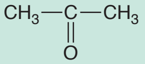
SOLUTION (a) Substitution: The products are $CH_3—CH_2—CH_2—OH + NaI$

(b) Substitution: The products are



$CH_3—CH_2—CH_2—\underset{\displaystyle CH_2—CH_3}{\underset{|}{NH}} + CH_3—CH_2—CH_2—\overset{+}{N}H_3Br^-$

(c) Elimination: (oxidation): The product is

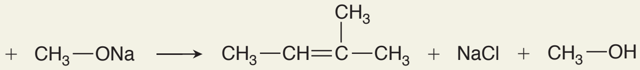


$CH_3—\underset{\displaystyle O}{\underset{\|}{C}}—CH_3$

CHECK The only changes should be at the functional group.

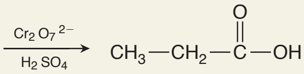
FOLLOW-UP PROBLEM 15.4 Fill in the blank in each reaction. (*Hint:* Examine any inorganic compounds and the organic product to determine the organic reactant.)

(a) _____



$\_\_\_\_\_ + CH_3—ONa \longrightarrow CH_3—CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}—CH_3 + NaCl + CH_3—OH$

(b) _____

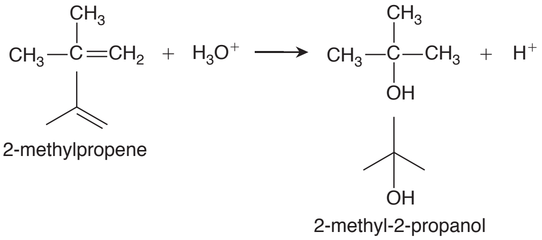


$\_\_\_\_\_ \xrightarrow[H_2SO_4]{Cr_2O_7^{2-}} CH_3—CH_2—\overset{\displaystyle O}{\overset{\|}{C}}—OH$

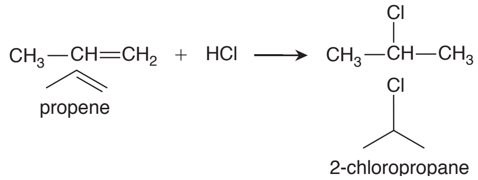
Functional Groups with Double Bonds

The most important functional groups with double bonds are the C═C of alkenes and the C═O of aldehydes and ketones. Both appear in many organic and biological molecules. *Their most common reaction type is addition.*

Comparing the Reactivity of Alkenes and Aromatic Compounds The C═C bond is the essential portion of the alkene functional group, $\rangle\mathrm{C{=}C}\langle$. Although they can be further unsaturated to alkynes, *alkenes typically undergo addition.* The electron-rich double bond is readily attracted to the partially positive H atoms of hydronium ions and hydrohalic acids, yielding alcohols and alkyl halides, respectively:



$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 + H_3O^+ \longrightarrow CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_3 + H^+}$$

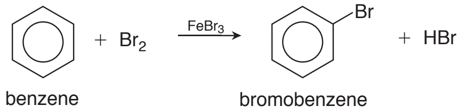


$$\mathrm{CH_3{-}CH{=}CH_2 + HCl \longrightarrow CH_3{-}\overset{\displaystyle Cl}{\overset{|}{C}H}{-}CH_3}$$

The *localized* unsaturation of alkenes is very different from the *delocalized* unsaturation of benzene. Despite the way we depict its resonance forms, benzene does *not* have double bonds. Thus, for example, benzene does not decolorize Br_2.

In general, aromatic rings are much *less* reactive than alkenes because they have delocalized π electrons. For example, let's compare the heats of reaction for the addition of H_2. Hydrogenation of cyclohexene, with one C═C bond, has a $\Delta H^\circ_{\mathrm{rxn}}$ of −120 kJ/mol. If we extrapolate to the imaginary molecule "cyclohexatriene," that is, the structure with three C═C bonds, its hypothetical $\Delta H^\circ_{\mathrm{rxn}}$ for hydrogenation is three times as much, or −360 kJ/mol. Hydrogenation of benzene has a $\Delta H^\circ_{\mathrm{rxn}}$ of −208 kJ/mol. Thus, the $\Delta H^\circ_{\mathrm{rxn}}$ for hydrogenation of benzene is 152 kJ/mol *less* than that for "cyclohexatriene," an energy difference attributed to the aromatic stabilization of benzene (Figure 15.17).

This extra energy needed to break up the delocalized π system means *addition* reactions with benzene occur rarely. But, benzene does undergo many *substitution* reactions in which the delocalization is retained when an H atom attached to a ring C is replaced by another group:



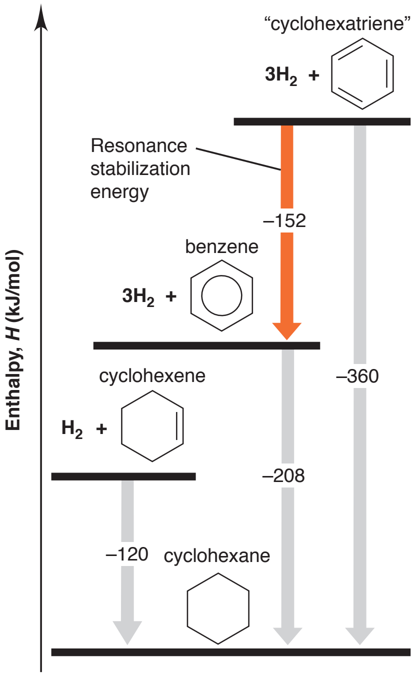
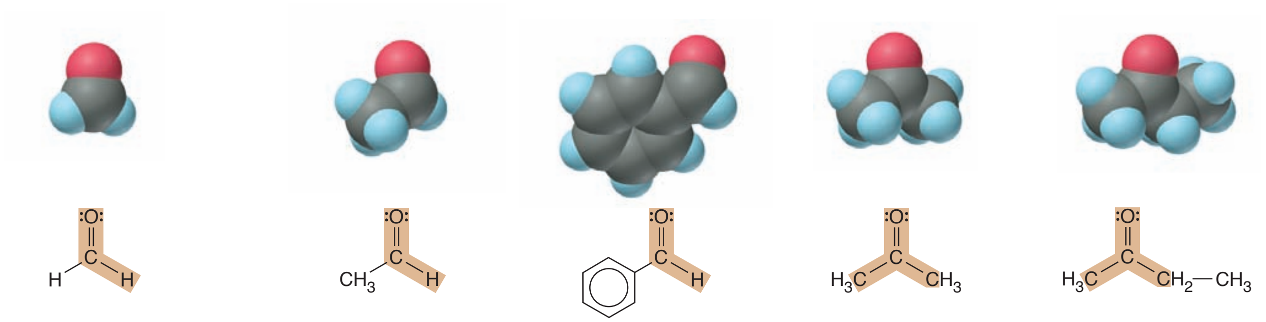


Figure 15.17 The stability of benzene. Because of the resonance stabilization caused by the aromatic π-electron system in benzene, the molecule releases 152 kJ/mol *less* energy when it is hydrogenated than would "cyclohexatriene," the analogous molecule with three separate double bonds.

Aldehydes and Ketones The C═O bond, or **carbonyl group,** is one of the most chemically versatile. In the **aldehyde** functional group, the carbonyl C is bonded to H (and often to another C), so it occurs *at the end of a chain,* $\mathrm{R{-}\overset{\displaystyle H}{\overset{|}{C}}{=}O}$. Aldehyde names drop the final *-e* from the alkane name and add *-al;* thus, the three-C aldehyde is propanal. In the **ketone** functional group, the carbonyl C is bonded to two other C atoms, $\mathrm{{-}\overset{|}{\underset{|}{C}}{-}\overset{:\ddot{O}:}{\overset{\|}{C}}{-}\overset{|}{\underset{|}{C}}{-}}$, so it occurs *within the chain.*



Methanal (formaldehyde)
Used to make resins in plywood, dishware, countertops; biological preservative

Ethanal (acetaldehyde)
Narcotic product of ethanol metabolism; used to make perfumes, flavors, plastics, other chemicals

Benzaldehyde
Artificial almond flavoring

2-Propanone (acetone)
Solvent for fat, rubber, plastic, varnish, lacquer; chemical feedstock

2-Butanone (methyl ethyl ketone)
Important solvent

Figure 15.18 Some common aldehydes and ketones.

Ketones, $R-\overset{\displaystyle O}{\overset{\|}{C}}-R'$, are named by numbering the carbonyl C, dropping the final *-e* from the alkane name, and adding *-one*. For example, the unbranched, five-C ketone with the carbonyl C as C-2 in the chain is named 2-pentanone. Figure 15.18 shows some common carbonyl compounds.

Like the C=C bond, the C=O bond is *electron rich;* unlike the C=C bond, it is *highly polar* ($\Delta EN = 1.0$). Figure 15.19 emphasizes this polarity with an electron density model and a charged resonance form. Aldehydes and ketones are formed by the oxidation of alcohols:

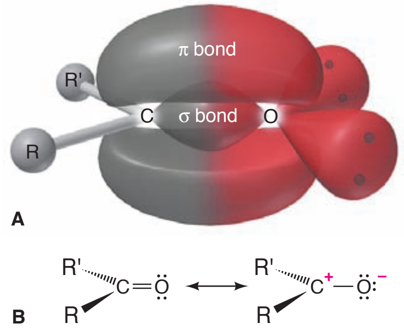
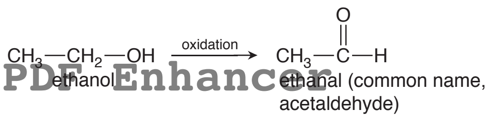
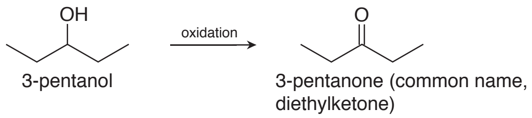
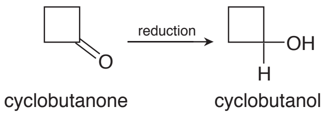


Figure 15.19 The carbonyl group. **A,** The σ and π bonds that make up the C=O bond of the carbonyl group. **B,** The charged resonance form shows that the C=O bond is polar (ΔEN = 1.0).

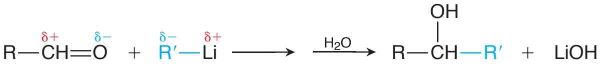




Conversely, as a result of their unsaturation, carbonyl compounds can undergo *addition* and be reduced to alcohols:

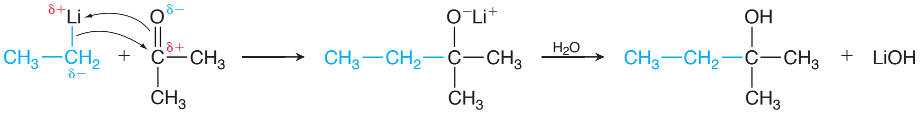


As a result of the bond polarity, addition often occurs with an electron-rich group bonding to the carbonyl C and an electron-poor group bonding to the carbonyl O. **Organometallic compounds,** which have a metal atom (usually Li or Mg) attached to an R group through a polar covalent bond (Sections 14.3 and 14.4), take part in this type of reaction. In a two-step sequence, they convert carbonyl compounds to alcohols with *different carbon skeletons:*



$$R-\overset{\delta+}{C}H=\overset{\delta-}{O} + \overset{\delta-}{R'}-\overset{\delta+}{Li} \longrightarrow \xrightarrow{H_2O} R-\underset{}{\overset{\displaystyle OH}{\overset{|}{C}H}}-R' + LiOH$$

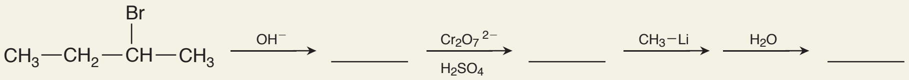
In the following reaction steps, for example, the electron-rich C bonded to Li in ethyllithium, CH_3CH_2-Li, attacks the electron-poor carbonyl C of 2-propanone, adding its ethyl group; at the same time, the Li adds to the carbonyl O. Treating the mixture with water forms the C—OH group:



Note that the product skeleton combines the two reactant skeletons. The field of *organic synthesis* often employs organometallic compounds to create molecules with different skeletons and, thus, synthesize new compounds.

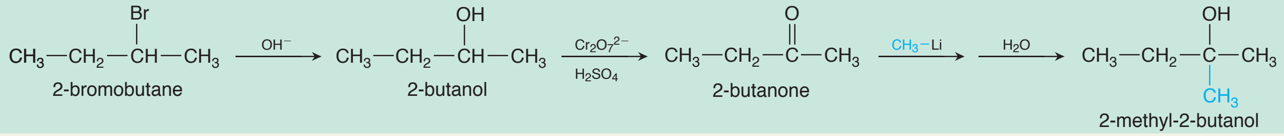
SAMPLE PROBLEM 15.5 Predicting the Steps in a Reaction Sequence

PROBLEM Fill in the blanks in the following reaction sequence:



PLAN For each step, we examine the functional group of the reactant and the reagent above the yield arrow to decide on the most likely product.

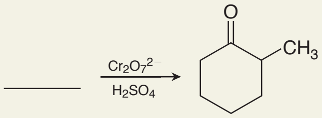
SOLUTION The sequence starts with an alkyl halide reacting with OH^-. Substitution gives an alcohol. Oxidation of this alcohol with acidic dichromate gives a ketone. Finally, a two-step reaction of a ketone with CH_3—Li and then water forms an alcohol with a carbon skeleton that has the CH_3— group attached to the carbonyl C:



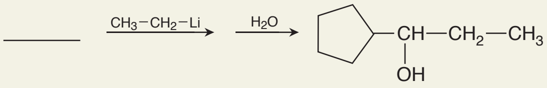
CHECK In this case, make sure that the first two reactions alter the functional group only and that the final steps change the C skeleton.

FOLLOW-UP PROBLEM 15.5 Choose reactants to obtain the following products:

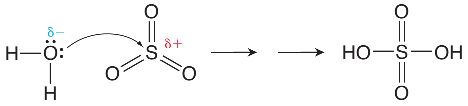
(a)



(b)

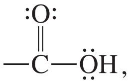
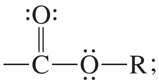
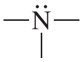
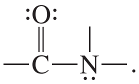


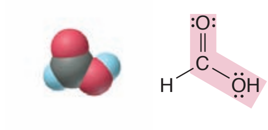
Variations on a Theme: Inorganic Compounds with Double Bonds Homonuclear (same kind of atom) double bonds are rare for atoms other than C. However, we've seen many double bonds between O and other nonmetals, for example, in the oxides of S, N, and the halogens. Like carbonyl compounds, these substances undergo addition reactions. For example, the partially negative O of water attacks the partially positive S of SO_3 to form sulfuric acid:



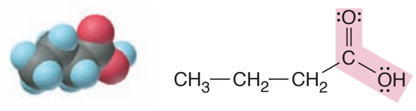
S bonded to 3 atoms S bonded to 4 atoms

Functional Groups with Both Single and Double Bonds

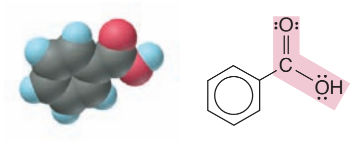
A family of three functional groups contains C double bonded to O (a carbonyl group) *and* single bonded to O or N. The parent of the family is the **carboxylic acid** group,  $-\overset{\overset{\large :O:}{\|}}{C}-\ddot{O}H$, also called the *carboxyl group* and written —COOH. *The most important reaction type of this family is substitution from one member to another.* Substitution for the —OH by the —OR of an alcohol gives the **ester** group,  $-\overset{\overset{\large :O:}{\|}}{C}-\ddot{\underset{..}{O}}-R$; substitution by the  $-\ddot{\underset{|}{N}}-$ of an amine gives the **amide** group,  $-\overset{\overset{\large :O:}{\|}}{C}-\underset{..}{\overset{|}{N}}-$.



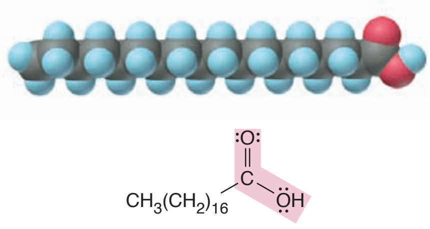
Methanoic acid (formic acid)
An irritating component
of ant and bee stings



Butanoic acid (butyric acid)
Odor of rancid butter;
suspected component of
monkey sex attractant



Benzoic acid
Calorimetric standard;
used in preserving food,
dyeing fabric, curing tobacco

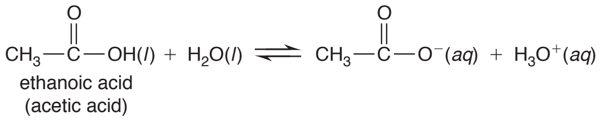


Octadecanoic acid (stearic acid)
Found in animal fats; used in
making candles and soaps

Figure 15.20 **Some molecules with the carboxylic acid functional group.**

Carboxylic Acids Carboxylic acids, $R{-}\overset{O}{\overset{\|}{C}}{-}OH$, are named by dropping the *-e* from the alkane name and adding *-oic acid;* however, many common names are used. For example, the four-C acid is butanoic acid (the carboxyl C is counted when choosing the root); its common name is butyric acid. Figure 15.20 shows some important carboxylic acids. The carboxyl C already has three bonds, so it forms only one other. In formic acid (methanoic acid), the carboxyl C bonds to an H, but in all other carboxylic acids it bonds to a chain or ring.

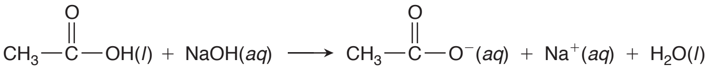
Carboxylic acids are weak acids in water:



$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH(l) + H_2O(l) \rightleftharpoons CH_3{-}\overset{O}{\overset{\|}{C}}{-}O^-(aq) + H_3O^+(aq)$$

ethanoic acid
(acetic acid)

At equilibrium in acid solutions of typical concentration, more than 99% of the acid molecules are undissociated at any given moment. In strong base, however, they react completely to form a salt and water:

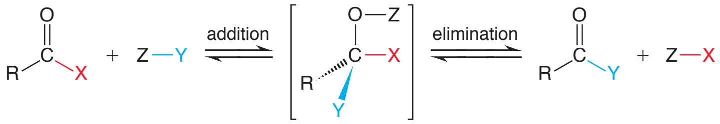


$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH(l) + NaOH(aq) \longrightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}O^-(aq) + Na^+(aq) + H_2O(l)$$

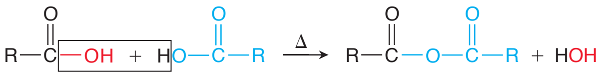
The anion is the *carboxylate ion,* named by dropping *-oic acid* and adding *-oate;* the sodium salt of butanoic acid, for instance, is sodium butanoate.

Carboxylic acids with long hydrocarbon chains are **fatty acids,** an essential group of compounds found in all cells. Animal fatty acids have saturated chains, whereas many from vegetable sources are unsaturated, usually with the C=C bonds in the *cis* configuration. The double bond makes them much easier to metabolize. Nearly all fatty acid skeletons have an even number of C atoms—16 and 18 carbons are very common—because cells use two-carbon units in synthesizing them. Fatty acid salts are soaps, with the cation usually from Group 1A(1) or 2A(2) (Section 13.2).

Substitution of carboxylic acids and other members of this family occurs through a two-step sequence: *addition plus elimination equals substitution.* Addition to the trigonal planar shape of the carbonyl group gives an unstable tetrahedral intermediate, which immediately undergoes elimination to revert to a trigonal planar product (in this case, X is OH):



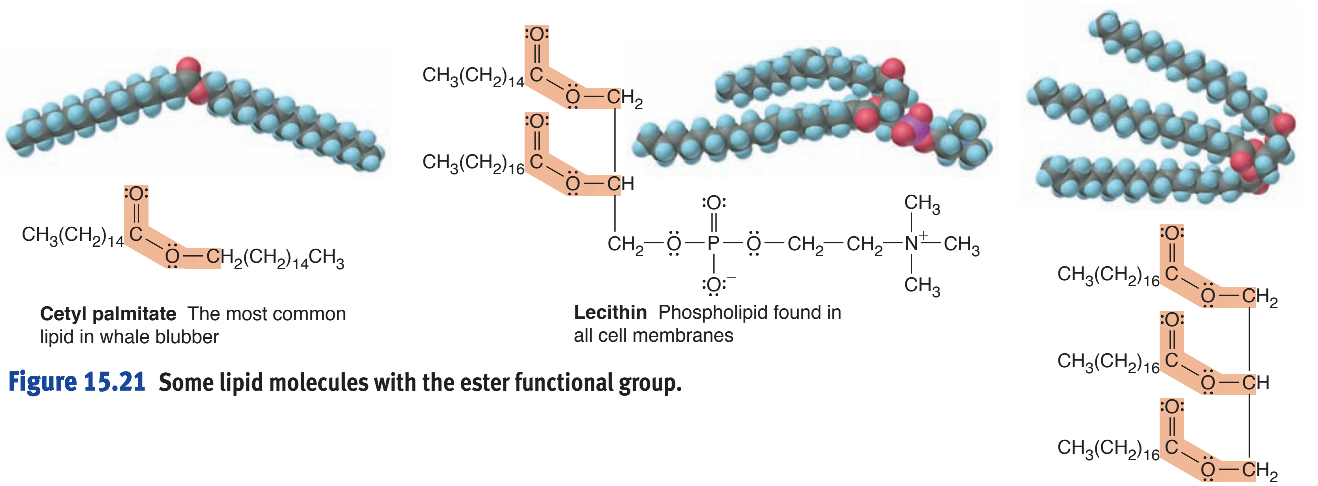
Strong heating of carboxylic acids forms an **acid anhydride** through a type of substitution called a *dehydration-condensation reaction* (Section 14.7), in which two molecules condense into one with loss of water:



$$R{-}\overset{O}{\overset{\|}{C}}\boxed{{-}OH + H}O{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow{\Delta} R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R + HOH$$

Esters *An alcohol and a carboxylic acid form an ester.* The first part of an ester name designates the alcohol portion and the second the acid portion (named in the same way as the carboxylate ion). For example, the ester formed between ethanol and ethanoic acid is ethyl ethanoate (common name, ethyl acetate), a solvent for nail polish and model glue.

The ester group occurs commonly in **lipids,** a large group of fatty biological substances. Most dietary fats are *triglycerides,* esters composed of three fatty acids linked to the alcohol 1,2,3-trihydroxypropane (common name, glycerol) that


Cetyl palmitate The most common lipid in whale blubber

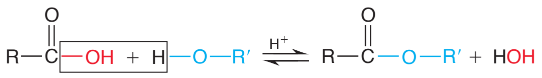
Lecithin Phospholipid found in all cell membranes

Tristearin Typical dietary fat used as an energy store in animals

Figure 15.21 **Some lipid molecules with the ester functional group.**

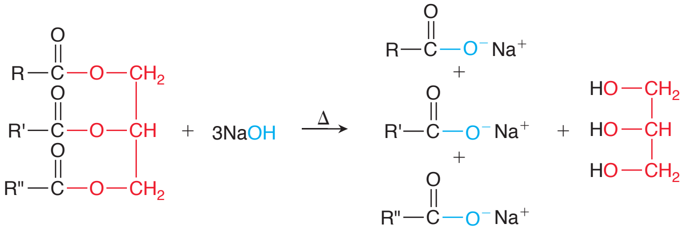
function as energy stores. Some important lipids are shown in Figure 15.21; lecithin is one of several phospholipids that make up the lipid bilayer in all cell membranes (Section 13.2).

Esters, like acid anhydrides, form through a dehydration-condensation reaction; in this case, it is called an *esterification*:

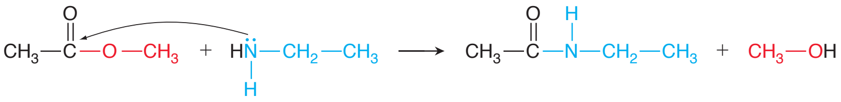

$$R-\overset{O}{\overset{\|}{C}}\boxed{-OH + H}-O-R' \xrightleftharpoons{H^+} R-\overset{O}{\overset{\|}{C}}-O-R' + HOH$$

In Chapter 16, we will discuss the role of H^+ in increasing the rate of this multistep reaction. ●

Note that the esterification reaction is reversible. The opposite of dehydration-condensation is called **hydrolysis,** in which the O atom of water is attracted to the partially positive C atom of the ester, cleaving (lysing) the molecule into two parts. One part receives water's —OH, and the other part receives water's other H. In the process of soap manufacture, or *saponification* (Latin *sapon,* "soap"), begun in ancient times, ester bonds in animal or vegetable fats are hydrolyzed with strong base:


a triglyceride 3 soaps glycerol

Amides The product of a substitution between an amine (or NH_3) and an ester is an amide. The partially negative N of the amine is attracted to the partially positive C of the ester, an alcohol (ROH) is lost, and an amide forms:


$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 + H\underset{H}{\underset{|}{\ddot{N}}}-CH_2-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-CH_2-CH_3 + CH_3-OH$$

methyl ethanoate (methyl acetate)

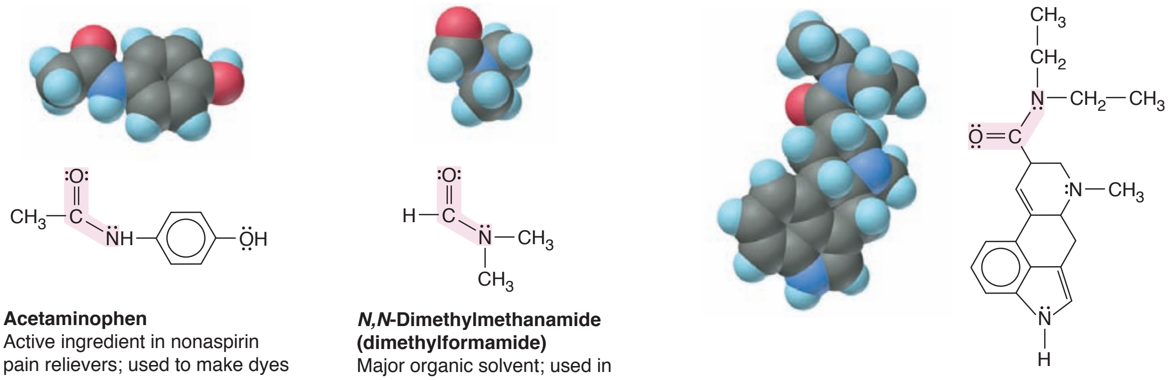
ethanamine (ethylamine)

N-ethylethanamide (*N*-ethylacetamide)

methanol

Amides are named by denoting the amine portion with *N*- and replacing *-oic acid* from the parent carboxylic acid with *-amide*. In the amide from the previous


● **A Pungent, Pleasant Banquet** Many organic compounds have strong odors, but none can rival the diverse odors of carboxylic acids and esters. From the pungent, vinegary odors of the one-C and two-C acids to the cheesy stench of slightly larger ones, carboxylic acids possess some awful odors. When butanoic acid reacts with ethanol, however, its rancid-butter smell becomes the peachy pineapple scent of ethyl butanoate, and when pentanoic acid reacts with pentanol, its Limburger cheese odor becomes the fresh apple aroma of pentyl pentanoate. Naturally occurring and synthetic esters are used to add fruity, floral, and herbal odors to foods, cosmetics, household deodorizers, and medicines.



Acetaminophen
Active ingredient in nonaspirin pain relievers; used to make dyes and photographic chemicals

***N,N*-Dimethylmethanamide (dimethylformamide)**
Major organic solvent; used in production of synthetic fibers

Lysergic acid diethylamide (LSD-25) A potent hallucinogen

Figure 15.22 Some molecules with the amide functional group.

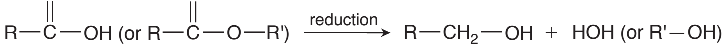
reaction, the ethyl group comes from the amine, and the acid portion comes from ethanoic acid (acetic acid). Some amides are shown in Figure 15.22.

Amides are hydrolyzed in hot water (or base) to a carboxylic acid and an amine. Thus, even though amides are not normally formed in the following way, they can be viewed as the result of a reversible dehydration-condensation:

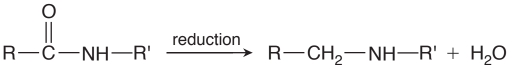
$$R-\overset{O}{\overset{\parallel}{C}}\boxed{-OH + H}-\overset{H}{\overset{|}{N}}-R' \rightleftharpoons R-\overset{O}{\overset{\parallel}{C}}-\overset{H}{\overset{|}{N}}-R' + HOH$$

The most important example of the amide group is the *peptide bond* (discussed in Sections 13.2 and 15.6), which links amino acids in a protein.

The carboxylic acid family also undergoes reduction to form other functional groups. For example, certain inorganic reducing agents convert acids or esters to alcohols and convert amides to amines:



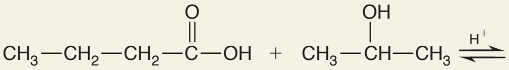
$$R-\overset{O}{\overset{\parallel}{C}}-OH \text{ (or } R-\overset{O}{\overset{\parallel}{C}}-O-R'\text{)} \xrightarrow{\text{reduction}} R-CH_2-OH + HOH \text{ (or } R'-OH\text{)}$$



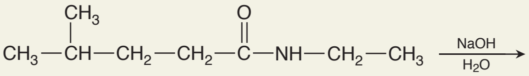
$$R-\overset{O}{\overset{\parallel}{C}}-NH-R' \xrightarrow{\text{reduction}} R-CH_2-NH-R' + H_2O$$

SAMPLE PROBLEM 15.6 Predicting Reactions of the Carboxylic Acid Family

PROBLEM Predict the product(s) of the following reactions:

(a)


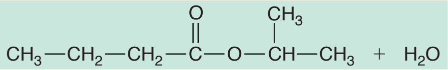
$$CH_3-CH_2-CH_2-\overset{O}{\overset{\parallel}{C}}-OH + CH_3-\overset{OH}{\overset{|}{CH}}-CH_3 \overset{H^+}{\rightleftharpoons}$$

(b)


$$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overset{O}{\overset{\parallel}{C}}-NH-CH_2-CH_3 \xrightarrow[H_2O]{NaOH}$$

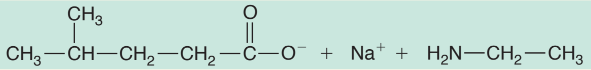
PLAN We discussed substitution reactions (including addition-elimination and dehydration-condensation) and hydrolysis. **(a)** A carboxylic acid and an alcohol react, so the reaction must be a substitution to form an ester and water. **(b)** An amide reacts with OH^-, so it is hydrolyzed to an amine and a sodium carboxylate.

SOLUTION **(a)** Formation of an ester:



$$CH_3-CH_2-CH_2-\overset{O}{\overset{\parallel}{C}}-O-\overset{CH_3}{\overset{|}{CH}}-CH_3 + H_2O$$

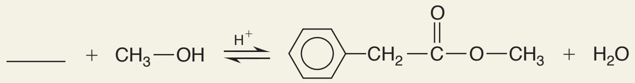
(b) Basic hydrolysis of an amide:

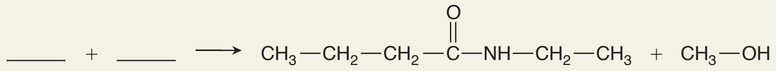


$$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overset{O}{\overset{\parallel}{C}}-O^- + Na^+ + H_2N-CH_2-CH_3$$

CHECK Note that in part (b), the carboxylate ion forms, rather than the acid, because the aqueous NaOH that is present reacts with the carboxylic acid.

FOLLOW-UP PROBLEM 15.6 Fill in the blanks in the following reactions:

(a)


(b)


$$\_\_\_\_ + \_\_\_\_ \longrightarrow CH_3{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_2{-}CH_3 + CH_3{-}OH$$

Variations on a Theme: Oxoacids, Esters, and Amides of Other Nonmetals

A nonmetal that is both double and single bonded to O occurs in most inorganic oxoacids, such as phosphoric, sulfuric, and chlorous acids. Those with additional O atoms are stronger acids than carboxylic acids.

Diphosphoric and disulfuric acids are acid anhydrides formed by dehydration-condensation reactions, just as a carboxylic acid anhydride is formed (Figure 15.23). Inorganic oxoacids form esters and amides that are part of many biological molecules. We already saw that certain lipids are phosphate esters (see Figure 15.21). The first compound formed when glucose is digested is a phosphate ester (Figure 15.24A); a similar phosphate ester is a major structural feature of nucleic acids, as we'll see shortly. Amides of organic sulfur-containing oxoacids, called *sulfonamides*, are potent antibiotics; the simplest of these is depicted in Figure 15.24B. More than 10,000 different sulfonamides have been synthesized.

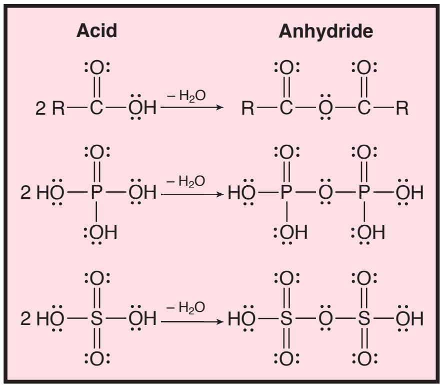
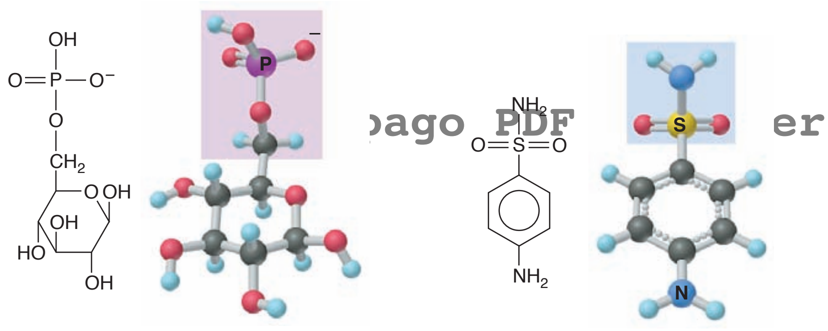


Figure 15.23 The formation of carboxylic, phosphoric, and sulfuric acid anhydrides.



A Glucose-6-phosphate **B Sulfanilamide**

Figure 15.24 An ester and an amide with another nonmetal. A, Glucose-6-phosphate contains a phosphate ester group. **B,** Sulfanilamide contains a sulfonamide group.

Functional Groups with Triple Bonds

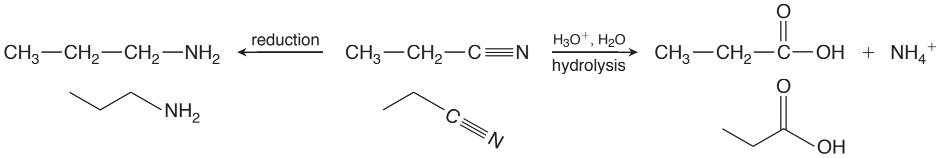
There are only two important functional groups with triple bonds. *Alkynes,* with an electron-rich —C≡C— group, undergo addition (by H_2O, H_2, HX, X_2, and so forth) to form double-bonded or saturated compounds:

$$\underset{\text{propyne}}{CH_3{-}C{\equiv}CH} \xrightarrow{H_2} \underset{\text{propene}}{CH_3{-}CH{=}CH_2} \xrightarrow{H_2} \underset{\text{propane}}{CH_3{-}CH_2{-}CH_3}$$

Nitriles (R—C≡N) contain the **nitrile** group (—C≡N:) and are made by substituting a CN^- (cyanide) ion for X^- in a reaction with an alkyl halide:

$$CH_3{-}CH_2{-}Cl + NaCN \longrightarrow CH_3{-}CH_2{-}C{\equiv}N + NaCl$$

This reaction is useful because it *increases the hydrocarbon chain by one C atom.* Nitriles are versatile because once they are formed, they can be reduced to amines or hydrolyzed to carboxylic acids:



$$CH_3{-}CH_2{-}CH_2{-}NH_2 \xleftarrow{\text{reduction}} CH_3{-}CH_2{-}C{\equiv}N \xrightarrow[\text{hydrolysis}]{H_3O^+,\ H_2O} CH_3{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}OH + NH_4^+$$

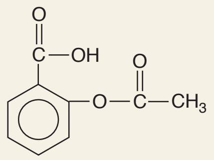
Variations on a Theme: Inorganic Compounds with Triple Bonds Triple bonds are as scarce in the inorganic world as in the organic world. Carbon monoxide (:C≡O:), elemental nitrogen (:N≡N:), and the cyanide ion ($[:C{\equiv}N:]^-$) are the only common examples.

You've seen quite a few functional groups by this time, and it is especially important that you can recognize them in a complex organic molecule. Sample Problem 15.7 provides some practice.

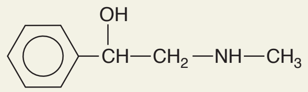
SAMPLE PROBLEM 15.7 Recognizing Functional Groups

PROBLEM Circle and name the functional groups in the following molecules:

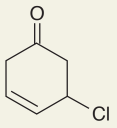
(a)



(b)



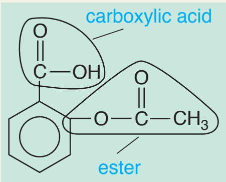
(c)



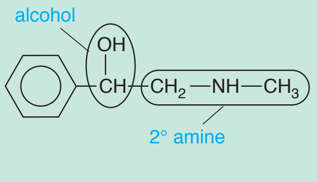
PLAN We use Table 15.5 (p. 651) to identify the various functional groups.

SOLUTION

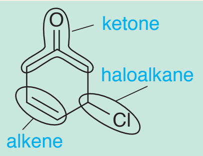
(a)



(b)

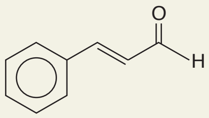


(c)

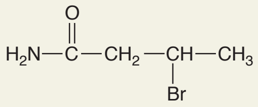


FOLLOW-UP PROBLEM 15.7 Circle and name the functional groups:

(a)



(b)



$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3$$

Section Summary

Organic reactions are initiated when regions of high and low electron density of different reactant molecules attract each other. • Groups containing only single bonds—alcohols, amines, and alkyl halides—take part in substitution and elimination reactions. • Groups with double or triple bonds—alkenes, aldehydes, ketones, alkynes, and nitriles—generally take part in addition reactions. • Aromatic compounds typically undergo substitution, rather than addition, because delocalization of the π electrons stabilizes the ring. • Groups with both double and single bonds—carboxylic acids, esters, and amides—generally take part in substitution reactions. • Many reactions change one functional group to another, but some, especially reactions with organometallic compounds and with the cyanide ion, change the C skeleton.

15.5 THE MONOMER-POLYMER THEME I: SYNTHETIC MACROMOLECULES

In our survey of advanced materials in Chapter 12, you saw that polymers are extremely large molecules that consist of many monomeric repeat units. In that chapter, we focused on the mass, shape, and physical properties of polymers. Now we'll see how polymers are named and discuss the two types of reactions that link monomers covalently into a chain. To name a polymer, just add the prefix *poly-* to the monomer name, as in *polyethylene* or *polystyrene*. When the monomer has a two-word name, parentheses are used, as in *poly(vinyl chloride)*.

Because synthetic polymers consist of petroleum-based monomers, a major shortage of raw materials for their manufacture is expected in the coming decades.

To avoid this and create renewable materials, green chemists are devising polymers based on corn, sugarcane, and even cashew-nut shells. Before such a method is embraced as a “green” technology, however, the total impact of growing, transporting, and manufacturing must be assessed.

The two major types of reaction processes that form synthetic polymers lend their names to the resulting classes of polymer—addition and condensation.

Addition Polymers

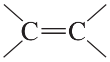
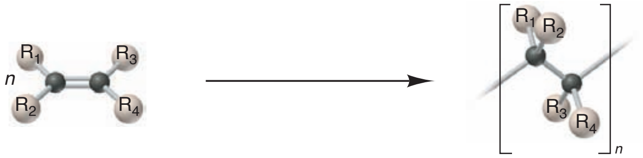
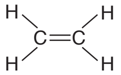
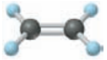
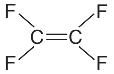
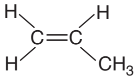
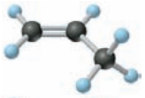
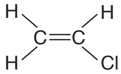
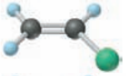
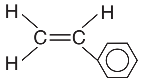
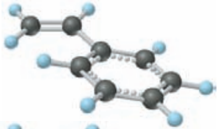
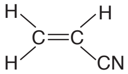
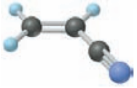
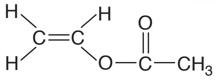
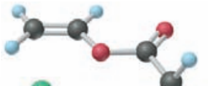
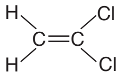
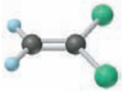
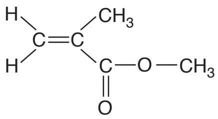
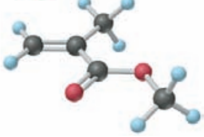
Addition polymers form when monomers undergo an addition reaction with one another. These are also called *chain-reaction* (or *chain-growth) polymers* because as each monomer adds to the chain, it forms a new reactive site to continue the process. The monomers of most addition polymers have the  grouping. As you can see from Table 15.6, the essential differences between an acrylic sweater, a plastic grocery bag, and a bowling ball are due to the different chemical groups that are attached to the double-bonded C atoms of the monomer.

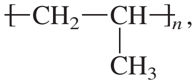
Table 15.6 Some Major Addition Polymers



Monomer		Polymer	Applications
		polyethylene	Plastic bags; bottles; toys
		polytetrafluoroethylene	Cooking utensils (e.g., Teflon)
		polypropylene	Carpeting (indoor-outdoor); bottles
		poly(vinyl chloride)	Plastic wrap; garden hose; indoor plumbing
		polystyrene	Insulation; furniture; packing materials
		polyacrylonitrile	Yarns, fabrics, and wigs (e.g., Orlon, Acrilan)
		poly(vinyl acetate)	Adhesives; paints; textile coatings; computer disks
		poly(vinylidene chloride)	Food wrap (e.g., Saran)
		poly(methyl methacrylate)	Glass substitute (e.g., Lucite, Plexiglas); bowling balls; paint

The *free-radical polymerization* of ethene (ethylene, $CH_2{=}CH_2$) to polyethylene is a simple example of the addition process. In Figure 15.25, the monomer reacts to form a *free radical,* a species with an unpaired electron, that seeks an electron from another monomer to form a covalent bond. The process begins when an *initiator,* usually a peroxide, generates a free radical that attacks the π bond of an ethylene unit, forming a σ bond with one of the p electrons and leaving the other unpaired. This new free radical then attacks the π bond of another ethylene, joining it to the chain end, and the backbone of the polymer grows. As each ethylene adds, it leaves an unpaired electron on the growing end to find an electron "mate" and make the chain one repeat unit longer. This process stops when two free radicals form a covalent bond or when a very stable free radical is formed by addition of an *inhibitor* molecule. Recent progress in controlling the high reactivity of free-radical species promises an even wider range of polymers. In a similar method, polymerization is initiated by the formation of a cation (or anion) instead of a free radical. The cationic (or anionic) reactive end of the chain attacks the π bond of another monomer to form a new cationic (or anionic) end, and the process continues.

The most important polymerization reactions take place under relatively mild conditions through the use of catalysts that incorporate transition metals. In 1963, Karl Ziegler and Giulio Natta received the Nobel Prize in chemistry for developing *Ziegler-Natta catalysts,* which employ an organoaluminum compound, such as $Al(C_2H_5)_3$, and the tetrachloride of titanium or vanadium. Today, chemists use organometallic catalysts that are *stereoselective* to create polymers whose repeat units have groups spatially oriented in particular ways. Through the use of these catalysts, polyethylene chains with molar masses of 10^4 to 10^5 g/mol are made by varying conditions and reagents.

Similar methods are used to make polypropylenes,  $\left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}\right]_n$, that have all the CH_3 groups of the repeat units oriented either on one side of the chain or on alternating sides. The different orientations lead to different packing efficiencies of the chains and, thus, different degrees of crystallinity, which lead to differences in such physical properties as density, rigidity, and elasticity (Section 12.7).

Condensation Polymers

The monomers of **condensation polymers** must have *two functional groups;* we can designate such a monomer as A—**R**—B (where **R** is the rest of the molecule). Most commonly, the monomers link when an A group on one undergoes a *dehydration-condensation reaction* with a B group on another:

$$\tfrac{1}{2}n\mathrm{H}\text{—}\mathrm{A}\text{—}\mathbf{R}\text{—}\mathrm{B}\text{—}\mathrm{OH} + \tfrac{1}{2}n\mathrm{H}\text{—}\mathrm{A}\text{—}\mathbf{R}\text{—}\mathrm{B}\text{—}\mathrm{OH} \xrightarrow{-(n-1)\mathrm{HOH}} \mathrm{H}\left[\mathrm{A}\text{—}\mathbf{R}\text{—}\mathrm{B}\right]_n\mathrm{OH}$$

Many condensation polymers are *copolymers,* those consisting of two or more different repeat units (Section 12.7). For example, condensation of carboxylic acid and amine monomers forms *polyamides (nylons),* whereas carboxylic acid and alcohol monomers form *polyesters.*

One of the most common polyamides is *nylon-66* (see the Gallery, p. 74), manufactured by mixing equimolar amounts of a six-C diamine (1,6-diaminohexane)

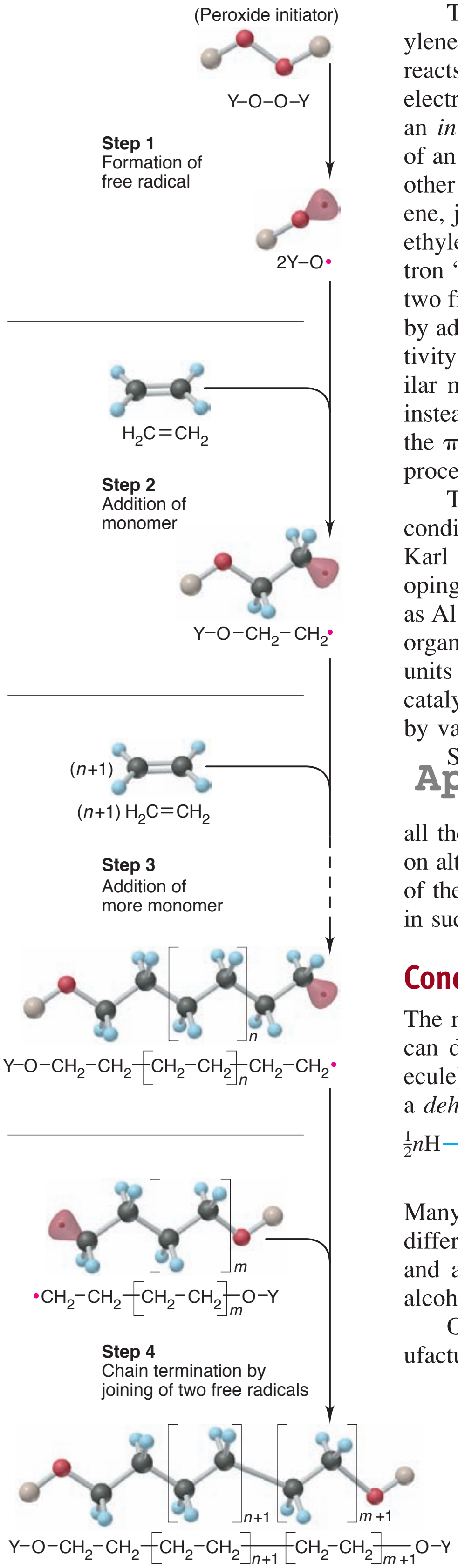
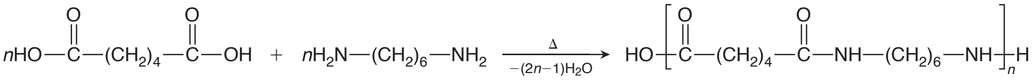


Figure 15.25 Steps in the free-radical polymerization of ethylene. In this polymerization method, free radicals initiate, propagate, and terminate the formation of an addition polymer. An initiator (Y—O—O—Y) is split to form two molecules of a free radical (Y—O·). The free radical attacks the π bond of a monomer and creates another free radical (Y—O—CH_2—CH_2·). The process continues, and the chain grows (propagates) until the system runs out of monomer and two free radicals combine.

and a six-C diacid (1,6-hexanedioic acid). The basic amine reacts with the acid to form a "nylon salt." Heating drives off water and forms the amide bonds:



$$n\mathrm{HO{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}OH} + n\mathrm{H_2N{-}(CH_2)_6{-}NH_2} \xrightarrow[-(2n-1)\mathrm{H_2O}]{\Delta} \mathrm{HO}\left[\mathrm{\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}NH{-}(CH_2)_6{-}NH}\right]_n\mathrm{H}$$

In the laboratory, this nylon is made without heating by using a more reactive acid component (Figure 15.26). Covalent bonds within the chains give nylons great strength, and H bonds between chains give them great flexibility. About half of all nylons are made to reinforce automobile tires; the others are used for rugs, clothing, fishing line, and so forth.

Dacron, a popular polyester fiber, is woven from polymer strands formed when equimolar amounts of 1,4-benzenedicarboxylic acid and 1,2-ethanediol react. Blending these polyester fibers with various amounts of cotton gives fabrics that are durable, easily dyed, and crease resistant. Extremely thin Mylar films, used for recording tape and food packaging, are also made from this polymer.

Variations on a Theme: Inorganic Polymers You already know that some synthetic polymers have inorganic backbones. In Chapter 14, we discussed the silicones, polymers with the repeat unit —$(R_2)Si$—O—. Depending on the chain crosslinks and the R groups, silicones range from oily liquids to elastic sheets to rigid solids and have applications that include artificial limbs and spacesuits. We also mentioned the polyphosphazenes in Chapter 14, which exist as flexible chains even at low temperatures and have the repeat unit —$(R_2)P{=}N$—.

Figure 15.26 The formation of nylon-66. Nylons are formed industrially by the reaction of diamine and diacid monomers. In this laboratory demonstration, the six-C diacid chloride, which is more reactive than the diacid, is used as one monomer; the polyamide forms between the two liquid phases.

Section Summary

Polymers are extremely large molecules that are made of repeat units called monomers. • Addition polymers are formed from unsaturated monomers that commonly link through free-radical reactions. • Most condensation polymers are formed by linking two types of monomer through a dehydration-condensation reaction. • Reaction conditions, catalysts, and monomers can be varied to produce polymers with different properties.

15.6 THE MONOMER-POLYMER THEME II: BIOLOGICAL MACROMOLECULES

The monomer-polymer theme was being played out in nature eons before humans employed it to such great advantage. Biological macromolecules are nothing more than condensation polymers created by nature's reaction chemistry and improved through evolution. These remarkable molecules are the greatest proof of the versatility of carbon and its handful of atomic partners.

Natural polymers are the "stuff of life"—polysaccharides, proteins, and nucleic acids. Some have structures that make wood strong, hair curly, fingernails hard, and wool flexible. Others speed up the myriad reactions that occur in every cell or defend the body against infection. Still others possess the genetic information organisms need to forge other biomolecules. Remarkable as these giant molecules are, the functional groups of their monomers and the reactions that link them are identical to those of other, smaller organic molecules. Moreover, as you saw in Section 13.2, the same intermolecular forces that dissolve smaller molecules stabilize these giant molecules in the aqueous medium of the cell.

Sugars and Polysaccharides

In essence, the same chemical change occurs when you burn a piece of wood or eat a piece of bread. Wood and bread are mixtures of *carbohydrates*, substances that provide energy through oxidation.

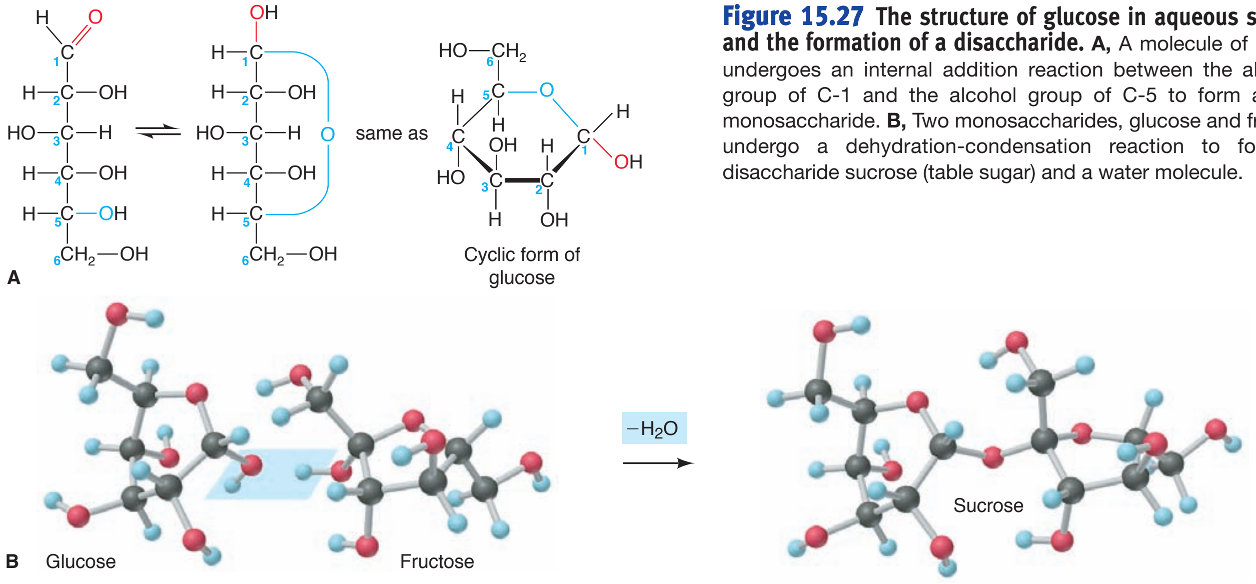


Figure 15.27 The structure of glucose in aqueous solution and the formation of a disaccharide. A, A molecule of glucose undergoes an internal addition reaction between the aldehyde group of C-1 and the alcohol group of C-5 to form a cyclic monosaccharide. **B,** Two monosaccharides, glucose and fructose, undergo a dehydration-condensation reaction to form the disaccharide sucrose (table sugar) and a water molecule.

Monomer Structure and Linkage Glucose and other simple sugars, from the three-C *trioses* to the seven-C *heptoses,* are called **monosaccharides** and consist of carbon chains with attached hydroxyl and carbonyl groups. In addition to their roles as individual molecules engaged in energy metabolism, they serve as the monomer units of **polysaccharides.** Most natural polysaccharides are formed from five- and six-C units. In aqueous solution, *an alcohol group and the aldehyde (or ketone) group of a given monosaccharide react with each other to form a cyclic molecule with either a five- or six-membered ring* (Figure 15.27A).

When two monosaccharides undergo a dehydration-condensation reaction, a **disaccharide** forms. For example, sucrose (table sugar) is a disaccharide of glucose (linked at C-1) and fructose (linked at C-2) (Figure 15.27B); lactose (milk sugar) is a disaccharide of glucose (C-1) and galactose (C-4); and maltose, used in brewing and as a sweetener, is a disaccharide of two glucose units (C-1 to C-4).

Types of Polysaccharides A polysaccharide consists of *many* monosaccharide units linked together. The three major natural polysaccharides—cellulose, starch, and glycogen—consist entirely of glucose units, but they differ in the ring positions of the links, in the orientation of certain bonds, and in the extent of crosslinking. Some other polysaccharides contain nitrogen in their attached groups. ●

● **Polysaccharide Skeletons of Lobsters and Roaches** The variety of polysaccharide properties that arises from simple changes in the monomers is amazing. For example, substituting an —NH_2 group for the —OH group at C-2 in glucose produces *glucosamine.* The amide that is formed from glucosamine and acetic acid (*N*-acetylglucosamine) is the monomer of *chitin* (pronounced "KY-tin"), a polysaccharide that is the main component of the tough, brittle, external skeletons of insects and crustaceans.

Cellulose is the most abundant organic chemical on Earth. More than 50% of the carbon in plants occurs in the cellulose of stems and leaves; wood is largely cellulose, and cotton is more than 90% cellulose (see Section 13.2). Cellulose consists of long chains of glucose. The great strength of wood is due largely to the H bonds between cellulose chains. The monomers are linked in a particular way from C-1 in one unit to C-4 in the next. Humans lack the enzymes to break this link, so we cannot digest cellulose (unfortunately!); however, microorganisms in the digestive tracts of some animals, such as cows, sheep, and termites, can.

Starch is a mixture of polysaccharides of glucose and serves as an *energy store* in plants. When a plant needs energy, some starch is broken down by hydrolysis of the bonds between units, and the released glucose is oxidized through a multistep metabolic pathway. Starch occurs in plant cells as insoluble granules of amylose, a helical molecule of several thousand glucose units, and amylopectin, a highly branched, bushlike molecule of up to a million glucose units. Most of the glucose units are linked by C-1 to C-4 bonds, as in cellulose, but a different orientation around the chiral C-1 allows our digestive enzymes to break starch down into monomers. A C-6 to C-1 crosslink joins chains every 24 to 30 units.

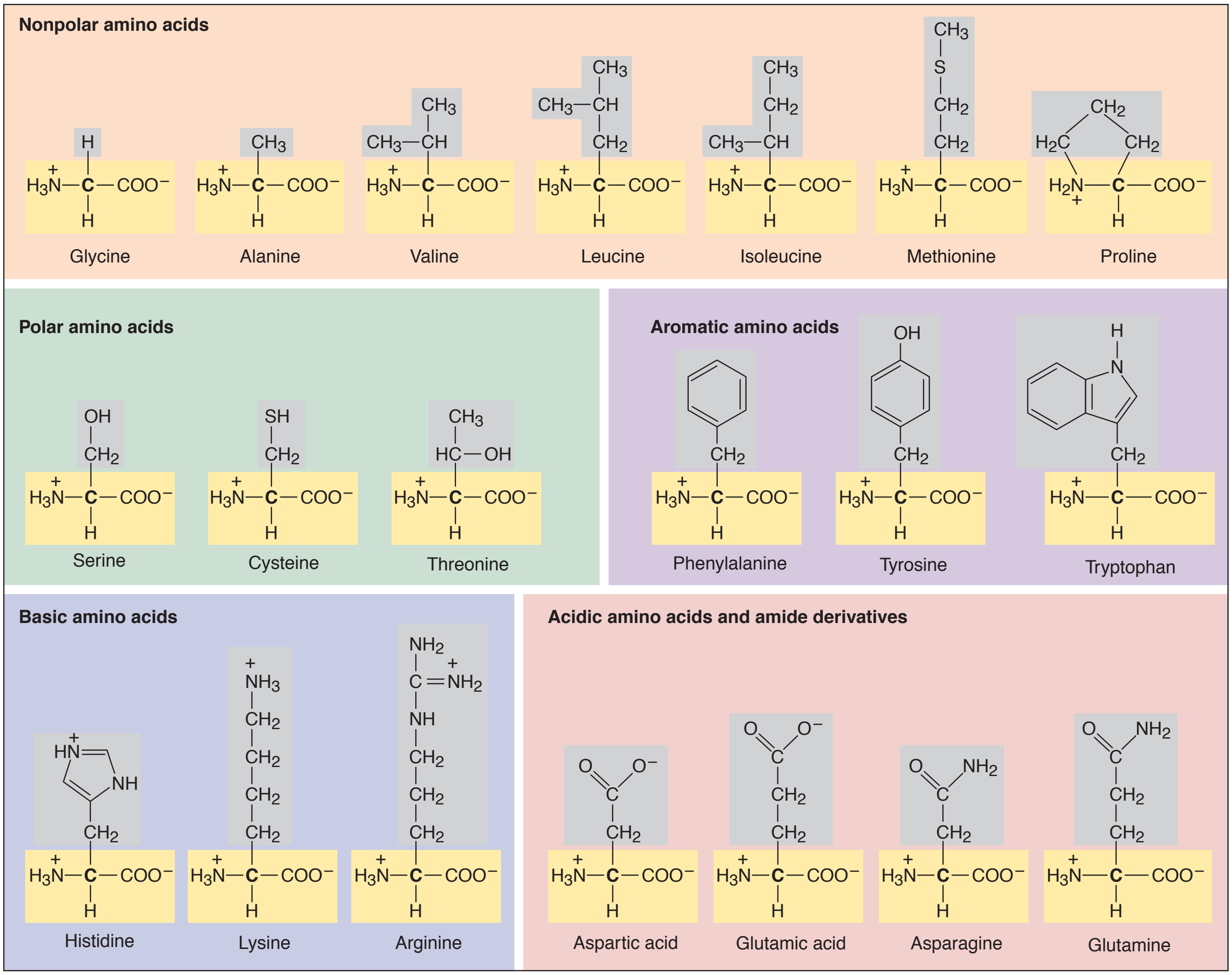
Glycogen functions as the energy storage molecule in animals. It occurs in liver and muscle cells as large, insoluble granules consisting of glycogen molecules made from 1000 to more than 500,000 glucose units. In glycogen, the units are also linked by C-1 to C-4 bonds, but the molecule is more highly crosslinked than starch, with C-6 to C-1 crosslinks every 8 to 12 units.

Amino Acids and Proteins

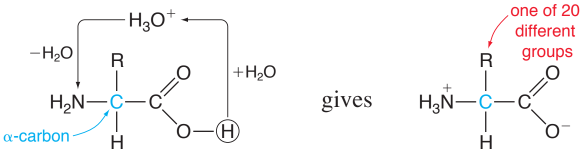
As you saw in Section 15.5, synthetic polyamides (such as nylon-66) are formed from two monomers, one with a carboxyl group at each end and the other with an amine group at each end. **Proteins,** the polyamides of nature, are unbranched polymers formed from monomers called **amino acids.** As we discussed in Section 13.2, *each amino acid has a carboxyl group and an amine group*.

Monomer Structure and Linkage An amino acid has both its carboxyl group and its amine group attached to the α*-carbon,* the second C atom in the chain. Proteins are made up of about 20 different types of amino acids, each with its own particular R group, ranging from an H atom to a polycyclic N-containing aromatic structure (Figure 15.28).

Figure 15.28 The common amino acids. About 20 different amino acids occur in proteins. The R groups are screened gray, and the α-carbons (*boldface*), with carboxyl and amino groups, are screened yellow. Here the amino acids are shown with the charges they have under physiological conditions. They are grouped by polarity, acid-base character, and presence of an aromatic ring. The R groups play a major role in the shape and function of the protein.



In the aqueous cell fluid, the NH_2 and COOH groups of amino acids are charged because the carboxyl group transfers an H^+ ion to H_2O to form H_3O^+, which transfers the H^+ to the amine group. The overall process is, in effect, an intramolecular acid-base reaction:



An H atom is the third group bonded to the α-carbon, and the fourth is the R group (also called the *side chain*).

Each amino acid is linked to the next through a *peptide (amide) bond* formed by a dehydration-condensation reaction in which the carboxyl group of one monomer reacts with the amine group of the next. Therefore, as noted in Section 13.2, the polypeptide chain—the backbone of the protein—has a repeating structure that consists of an *α-carbon bonded to an amide group bonded to the next α-carbon bonded to the next amide group,* and so forth (see Figure 13.6, p. 508). The various R groups dangle from the α-carbons on alternate sides of the chain.

The Hierarchy of Protein Structure *Each type of protein has its own amino acid composition,* a specific number and proportion of various amino acids. However, it is not the composition that defines the protein's role in the cell; rather, *the sequence of amino acids determines the protein's shape and function.* Proteins range from about 50 to several thousand amino acids, yet from a purely mathematical point of view, even a small protein of 100 amino acids has a virtually limitless number of possible sequences of the 20 types of amino acids ($20^{100} \approx 10^{130}$). In fact, though, only a tiny fraction of these possibilities occur in actual proteins. For example, even in an organism as complex as a human being, there are only about 10^5 different types of protein.

A protein folds into its *native shape* as it is being synthesized in the cell. Some shapes are simple—long rods or undulating sheets. Others are far more complex—baskets, Y shapes, spheroid blobs, and countless other globular forms. Biochemists define a hierarchy for the overall structure of a protein (Figure 15.29):

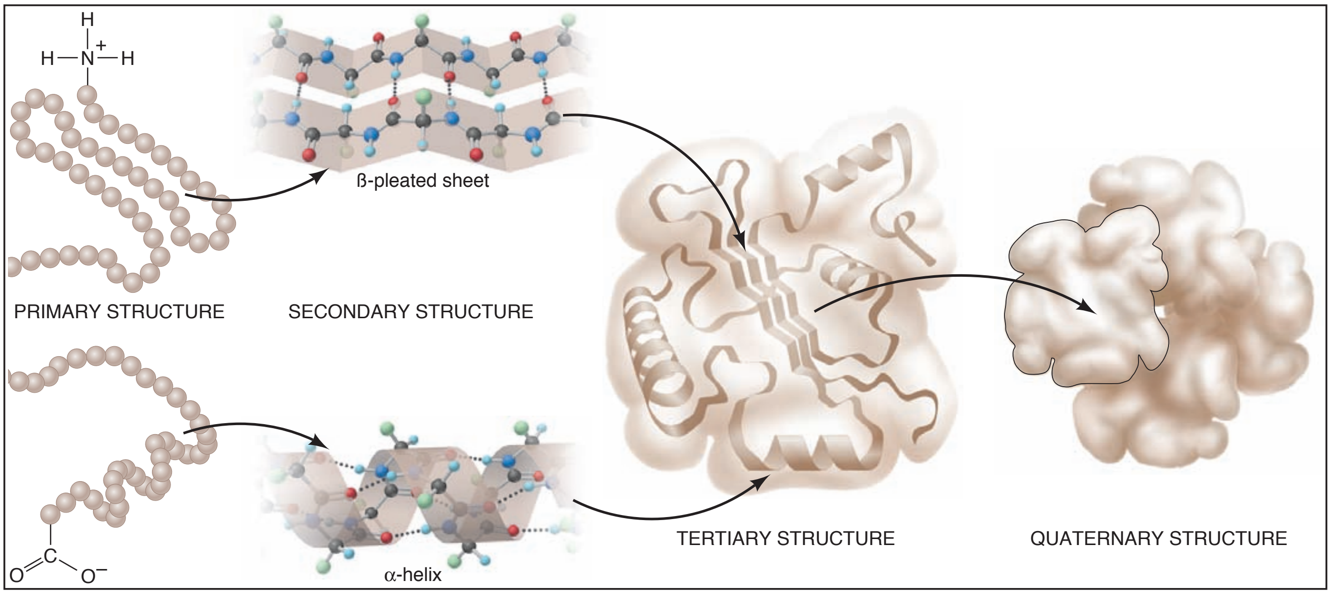


Figure 15.29 The structural hierarchy of proteins. A typical protein's structure can be viewed at different levels. Primary structure (shown as a long string of balls leaving and returning to the picture frame) is the sequence of amino acids. Secondary structure consists of highly ordered regions that occur as an α-helix or a β-sheet. Tertiary structure combines these regions with random coil sections. In many proteins, several tertiary units interact to give the quaternary structure.

1. *Primary (1°) structure*, the most basic level, refers to the sequence of covalently bonded amino acids in the polypeptide chain.
2. *Secondary (2°) structure* refers to sections of the chain that, as a result of H bonding between nearby peptide groupings, adopt shapes called α-helices and β-pleated sheets.
3. *Tertiary (3°) structure* refers to the three-dimensional folding of the whole polypeptide chain. In some proteins, certain folding patterns form characteristic regions that play a role in the protein's function—binding a hormone, attaching to a membrane, forming a polar channel, and so forth.
4. *Quaternary (4°) structure*, the most complex level, occurs in proteins made up of several polypeptide chains (subunits) and refers to the way the chains assemble into the overall protein.

Note that *only the 1° structure involves covalent bonds; the 2°, 3°, and 4° structures rely primarily on intermolecular forces*, as discussed in Section 13.2.

The Relation Between Structure and Function Two broad classes of proteins differ in the complexity of their amino acid compositions and sequences and, therefore, in their structure and function:

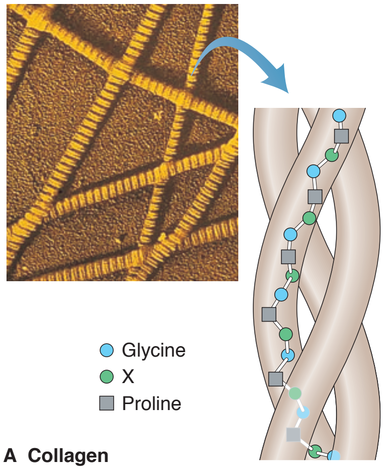
1. *Fibrous proteins* have relatively simple amino acid compositions and correspondingly simple structures. They are key components of hair, wool, skin, and connective tissue—materials that require strength and flexibility. Like synthetic polymers, these proteins have a small number of different amino acids in a repeating sequence. Consider collagen, the most common animal protein, which makes up as much as 40% of human body weight. More than 30% of its amino acids are glycine (G) and another 20% are proline (P). It exists as three chains, each an extended helix, that wind tightly around each other as the peptide C=O groups in one chain form H bonds to the peptide N—H groups in another. The result is a long, triple-helical cable with the sequence —G—X—P—G—X—P— and so on (where X is another amino acid), as shown in Figure 15.30A. As the main component of tendons, skin, and blood vessels, collagen has a high tensile strength; in fact, a 1-mm thick strand can support a 10-kg weight!

In silk fibroin, secreted by the silk moth caterpillar, more than 85% of the amino acids are glycine, alanine, and serine (Figure 15.30B). Fibroin chain segments bend back and forth, running alongside each other, and form interchain H bonds to create a *pleated sheet*. Stacks of sheets interact through dispersion forces, which make fibroin strong and flexible but not very extendable—perfect for a silkworm's cocoon.

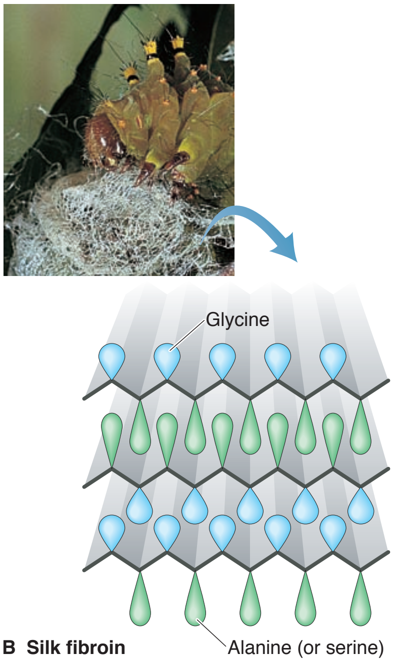
2. *Globular proteins* have much more complex compositions, often containing all 20 amino acids in varying proportions. As the name implies, globular proteins are typically more rounded and compact, with a wide variety of shapes and a correspondingly wide range of functions: defenders against bacterial invasion, messengers that trigger cell actions, catalysts of chemical change, membrane gatekeepers that maintain aqueous concentrations, and many others. The locations of particular amino-acid R groups are crucial to the protein's function. For example, in catalytic proteins, a few R groups form a crevice that closely matches the shapes of reactant molecules. These groups typically hold the reactants through intermolecular forces and speed their reaction to products by bringing them together and twisting and stretching their bonds. Experiment has shown repeatedly that a slight change in one of these critical R groups decreases function dramatically. This fact supports the essential idea that *the protein's amino acid sequence determines its structure, which in turn determines its function*:

SEQUENCE ⟹ STRUCTURE ⟹ FUNCTION

Next, we'll see how the amino acid sequence of every protein in every organism is prescribed by the genetic information that is held within the organism's nucleic acids.



A Collagen



B Silk fibroin

Figure 15.30 The shapes of fibrous proteins. Fibrous proteins have largely structural roles in an organism, and their amino acid sequence is relatively simple. **A,** The triple helix of a collagen molecule has a glycine as every third amino acid along the chain. **B,** The pleated sheet structure of silk fibroin has a repeating sequence of glycine alternating with either alanine or serine. The sheets interact through dispersion forces.

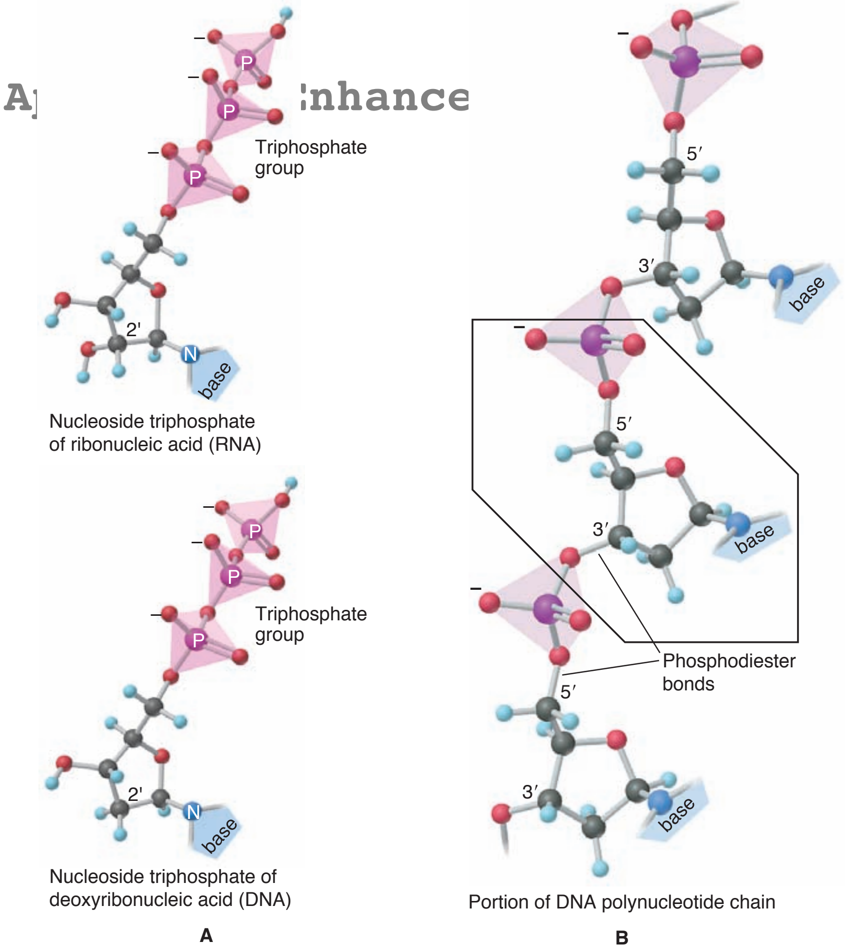
Nucleotides and Nucleic Acids

An organism's nucleic acids construct its proteins. And, given that the proteins determine how the organism looks and behaves, no job could be more essential.

Monomer Structure and Linkage **Nucleic acids** are unbranched polymers that consist of linked monomer units called **mononucleotides,** which consist of an N-containing base, a sugar, and a phosphate group. The two types of nucleic acid, ***r**ibo**n**ucleic **a**cid* (RNA) and ***d**eoxyribo**n**ucleic **a**cid* (DNA), differ in the sugar portions of their mononucleotides. RNA contains *ribose,* a five-C sugar, and DNA contains *deoxyribose,* in which —H substitutes for —OH on the 2′ position of ribose. (Carbon atoms in the sugar portion are given numbers with a prime to distinguish them from carbon atoms in the base.)

The cellular precursors that form a nucleic acid are *nucleoside triphosphates* (Figure 15.31A). Dehydration-condensation reactions between them release inorganic diphosphate ($H_2P_2O_7^{2-}$) and create *phosphodiester* bonds to form a polynucleotide chain. Therefore, the repeating pattern of the nucleic acid backbone is *—sugar—phosphate—sugar—phosphate—,* and so on (Figure 15.31B). Attached to each sugar is one of four N-containing bases, either a pyrimidine (six-membered ring) or a purine (six- and five-membered rings sharing a side). The pyrimidines are thymine (T) and cytosine (C); the purines are guanine (G) and adenine (A); in RNA, uracil (U) substitutes for thymine. The bases dangle off the sugar-phosphate chain, much as R groups dangle off the polypeptide chain of a protein.

Figure 15.31 Nucleic acid precursors and their linkage. A, In the cell, nucleic acids are constructed from nucleoside triphosphates, precursors of the mononucleotide units. Each one consists of an N-containing base (structure not shown), a sugar, and a triphosphate group. In RNA (*top*), the sugar is ribose; in DNA, it is 2′-deoxyribose (note the absence of an —OH group on C-2 of the ring). **B,** A tiny segment of the polynucleotide chain of DNA (with one, mononucleotide unit boxed) shows the phosphodiester bonds that link the 5′-OH group of one sugar to the 3′-OH group of the next and are formed through dehydration-condensation reactions (which also release diphosphate ion). The bases dangle off the chain.



Nucleoside triphosphate of ribonucleic acid (RNA)

Nucleoside triphosphate of deoxyribonucleic acid (DNA)

A

Portion of DNA polynucleotide chain

B

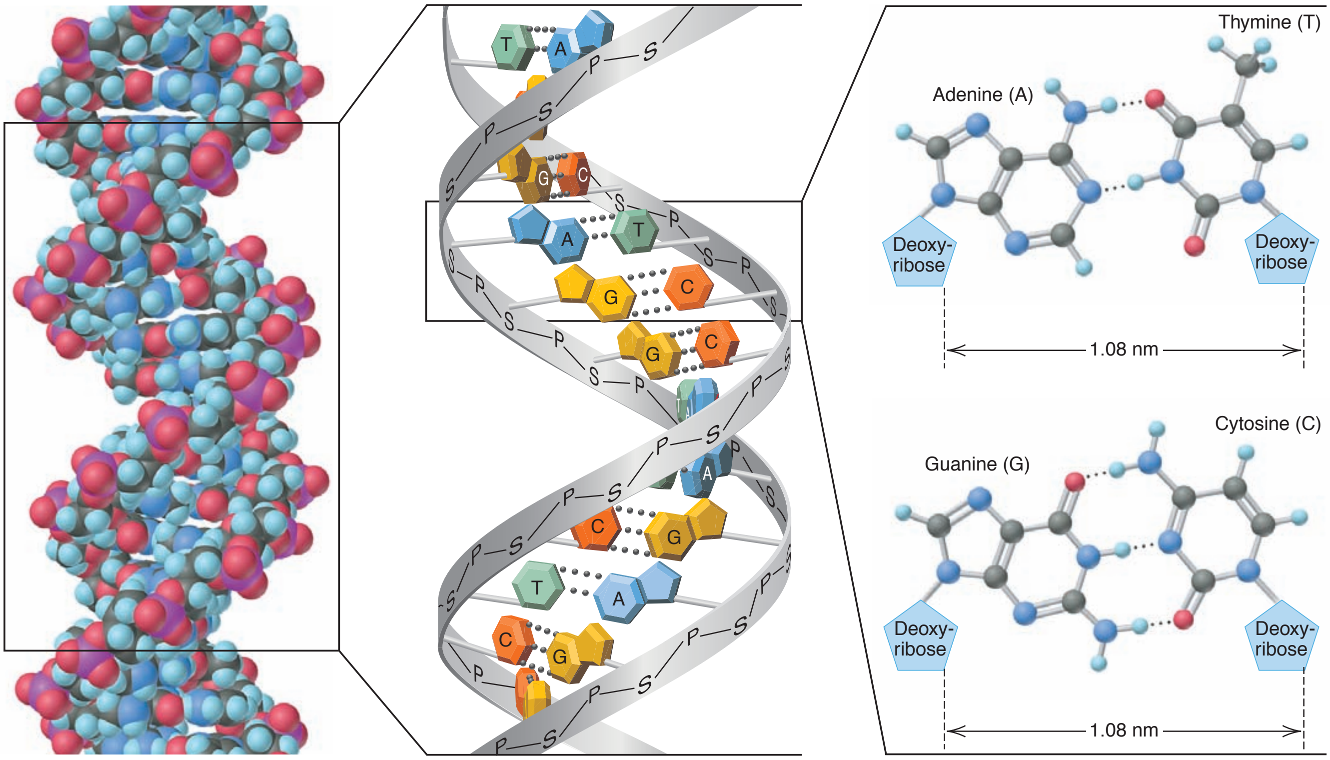


Figure 15.32 The double helix of DNA. A segment of DNA is shown as a space-filling model (*left*). The boxed area is expanded (*center*) to show how the polar sugar-phosphate (—S—P—) backbone faces the watery outside, and the nonpolar bases form H bonds to each other in the DNA core. The boxed area is expanded (*right*) to show how a pyrimidine and a purine always form H-bonded base pairs to maintain the double helix width. The members of the pairs are always the same: A pairs with T, and G pairs with C.

The Central Importance of Base Pairing In the nucleus of the cell, DNA exists as two chains wrapped around each other in a **double helix** (Figure 15.32). Each base in one chain "pairs" with a base in the other through H bonding. A double-helical DNA molecule may contain many millions of H-bonded bases in specified pairs. Two features of these **base pairs** are crucial to the structure and function of DNA:

- A pyrimidine and a purine are always paired, which gives the double helix a constant diameter.
- Each base is always paired with the same partner: A with T and G with C. Thus, *the base sequence on one chain is the complement of the sequence on the other.* For example, the sequence A—C—T on one chain is *always* paired with T—G—A on the other: A with T, C with G, and T with A.

Each DNA molecule is folded into a tangled mass that forms one of the cell's *chromosomes.* The DNA molecule is amazingly long and thin: if the largest human chromosome were stretched out, it would be 4 cm long; in the cell nucleus, however, it is wound into a structure only 5 nm long—8 million times shorter! Segments of the DNA chains are the *genes* that contain the chemical information for synthesizing the organism's proteins.

An Outline of Protein Synthesis *The information content of a gene resides in its base sequence.* In the **genetic code,** each base acts as a "letter," each three-base sequence as a "word," and *each word codes for a specific amino acid.* For example, the sequence C—A—C codes for the amino acid histidine, A—A—G codes for lysine, and so on. Through a complex series of interactions, greatly simplified

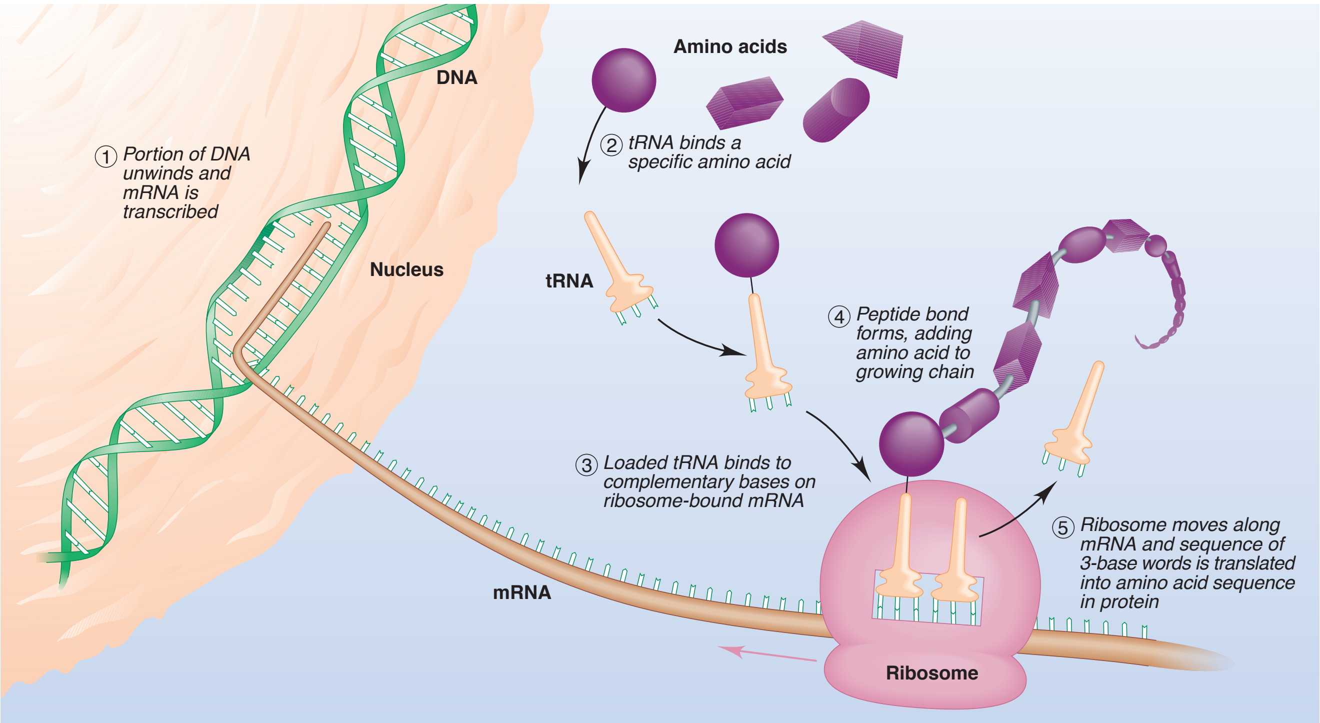


Figure 15.33 **Key stages in protein synthesis.**

in the overview in Figure 15.33, one amino acid at a time is positioned and linked to the next in the process of protein synthesis. To fully appreciate this aspect of the chemical basis of biology, keep in mind that *this amazingly complex process occurs largely through H bonding between base pairs.*

Here is an outline of *protein synthesis.* DNA occurs in the cell nucleus, but the genetic message is decoded outside it, so the information must be sent to the synthesis site. RNA serves in this messenger role, as well as in several others. A portion of the DNA is temporarily unwound and one chain segment acts as a *template* for the formation of a complementary chain of *messenger RNA* (mRNA) made by individual mononucleoside triphosphates linking together; thus, *the DNA code words are transcribed into RNA code words* through base pairing. The mRNA leaves the nucleus and binds, again through base pairing, to an RNA-rich particle in the cell called a *ribosome.* The words (three-base sequences) in the mRNA are then decoded by molecules of *transfer RNA* (tRNA). These smaller nucleic acid "shuttles" have two key portions on opposite ends of their structures:

- A three-base sequence that is the complement of a word on the mRNA
- A binding site for the amino acid coded by that word

The ribosome moves along the bound mRNA, one word at a time, while tRNAs bind to the mRNA and position their amino acids near one another in preparation for peptide bond formation and synthesis of the protein.

In essence, then, protein synthesis involves the DNA message of three-base words being transcribed into the RNA message of three-base words, which is then translated into a sequence of amino acids that are linked to make a protein:

DNA BASE SEQUENCE ⇒ RNA BASE SEQUENCE ⇒ PROTEIN AMINO ACID SEQUENCE

An Outline of DNA Replication Another complex series of interactions allows *DNA replication,* the ability of DNA to copy itself. When a cell divides, its chromosomes are replicated, or reproduced, ensuring that the new cells have the same number and types of chromosomes. In this process, a small portion of the double helix is

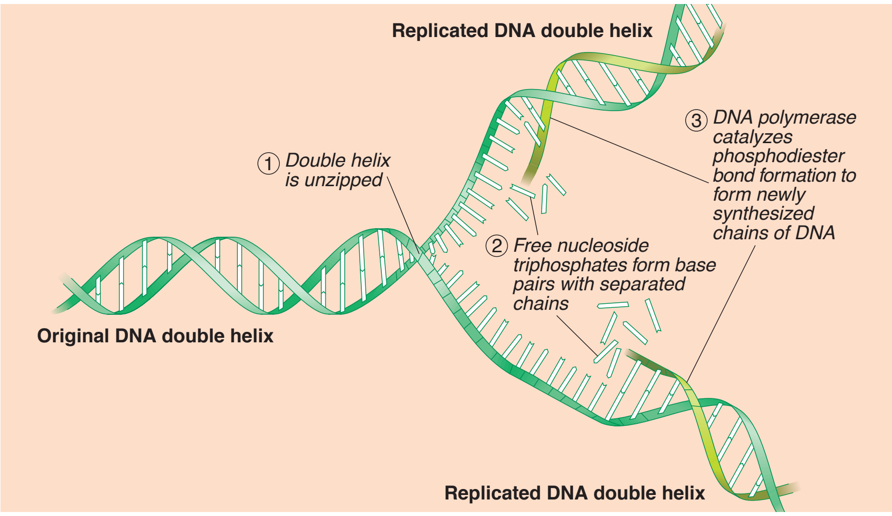


Figure 15.34 Key stages in DNA replication.

"unzipped," and each DNA chain acts as a template for the base pairing of its mononucleotide monomers with free mononucleoside triphosphates (Figure 15.34). These new units, H-bonded to their complements, are linked through phosphodiester bonds into a chain by an enzyme called *DNA polymerase*. Gradually, each of the unzipped chains forms the complementary half of a double helix, leading to *two* double helices. Because each base always pairs with its complement, the original double helix is copied and the genetic makeup of the cell preserved. (Base pairing is central to methods for learning the sequence of nucleotides in our genes, as the upcoming Chemical Connections essay shows.)

The biopolymers provide striking evidence for the folly of vitalism—that some sort of vital force exists only in substances from living systems. No unknowable force is required to explain the marvels of the living world. The same atomic properties that give rise to covalent bonds, molecular shape, and intermolecular forces provide the means for all life forms to flourish.

Section Summary

The three types of natural polymers—polysaccharides, proteins, and nucleic acids—are formed by dehydration-condensation reactions. • Polysaccharides are formed from cyclic monosaccharides, such as glucose. Cellulose, starch, and glycogen have structural or energy-storage roles. • Proteins are polyamides formed from as many as 20 different types of amino acids. Fibrous proteins have extended shapes and play structural roles. Globular proteins have compact shapes and play metabolic, immunologic, and hormonal roles. The amino acid sequence of a protein determines its shape and function. • Nucleic acids (DNA and RNA) are polynucleotides consisting of four different mononucleotides. The base sequence of the DNA chain determines the sequence of amino acids in an organism's proteins. Hydrogen bonding between specific base pairs is the key to protein synthesis and DNA replication. • DNA sequencing is used to determine the identity and order of nucleotides; DNA fingerprinting is used to identify a person from the characteristic pattern of gene fragments in a sample of cells.

Chapter Perspective

The amazing diversity of organic compounds highlights the importance of atomic properties. While gaining an appreciation for the special properties of carbon, you've seen similar types of bonding, molecular shapes, intermolecular forces, and reactivities in organic and inorganic compounds. Upcoming chapters focus on the dynamic aspects of all reactions—their speed, extent, and direction—as we explore the kinetics, equilibrium, and thermodynamics of chemical and physical change. We'll have many opportunities to exemplify these topics with organic compounds and biochemical systems.

***Chemical Connections** to Genetics and Forensics*

DNA Sequencing and Fingerprinting

As a result of one of the most remarkable achievements in modern science, we now know the sequence of the 3 billion nucleotide base pairs in the DNA of the entire human genome! The *genome* consists of DNA molecules; segments of their chains are the genes, the functional units of heredity. The DNA exists in each cell's nucleus as tightly coiled threads arranged, in the human, into 23 pairs of chromosomes (Figure B15.6). The potential benefits of this knowledge are profound, and central to the accomplishment is *DNA sequencing,* the process used to determine the identity and order of bases. Sequencing is indispensable to molecular biology and biochemical genetics.

Just as indispensable to forensic science is *DNA fingerprinting* (or *DNA profiling*), a different process but one that employs some similar methods. In 1985, British scientists discovered that portions of an individual's DNA are as unique as fingerprints. The technique has been applied in countless situations, from parental custody claims to crime scene investigations to identifying the remains of victims of the September 11, 2001, terrorist attacks.

An Outline of DNA Sequencing

A given chromosome may have 100 million nucleotide bases, but the sequencing process can handle, at one time, DNA fragments only about 2000 bases long. Therefore, the chromosome is first broken into pieces by enzymes that cleave at specific sites. Then, to obtain enough sample for analysis, the DNA is replicated through a variety of "amplification" methods, which make many copies of the individual DNA "target" fragments.

The most popular sequencing method is the *Sanger chain-termination method*, which uses chemically altered bases to stop the growth of a complementary DNA chain at specific locations. As you've seen in the previous text discussion, the chain consists of linked 2′-deoxyribonucleoside monophosphate units (dNMP, where N represents A, T, G, or C). The link is a phosphodiester bond from the 3′-OH of one unit to the 5′-OH of the next. The free monomers used to construct the chain are 2′-deoxyribonucleoside triphosphates (dNTP) (Figure B15.7A). The Sanger method uses a modified monomer, called a *di*deoxyribonucleoside triphosphate (ddNTP), in which the 3′-OH group is also missing from the ribose unit (Figure B15.7B). As soon as the ddNTP is incorporated into the growing chain, polymerization stops because there is no —OH group on the 3′ position to form a phosphodiester bond to the next dNTP unit.

The procedure is shown in Figure B15.8. After several preparation steps, the sample to be sequenced consists of a single-stranded DNA target fragment, which is attached to one strand of a double-stranded segment of DNA (Figure B15.8A). This sample is divided into four tubes, and to each tube is added a mixture of DNA polymerase, large amounts of all four dNTP's, and a small amount of one of the four ddNTP's. Thus, tube 1 contains polymerase, dATP, dGTP, dCTP, and dTTP, and, say, ddATP; tube 2 contains the same, except ddGTP instead of ddATP; and so forth. After the polymerization reaction is complete, each tube contains the original target fragment paired to complementary chains of varying length (Figure B15.8B). The chain lengths vary because in tube 1, each complementary chain ends in ddA (designated **A** in the figure); in tube 2, each ends in ddG (**G**); in tube 3, each ends in ddC (**C**); and in tube 4, each ends in ddT (**T**).

Each double-stranded product is divided into single strands, and then the complementary chains are separated by means of *high-resolution polyacrylamide-gel electrophoresis.* This technique applies an electric field to separate charged species through differences in their rate of migration through pores in a gel: the smaller the species, the faster it moves. Polynucleotide fragments are commonly separated by electrophoresis because they have charged phosphate groups. High-resolution gels can be made with pores that vary so slightly in size that they can separate fragments differing by only a single nucleotide.

In this step, each sample is applied to its own "lane" on a gel, and, after electrophoresis, the gel is scanned to locate the chains,

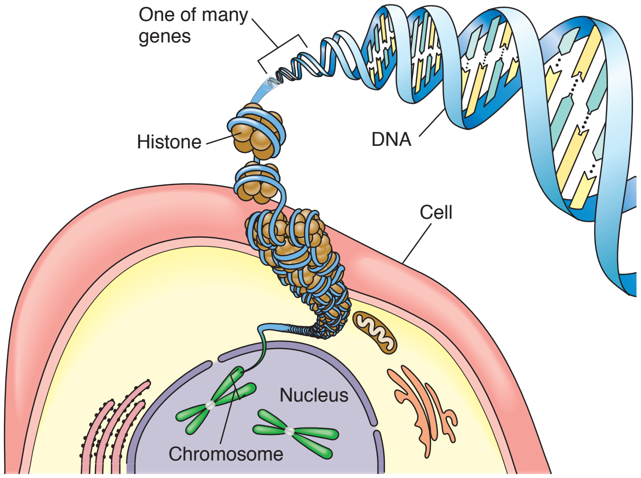


Figure B15.6 DNA, the genetic material. In the cell nucleus, each chromosome consists of a DNA molecule wrapped around globular proteins called histones. Segments of the DNA chains are genes.

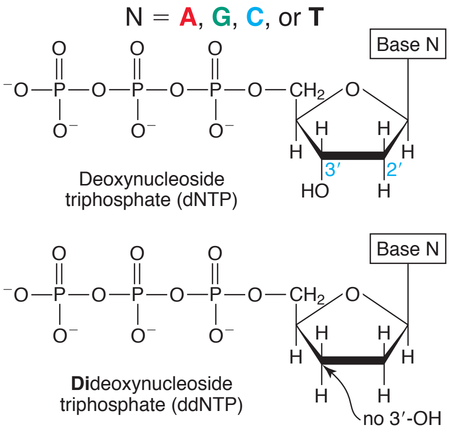


Figure B15.7 Nucleoside triphosphate monomers. The normal *deoxy* monomer (dNTP; *top*) has no 2′-OH group but *does* have a 3′-OH group to continue growth of the polynucleotide chain. The modified *dideoxy* monomer in the Sanger method (ddNTP; *bottom*) also lacks the 3′-OH group.

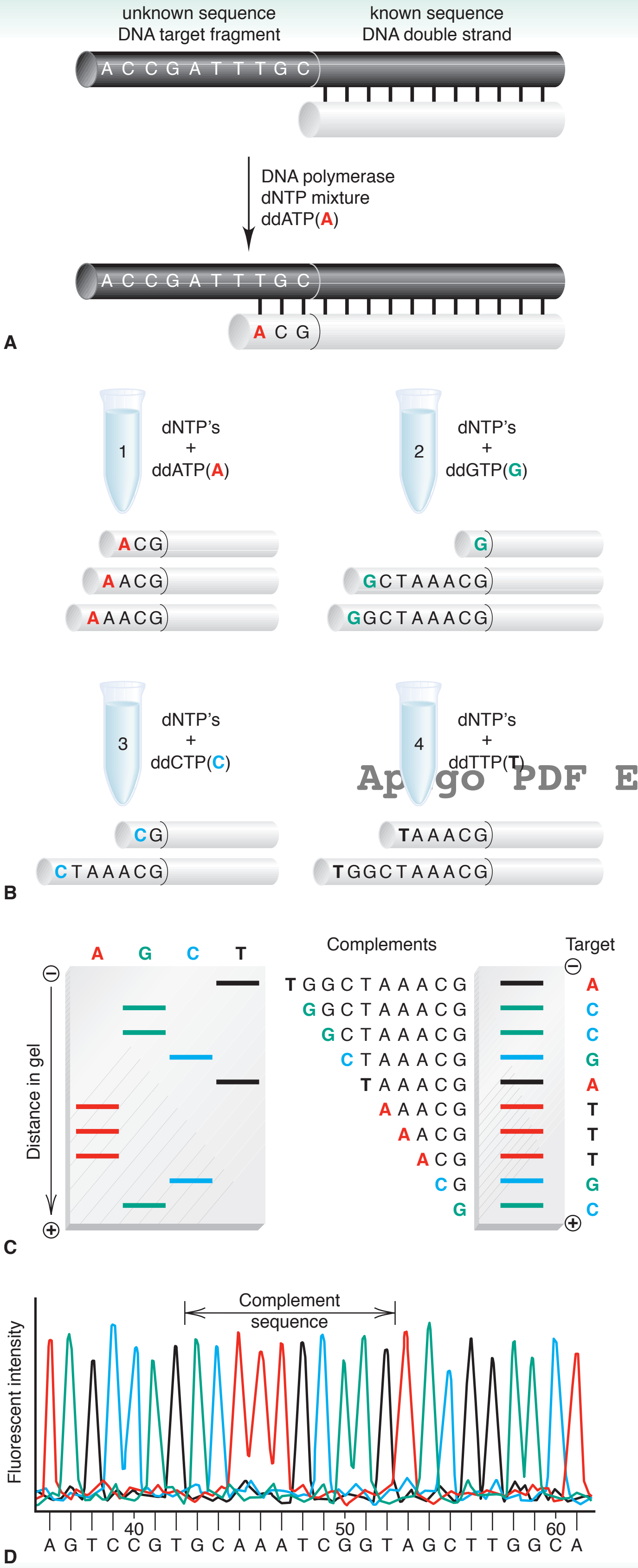


Figure B15.8 **Steps in the Sanger method of DNA sequencing.** (See text for full discussion.)

which appear in bands. Because all four ddNTP's were used, all possible chain fragments are formed, so the sequence of the original DNA fragment can be determined (Figure B15.8C).

An automated approach begins with each ddNTP tagged with a different fluorescent dye that emits light of a distinct color. The entire mixture of complementary chains is introduced onto the gel and separated. The gel is scanned by a laser, which activates the dyes. The fluorescent intensity versus distance along the chain is detected and plotted by a computer (Figure B15.8D).

An Outline of DNA Fingerprinting

Biological samples collected at a crime scene are often very small, so, as with sequencing, the first step to obtain enough DNA for forensic analysis involves amplification. Modern techniques require less than 1 ng of DNA. Thus, in addition to blood and semen, licked stamps and envelopes, gum, and clothing containing dead skin cells can also be used as sources for the DNA.

Currently, the most successful and widely used DNA profiling procedure is called *short tandem repeat (STR) analysis*. STRs are specific areas on a chromosome that contain short (3–7 bases) sequences that repeat themselves within the DNA molecule. There are hundreds of different types of STRs, but each person has a unique number and assortment of types. Therefore, the more STRs that are characterized, the more discriminating the analysis. Once the STRs have been amplified, they are separated by electrophoresis, and an analyst determines the number of base repeats within each STR (Figure B15.9).

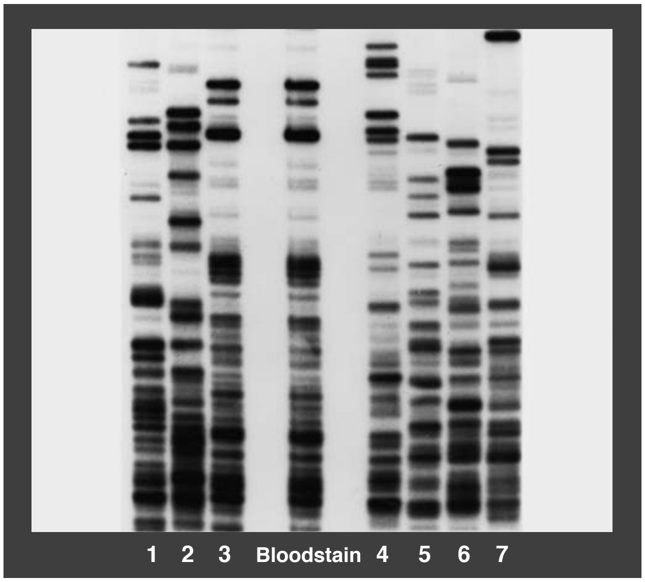


Figure B15.9 **STR analysis of DNA in a blood stain.** Stained gels containing the STRs of DNA in blood samples from several suspects are compared with those from the blood found at the crime scene. Suspect 3 has an identical pattern of STRs to those in the blood stain.

CHAPTER REVIEW GUIDE

The following sections provide many aids to help you study this chapter. (Numbers in parentheses refer to pages, unless noted otherwise.)

Learning Objectives

These are concepts and skills you should know after studying this chapter.

Relevant section and/or sample problem (SP) numbers appear in parentheses.

Understand These Concepts

1. How carbon's atomic properties give rise to its ability to form four strong covalent bonds, multiple bonds, and chains, which results in the great structural diversity of organic compounds (15.1)
2. How carbon's atomic properties give rise to its ability to bond to various heteroatoms, which creates regions of charge imbalance that result in functional groups (15.1)
3. Structures and names of alkanes, alkenes, and alkynes (15.2)
4. The distinctions among constitutional, optical, and geometric isomers (15.2)
5. The importance of optical isomerism in organisms (15.2)
6. The effect of restricted rotation around a π bond on the structures and properties of alkenes (15.2)
7. The nature of organic addition, elimination, and substitution reactions (15.3)
8. The properties and reaction types of the various functional groups (15.4):
   - Substitution and elimination for alcohols, alkyl halides, and amines
   - Addition for alkenes, alkynes, and aldehydes and ketones
   - Substitution for the carboxylic acid family (acids, esters, and amides)
9. Why delocalization of electrons causes aromatic rings to have lower reactivity than alkenes (15.4)
10. The polarity of the carbonyl bond and the importance of organometallic compounds in addition reactions of carbonyl compounds (15.4)
11. How addition plus elimination lead to substitution in the reactions of the carboxylic acid family (15.4)
12. How addition and condensation polymers form (15.5)
13. The three types of biopolymers and their monomers (15.6)
14. How amino acid sequence determines protein shape, which determines function (15.6)
15. How complementary base pairing controls the processes of protein synthesis and DNA replication (15.6)
16. How DNA base sequence determines RNA base sequence, which determines amino acid sequence (15.6)

Master These Skills

1. Drawing hydrocarbon structures given the number(s) of C atoms, multiple bonds, and rings (SP 15.1)
2. Naming hydrocarbons and drawing expanded, condensed, and carbon skeleton formulas (15.2 and SP 15.2)
3. Drawing geometric isomers and identifying chiral centers of molecules (SP 15.2)
4. Recognizing the type of reaction from the structures of reactants and products (SP 15.3)
5. Recognizing a reaction as an oxidation or reduction from the structures of reactants and products (15.3)
6. Determining the reactants and products of the reactions of alcohols, alkyl halides, and amines (SP 15.4 and Follow-up)
7. Determining the products in a stepwise reaction sequence (SP 15.5)
8. Determining the reactants of the reactions of aldehydes and ketones (Follow-up Problem 15.5)
9. Determining the reactants and products of the reactions of the carboxylic acid family (SP 15.6 and Follow-up)
10. Recognizing and naming the functional groups in an organic molecule (SP 15.7)
11. Drawing an abbreviated synthetic polymer structure based on monomer structures (15.5)
12. Drawing small peptides from amino acid structures (15.6)
13. Using the base-paired sequence of one DNA strand to predict the sequence of the other (15.6)

Key Terms

These important terms appear in boldface in the chapter and are defined again in the Glossary.

organic compound (629)

Section 15.1

heteroatom (631)
functional group (631)

Section 15.2

hydrocarbon (632)
alkane (C_nH_{2n+2}) (635)
homologous series (635)
saturated hydrocarbon (635)
cyclic hydrocarbon (637)
isomers (637)
constitutional (structural) isomers (637)
stereoisomers (639)
optical isomers (639)
chiral molecule (639)
polarimeter (640)
optically active (640)
alkene (C_nH_{2n}) (640)
unsaturated hydrocarbon (640)
geometric (*cis-trans*) isomers (641)
alkyne (C_nH_{2n-2}) (643)
aromatic hydrocarbon (644)
nuclear magnetic resonance (NMR) spectroscopy (646)

Section 15.3

alkyl group (646)
addition reaction (647)
elimination reaction (648)
substitution reaction (648)

Section 15.4

alcohol (650)
haloalkane (alkyl halide) (652)
amine (652)
carbonyl group (655)
aldehyde (655)
ketone (655)
organometallic compound (656)
carboxylic acid (657)
ester (657)
amide (657)
fatty acid (658)
acid anhydride (658)
lipid (658)
hydrolysis (659)
nitrile (661)

Section 15.5

addition polymer (663)
condensation polymer (664)

Section 15.6

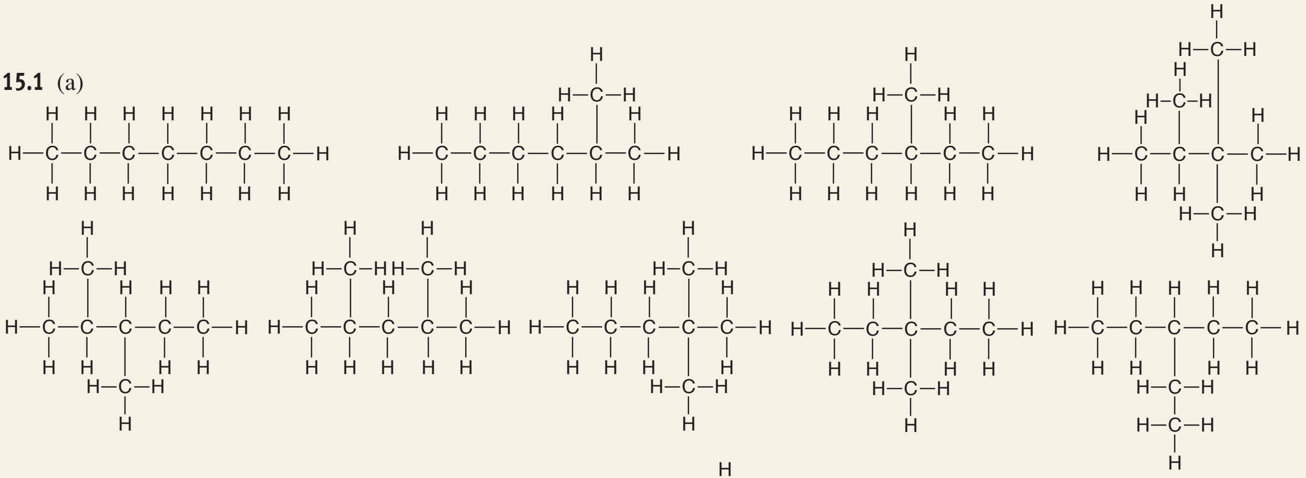
monosaccharide (666)
polysaccharide (666)
disaccharide (666)
protein (667)
amino acid (667)
nucleic acid (670)
mononucleotide (670)
double helix (671)
base pair (671)
genetic code (671)

Highlighted Figures and Tables These figures (F) and tables (T) provide a visual review of key ideas.

F15.4	Adding H-atom skin to C-atom skeleton (633)
T15.1	Numerical roots for carbon chains and branches (635)
T15.2	Rules for naming an organic compound (636)
T15.5	Important organic functional groups (651)
F15.31	Nucleic acid precursors and their linkage (670)

Brief Solutions to FOLLOW-UP PROBLEMS Compare your solutions to these calculation steps and answers.

15.1 (a)



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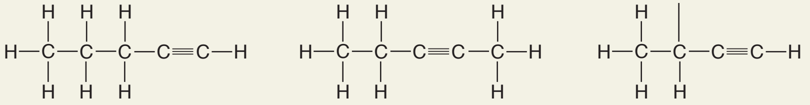
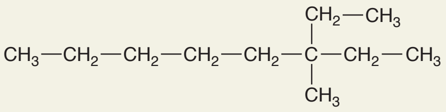
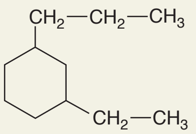


15.2 (a)

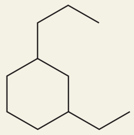


$CH_3-CH_2-CH_2-CH_2-CH_2-\underset{CH_3}{\overset{CH_2-CH_3}{C}}-CH_2-CH_3$

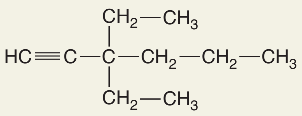
(b)



and

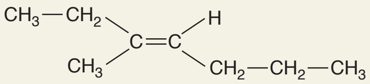


(c)

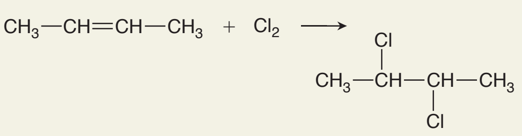


$HC\equiv C-\underset{CH_2-CH_3}{\overset{CH_2-CH_3}{C}}-CH_2-CH_2-CH_3$

(d)



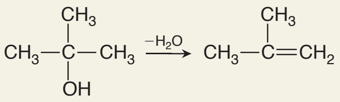
15.3 (a)



$CH_3-CH=CH-CH_3 + Cl_2 \longrightarrow CH_3-\overset{Cl}{CH}-\underset{Cl}{CH}-CH_3$

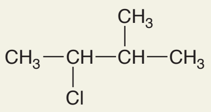
(b) $CH_3-CH_2-CH_2-Br + OH^- \longrightarrow CH_3-CH_2-CH_2-OH + Br^-$

(c)



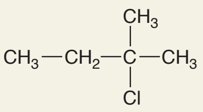
$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow{-H_2O} CH_3-\overset{CH_3}{C}=CH_2$

15.4 (a)



$CH_3-\underset{Cl}{CH}-\overset{CH_3}{CH}-CH_3$

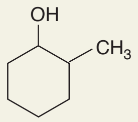
or



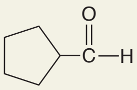
$CH_3-CH_2-\underset{Cl}{\overset{CH_3}{C}}-CH_3$

(b) $CH_3-CH_2-CH_2-OH$

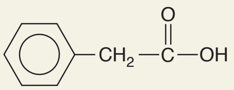
15.5 (a)



(b)



15.6 (a)



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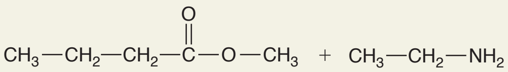
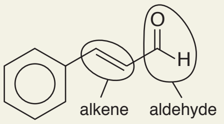
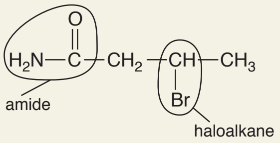


$CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3 + CH_3-CH_2-NH_2$

15.7 (a)



(b)



PROBLEMS

Problems with **colored** numbers are answered in Appendix E and worked in detail in the Student Solutions Manual. Problem sections match those in the text and provide the numbers of relevant sample problems. Most offer Concept Review Questions, Skill-Building Exercises (grouped in pairs covering the same concept), and Problems in Context. The Comprehensive Problems are based on material from any section or previous chapter.

The Special Nature of Carbon and the Characteristics of Organic Molecules

Concept Review Questions

15.1 Give the names and formulas of two carbon compounds that are organic and two that are inorganic.

15.2 Through the first quarter of the 19th century, the concept of vitalism—that a key difference existed between substances isolated from animate sources and those from inanimate sources—was widely accepted. What was the central notion of vitalism? Give an example of a finding that led to its eventual downfall.

15.3 Explain each statement in terms of atomic properties:
(a) Carbon engages in covalent rather than ionic bonding.
(b) Carbon has four bonds in all its organic compounds.
(c) Carbon forms neither stable cations, like many metals, nor stable anions, like many nonmetals.
(d) Carbon bonds to itself more extensively than does any other element.
(e) Carbon forms stable multiple bonds.

15.4 Carbon bonds to many elements other than itself.
(a) Name six elements that commonly bond to carbon in organic compounds.
(b) Which of these elements are heteroatoms?
(c) Which of these elements are more electronegative than carbon? Less electronegative?
(d) How does bonding of carbon to heteroatoms increase the number of organic compounds?

15.5 Silicon lies just below carbon in Group 4A(14) and also forms four covalent bonds. Why aren't there as many silicon compounds as carbon compounds?

15.6 What is the range of oxidation states for carbon? Name a compound in which carbon has its highest oxidation state and one in which it has its lowest.

15.7 Which of these bonds to carbon would you expect to be relatively reactive: C—H, C—C, C—I, C═O, C—Li? Explain.

The Structures and Classes of Hydrocarbons

(Sample Problems 15.1 and 15.2)

Concept Review Questions

15.8 (a) What structural feature is associated with each type of hydrocarbon: an alkane; a cycloalkane; an alkene; an alkyne?
(b) Give the general formula for each type.
(c) Which hydrocarbons are considered saturated?

15.9 Define each type of isomer: (a) constitutional; (b) geometric; (c) optical. Which types of isomers are stereoisomers?

15.10 Among alkenes, alkynes, and aromatic hydrocarbons, only alkenes exhibit *cis-trans* isomerism. Why don't the others?

15.11 Which objects are asymmetric (have no plane of symmetry): (a) a circular clock face; (b) a football; (c) a dime; (d) a brick; (e) a hammer; (f) a spring?

15.12 Explain how a polarimeter works and what it measures.

15.13 How does an aromatic hydrocarbon differ from a cycloalkane in terms of its bonding? How does this difference affect structure?

Skill-Building Exercises *(grouped in similar pairs)*

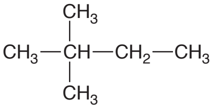
15.14 Draw all possible skeletons for a 7-C compound with
(a) A 6-C chain and 1 double bond
(b) A 5-C chain and 1 double bond
(c) A 5-C ring and no double bonds

15.15 Draw all possible skeletons for a 6-C compound with
(a) A 5-C chain and 2 double bonds
(b) A 5-C chain and 1 triple bond
(c) A 4-C ring and no double bonds

15.16 Add the correct number of hydrogens to each of the skeletons in Problem 15.14.

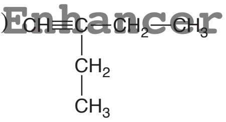
15.17 Add the correct number of hydrogens to each of the skeletons in Problem 15.15.

15.18 Draw correct structures, by making a single change, for any that are incorrect:

(a) 

$CH_3—\overset{CH_3}{\underset{CH_3}{CH}}—CH_2—CH_3$

(b) $CH_3═CH—CH_2—CH_3$

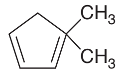
(c) 

$CH≡\underset{\underset{CH_3}{CH_2}}{C}—CH_2—CH_3$

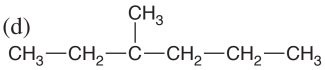
(d) 

15.19 Draw correct structures, by making a single change, for any that are incorrect:

(a) $CH_3—CH═CH—CH_2—CH_3$

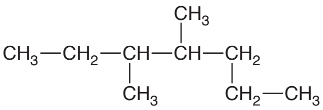
(b) 

(c) $CH_3—C≡CH—CH_2—CH_3$

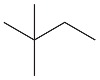
(d) 

$CH_3—CH_2—\overset{CH_3}{C}—CH_2—CH_2—CH_3$

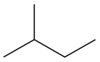
15.20 Draw the structure or give the name of each compound:
(a) 2,3-dimethyloctane (b) 1-ethyl-3-methylcyclohexane

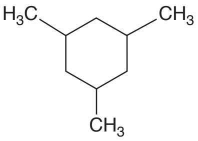
(c) 

$CH_3—CH_2—\underset{CH_3}{CH}—\overset{CH_3}{CH}—\underset{CH_2—CH_3}{CH_2}$

(d) 

15.21 Draw the structure or give the name of each compound:

(a) 

(b) 

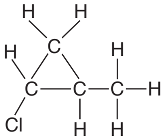
(c) 1,2-diethylcyclopentane (d) 2,4,5-trimethylnonane

15.22 Each of the following names is wrong. Draw structures based on them, and correct the names:
(a) 4-methylhexane (b) 2-ethylpentane
(c) 2-methylcyclohexane (d) 3,3-methyl-4-ethyloctane

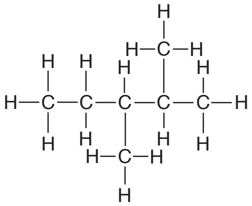
15.23 Each of the following names is wrong. Draw structures based on them, and correct the names:
(a) 3,3-dimethylbutane (b) 1,1,1-trimethylheptane
(c) 1,4-diethylcyclopentane (d) 1-propylcyclohexane

15.24 Each of the following compounds can exhibit optical activity. Circle the chiral center(s) in each:

(a)

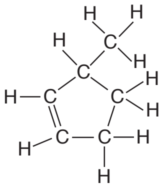


(b)

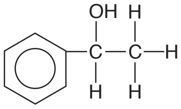


15.25 Each of the following compounds can exhibit optical activity. Circle the chiral center(s) in each:

(a)



(b)



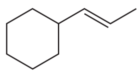
15.26 Draw structures from the following names, and determine which compounds are optically active:
(a) 3-bromohexane (b) 3-chloro-3-methylpentane
(c) 1,2-dibromo-2-methylbutane

15.27 Draw structures from the following names, and determine which compounds are optically active:
(a) 1,3-dichloropentane (b) 3-chloro-2,2,5-trimethylhexane
(c) 1-bromo-1-chlorobutane

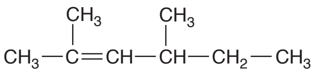
15.28 Which of the following structures exhibit geometric isomerism? Draw and name the two isomers in each case:

(a) $CH_3—CH_2—CH=CH—CH_3$

(b)



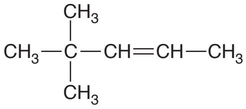
(c)



$CH_3—\overset{CH_3}{\overset{|}{C}}=CH—\overset{CH_3}{\overset{|}{CH}}—CH_2—CH_3$

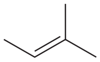
15.29 Which of the following structures exhibit geometric isomerism? Draw and name the two isomers in each case:

(a)

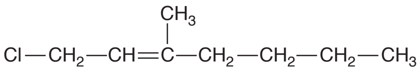


$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—CH=CH—CH_3$

(b)



(c)



$Cl—CH_2—CH=\overset{CH_3}{\overset{|}{C}}—CH_2—CH_2—CH_2—CH_3$

15.30 Which compounds exhibit geometric isomerism? Draw and name the two isomers in each case:
(a) propene (b) 3-hexene
(c) 1,1-dichloroethene (d) 1,2-dichloroethene

15.31 Which compounds exhibit geometric isomerism? Draw and name the two isomers in each case:
(a) 1-pentene (b) 2-pentene
(c) 1-chloropropene (d) 2-chloropropene

15.32 Draw and name all the constitutional isomers of dichlorobenzene.

15.33 Draw and name all the constitutional isomers of trimethylbenzene.

● Problems in Context

15.34 Butylated hydroxytoluene (BHT) is a common preservative added to cereals and other dry foods. Its systematic name is 1-hydroxy-2,6-di-*tert*-butyl-4-methylbenzene (where "*tert*-butyl" is 1,1-dimethylethyl). Draw the structure of BHT.

15.35 There are two compounds with the name 2-methyl-3-hexene, but only one with the name 2-methyl-2-hexene. Explain with structures.

15.36 Any tetrahedral atom with four different groups attached can be a chiral center. Which of these species is optically active?
(a) $CHClBrF$
(b) $NBrCl_2H^+$
(c) $PFClBrI^+$
(d) $SeFClBrH$

15.37 The number of peaks in the ^1H-NMR spectrum of a compound depends on the number of different kinds (environments) of H atoms. How many peaks appear in the spectrum of each isomer of C_4H_{10} and of C_5H_{12} (see Table 15.3, p. 638)?

Some Important Classes of Organic Reactions

(Sample Problem 15.3)

● Concept Review Questions

15.38 In terms of numbers of reactant and product substances, which organic reaction type corresponds to (a) a combination reaction, (b) a decomposition reaction, (c) a displacement reaction?

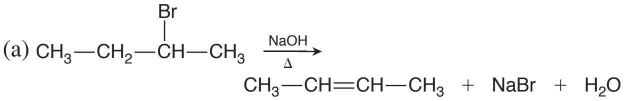
15.39 The same type of bond is broken in an addition reaction and formed in an elimination reaction. Name the type.

15.40 Can a redox reaction also be an addition, elimination, or substitution reaction? Explain with examples.

● Skill-Building Exercises *(grouped in similar pairs)*

15.41 Determine the type of each of the following reactions:

(a)

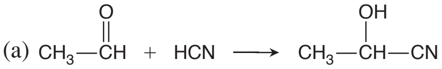


$CH_3—CH_2—\overset{Br}{\overset{|}{CH}}—CH_3 \xrightarrow[\Delta]{NaOH} CH_3—CH=CH—CH_3 + NaBr + H_2O$

(b) $CH_3—CH=CH—CH_2—CH_3 + H_2 \xrightarrow{Pt} CH_3—CH_2—CH_2—CH_2—CH_3$

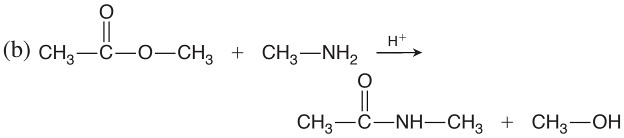
15.42 Determine the type of each of the following reactions:

(a)



$CH_3—\overset{O}{\overset{\|}{C}}H + HCN \longrightarrow CH_3—\overset{OH}{\overset{|}{CH}}—CN$

(b)



$CH_3—\overset{O}{\overset{\|}{C}}—O—CH_3 + CH_3—NH_2 \xrightarrow{H^+} CH_3—\overset{O}{\overset{\|}{C}}—NH—CH_3 + CH_3—OH$

15.43 Write equations for the following: (a) an addition reaction between H_2O and 3-hexene (H^+ is a catalyst); (b) an elimination reaction between 2-bromopropane and hot potassium ethoxide, $CH_3—CH_2—OK$ (KBr and ethanol are also products); (c) a light-induced substitution reaction between Cl_2 and ethane to form 1,1-dichloroethane.

15.44 Write equations for the following: (a) a substitution reaction between 2-bromopropane and KI; (b) an addition reaction between cyclohexene and Cl_2; (c) an addition reaction between 2-propanone and H_2 (Ni metal is a catalyst).

15.45 Based on the number of bonds and the nature of the bonded atoms, state whether each of the following changes is an oxidation or a reduction:

(a) $=CH_2$ becomes $—CH_2—OH$

(b) $=CH—$ becomes $—CH_2—$

(c) $\equiv C—$ becomes $—CH_2—$

15.46 Based on the number of bonds and the nature of the bonded atoms, state whether each of the following changes is an oxidation or a reduction:

(a) 
$—\overset{|}{\underset{|}{C}}—OH$ becomes $—\underset{|}{C}=O$

(b) $—CH_2—OH$ becomes $=CH_2$

(c) 
$—\overset{O}{\overset{\|}{C}}—\underset{|}{C}—$ becomes $—\overset{O}{\overset{\|}{C}}—O—$

15.47 Is the organic reactant oxidized, reduced, or neither in each of the following reactions?

(a) 2-hexene $\xrightarrow[\text{cold } OH^-]{KMnO_4}$ 2,3-dihydroxyhexane

(b) cyclohexane $\xrightarrow[\text{catalyst}]{\Delta}$ benzene + $3H_2$

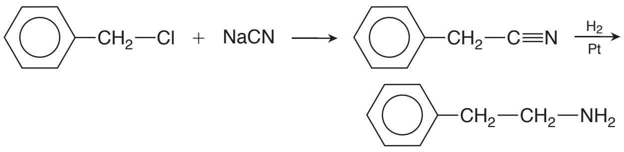
15.48 Is the organic reactant oxidized, reduced, or neither in each of the following reactions?

(a) 1-butyne + H_2 $\xrightarrow{Pt}$ 1-butene

(b) toluene $\xrightarrow[H_3O^+,\ \Delta]{KMnO_4}$ benzoic acid

Problems in Context

15.49 Phenylethylamine is a natural substance that is structurally similar to amphetamine. It is found in sources as diverse as almond oil and human urine, where it occurs at elevated concentrations as a result of stress and certain forms of schizophrenia. One method of synthesizing the compound for pharmacological and psychiatric studies involves two steps:



phenylethylamine

Classify each step as an addition, elimination, or substitution.

Properties and Reactivities of Common Functional Groups

(Sample Problems 15.4 to 15.7)

Concept Review Questions

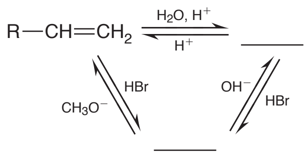
15.50 Compounds with nearly identical molar masses often have very different physical properties. Choose the compound with the higher value for each of the following properties, and explain your choice.

(a) Solubility in water: chloroethane or methylethylamine

(b) Melting point: diethyl ether or 1-butanol

(c) Boiling point: trimethylamine or propylamine

15.51 Fill in each blank with a general formula for the type of compound formed:



15.52 Of the three major types of organic reactions, which do *not* occur readily with benzene? Why?

15.53 Why does the C=O group react differently from the C=C group? Show an example of the difference.

15.54 Many substitution reactions involve an initial electrostatic attraction between reactants. Show where this attraction arises in the formation of an amide from an amine and an ester.

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

15.56 What reaction type is common to the formation of esters and acid anhydrides? What is the other product?

15.57 Both alcohols and carboxylic acids undergo substitution, but the processes are very different. Explain.

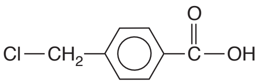
Skill-Building Exercises *(grouped in similar pairs)*

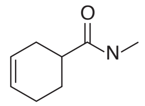
15.58 Name the type of organic compound from the following description of its functional group: (a) polar group that has only single bonds and does not include O or N; (b) group that is polar and has a triple bond; (c) group that has single and double bonds and is acidic in water; (d) group that has a double bond and must be at the end of a C chain.

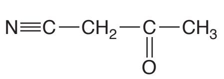
15.59 Name the type of organic compound from the following description of its functional group: (a) N-containing group with single and double bonds; (b) group that is not polar and has a double bond; (c) polar group that has a double bond and cannot be at the end of a C chain; (d) group that has only single bonds and is basic in water.

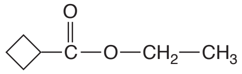
15.60 Circle and name the functional group(s) in each compound:

(a) $CH_3—CH=CH—CH_2—OH$

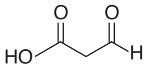
(b) 

(c) 

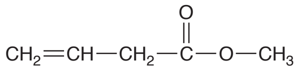
(d) 
$N\equiv C—CH_2—\underset{O}{\underset{\|}{C}}—CH_3$

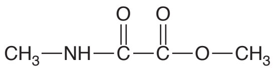
(e) 

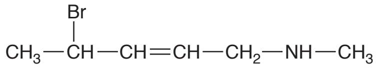
15.61 Circle and name the functional group(s) in each compound:

(a) 

(b) $I—CH_2—CH_2—C\equiv CH$

(c) 
$CH_2=CH—CH_2—\overset{O}{\overset{\|}{C}}—O—CH_3$

(d) 
$CH_3—NH—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—O—CH_3$

(e) 
$CH_3—\overset{Br}{\overset{|}{C}H}—CH=CH—CH_2—NH—CH_3$

15.62 Draw all alcohols with the formula $C_5H_{12}O$.

15.63 Draw all aldehydes and ketones with the formula $C_5H_{10}O$.

15.64 Draw all amines with the formula $C_4H_{11}N$.

15.65 Draw all carboxylic acids with the formula $C_5H_{10}O_2$.

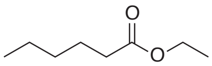
15.66 Draw the product resulting from mild oxidation of (a) 2-butanol; (b) 2-methylpropanal; (c) cyclopentanol.

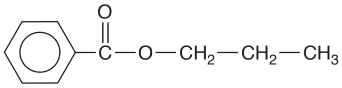
15.67 Draw the alcohol you'd oxidize to produce (a) 2-methylpropanal; (b) 2-pentanone; (c) 3-methylbutanoic acid.

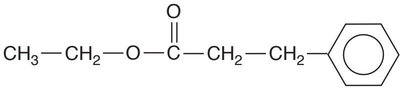
15.68 Draw the organic product formed when the following compounds undergo a substitution reaction: (a) acetic acid and methylamine; (b) butanoic acid and 2-propanol; (c) formic acid and 2-methyl-1-propanol.

15.69 Draw the organic product formed when the following compounds undergo a substitution reaction: (a) acetic acid and 1-hexanol; (b) propanoic acid and dimethylamine; (c) ethanoic acid and diethylamine.

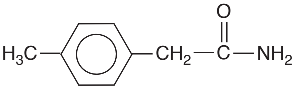
15.70 Draw condensed formulas for the carboxylic acid and alcohol that form the following esters:

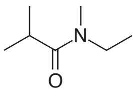
(a) 

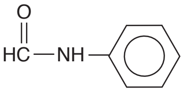
(b) 

(c) 

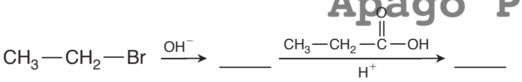
15.71 Draw condensed formulas for the carboxylic acid and amine that form the following amides:

(a) 

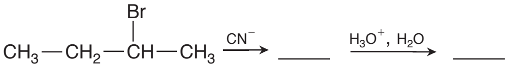
(b) 

(c) 

15.72 Fill in the expected organic substances:

(a) 

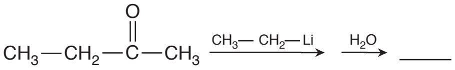
$$CH_3-CH_2-Br \xrightarrow{OH^-} \underline{\quad\quad} \xrightarrow[H^+]{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH} \underline{\quad\quad}$$

(b) 

$$CH_3-CH_2-\overset{Br}{\overset{|}{C}H}-CH_3 \xrightarrow{CN^-} \underline{\quad\quad} \xrightarrow{H_3O^+,\ H_2O} \underline{\quad\quad}$$

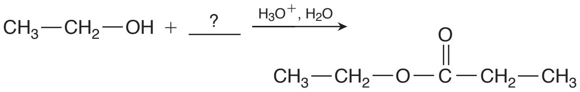
15.73 Fill in the expected organic substances:

(a) $CH_3-CH_2-CH=CH_2 \xrightarrow{H^+,\ H_2O} \underline{\quad\quad} \xrightarrow{Cr_2O_7^{2-},\ H^+} \underline{\quad\quad}$

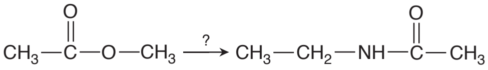
(b) 

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{CH_3-CH_2-Li} \xrightarrow{H_2O} \underline{\quad\quad}$$

15.74 Supply the missing organic and/or inorganic substances:

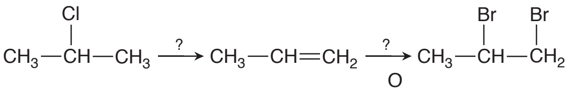
(a) 

$$CH_3-CH_2-OH + \underline{\ ?\ } \xrightarrow{H_3O^+,\ H_2O} CH_3-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

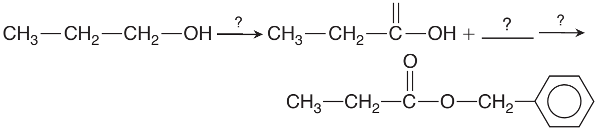
(b) 

$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 \xrightarrow{?} CH_3-CH_2-NH-\overset{O}{\overset{\|}{C}}-CH_3$$

15.75 Supply the missing organic and/or inorganic substances:

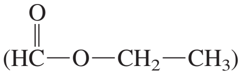
(a) 

$$CH_3-\overset{Cl}{\overset{|}{C}H}-CH_3 \xrightarrow{?} CH_3-CH=CH_2 \xrightarrow{?} CH_3-\overset{Br}{\overset{|}{C}H}-\overset{Br}{\overset{|}{C}H_2}$$

(b) 

Problems in Context

15.76 (a) Draw the four isomers of $C_5H_{12}O$ that can be oxidized to an aldehyde. (b) Draw the three isomers of $C_5H_{12}O$ that can be oxidized to a ketone. (c) Draw the isomers of $C_5H_{12}O$ that cannot be easily oxidized to an aldehyde or ketone. (d) Name any isomer that is an alcohol.

15.77 Ethyl formate  $(H\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3)$ is added to foods to give them the flavor of rum. How would you synthesize ethyl formate from ethanol, methanol, and any inorganic reagents?

The Monomer-Polymer Theme I: Synthetic Macromolecules

Concept Review Questions

15.78 Name the reaction processes that lead to the two types of synthetic polymers.

15.79 Which functional group occurs in the monomers of addition polymers? How are these polymers different from one another?

15.80 What is a free radical? How is it involved in polymer formation?

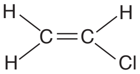
15.81 Which intermolecular force is primarily responsible for the different types of polyethylene? Explain.

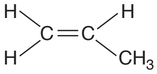
15.82 Which of the two types of synthetic polymer is more similar chemically to biopolymers? Explain.

15.83 Which functional groups react to form nylons? Polyesters?

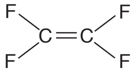
Skill-Building Exercises *(grouped in similar pairs)*

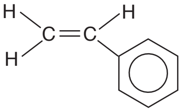
15.84 Draw an abbreviated structure for the following polymers, with brackets around the repeat unit:

(a) Poly(vinyl chloride) (PVC) from 

(b) Polypropylene from 

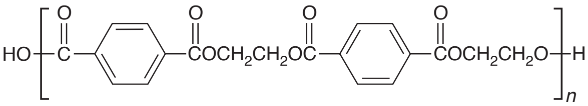
15.85 Draw an abbreviated structure for the following polymers, with brackets around the repeat unit:

(a) Teflon from 

(b) Polystyrene from 

Problems in Context

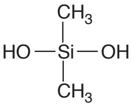
15.86 Polyethylene terephthalate (PET) is used to make synthetic fibers, such as Dacron, thin films, such as Mylar, and bottles for carbonated beverages.



PET

PET is produced from ethylene glycol and either of two monomers, depending on whether the reaction proceeds by dehydration-condensation or by displacement. Write equations for the two syntheses. (*Hint:* The displacement is reversed by adding methanol to PET at high *T* and *P*.)

15.87 Write a balanced equation for the reaction of dihydroxydimethylsilane *(right)* to form the condensation polymer known as Silly Putty.



$$HO-\overset{CH_3}{\underset{CH_3}{Si}}-OH$$

The Monomer-Polymer Theme II: Biological Macromolecules

Concept Review Questions

15.88 Which type of polymer is formed from each of the following monomers: (a) amino acids; (b) alkenes; (c) simple sugars; (d) mononucleotides?

15.89 What is the key structural difference between fibrous and globular proteins? How is it related, in general, to the proteins' amino acid composition?

15.90 Protein shape, function, and amino acid sequence are interrelated. Which determines which?

15.91 What linkage joins the monomers in each strand of DNA?

15.92 What is base pairing? How does it pertain to DNA structure?

15.93 RNA base sequence, protein amino acid sequence, and DNA base sequence are interrelated. Which determines which in the process of protein synthesis?

Skill-Building Exercises *(grouped in similar pairs)*

15.94 Draw the R group of (a) alanine; (b) histidine; (c) methionine.

15.95 Draw the R group of (a) glycine; (b) isoleucine; (c) tyrosine.

15.96 Draw the structure of each of the following tripeptides:
(a) Aspartic acid-histidine-tryptophan
(b) Glycine-cysteine-tyrosine with the charges existing in cell fluid

15.97 Draw the structure of each of the following tripeptides:
(a) Lysine-phenylalanine-threonine
(b) Alanine-leucine-valine with the charges that exist in cell fluid

15.98 Write the sequence of the complementary DNA strand that pairs with each of the following DNA base sequences:
(a) TTAGCC (b) AGACAT

15.99 Write the sequence of the complementary DNA strand that pairs with each of the following DNA base sequences:
(a) GGTTAC (b) CCCGAA

15.100 Write the base sequence of the DNA template from which this RNA sequence was derived: UGUUACGGA. How many amino acids are coded for in this sequence?

15.101 Write the base sequence of the DNA template from which this RNA sequence was derived: GUAUCAAUGAACUUG. How many amino acids are coded for in this sequence?

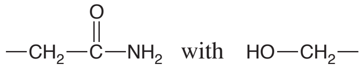
Problems in Context

15.102 Protein shapes are maintained by a variety of forces that arise from interactions between the amino-acid R groups. Name the amino acid that possesses each R group and the force that could arise in each of the following interactions:

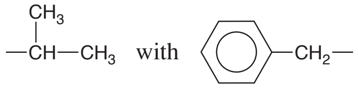
(a) $-CH_2-SH$ with $HS-CH_2-$

(b) 

$-(CH_2)_4-NH_3^+$ with $^-O-\overset{\overset{O}{\|}}{C}-CH_2-$

(c) 

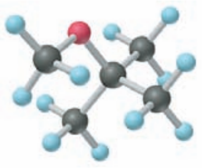
$-CH_2-\overset{\overset{O}{\|}}{C}-NH_2$ with $HO-CH_2-$

(d) 

15.103 Amino acids have an average molar mass of 100 g/mol. How many bases on a single strand of DNA are needed to code for a protein with a molar mass of 5×10^5 g/mol?

Comprehensive Problems

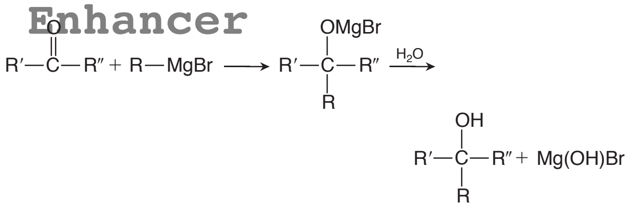
15.104 A synthesis of 2-butanol was performed by treating 2-bromobutane with hot sodium hydroxide solution. The yield was 60%, indicating that a significant portion of the reactant was converted into a second product. Predict what this other product might be. What simple test would support your prediction?



15.105 Ethers (general formula R—O—R′) have many important uses. Until recently, methyl *tert*-butyl ether (MTBE, *right*) was used as an octane booster and fuel additive for gasoline. It increases the oxygen content of the fuel, which reduces CO emissions. MTBE is synthesized by the catalyzed reaction of 2-methylpropene with methanol.
(a) Write a balanced equation for the synthesis of MTBE. (*Hint:* Alcohols add to alkenes similarly to the way water does.)
(b) If the government required that auto fuel mixtures contain 2.7% oxygen by mass to reduce CO emissions, how many grams of MTBE would have to be added to each 100. g of gasoline?
(c) How many liters of MTBE would be in each liter of fuel mixture? (The density of both gasoline and MTBE is 0.740 g/mL.)
(d) How many liters of air (21% O_2 by volume) are needed at 24°C and 1.00 atm to fully combust 1.00 L of MTBE?

15.106 An alcohol is oxidized to a carboxylic acid, and 0.2003 g of the acid is titrated with 45.25 mL of 0.03811 *M* NaOH. (a) What is the molar mass of the acid? (b) What are the molar mass and molecular formula of the alcohol?

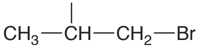
15.107 Some of the most useful compounds for organic synthesis are Grignard reagents (general formula R—MgX, where X is a halogen), which are made by combining an alkyl halide, R—X, with Mg. They are used to change the carbon skeleton of a starting carbonyl compound in a reaction similar to that with R—Li:



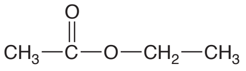
$$R'-\overset{\overset{O}{\|}}{C}-R'' + R-MgBr \longrightarrow R'-\underset{\underset{R}{|}}{\overset{\overset{OMgBr}{|}}{C}}-R'' \xrightarrow{H_2O} R'-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-R'' + Mg(OH)Br$$

(a) What is the product, after a final step with water, of the reaction between ethanal and the Grignard reagent of bromobenzene? (b) What is the product, after a final step with water, of the reaction between 2-butanone and the Grignard reagent of 2-bromopropane? (c) There are often two (or more) combinations of Grignard reagent and carbonyl compound that will give the same product. Choose another pair of reactants to give the product in (a). (d) What carbonyl compound must react with a Grignard reagent to yield a product with the —OH group at the *end* of the carbon chain? (e) What Grignard reagent and carbonyl compound would you use to prepare 2-methyl-2-butanol?

15.108 Starting with the given organic reactant and any necessary inorganic reagents, explain how you would perform each of the following syntheses:

(a) From $CH_3-CH_2-CH_2-OH$, make 

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

(b) From CH_3-CH_2-OH, make 

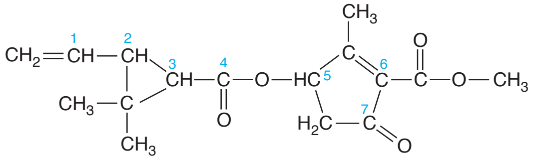
$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

15.109 Compound A, composed of C, H, and O, is heated in a 1.00-L flask to 160.°C until all of the A has vaporized and displaced the air. The flask is then cooled, and 2.48 g of A remains. When 0.500 g of A burns in O_2, 0.409 g of H_2O and 1.00 g of CO_2 are produced. Compound A is not acidic, but it can be oxidized to compound B, which is weakly acidic: 1.000 g of B is neutralized with 33.9 mL of 0.5 *M* sodium hydroxide. When B is heated to 260°C, it gives off water and forms C, whose solution in $CDCl_3$ (where D is deuterium, ^2H) has one peak in its ^1H-NMR spectrum. (a) What are the structures of A, B, and C? (b) Compound A is a controlled substance because it is metabolized to the weakly acidic "date rape" drug GHB, $C_4H_8O_3$. What are the structure and name of GHB?

15.110 Cadaverine (1,5-diaminopentane) and putrescine (1,4-diaminobutane) are two compounds that are formed by bacterial action and are responsible for the odor of rotting flesh. Draw their structures. Suggest a series of reactions to synthesize putrescine from 1,2-dibromoethane and any inorganic reagents.

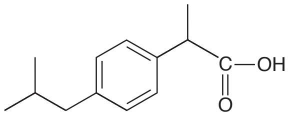
15.111 Pyrethrins, such as jasmolin II *(below)*, are a group of natural compounds synthesized by flowers of the genus *Chrysanthemum* (known as pyrethrum flowers) to act as insecticides.

(a) Circle and name the functional groups in jasmolin II.
(b) What is the hybridization of the numbered carbons?
(c) Which, if any, of the numbered carbons are chiral centers?

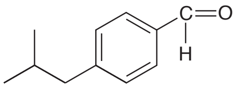


15.112 Compound A is branched and optically active and contains C, H, and O. (a) A 0.500-g sample burns in excess O_2 to yield 1.25 g of CO_2 and 0.613 g of H_2O. Determine the empirical formula. (b) When 0.225 g of compound A vaporizes at 755 torr and 97°C, the vapor occupies 78.0 mL. Determine the molecular formula. (c) Careful oxidation of the compound yields a ketone. Name and draw compound A, and circle the chiral center.

15.113 Ibuprofen is one of the most common anti-inflammatory drugs. (a) Identify the functional group(s) and chiral center(s) in ibuprofen. (b) Write a four-step synthesis of a racemic mixture of ibuprofen from 4-isobutylbenzaldehyde, using inorganic reactants and one organometallic reactant (see Problem 15.107).



ibuprofen



4-isobutylbenzaldehyde

15.114 Combustion of gasoline releases almost all of the carbon it contains as CO_2, the major greenhouse gas. As a simplification, assume that gasoline consists of eight-C alkanes (average $d = 0.74$ g/mL). How many metric tons of CO_2 are released in a year by an SUV that gets 15 mpg and is driven 18,000 miles?

15.115 Which features of retinal make it so useful as a photon absorber in the visual systems of organisms?

15.116 The polypeptide chain in proteins does not exhibit free rotation because of the partial double-bond character of the peptide bond. Explain this fact with resonance structures.

15.117 Other nonmetals form compounds that are structurally analogous to those of carbon, but these inorganic compounds are usually more reactive. Predict any missing products and write balanced equations for each reaction: (a) the decomposition and chlorination of diborane to boron trichloride; (b) the combustion of pentaborane (B_5H_9) in O_2; (c) the addition of water to borazine's double bonds ($B_3N_3H_6$, Figure 14.9B, p. 583) (*Hint:* The —OH group bonds to B); (d) the hydrolysis of trisilane (Si_3H_8) to silica (SiO_2) and H_2; (e) the complete halogenation of disilane with Cl_2; (f) the thermal decomposition of H_2S_5 to hydrogen sulfide and sulfur molecules; (g) the hydrolysis of PCl_5.

15.118 The genetic code consists of a series of three-base words that each code for a given amino acid.

(a) Using the selections from the genetic code shown below, determine the amino acid sequence coded by the following segment of RNA: UCCACAGCCUAUAUGGCAAACUUGAAG

AUG = methionine
UGG = tryptophan
GCC = alanine
UGU = cysteine
UCC = serine
CCU = proline
AAG = lysine
UUG = leucine
AAC = asparagine
GCA = alanine
CAU = histidine
UAU = tyrosine
CGG = arginine
ACA = threonine
UCA = serine

(b) What is the complementary DNA sequence from which this RNA sequence was made? (c) If you were sequencing the DNA fragment in part (b), how many complementary chain pieces would you obtain in the tube containing ddATP?

15.119 In addition to their use in water treatment, ion-exchange resins are used to extract Au, Ag, and Pt ions from solution. One of the most common resins consists of a polymer with a benzene-containing backbone to which sulfonic acid groups (—SO_3H) are then added. (a) What monomer can be used to prepare the polymer backbone? (b) This polymer typically contains 4–16% crosslinking. Draw the structure of the benzene-containing monomer used to crosslink the polymer.

15.120 Complete hydrolysis of a 100.00-g sample of a peptide gave the following amounts of individual amino acids (molar masses, in g/mol, appear in parentheses):

3.00 g of glycine (75.07)
3.70 g of valine (117.15)
7.30 g of serine (105.10)
0.90 g of alanine (89.10)
6.90 g of proline (115.13)
86.00 g of arginine (174.21)

(a) Why does the total mass of amino acids exceed the mass of peptide? (b) What are the relative numbers of amino acids in the peptide? (c) What is the minimum molar mass of the peptide?

15.121 Aircraft de-icing agents, such as propylene glycol [1,2-propanediol; $CH_3CH(OH)CH_2OH$; $d = 1.036$ g/mL], are used to remove ice and snow prior to winter flights, but their presence in runoff depletes O_2 in natural waters. (a) Write a balanced equation for the complete oxidation of propylene glycol by O_2. (b) What is the "theoretical oxygen demand," in grams of O_2 required per gram of propylene glycol oxidized? (c) What is the theoretical oxygen demand, in grams of O_2 required per liter of solution, of 90.0% by volume aqueous propylene glycol?

15.122 2-Butanone is reduced by hydride ion donors, such as sodium borohydride ($NaBH_4$), to the alcohol 2-butanol. Even though the alcohol has a chiral center, the product isolated from the redox reaction is not optically active. Explain.

15.123 Biphenyl consists of two benzene rings connected by a single bond. When Cl atoms substitute for some of the H atoms, polychlorinated biphenyls (PCBs) are formed. There are over 200 different PCBs, but only six with one Cl on each ring. Draw these constitutional isomers.

15.124 Wastewater from a cheese factory has the following composition: 8.0 g/L protein ($C_{16}H_{24}O_5N_4$); 12 g/L carbohydrate (CH_2O); and 2.0 g/L fat ($C_8H_{16}O$). What is the total organic carbon (TOC) of the wastewater in g of C/L?