

28

Organic Chemistry II: Shapes, Selected Reactions, and Biopolymers



OUTLINE

Shapes of Organic Molecules

- 28-1 Constitutional Isomers
- 28-2 Stereoisomers
- 28-3 Conformations

Selected Reactions

- 28-4 Reactions of Brønsted–Lowry Acids and Bases
- 28-5 Oxidation–Reduction Reactions

28-6 Formation of Carboxylic Acid Derivatives

28-7 Hydrolysis of Esters

Biopolymers

28-8 Carbohydrates

28-9 Polypeptides and Proteins

28-10 Nucleic Acids



Capsaicin, the substance responsible for the “hot” in peppers, has phenol, ester, and amide functional groups. In addition to acting as an inflammatory agent, it can act as a pain reliever, presumably by blocking nerve endings involved in the transmission of pain.

OBJECTIVES

After you have studied this chapter, you should be able to

- Describe the differences between constitutional isomers and stereoisomers
- Distinguish between isomers and conformations
- Describe some common organic acids and bases and their relative strengths
- Recall some reactions that involve oxidation and reduction of organic compounds
- Recall reactions that form carboxylic acid derivatives
- Recall reactions in which esters and amides are formed
- Write equations in which carbonyl groups are used to produce other functional groups
- Write equations showing the hydrolysis of esters (saponification)
- Describe the structure of carbohydrates
- Describe the structure of proteins
- Describe the structure of nucleic acids

SHAPES OF ORGANIC MOLECULES

As we learned in Chapters 25 and 27, the chemical and physical properties of a substance depend on the arrangements, as well as the identities, of its atoms.

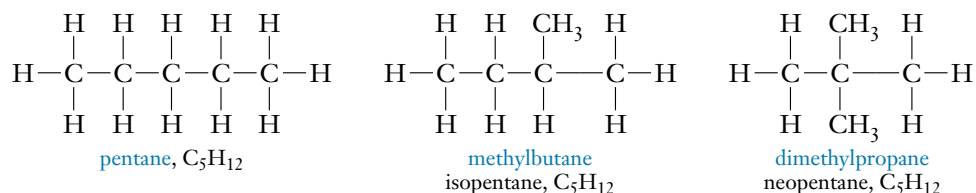
Isomers are substances that have the same number and kind of atoms—that is, the same *molecular formula*—but with different structural formulas. *Because their structures are different, isomers are different substances and have different properties.*

Isomers can be broadly divided into two major classes: constitutional isomers and stereoisomers. In Chapter 25 we discussed isomerism in coordination compounds, and in Chapter 27 we learned about some isomeric organic compounds. In this chapter we will take a more systematic look at some three-dimensional aspects of organic structures—a subject known as **stereochemistry** (“spatial chemistry”).

28-1 CONSTITUTIONAL ISOMERS

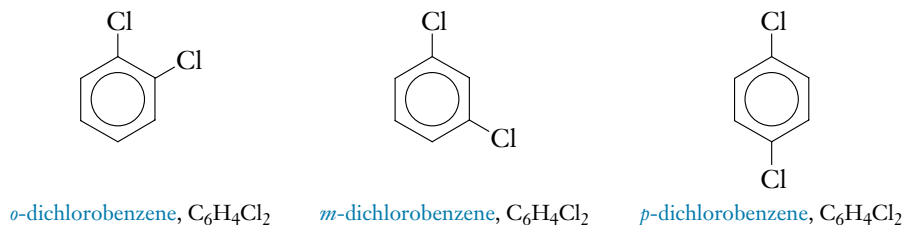
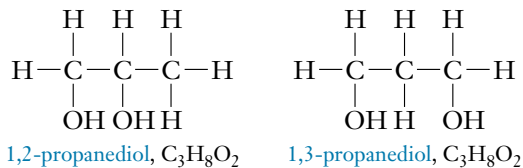
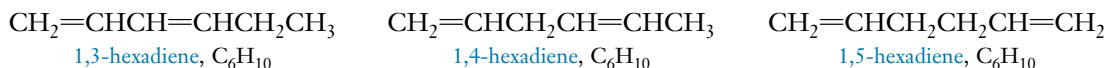
Constitutional (or **structural**) **isomers** differ in the *order* in which their atoms are bonded together.

In our studies of hydrocarbons in Sections 27-1 through 27-7, we saw some examples of constitutional isomerism. Recall that there are three isomers of C_5H_{12} .



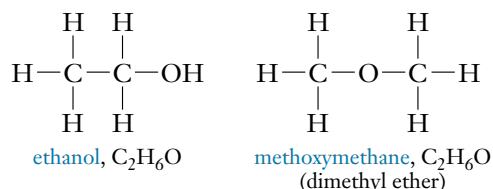
These three isomers differ in the lengths of their base chains but not in the functional groups present (i.e., only alkyl groups are present in this case). As a result, they differ somewhat in their melting and boiling points but differ only very slightly in the reactions they undergo.

In one kind of constitutional isomerism, the compounds have the same *number* and *kind* of functional groups on the *same base chain* or the *same ring* but in different positions. Isomers that vary only in the location of groups of atoms usually have very similar chemical and physical properties differing mainly in physical properties such as melting and boiling points. The following groups of isomers are examples in which the type of functional group does not change.

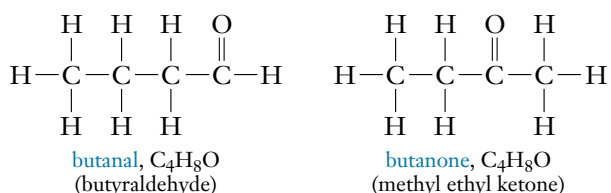


Sometimes the different order of arrangements of atoms results in different functional groups. Some examples of this type of constitutional isomerism follow.

An alcohol and an ether:



An aldehyde and a ketone:



28-2 STEREOISOMERS

In **stereoisomers** the atoms are linked together in the same atom-to-atom order, but their arrangements in space are different.

There are two types of stereoisomers: geometric and optical.

Geometric Isomers

Geometric isomers (or *cis-trans* isomers) differ only in the spatial orientation of groups about a plane or direction. Two geometric isomers have the same molecular formula, the same functional groups, the same base chain or ring, and the same order of attachment of atoms; they differ in orientation either (1) around a double bond or (2) across the ring in a cyclic compound. If the larger groups are on opposite sides of the ring or the double bond, the designation *trans* appears in the name; if they are on the same side, the designation is *cis*. We learned in Section 27-3 about the geometric isomerism associated with the double bond in alkenes such as the 1,2-dichloroethenes (Figure 27-9). Similarly, two or more substituents can be either on the same side or on opposite sides of the ring, as shown in Figures 28-1 and 28-2. This kind of isomerism is possible when substituents have replaced an H from a $-\text{CH}_2-$ unit in a ring. Because substituents on an aromatic ring are bonded in the plane of the ring, such substitutions do not lead to geometric isomerism.

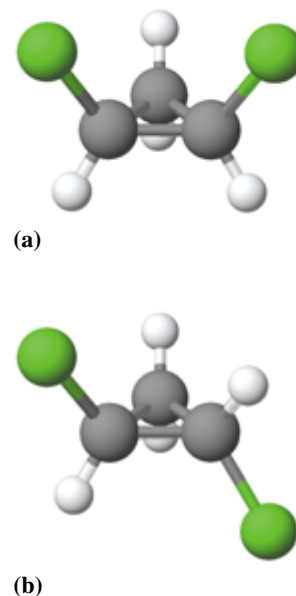


Figure 28-1 Models of (a) *cis*-dichlorocyclopropane and (b) *trans*-dichlorocyclopropane.

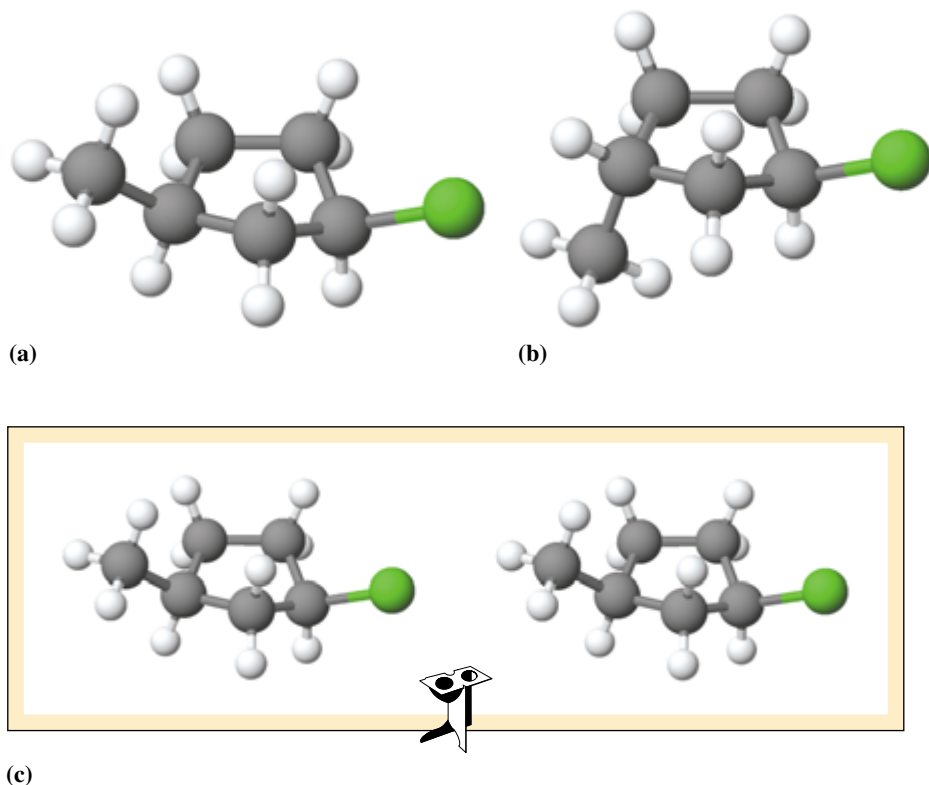


Figure 28-2 Models of (a) *cis*-1-chloro-3-methylcyclopentane, (b) *trans*-1-chloro-3-methylcyclopentane, and (c) *cis*-1-chloro-3-methylcyclopentane (stereoview).

Optical Isomers

Many objects are mirror images of each other and cannot be superimposed. Your two hands are a familiar example of this; each hand is a nonsuperimposable mirror image of the other (Figure 28-3). “Superimposable” means that if one object is placed over the other, the positions of all parts will match.

An object that is *not* superimposable with its mirror image is said to be **chiral** (from the Greek word *cheir*, meaning “hand”); an object that *is* superimposable with its mirror image is said to be **achiral**. Examples of familiar objects that are chiral are a screw, a propeller, a foot, an ear, and a spiral staircase; examples of common objects that are achiral are a plain cup with no decoration, a pair of eyeglasses, and a sock.

We speak of a screw or a propeller as being “right-handed” or “left-handed.”

Optical isomers that are nonsuperimposable mirror images of each other (chiral) are called **enantiomers** of one another. Enantiomers can exist in two forms that bear the same relationship to each other as do left and right hands.

As an example of this, consider first the two models of bromochloromethane, CH_2BrCl , shown in Figure 28-4. They are mirror images of each other, and they can be superimposed. Thus, this molecule is *achiral* and is not capable of optical isomerism. Now consider

Figure 28-3 Mirror images. Place your left hand in front of a mirror; you will observe that it looks like your right hand. We say that the two hands are mirror images of each other; each hand is in every way the “reverse” of the other. Now try placing one hand directly over the other; they are not identical. Hence, they are nonsuperimposable mirror images. Each hand is a *chiral* object.



bromochloriodomethane, CHBrClI (Figure 28-5). This molecule is not superimposable with its mirror image, so it is *chiral*, and the two forms are said to be enantiomers of each other. Any compound that contains four different atoms or groups bonded to the same carbon atom is chiral; that is, it exhibits optical isomerism. Such a carbon is said to be *asymmetric* (meaning “without symmetry”). Most simple chiral molecules contain at least one asymmetric carbon atom, although there are other ways in which molecular chirality can occur.

Stereoisomers have the same type and number of atoms, connected in the same order, but arranged differently in space. Optical isomers (enantiomers) and geometric isomers are subgroups of stereoisomers. They differ, however, in that geometric isomers have *different* physical and chemical properties, whereas optical isomers have physical properties that are identical (e.g., melting point, boiling point, and density). Optical isomers also undergo the same chemical reactions, except when they interact with other chiral compounds. Consequently, their properties in biological systems may be very different. They also often exhibit different solubilities in solvents that are composed of chiral molecules.

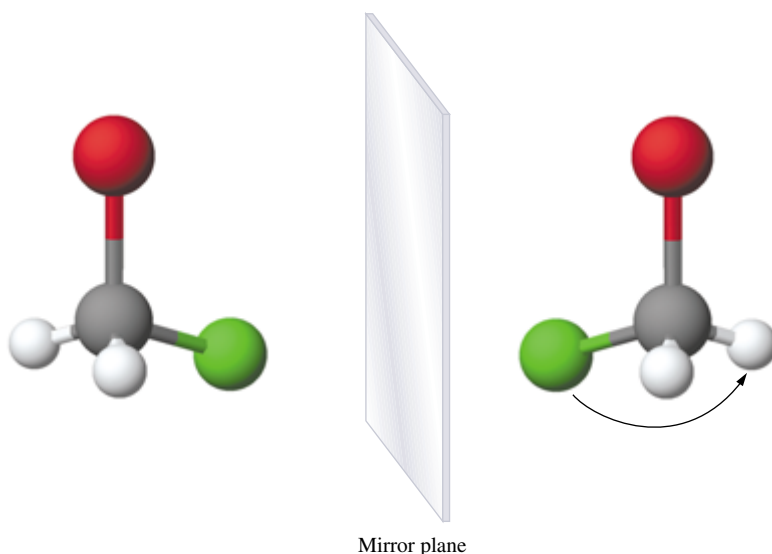
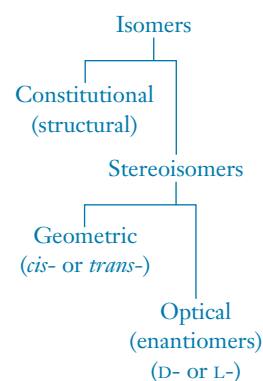
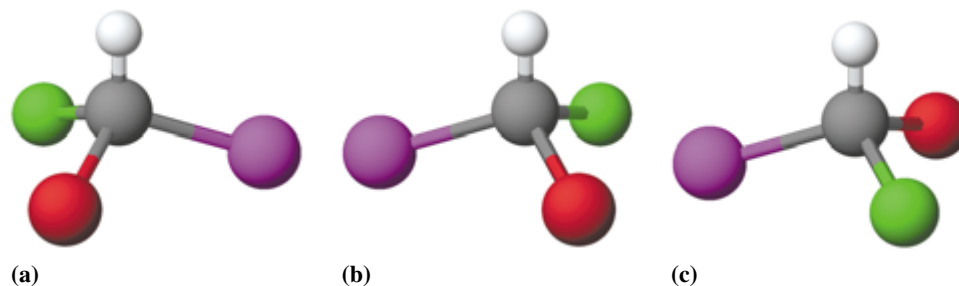


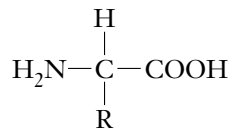
Figure 28-4 Models of two mirror-image forms of bromochloromethane, CH_2BrCl . The two models are the same (superimposable), so they are achiral. CH_2BrCl does *not* exhibit optical isomerism.

Figure 28-5 (a, b) Models of the two mirror-image forms of bromochloriodomethane, CHBrClI . (Colors: Cl, *green*; Br, *red*; I, *purple*.) (c) The same model as in (a), turned so that H and I point the same as in (b); however, the Br and Cl atoms are not in the same positions in (b) and (c). The two models in (a) and (b) cannot be superimposed on each other no matter how we rotate them, so they are chiral. These two forms of CHBrClI represent *different compounds* that are optical isomers of each other.

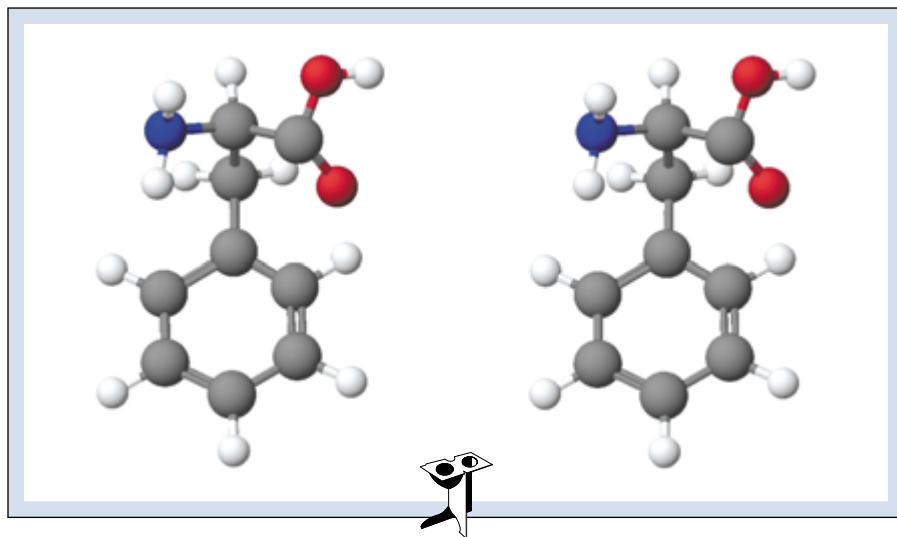


Optical isomers also differ from each other in one notable physical property: They interact with polarized light in different ways. The main features of this subject were presented in Chapter 25. Separate equimolar solutions of two optical isomers rotate a plane of polarized light (Figures 25-4 and 25-5) by equal amounts but in opposite directions. One of the optical isomers is designated as the *D*-isomer and its nonsuperimposable mirror image is designated as the *L*-isomer. The phenomenon in which a plane of polarized light is rotated by samples of either isomer is called **optical activity**. It can be measured with a polarimeter (Figure 25-5). A **racemic mixture** is a single sample containing equal amounts of the two optical isomers of a compound. Such a solution does not rotate a plane of polarized light because the equal and opposite effects of the two isomers exactly cancel. The isomers must be separated from each other to exhibit optical activity.

One very important way in which optical isomers differ chemically from one another is in their biological activities. α -Amino acids have the general structure



where *R* represents any of a number of common substituents. The central carbon atom has four atoms or groups bonded to it. In α -amino acids the four groups are all different, so each amino acid can exist as two optical isomers. The exception is glycine, in which



Stereoview of *L*-phenylalanine.

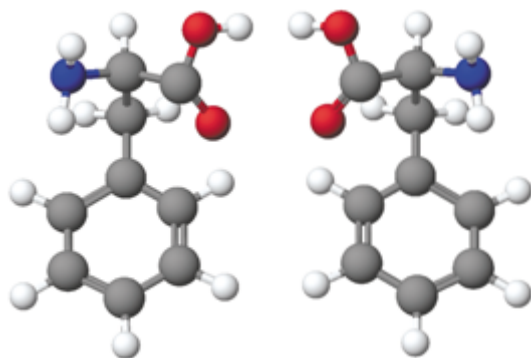


Figure 28-6 Models of the two optical isomers of phenylalanine. The naturally occurring phenylalanine in all living systems is the form shown on the left.

$R = H$. Figure 28-6 shows this mirror-image relationship for optical isomers of phenylalanine, in which $R = -CH_2C_6H_5$. All naturally occurring phenylalanine in living systems is the L-form. In fact, only one isomer of each of the various optically active amino acids is found in proteins.

28-3 CONFORMATIONS

The **conformations** of a compound differ from one another in the *extent of rotation about one or more single bonds*. The C—C single bond length, 1.54 \AA , is relatively independent of the structure of the rest of the molecule.

Rotation about a single C—C bond is possible; in fact, at room temperature it occurs very rapidly. In drawings and models, like those in Figure 28-7, it might at first appear that rotation about a single bond would be unrestricted. The electrons of the groups

As we saw in Section 27-3, rotation does not occur around carbon-carbon double bonds at room temperature.

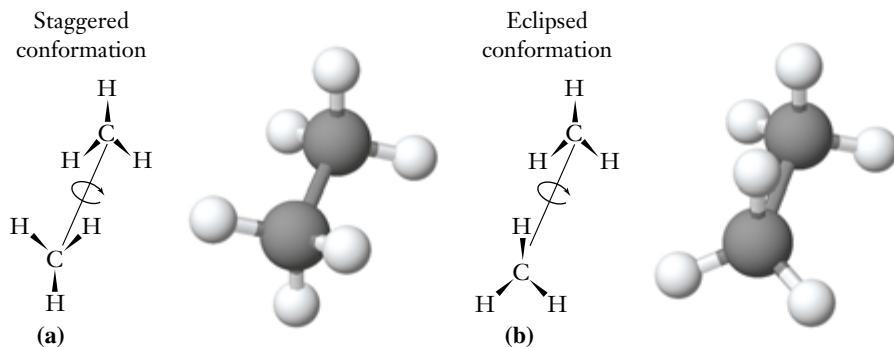


Figure 28-7 Two possible conformations of ethane. (a) Staggered. (b) Eclipsed. Rotation of one CH_3 group about the C—C single bond, as shown by the curved arrows, converts one conformation to the other.

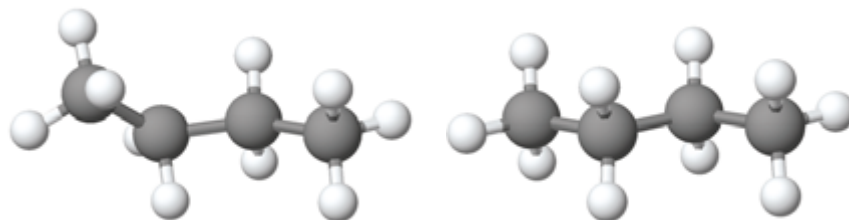


Figure 28-8 Two staggered conformations of butane, C_4H_{10} .

attached to the carbon atoms do repel one another somewhat, however. At room temperature ethane molecules possess sufficient energy to cause rapid rotation about the single carbon–carbon bond from one conformation to another. The staggered conformation of ethane is slightly more stable (of lower energy) than the eclipsed conformation (see Figure 28-7); in the eclipsed conformation there is a slightly stronger repulsion between H atoms on adjacent C atoms.

Consider the two conformations of butane shown in Figure 28-8. Again, staggered conformations are *slightly* more stable than eclipsed ones. At room temperature many conformations are present in a sample of butane.

Take care to distinguish between conformational differences and isomerism. The two forms of butane shown in Figure 28-8 are *not* isomers of each other. Either form can be converted to the other by rotation about a single bond, which is a very easy process that does not involve breaking any bonds. By contrast, at least one chemical bond would have to be broken and then re-formed to convert one isomer to another. This is most obvious with isomerism in which a conversion would change the order of attachment of the atoms. It is also true for geometric isomers that differ in orientation about a double bond. To convert such a *cis* isomer to a *trans* isomer, it would be necessary to rotate part of the molecule about the double bond. Such a rotation would move the *p* orbitals out of the parallel alignment that is necessary to form the pi component of the double bond (Section 8-13). The breaking of this pi bond is quite costly in terms of energy; it occurs only with the input of energy in the form of heat or light.

We saw in Section 27-1 that cyclohexane adopts a folded or “puckered” form. Cyclohexane actually exists in two forms called the *chair* and *twist boat* forms (Figure 28-9). The chair form is the more stable of the two because, on the average, the hydrogens (or other substituents) are farther from one another than in the boat form. Chair and boat cyclohexane, however, *are not* different compounds. Either form is easily converted into the other by rotation around single bonds without breaking any bonds, and the two forms cannot be separated. Thus, they are different *conformations* of cyclohexane.

SELECTED REACTIONS

Organic compounds can have quite different abilities to react, ranging from the limited reactivity of hydrocarbons and fluorocarbons to the great variety of reactions undergone by the thousands of organic molecules that contain several functional groups. Reactivity depends on structure. We can usually predict the kinds of reactions a compound can undergo by identifying the functional groups it contains.

In Chapter 27 we saw three fundamental classes of organic reactions and we associated the fundamental reactions with specific functional groups. In this chapter we will present some additional types of organic reactions.

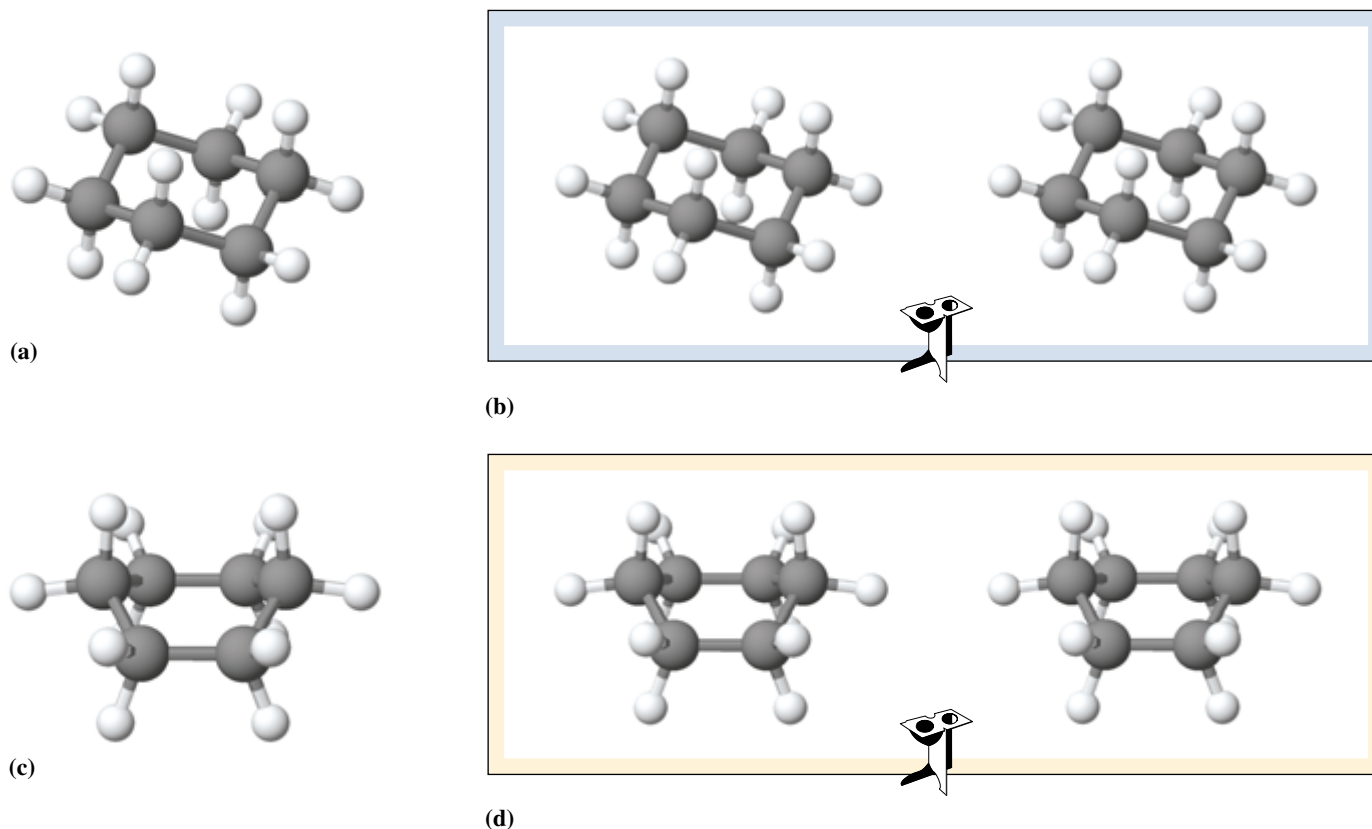


Figure 28-9 The two conformations of cyclohexane. (a) Chair, (b) stereoview of the chair conformation, (c) twist boat and (d) stereoview of the twist boat conformation.

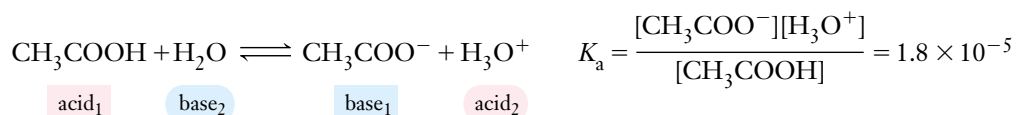
28-4 REACTIONS OF BRØNSTED–LOWRY ACIDS AND BASES

Many organic compounds can act as weak Brønsted–Lowry acids or bases. Their reactions involve the transfer of H^+ ions, or *protons* (Section 10-4). Like similar reactions of inorganic compounds, these acid–base reactions of organic acids and bases are usually fast and reversible. Consequently, we can discuss the acidic or basic properties of organic compounds in terms of equilibrium constants (Section 18-4).

In the Brønsted–Lowry description, an *acid* is a *proton donor* and a *base* is a *proton acceptor*. Review the terminology of conjugate acid–base pairs in Section 10-4.

Some Organic Acids

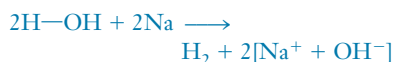
The most important organic acids contain carboxyl groups, $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—O—H}$. They are called carboxylic acids (Section 27-13). They ionize slightly when dissolved in water, as illustrated with acetic acid.





Sources of some naturally occurring carboxylic acids.

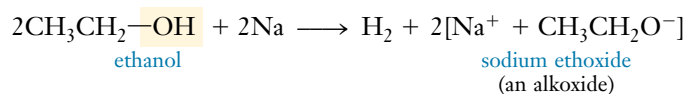
This is similar to the reaction of water with active metals.



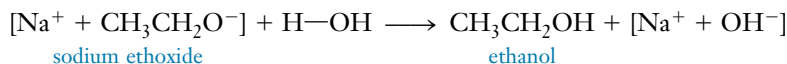
Acetic acid is 1.3% ionized in 0.10 *M* solution. Regardless of the lengths of the chains, the acid strengths of the monocarboxylic acids are approximately the same, with K_a values (in water) in the range 10^{-5} to 10^{-4} . Their acid strengths increase dramatically when electronegative substituents are present on the α -carbon atom (K_a values in water range from 10^{-3} to 10^{-1}). Compare acetic acid and the three substituted acetic acids in Table 28-1. There are two main reasons for this increase: (1) the electronegative substituents pull electron density from the carboxylic acid group, and (2) the more electronegative substituents help to stabilize the resulting carboxylate anion by spreading the negative charge over more atoms.

The alcohols are so *very weakly acidic* that they do not react with strong bases. They have about the same acid strength as water (see Table 28-1), and some of their reactions are analogous to those of water.

The reactive metals react with alcohols to form **alkoxides** with the liberation of hydrogen.



Alkoxides are strong bases that react with water (hydrolyze) to form the parent alcohol and a metal hydroxide.



Phenols react with metallic sodium to produce **phenoxides**; the reactions are analogous to those of alcohols. Because phenols are more acidic than alcohols, their reactions are more vigorous.

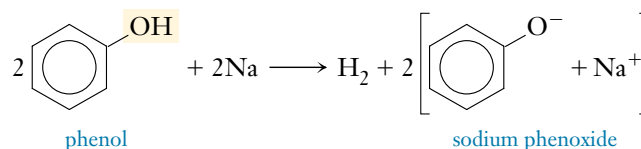


TABLE 28-1 K_a and $\text{p}K_a$ Values of Some Carboxylic Acids

Name	Formula	K_a	$\text{p}K_a$
formic acid	HCOOH	1.8×10^{-4}	3.74
acetic acid	CH_3COOH	1.8×10^{-5}	4.74
propanoic acid	$\text{CH}_3\text{CH}_2\text{COOH}$	1.4×10^{-5}	4.85
monochloroacetic acid	ClCH_2COOH	1.5×10^{-3}	2.82
dichloroacetic acid	Cl_2CHCOOH	5.0×10^{-2}	1.30
trichloroacetic acid	Cl_3CCOOH	2.0×10^{-1}	0.70
benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	6.3×10^{-5}	4.20
phenol*	$\text{C}_6\text{H}_5\text{OH}$	1.3×10^{-10}	9.89
ethanol*	$\text{CH}_3\text{CH}_2\text{OH}$	$\approx 10^{-18}$	≈ 18

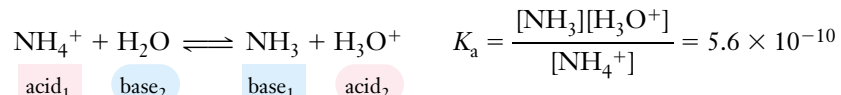
*Phenol and ethanol are not carboxylic acids. Phenol is weakly acidic compared with carboxylic acids, whereas ethanol is even weaker than water.

In Section 18-3 we defined

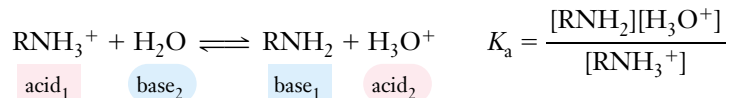
$$\text{p}K_a = -\log K_a$$

When K_a goes up by a factor of 10, $\text{p}K_a$ goes down by one unit. We see that the stronger an acid, the lower its $\text{p}K_a$ value.

We saw in Section 18-9 that salts derived from strong acids and weak bases react with water (hydrolyze) to give acidic solutions. The example given there involved the acidic character of the ammonium ion.



Similar hydrolysis reactions occur with organic ammonium salts.



We recall from Chapter 18 that the relationship $K_w = K_a K_b$ describes the strengths of any conjugate acid-base pair in aqueous solution. For instance, we can use this relationship for the $\text{CH}_3\text{NH}_3^+/\text{CH}_3\text{NH}_2$ pair (we obtain K_b for methylamine, CH_3NH_2 , from Appendix G).

$$K_{a(\text{CH}_3\text{NH}_3^+)} = \frac{K_w}{K_{b(\text{CH}_3\text{NH}_2)}} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-4}} = 2.0 \times 10^{-11}$$

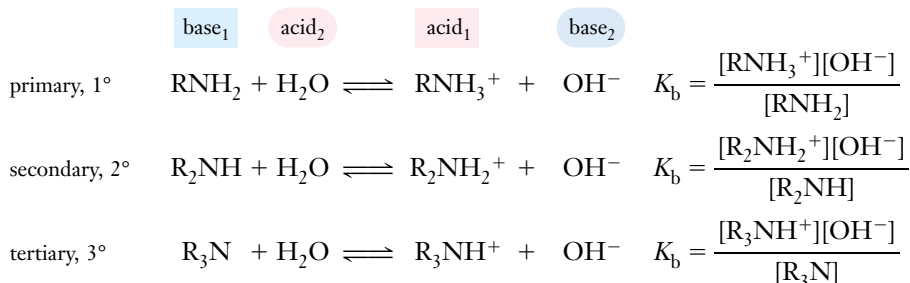
In summary, we can rank the acid strengths of these classes of organic species.

carboxylic acids > phenols > substituted ammonium ions > alcohols

Our discussion has emphasized water solutions of these acids. Many organic compounds are soluble in numerous other solvents. The properties of acids and bases in other solvents depend on solvent properties such as polarity, acidity or basicity, and polarizability.

Some Organic Bases

The most important organic bases are the amines. When dissolved in water, they are partially converted to substituted ammonium ions. This equilibrium is defined as shown in the following equations for the ionization of primary, secondary, and tertiary amines.



Most low-molecular-weight aliphatic amines are somewhat stronger bases than ammonia. Table 28-2 shows that aliphatic amines are much stronger bases than aromatic and heterocyclic amines. The basicities of amines often decrease roughly in the order tertiary > secondary > primary. Other structural factors and solvation effects, however, may outweigh this tendency, especially with tertiary amines.

The weaker a base, the stronger its conjugate acid (Section 10-4).



Reaction of sodium metal with ethanol gives sodium ethoxide and hydrogen.

The formula of a quaternary ammonium salt is R_4NCl .



Several antibacterial mouthwashes that contain a quaternary pyridinium chloride salt.

$$pK_b = -\log K_b$$

The weaker a base, the higher its pK_b value.

TABLE 28-2 Basicities of Ammonia and Some Amines in Water

Name	Formula	K_b	pK_b
ammonia	NH_3	1.8×10^{-5}	4.74
methylamine	CH_3NH_2	5.0×10^{-4}	3.30
dimethylamine	$(\text{CH}_3)_2\text{NH}$	7.4×10^{-4}	3.13
trimethylamine	$(\text{CH}_3)_3\text{N}$	7.4×10^{-5}	4.13
ethylamine	$\text{CH}_3\text{CH}_2\text{NH}_2$	4.7×10^{-4}	3.33
aniline	$\text{C}_6\text{H}_5\text{NH}_2$	4.2×10^{-10}	9.38
ethylenediamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	8.5×10^{-5} (K_{b1})	4.07
pyridine	$\text{C}_5\text{H}_5\text{N}$	1.5×10^{-9}	8.82

We can rank the base strengths of common organic bases as:

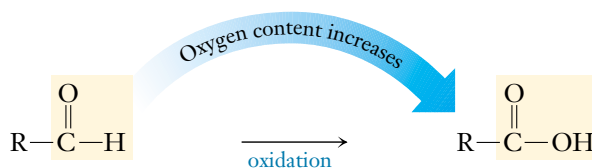
alkoxides > aliphatic amines \approx phenoxides > carboxylates \approx aromatic amines \approx heterocyclic amines

28-5 OXIDATION-REDUCTION REACTIONS

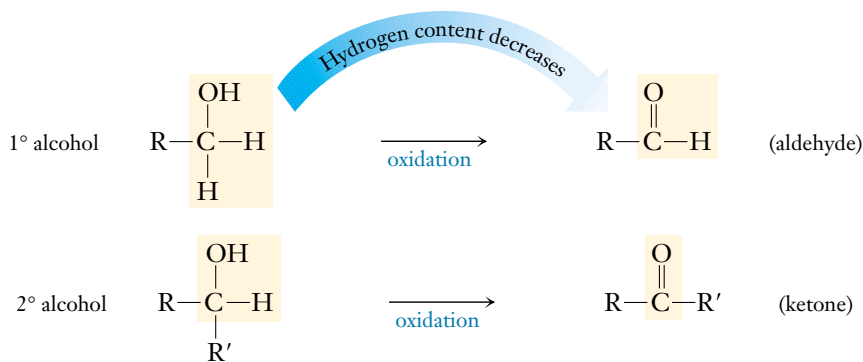
We could describe the oxidation and reduction of organic compounds in terms of changes in oxidation numbers, just as we did for inorganic compounds in Sections 4-4 through 4-5. Formal application of oxidation number rules to organic compounds often leads to fractional oxidation numbers for carbon. For organic species, the descriptions in terms of increase or decrease of oxygen or hydrogen are usually easier to apply.

Oxidation of an organic molecule usually corresponds to *increasing* its *oxygen* content or *decreasing* its *hydrogen* content. **Reduction** of an organic molecule usually corresponds to *decreasing* its *oxygen* content or *increasing* its *hydrogen* content.

For example, the oxygen content increases when an aldehyde is converted to a carboxylic acid, so this process is an oxidation.



Converting a primary alcohol to an aldehyde or a secondary alcohol to a ketone is also an oxidation; the hydrogen content decreases.



The notation R' emphasizes that the two R groups may be the same ($R = R'$, e.g., in the formation of

acetone, $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$) or different

($R \neq R'$, e.g., in the formation of methyl ethyl ketone,

$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_3$).



Research & Technology

Chemical Communication

The geometries of molecules play important roles in chemical reactivity. Molecular geometry is particularly important in a group of substances known as pheromones. *Pheromones* are chemicals used for communication between members of the same species. Pheromone activity has been observed in many forms of life, from insects to humans, and pheromone research is being done at many scholarly institutions.

If you've ever observed lines of ants moving in opposite directions, you have observed the influence of pheromones on insect behavior. When an ant finds food, it immediately heads toward its nest while secreting 9-oxy-2-decenoic acid from an abdominal gland. When other ants cross this acid trail, they compulsively follow it to the food source and carry the nourishment back to their nest. Soon, many ants will be following the acid trail and reinforcing it with their own 9-oxy-2-decenoic acid secretions. Eventually, the food source becomes exhausted, trail reinforcement stops, and the acid trail evaporates. Ants are so dependent on the acid trail that if a part of it were wiped away the ants following the trail in both directions would come to a complete stop. They wouldn't know where to go.

Perhaps an even more impressive example than the total dependence on chemical communication by ants is demonstrated with the so-called "death pheromone." Immediately upon the death of an ant, fellow ants continue to groom the dead ant and treat it as if it were still living. This attention continues until the dead ant's body produces the death pheromone, 10-octadecenoic acid. On sensing this pheromone, colleagues carry the dead ant to the nearest garbage site. Interestingly, if 10-octadecenoic acid is applied to a living ant, the living ant is similarly dumped into the garbage. The discarded ant will quickly return only to be carried off again, and this process continues until the death pheromone evaporates.

Because pheromones are used by female insects to indicate their state of fertile readiness, pheromones have proven to be an effective weapon in controlling some crop-damaging insects. For example, when a specific mating pheromone is applied to crops, male cotton bollworms and female tobacco budworms compulsively mate with one another. Because of physical incompatibilities, their bodies become interlocked and both insects eventually die. Less drastic uses of pheromones to control crop damage involve baiting traps



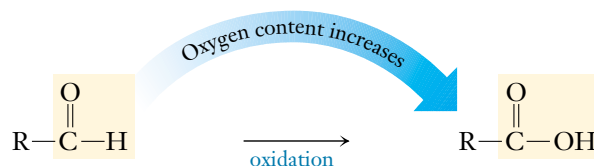
with sex pheromones to lure and trap male insects. Trapping males eventually slows reproduction, and the insect population may decrease to controllable levels. Some of these sex pheromones are so powerful that a single drop has the potential of attracting millions of males. In fact, some male insects can detect a single molecule of female pheromone from a great distance and then successfully seek out and find the female.

Chemical communication is not confined to the insect world. Female dogs secrete the chemical *p*-hydroxybenzoate to attract males. Just like the ants and cotton bollworms, who are dependent on detecting chemicals for their actions, male dogs will attempt to mate with various objects to which *p*-hydroxybenzoate has been applied.

When we examine the molecular structures and functional groups of known pheromones, we find that they have little in common. Some pheromones contain stereoisomers, and some insects can distinguish between the stereoisomers. The structures of pheromones play vital roles in their activity. Part of the structure is an upper limit of about 20 carbon atoms, a limit probably imposed by Graham's Law. Most pheromones must travel through the air; those with low molecular weights are often more volatile. Scientists suspect that the physical motions of pheromone molecules, which are also a function of molecular structure, play an important role in the communication mechanism.

Ronald DeLorenzo
Middle Georgia College

An aldehyde can be oxidized to a carboxylic acid.



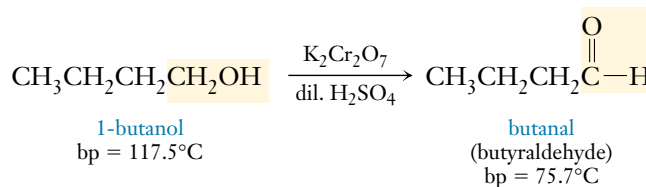
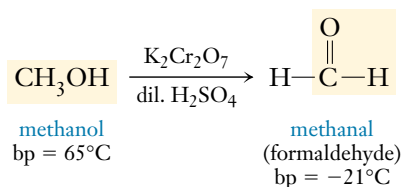
In each of these “oxidation” reactions, something else must act as the oxidizing agent (which is reduced). These oxidizing agents are often inorganic species such as dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$. The reverse of each of the preceding reactions is a reduction of the organic molecule. In this reverse reaction, the reducing agent (the substance that is oxidized) is often an inorganic compound.

Let us look at a few important types of organic oxidations and reductions.

Oxidation of Alcohol

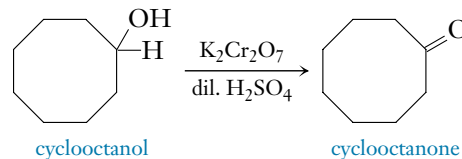
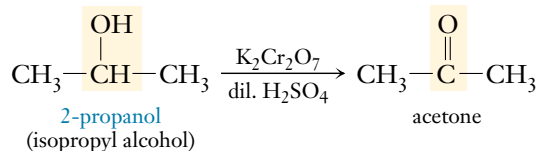
Aldehydes can be prepared by the oxidation of *primary* alcohols. The reaction mixture is heated to a temperature slightly above the boiling point of the aldehyde so that the aldehyde distills out as soon as it is formed. Potassium dichromate in the presence of dilute sulfuric acid is the common oxidizing agent.

Aldehydes are easily oxidized to carboxylic acids. They must therefore be removed from the reaction mixture as soon as they are formed. Aldehydes have lower boiling points than the alcohols from which they are formed, so the removal of aldehydes is easily accomplished.



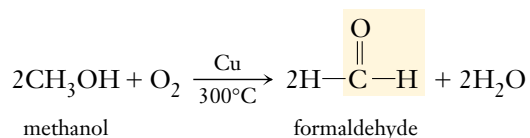
Ketones are not as easily oxidized as aldehydes, because oxidation of a ketone requires the breaking of a carbon-carbon bond. Thus, it is not as important that they be quickly removed from the reaction mixture.

Ketones can be prepared by the oxidation of *secondary* alcohols. Ketones are not as susceptible to oxidation as are aldehydes.



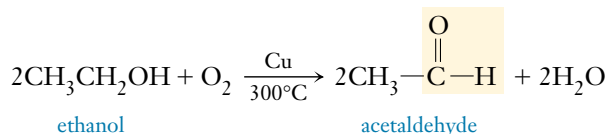
These two reactions can also be described as a type of *elimination* reaction (Section 27-18). Two hydrogen atoms are eliminated to form a C=O double bond.

Aldehydes and ketones can be prepared by a catalytic process that involves passing alcohol vapors and air over a copper gauze or powder catalyst at approximately 300°C . Here the oxidizing agent is O_2 .



Formaldehyde is quite soluble in water; the gaseous compound can be dissolved in water to give a 40% solution.

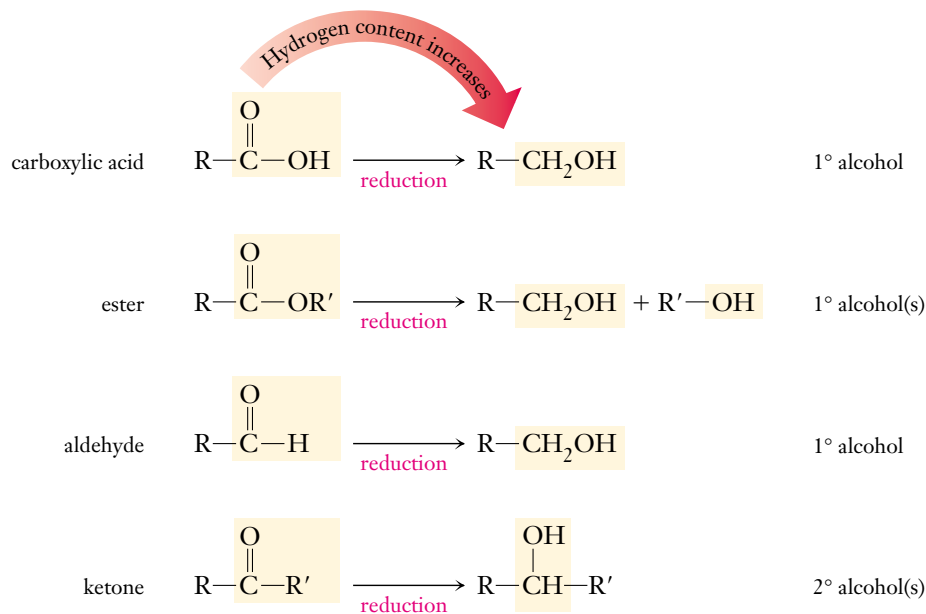
Acetaldehyde can be prepared by the similar oxidation of ethanol.



Oxidation of tertiary alcohols is difficult because the breaking of a carbon–carbon bond is required. Such oxidations are of little use in synthesis.

Reduction of Carbonyl Compounds

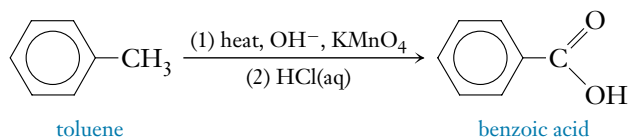
Reduction of a variety of compounds that contain the carbonyl group provides synthetic methods to produce primary and secondary alcohols. A common, very powerful reducing agent is lithium aluminum hydride, LiAlH_4 ; other reducing agents include sodium in alcohol and sodium borohydride, NaBH_4 .



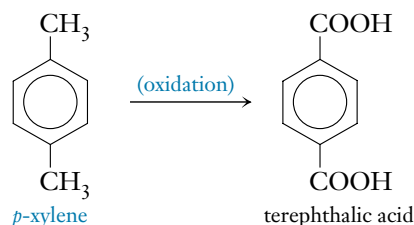
Organic reactions are sometimes written in extremely abbreviated form. This is often the case when a variety of common oxidizing or reducing agents will accomplish the desired conversion.

Oxidation of Alkylbenzenes

Unsubstituted aromatic hydrocarbons (Sections 27-5, 27-6) are quite resistant to oxidation by chemical oxidizing agents. The reactions of strong oxidizing agents with alkylbenzenes illustrate the stability of the benzene ring system. Heating toluene with a basic solution of KMnO_4 results in a nearly 100% yield of benzoic acid. The ring itself remains intact; only the nonaromatic portion of the molecule is oxidized.



Two such alkyl groups on an aromatic ring are oxidized to give a diprotic acid, as the following example illustrates.



Terephthalic acid is used to make “polyesters,” an important class of polymers (Section 27-19).

Combustion of Organic Compounds

The most extreme oxidation reactions of organic compounds occur when they burn in O_2 . Such *combustion reactions* (Section 6-8) are highly exothermic. When the combustion takes place in excess O_2 , the products are CO_2 and H_2O . Examples of alkane combustions are

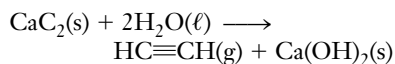


The **heat of combustion** is the amount of energy *liberated* per mole of hydrocarbon burned. Heats of combustion are assigned positive values *by convention* (Table 28-3) and are therefore equal in magnitude, but opposite in sign, to ΔH^0 values for combustion reactions. The combustion of hydrocarbons produces large volumes of O_2 and H_2O in addition to large amounts of heat. The rapid formation of these gases at high temperature and pressure drives the pistons or turbine blades in internal combustion engines.

Recall that ΔH^0 is negative for an exothermic process.



Acetylene is produced by the slow addition of water to calcium carbide.



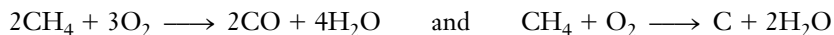
The light of one kind of headlamp used by miners and cave explorers is given off by the combustion of acetylene.

TABLE 28-3 Heats of Combustion of Some Alkanes

Hydrocarbon	Heat of Combustion		
	<i>kJ/mol</i>	<i>J/g</i>	
methane	CH_4	891	55.7
propane	C_3H_8	2220	50.5
pentane	C_5H_{12}	3507	48.7
octane	C_8H_{18}	5450	47.8
decane	$\text{C}_{10}\text{H}_{22}$	6737	47.4
ethanol*	$\text{C}_2\text{H}_5\text{OH}$	1372	29.8

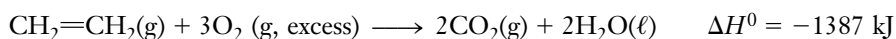
*Not an alkane; included for comparison only.

In the absence of sufficient oxygen, partial combustion of hydrocarbons occurs. The products may be carbon monoxide (a very poisonous gas) or carbon (which deposits on spark plugs, in the cylinder head, and on the pistons of automobile engines). Many modern automobile engines now use microcomputer chips and sensors to control the air supply and to optimize the fuel/O₂ ratio. The reactions of methane with insufficient oxygen are



All hydrocarbons undergo similar reactions.

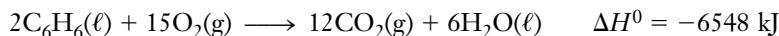
The alkenes, like the alkanes, burn in *excess* oxygen to produce carbon dioxide and water in exothermic reactions.



When an alkene (or any other unsaturated organic compound) is burned in air, a yellow, luminous flame is observed, and considerable soot (unburned carbon) is formed. This reaction provides a qualitative test for unsaturation. Saturated hydrocarbons burn in air without forming significant amounts of soot.

Acetylene lamps are charged with calcium carbide. Very slow addition of water produces acetylene, which is burned as it is produced. Acetylene is also used in the oxyacetylene torch for welding and cutting metals. When acetylene is burned with oxygen, the flame reaches temperatures of about 3000°C.

Like other hydrocarbons, the *complete combustion* of aromatic hydrocarbons, such as benzene, releases large amounts of energy.

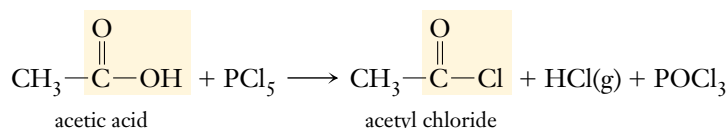
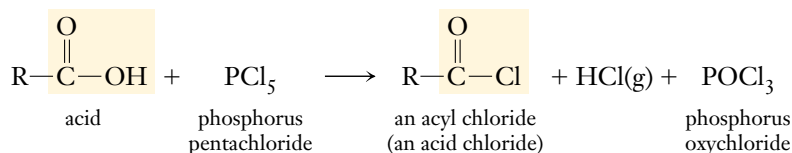


Because they are so unsaturated, aromatic hydrocarbons burn *in air* with a yellow, sooty flame.



28-6 FORMATION OF CARBOXYLIC ACID DERIVATIVES

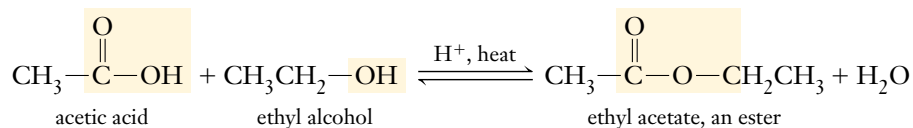
The carboxylic acid derivatives introduced in Section 27-14 can be formed by *substitution* of another group in place of —OH in the carboxyl group. The acyl halides (acid halides) are usually prepared by treating acids with PCl₃, PCl₅, or SOCl₂ (thionyl chloride). In general terms, the reaction of acids with PCl₅ may be represented as



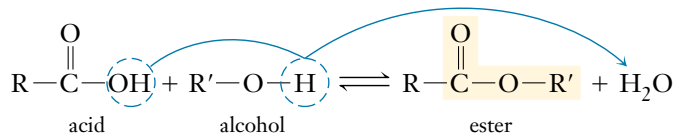
The acyl halides are much more reactive than their parent acids. Consequently, they are often used in reactions to introduce an acyl group into another molecule.

When an organic acid is heated with an alcohol, an equilibrium is established with the resulting *ester* and water. The reaction is catalyzed by traces of strong inorganic acids, such as a few drops of concentrated H₂SO₄.

Hexane, C₆H₁₄, an alkane, burns cleanly in air to give CO₂ and H₂O (*top*). 1-Hexene, C₆H₁₂, an alkene, burns with a flame that contains soot (*middle*). Burning *o*-xylene, an aromatic hydrocarbon, produces large amounts of soot (*bottom*).

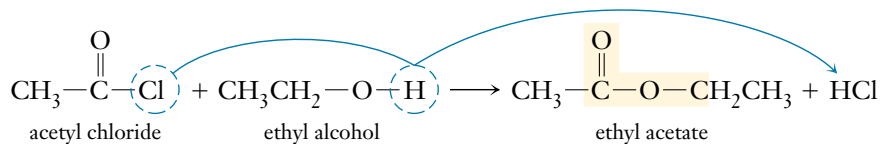


In general terms, the reaction of an organic acid and an alcohol may be represented as

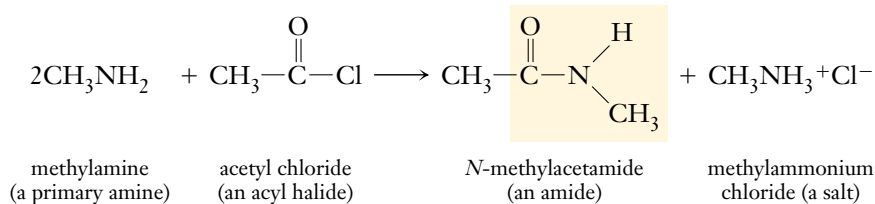


(R and R' may be the same or different groups.)

Reactions between acids and alcohols are usually quite slow and require prolonged boiling (refluxing). The reactions between most acyl halides and most alcohols, however, occur very rapidly without requiring the presence of an acid catalyst.



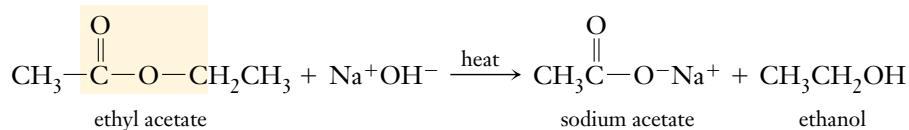
Amides are usually *not* prepared by the reaction of an amine with an organic acid. Acyl halides react readily with primary and secondary amines to produce amides. The reaction of an acyl halide with a primary or secondary amine produces an amide and a salt of the amine.



In this preparation, one half of the amine is converted to an amide and the other half to a salt.

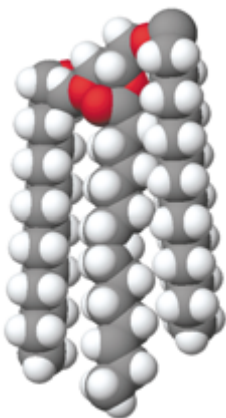
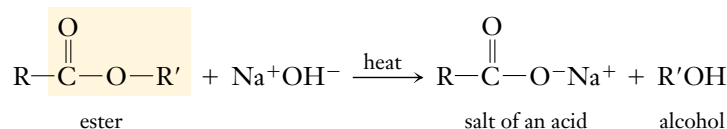
28-7 HYDROLYSIS OF ESTERS

Because most esters are not very reactive, strong reagents are required for their reactions. Esters can be hydrolyzed by refluxing with solutions of strong bases.



The hydrolysis of esters in the presence of strong bases is called **saponification** (soap-making).

In general terms, the hydrolysis of esters may be represented as




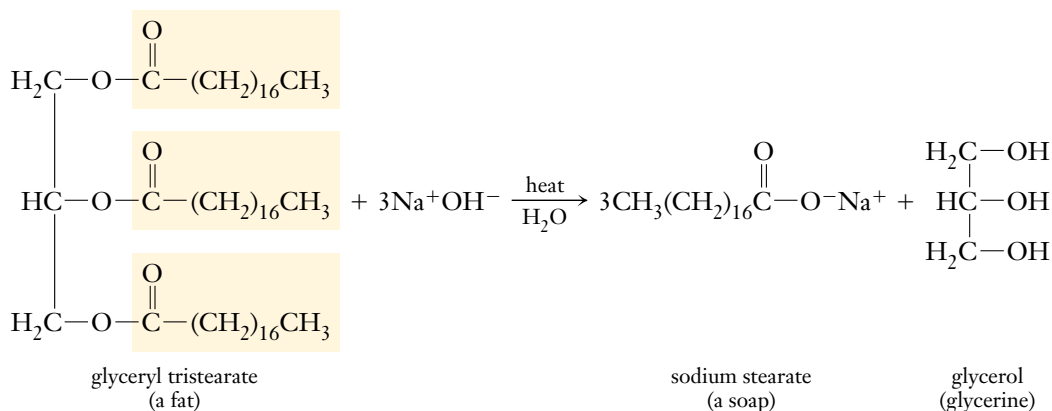
Tripalmitin, a triglyceride.



American pioneers prepared their soaps by boiling animal fat with an alkaline solution obtained from the ashes of hardwood. The resulting soap could be “salted out” by adding sodium chloride, making use of the fact that soap is less soluble in a salt solution than in water.

Like other esters, fats and oils (Section 27-14) can be hydrolyzed in strongly basic solution to produce salts of the acids and the trihydric alcohol glycerol. The resulting sodium salts of long-chain fatty acids are soaps. In Section 14-18 we described the cleansing action of soaps and detergents.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 11.7, Functional Groups 2: Fats and Oils.



BIOPOLYMERS

As we study the molecules and ions in living organisms such as humans, we learn that substances with a huge range of sizes and complexities are involved. These include small molecules and ions such as sodium ions, trace metals, ketones, alcohols, and carboxylic acids. Steroids, hormones, vitamins, fats, and oils are somewhat larger. As we continue up the scale of sizes of substances present in living systems, we encounter the mammoth polymers (biopolymers, or polymers found in biological systems). Concepts discussed in the first 27 chapters and the first half of this chapter can be applied to large molecules and ions as well as small ones. In the following sections we will look briefly at three classes of biopolymers (carbohydrates, proteins, and nucleic acids), keeping in mind that almost all of the chemical concepts used in these discussions were introduced earlier in this text.

28-8 CARBOHYDRATES

The word *saccharide* comes from the Latin *saccharum*, for “sugar” or “sweet.”

Carbohydrates have the general formula $C_n(H_2O)_m$, thus the name hydrated carbons or, more commonly, carbohydrates. **Monosaccharides**, or simple sugars, are the monomers from which more complex carbohydrates are constructed. The most important simple sugars contain either five or six carbon atoms. Monosaccharides that contain an aldehyde group are called **aldoses**, and those that contain a ketone group are called **ketoses**. The most commonly encountered monosaccharide is glucose, $C_6H_{12}O_6$, also known as dextrose or blood sugar. Figure 28-10a shows glucose as it is often written to emphasize its aldehyde functional group. We can see from this formula that carbons 2, 3, 4, and 5 in glucose each have four *different* groups and are, therefore, chiral. Each different monosaccharide has a unique arrangement of atoms about its chiral atoms. Some important monosaccharides are shown in Table 28-4.

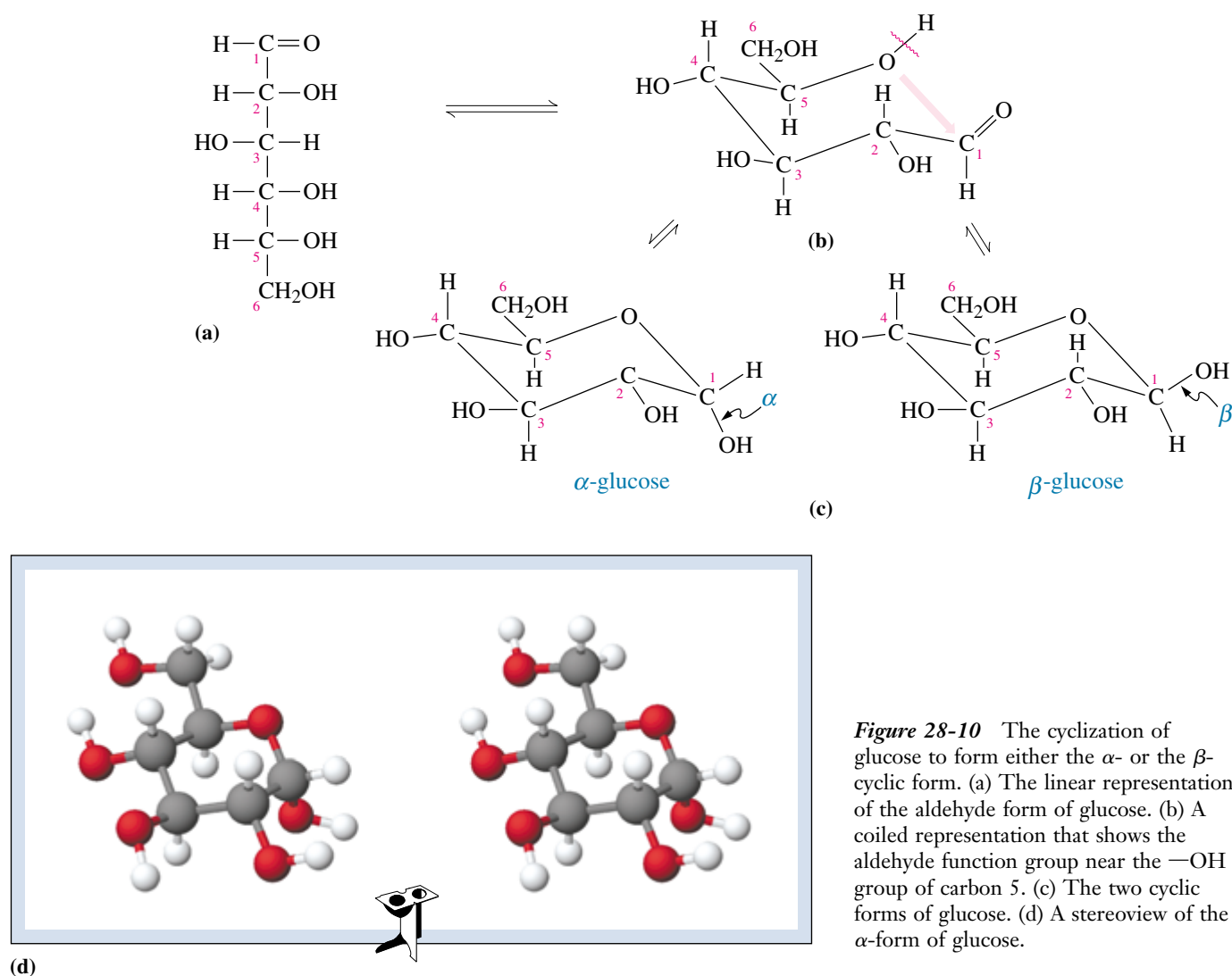


Figure 28-10 The cyclization of glucose to form either the α - or the β -cyclic form. (a) The linear representation of the aldehyde form of glucose. (b) A coiled representation that shows the aldehyde function group near the —OH group of carbon 5. (c) The two cyclic forms of glucose. (d) A stereoview of the α -form of glucose.

TABLE 28-4 Some Important Monosaccharides

Five Carbon Atom Monosaccharides			
ribose $\begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	arabinose $\begin{array}{c} \text{CHO} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	ribulose $\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	
Six Carbon Atom Monosaccharides			
glucose $\begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	mannose $\begin{array}{c} \text{CHO} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	galactose $\begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	fructose $\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$

Besides their aldehyde or ketone form, saccharides can also exist in a cyclic form. Figure 28-10 shows the interconversion of glucose between its linear form and its cyclic form. Figure 28-10b shows the molecule rotated into a conformation that brings the hydroxyl group of carbon 5 near the aldehyde carbon. In this conformation, a reversible reaction occurs in which a hydrogen is moved from the hydroxyl group to the carbonyl oxygen, and an ether bond is formed between the two carbons (Figure 28-10c). During the formation of the ether bond, a ring is also formed and carbon atom 1 becomes chiral. This new chiral center can exist as either of two isomers; the resulting stereoisomers are referred to as α - or β -forms.

Most naturally occurring carbohydrates contain more than one monosaccharide unit. Complex carbohydrates are formed when two or more monosaccharides are linked. This linkage between two monosaccharides occurs by elimination of a molecule of water and the formation of an ether bond between two of the cyclic structures, as shown in Figure 28-11. The newly formed C—O bond linking the rings is called the **glycosidic bond**. Figure 28-11 illustrates the linkage of α -glucose and β -fructose to form sucrose. Fructose is a ketone-containing carbohydrate that exists in the cyclic form shown. A **disaccharide** is a molecule consisting of two monosaccharides joined together by a glycosidic bond. Sucrose is a disaccharide; two other disaccharides, each involving only glucose units, are shown in Figure 28-12. In such a molecule, the C—O—C linkage between the monosaccharide units involves carbon number 1 or 2 of one monosaccharide and carbon number 1, 4, or 6 of the other monosaccharide. The arrangement about the carbon number 1 or 2 is what is described as the α - or β -linkage. Using these notations, we describe maltose as consisting of two glucose units joined by an α -1,4-linkage. Lactose has a β -1,4-linkage. Table 28-5 lists some of the common sugars.

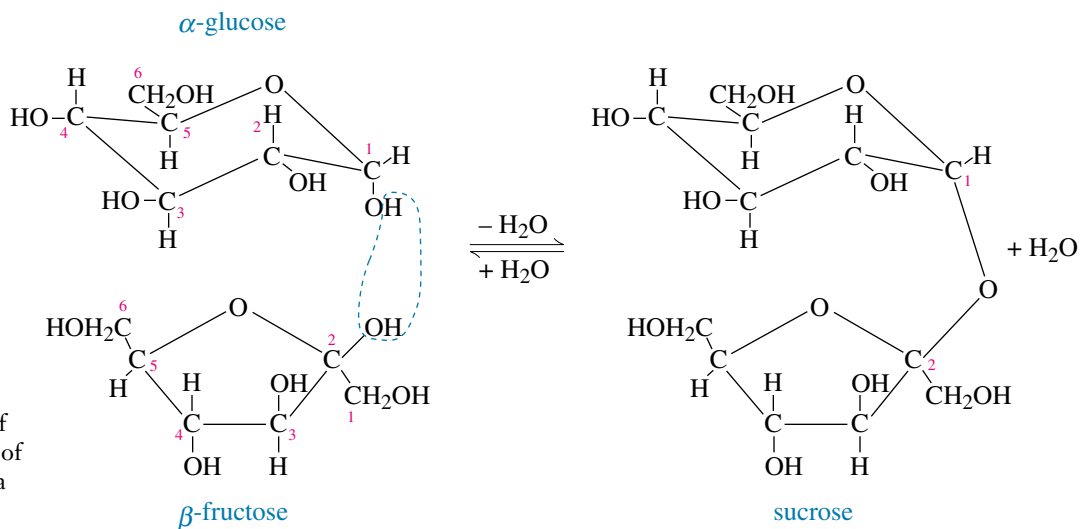


Figure 28-11 Formation of sucrose by the condensation of an *α*-glucose molecule with a *β*-fructose molecule.

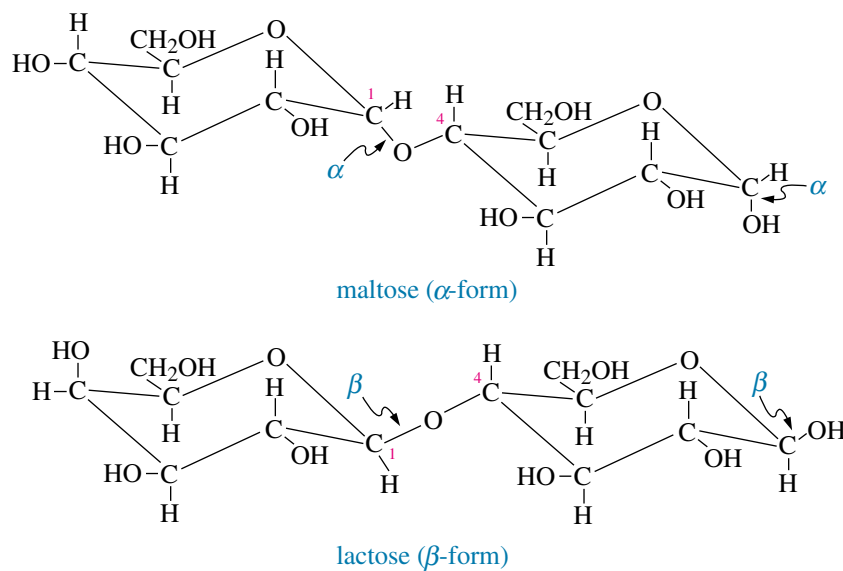


Figure 28-12 Two disaccharides: maltose and lactose. Each involves two glucose units. Maltose has *α*-1,4-linkage and lactose has *β*-1,4-linkage.

TABLE 28-5 Sweetness of Common Sugars Relative to Sucrose

Substance	Sweetness Relative to Sucrose at 1.00
lactose (milk sugar, a disaccharide)	0.16
galactose (a monosaccharide in milk sugar)	0.32
maltose (a disaccharide used in beer making)	0.33
glucose (dextrose, a common monosaccharide)	0.74
sucrose (table sugar, a disaccharide)	1.00
fructose (fruit sugar, a monosaccharide)	1.74

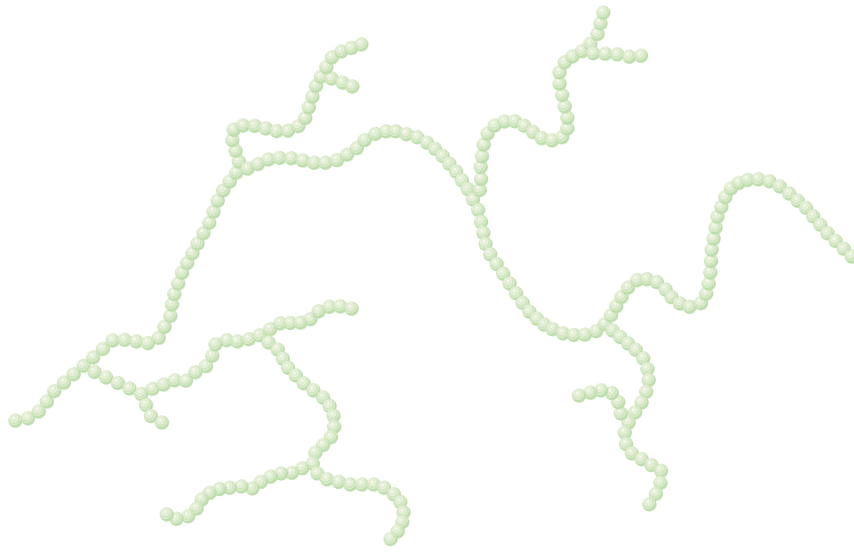


Figure 28-13 Amylopectin, or glycogen.

A carbohydrate that contains three monosaccharides is called a **trisaccharide**, and so on. Carbohydrates that contain from four to ten monosaccharides are usually called by the general term **oligosaccharides**. Carbohydrates that contain larger numbers of monosaccharide units are called **polysaccharides**.

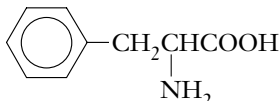
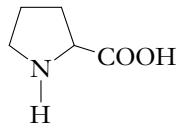
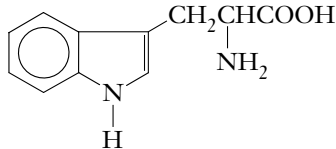
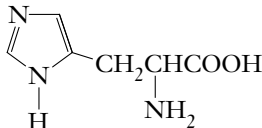
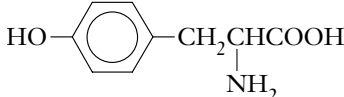
Amylose, a type of starch found in plants, is a polysaccharide. It consists of a linear combination of several thousand glucose units joined by α -1,4-linkages. In our bodies we store glucose in a form known as amylopectin, or glycogen. Glycogen is similar to amylose; it typically contains about 30,000 glucose monomers with the majority linked via an α -1,4-linkage but, unlike amylose, it contains occasional branches via α -1,6-linkages. In Figure 28-13 each sphere represents a glucose unit. All links are α -1,4 except where branching takes place; branching utilizes an α -1,6-linkage. Our digestive systems contain enzymes (see Sections 16-9, 28-9) that can break this biopolymer, glycogen, into its monomeric glucose units as we need energy to drive other biological processes.

Cellulose, the structural biopolymer found in plants, contains the β -1,4-linkage of glucose units. Our digestive systems are incapable of breaking the β -1,4-linkage, so we cannot utilize cellulose as a source of stored glucose. Some animals such as termites and cattle are able to digest cellulose.

Bacteria in the digestive tracts of termites and cattle produce an enzyme that allows them to digest the cellulose in wood and grass.

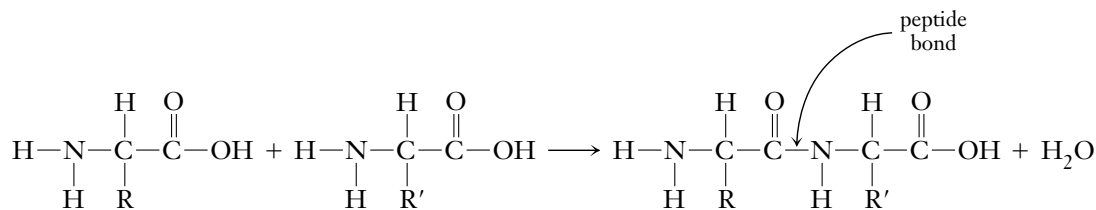


TABLE 28-6 *The 20 Common Amino Acids Found in Proteins*

Nonpolar R Groups			
alanine (Ala)	$\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$	phenylalanine (Phe)	
glycine (Gly)	$\text{HCH}(\text{NH}_2)\text{COOH}$	proline (Pro)	
isoleucine (Ile)	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{COOH}$	tryptophan (Trp)	
leucine (Leu)	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}$	valine (Val)	$(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{COOH}$
methionine (Met)	$\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$		
Polar, Neutral R Groups			
asparagine (Asn)	$\text{H}_2\text{NC}(\text{O})\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$	serine (Ser)	$\text{HOCH}_2\text{CH}(\text{NH}_2)\text{COOH}$
glutamine (Gln)	$\text{H}_2\text{NC}(\text{O})\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$	threonine (Thr)	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}$
Polar, Acidic R Groups		Polar, Basic R Groups	
aspartic acid (Asp)	$\text{HOOCCH}_2\text{CH}(\text{NH}_2)\text{COOH}$	arginine (Arg)	$\text{H}_2\text{NC}(\text{NH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
glutamic acid (Glu)	$\text{HOOCCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$	histidine (His)	
cysteine (Cys)	$\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$	lysine (Lys)	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
tyrosine (Tyr)			

28-9 POLYPEPTIDES AND PROTEINS

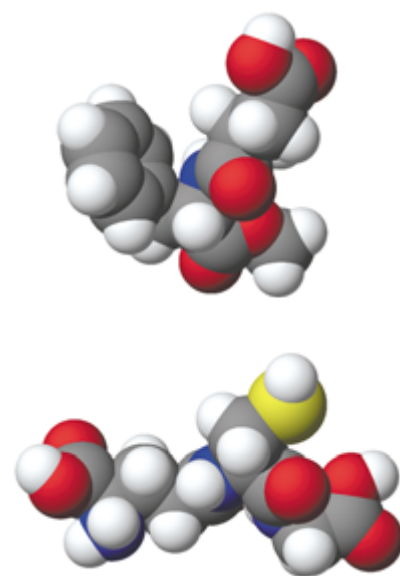
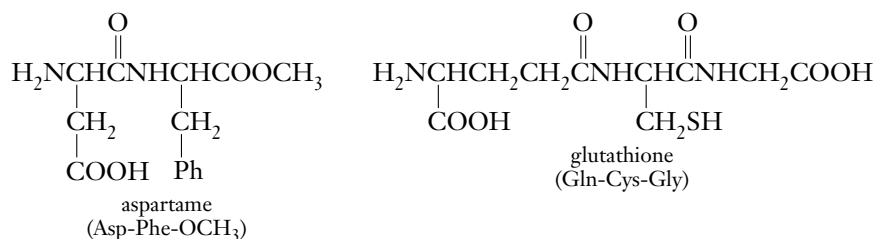
Two amino acids can react to form an amide bond (see Section 27-19). Compounds formed by the linking of small numbers of amino acids are called **peptides**, and the amide bond linking the amino acid monomers is called the **peptide bond**.



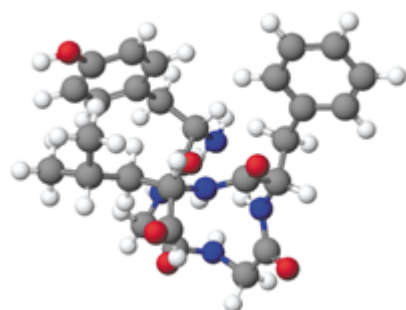
Prefixes di-, tri-, and so on are used to indicate the number of amino acid monomers that are joined to form the peptide. The compound indicated in the preceding formula is a **dipeptide**.

Twenty different α -amino acids (see Section 27-13) are found widely in nature. Each amino acid is commonly given a three-letter abbreviation. These acids differ in the R groups attached to the α -carbon (the carbon adjacent to the $-\text{COOH}$ group). Differences in R groups lead to differences in the properties of the α -amino acids. The amino acids are usually classified by their R groups, or side chains, according to two criteria. The first classification depends on whether the R groups are polar or nonpolar, the second describes whether the R group contains an acidic or basic group. The 20 common amino acids are shown, according to these classifications, in Table 28-6.

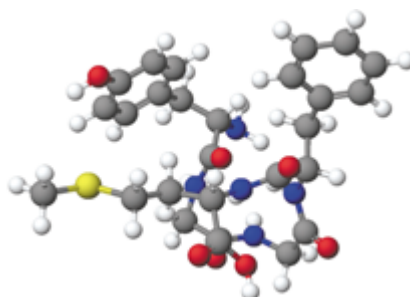
Many small peptides are known to have physiological significance. Aspartame, a common artificial sweetener, is a dipeptide. Glutathione, a tripeptide, acts as a scavenging agent for harmful oxidizing agents believed to cause cancer. Enkephalins, which are naturally occurring analgesics (pain relievers) that occur in the brain, are pentapeptides. The antibiotics gramicidin-S and tyrocidine A are cyclic decapeptides (i.e., they contain ten amino acids linked into a ring by peptide bonds) produced by a bacterium.



Space-filling models of aspartame (*top*) and glutathione (*bottom*).



Tyr-Gly-Gly-Phe-Leu
leucine enkephalin



Tyr-Gly-Gly-Phe-Met
methionine enkephalin

Some organisms such as bacteria also produce D-amino acids.

A **protein** is a biopolymer, of molecular weight typically 5000 g/mol or greater, consisting of one or more polypeptide chains. The α -amino acids that occur in nearly all proteins are the L optical isomer.

An **enzyme** is a protein that catalyzes a biological reaction.

Each protein consists of one or more polypeptide chains with a unique sequence of amino acids. The order of these monomers is termed the **primary structure** of the protein. The many possible interactions between different amino acids in the polypeptide chain cause each protein molecule to adopt a characteristic shape, usually depending on its environment. The **secondary structure** of a protein is the arrangement in space of the polypeptide backbone, without reference to the conformations of the side chains (R groups). Myoglobin is the oxygen-storing protein in muscles. Its amino acid sequence (primary structure) and a three-dimensional representation of its secondary structure are shown in Figure 28-14. The **tertiary structure** of a protein describes the overall shape of the protein, including the side chains and any other nonpeptide components of the protein. Myoglobin is referred to as a globular protein. Some proteins consist of multiple polypeptide units called *subunits*. These subunits are held to one another by noncovalent interactions such as hydrogen bonding, dipole–dipole interactions, or ionic attractions, to form the **quaternary structure** of the protein.

Val-Leu-Ser-Glu-Gly-Glu-Trp-Gln-Leu-Val-Leu-His-Val-Trp-Ala-Lys-Val-
Glu-Ala-Asp-Val-Ala-Gly-His-Gly-Gln-Asp-Ile-Leu-Ile-Arg-Leu-Phe-Lys-
Ser-His-Pro-Glu-Thr-Leu-Glu-Lys-Phe-Asp-Arg-Phe-Lys-His-Leu-Lys-
Thr-Glu-Ala-Glu-Met-Lys-Ala-Ser-Glu-Asp-Leu-Lys-Lys-His-Gly-Val-Thr-
Val-Leu-Thr-Ala-Leu-Gly-Ala-Ile-Leu-Lys-Lys-Lys-Gly-His-His-Glu-Ala-
Glu-Leu-Lys-Pro-Leu-Ala-Gln-Ser-His-Ala-Thr-Lys-His-Lys-Ile-Pro-Ile-Lys-
Tyr-Leu-Glu-Phe-Ile-Ser-Glu-Ala-Ile-Ile-His-Val-Leu-His-Ser-Arg-His-
Pro-Gly-Asn-Phe-Gly-Ala-Asp-Ala-Gln-Gly-Ala-Met-Asn-Lys-Ala-Leu-
Glu-Leu-Phe-Arg-Lys-Asp-Ile-Ala-Ala-Lys-Tyr-Lys-Glu-Leu-Gly-Tyr-Gln-Gly

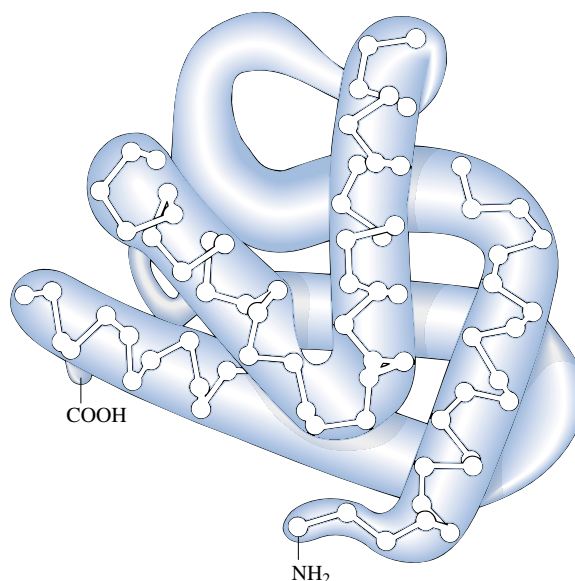
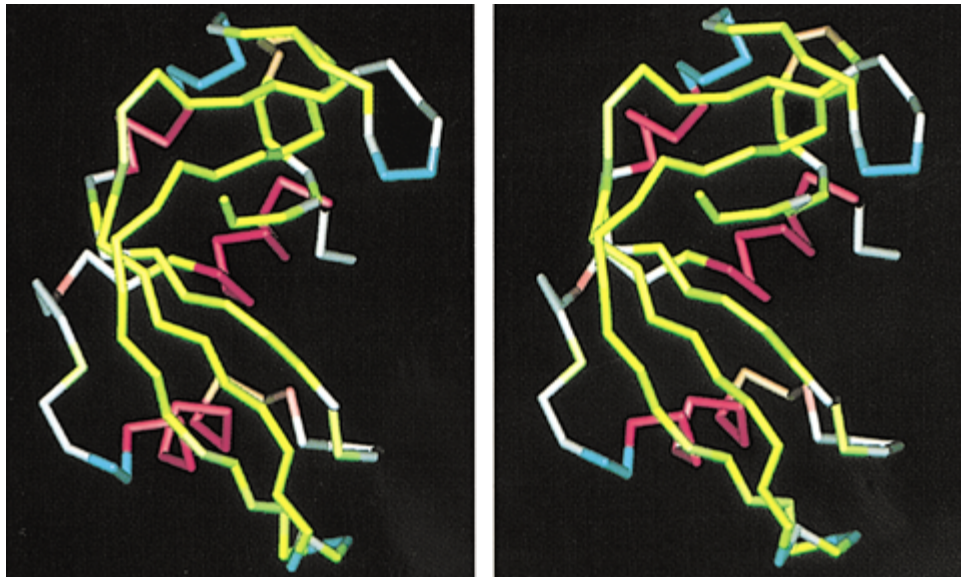


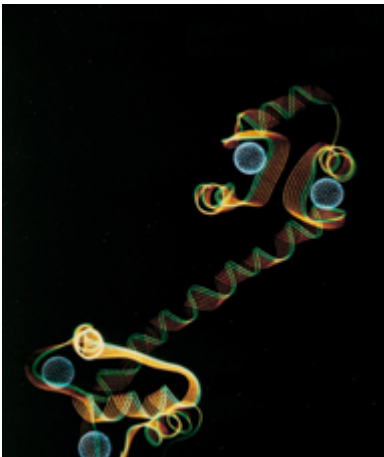
Figure 28-14 The amino acid sequence and the three-dimensional representation of myoglobin, the oxygen-storing protein in muscles.

A model of the protein ribonuclease A in stereoview. The different colors represent regions within the folding and coiling patterns.



The folding and coiling patterns of a protein often affect its biological activity, for instance, its effectiveness as an enzyme. Forces such as heat and ionic environment can alter the pattern of folding and coiling, causing the enzyme to become inactive, or *denatured*.

Proteins make up more than 50% of the dry weight of animals and bacteria. They perform many important functions in living organisms, a few of which are indicated in Table 28-7. Each protein carries out a specific biochemical function. Each is a polypeptide with its own unique *sequence* of amino acids. The amino acid sequence of a protein determines exactly how it folds up in a three-dimensional conformation and how it performs its precise biochemical task.



A “ribbon” model of the protein calmodulin. In this type of model, the ribbon represents the polypeptide chain. This protein coordinates with Ca^{2+} ions (white spheres) and aids in transporting them in living systems.

TABLE 28-7 *Some Functions of Proteins*

Example	Function
Enzymes	
amylase	converts starch to glucose
DNA polymerase I	repairs DNA molecule
trans aminase	transfers amino group from one amino acid to another
Structural Proteins	
viral coat proteins	outer covering of virus
keratin	hair, nails, horns, hoofs
collagen	tendons, cartilage
Hormones	
insulin, glucagon	regulate glucose metabolism
oxytocin	regulates milk production in female mammals
vasopressin	increases retention of water by kidney
Contractile Proteins	
actin	thin contractile filaments in muscle
myosin	thick filaments in muscle
Storage Proteins	
casein	a nutrient protein in milk
ferritin	stores iron in spleen and egg yolk
Transport Proteins	
hemoglobin	carries O ₂ in blood
myoglobin	carries O ₂ in muscle
serum albumin	carries fatty acids in blood
cytochrome <i>c</i>	transfers electrons
Immunological Proteins	
γ -globulins	form complexes with foreign proteins
Toxins	
neurotoxin	blocker of nerve function in cobra venom
ricin	nerve toxin in South American frog (most toxic substance known—0.000005 g is fatal to humans)

28-10 NUCLEIC ACIDS

We have seen that polysaccharides are polymers composed of a single type of monomer (carbohydrates), as are proteins (amino acids). The third type of biopolymer is more complex. Nucleic acids use three very different types of monomers: the phosphate group, one of two simple carbohydrate units (deoxyribose or ribose), and selected organic bases (Figure 28-15). A typical segment of the resulting polymer is shown in Figure 28-16.

There are two types of nucleic acids: ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). One of the ways in which they differ is in the carbohydrate that they contain.

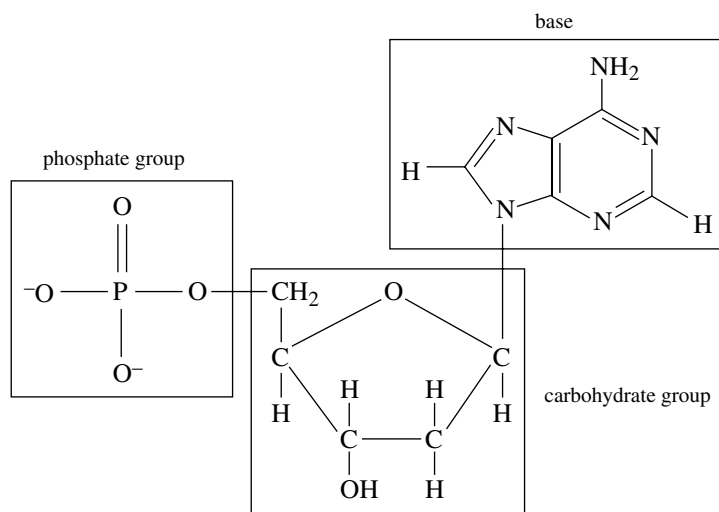


Figure 28-15 The three kinds of units that are polymerized to form nucleic acids.

The two carbohydrates in nucleic acids are ribose (contained in RNA) and 2-deoxyribose (contained in DNA); these carbohydrates differ in the presence or absence of an oxygen atom on carbon 2.

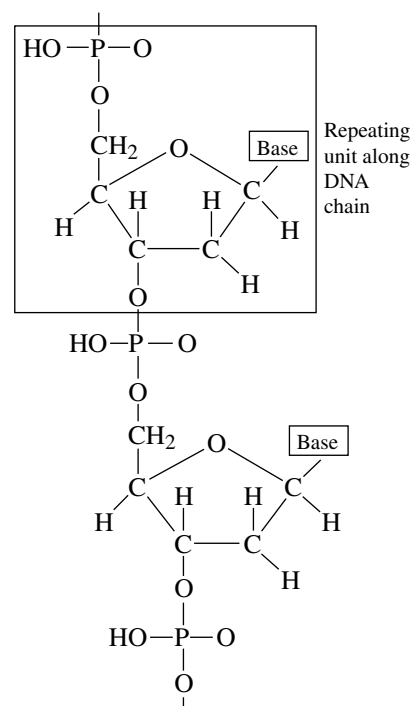


Figure 28-16 A short segment of DNA (deoxyribonucleic acid).

The bases found in nucleic acids are shown in Figure 28-17. Each type of nucleic acid contains two pyrimidine bases and two purine bases. The two purine bases adenine (A) and guanine (G) and the pyrimidine base cytosine (C) are found in both RNA and DNA.

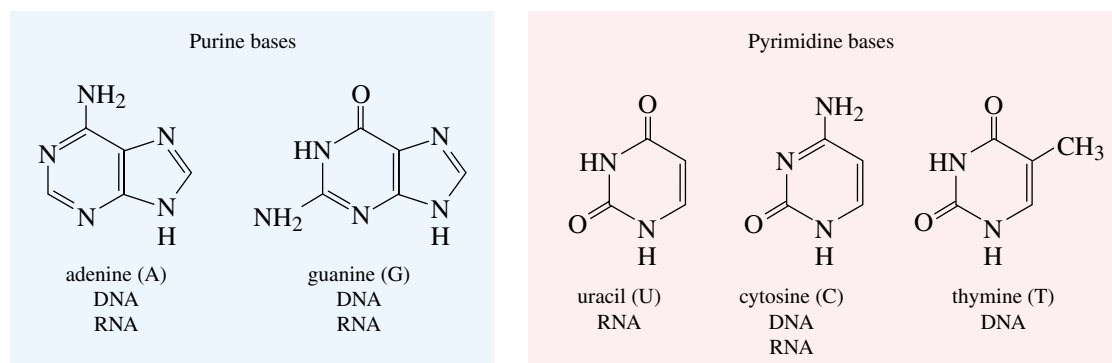
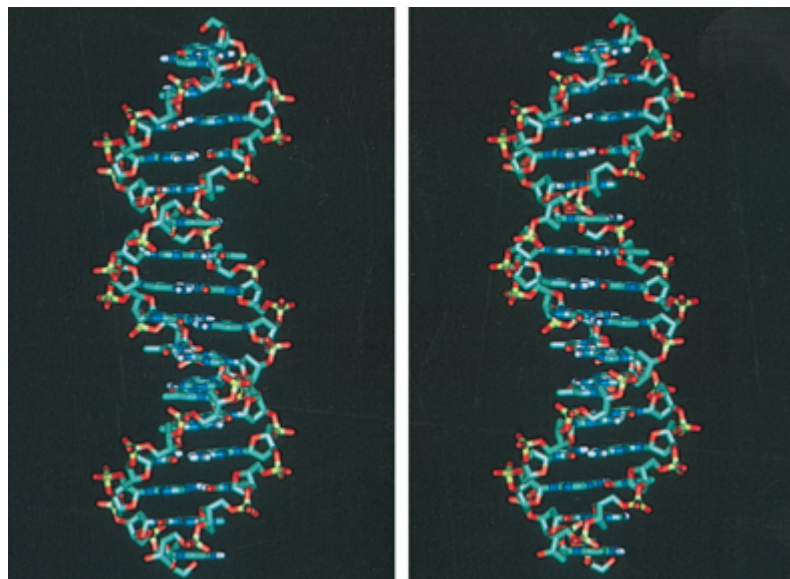
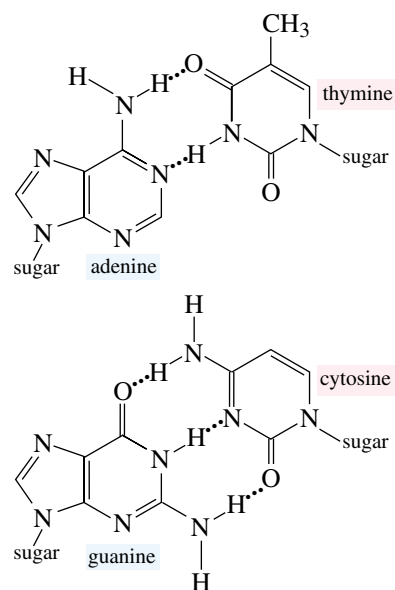


Figure 28-17 The bases found in DNA and RNA.



A stereoview of an idealized model of DNA.

In RNA, the other pyrimidine base is uracil (U), whereas DNA contains thymine (T). Specific pairs of these bases hydrogen bond to each other in particularly favorable arrangements, so they always occur in distinctive hydrogen-bonded base pairs. Adenine and thymine (in DNA) or uracil (in RNA) each form two hydrogen bonds, so they are always paired together; similarly, guanine and cytosine each form three hydrogen bonds, so they always pair to each other (Figure 28-18). The resulting **complementary base-pairing** links two strands of the polymer in a very specific order to form a double helix. This order is the key to nucleic acid function. Figure 28-19 shows a short segment of the double strand of DNA. In that figure, we see that adenine is paired with thymine and guanine is paired with cytosine. In RNA, adenine forms base pairs with uracil instead of with thymine.



DNA is one of the largest molecules known. Human DNA is estimated to have up to three billion base pairs, resulting in a molecular weight in the tens of billions. RNA is smaller and more variable, with molecular weights of 20,000 to 40,000. Genetic information for each organism is stored in its DNA as a result of the locations and sequence of the base pairs. The information is replicated when the strands unravel and new complementary strands are formed. The genetic information of the DNA is used to guide the many syntheses that occur in a living cell. For example, for the synthesis of a specific protein, a specific portion of the DNA double helix unwinds. Then an RNA molecule is built using the sequence of base pairs of the DNA as a pattern. The RNA then migrates from the cell's nucleus to the location where the protein is to be synthesized. There the base sequence of the RNA determines the sequence of amino acids to be used in the protein construction. With its many possible sequences of the same base pairs to transmit information to control synthesis of other molecules, DNA contains a vast amount of genetic information.

Figure 28-18 The two kinds of hydrogen-bonded base-pairing that occur in DNA. In RNA, adenine forms a base pair with uracil instead of with thymine.

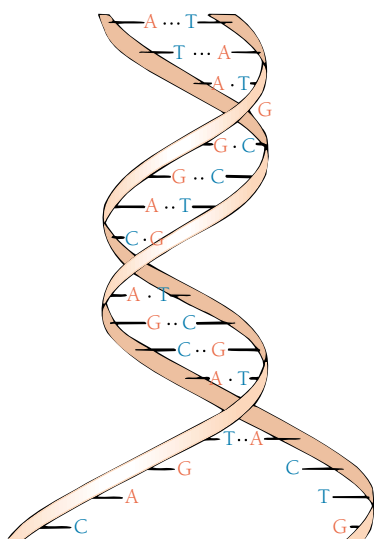


Figure 28-19 A short segment of the double strand of a DNA molecule.

Key Terms

Achiral Describes an object that *can* be superimposed with its mirror image.

Aldose A monosaccharide that contains an aldehyde group.

Base pairing The complementary hydrogen bonding of cytosine with guanine and of adenine with thymine (in DNA) or with uracil (in RNA).

Biopolymer Polymers found in biological systems.

Brønsted–Lowry acid A species that acts as a proton donor.

Brønsted–Lowry base A species that acts as a proton acceptor.

Carbohydrate A biopolymer made up of saccharide units.

Chiral Describes an object that *cannot* be superimposed with its mirror image.

Conformation One specific geometry of a molecule. The conformations of a compound differ from one another only by rotation about single bonds.

Constitutional isomers Compounds that contain the same number of the same kinds of atoms but that differ in the order in which their atoms are bonded together. Also known as *structural isomers*.

2-Deoxyribose The carbohydrate found in DNA.

Dipeptide A compound in which two amino acid monomers have joined to form the peptide.

Disaccharide A molecule consisting of two monosaccharides joined together by a glycosidic bond.

DNA Deoxyribonucleic acid; a nucleic acid consisting of phosphate, 2-deoxyribose, and the four bases adenine, cytosine, guanine, and thymine.

Enantiomers See *Optical isomers*.

Enzyme A protein that catalyzes a biological reaction.

Geometric isomers Compounds with different arrangements of groups on the opposite sides of a bond with restricted rotation, such as a double bond or a single bond in a ring; for example, *cis–trans* isomers of certain alkenes.

Glycosidic bond A bond linking monomers in a polysaccharide.

Ketose A monosaccharide that contains a ketone group.

Monomers The small molecules from which polymers are formed.

Monosaccharide Simple sugars (monomers) from which more complex carbohydrates are constructed.

Nucleic acid A biopolymer consisting of repeating units of ribose or deoxyribose, phosphate, and selected bases.

Oligosaccharide A molecule consisting of four to ten monosaccharides joined together by glycosidic bonds.

Optical isomers Molecules that are nonsuperimposable mirror images of each other, that is, that bear the same relationship to each other as do left and right hands; also called *enantiomers*.

Oxidation (as applied to organic compounds) The increase of oxygen content or the decrease of hydrogen content of an organic molecule.

Peptide bond A bond formed by elimination of a molecule of water between the amino group of one amino acid and the carboxylic acid group of another.

Peptides Compounds formed by the linking of small numbers of amino acids.

Polymerization The combination of many small molecules (monomers) to form large molecules (polymers).

Polymers Large molecules formed by the combination of many small molecules (monomers).

Polypeptide A polymer composed of amino acids linked by peptide bonds.

Polysaccharide Carbohydrates that contain more than ten monosaccharide units.

Primary structure The sequence of the monomeric units in proteins, carbohydrates, and so on.

Protein A naturally occurring polymeric chain of L-amino acids linked together by peptide bonds.

Racemic mixture A single sample containing equal amounts of the two enantiomers (optical isomers) of a compound; does not rotate the plane of polarized light.

Reduction (as applied to organic compounds) The decrease of oxygen content or the increase of hydrogen content of an organic molecule.

Ribose The carbohydrate found in RNA.

RNA Ribonucleic acid, a nucleic acid consisting of phosphate, ribose, and the four bases adenine, cytosine, guanine, and uracil.

Saponification The hydrolysis of esters in the presence of strong bases.

Soap The sodium salt of a long-chain fatty acid.

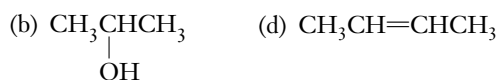
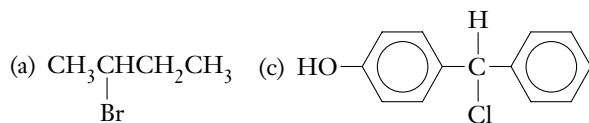
Stereoisomers Isomers in which the atoms are linked together in the same atom-to-atom order, but with different arrangements in space. See *Geometric isomers*, *Optical isomers*.

Trisaccharide A molecule consisting of three monosaccharides joined together by glycosidic bonds.

Exercises

Geometries of Organic Molecules

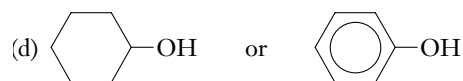
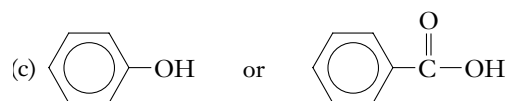
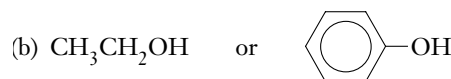
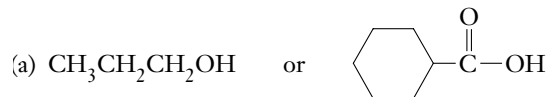
- Distinguish between two types of constitutional isomerism. Give an example of each type.
- Distinguish between two types of stereoisomerism. Give an example of each type.
- Which of the following compounds can exist as *cis* and *trans* isomers? Draw them. (a) 2,3-dimethyl-2-butene; (b) 2-chloro-2-butene; (c) dichlorobenzene; (d) 1,1-dichlorocyclobutane.
- Which of the following compounds can exist as *cis* and *trans* isomers? Draw them. (a) 1-butene; (b) 2-bromo-1-butene; (c) 2-bromo-2-butene; (d) 1,2-dichlorocyclopentane.
- Distinguish between conformations and isomers.
- What is optical isomerism? What are enantiomers?
- Which of the following compounds would exhibit optical isomerism?



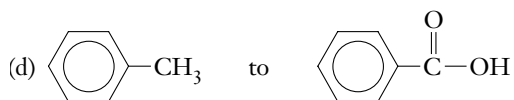
- Draw three-dimensional representations of the enantiomeric pairs in Exercise 7.
- Write formulas and names for the isomers of (a) bromochlorobenzene, (b) trifluorobenzene, and (c) chlorotoluene. What kind of isomerism is illustrated by each of these sets of compounds?
- Write formulas and names for the isomers of (a) propanol, (b) pentachloropropene, and (c) chlorofluoroethane.
- Draw structural representations of two conformations of butane. Indicate the one having the lower potential energy.
- Draw structural representations of two conformations of cyclohexane. Give the name commonly applied to each.

Selected Reactions

- (a) List the four most acidic organic functional groups. (b) List the four common organic functional groups that are bases.
 - Why are aqueous solutions of amines basic? Show, with equations, how the dissolution of an amine in water is similar to the dissolution of ammonia in water.
 - Show that the reaction of amines with inorganic acids such as HCl are similar to the reactions of ammonia with inorganic acids.
 - What are the equilibrium concentrations of the species present in a 0.10 M solution of aniline? $K_b = 4.2 \times 10^{-10}$
- $$\text{C}_6\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$$
- Which solution would be more acidic: a 0.10 M solution of aniline hydrochloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ ($K_b = 4.2 \times 10^{-10}$ for aniline, $\text{C}_6\text{H}_5\text{NH}_2$), or a 0.10 M solution of methylamine hydrochloride, $\text{CH}_3\text{NH}_3\text{Cl}$ ($K_b = 5.0 \times 10^{-4}$ for methylamine, CH_3NH_2)? Justify your choice.
 - Choose the compound that is the stronger acid in each set.



19. (a) What are alkoxides? (b) What do we mean when we say that the low-molecular-weight alkoxides are strong bases?
20. (a) Write equations for the reactions of three alcohols with metallic sodium. (b) Name all compounds in these equations. (c) Are these reactions similar to the reaction of metallic sodium with water? How?
21. Which physical property of aldehydes is used to advantage in their production from alcohols?
22. The K_b for lidocaine (a monobasic organic compound, MW = 234.3) is 7.0×10^{-6} . What is the pH of a 1.5 percent solution of lidocaine? The density of the solution is 1.00 g/mL.
23. How are the terms "oxidation" and "reduction" often used in organic chemistry? Classify the following changes as either oxidation or reduction: (a) CH_4 to CH_3OH ; (b) $\text{CH}_2=\text{CH}_2$ to CH_3-CH_3 ; (c) $\text{CH}_3\text{CH}_2\text{CHO}$ to $\text{CH}_3\text{CH}_2\text{CH}_3$;

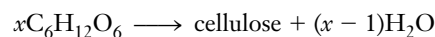


24. Classify the following changes as either oxidation or reduction: (a) CH_3OH to CO_2 and H_2O ; (b) CH_2CH_2 to CH_3CHO ; (c) CH_3COOH to CH_3CHO ; (d) $\text{CH}_3\text{CH}=\text{CH}_2$ to $\text{CH}_3\text{CH}_2\text{CH}_3$.
25. Write equations to illustrate the oxidation of the following aromatic hydrocarbons by potassium permanganate in basic solution: (a) toluene; (b) ethylbenzene; (c) 1,2-dimethylbenzene.
26. (a) Do you expect toluene to produce soot as it burns? Why? (b) Would you expect the flames to be blue or yellow?
27. Describe the preparation of three aldehydes from alcohols, and write appropriate equations. Name all reactants and products.
28. Describe the preparation of three ketones from alcohols, and write appropriate equations. Name all reactants and products.
29. An ester is the product of the reaction of an alcohol with a carboxylic acid and is the organic version of an inorganic salt. What is an inorganic ester?
30. (a) Write equations for the formation of three inorganic esters. (b) Name the inorganic ester formed in each case.
31. (a) What is nitroglycerine? (b) Write the chemical equation that shows the preparation of nitroglycerine. (c) List two important uses for nitroglycerine. Are they similar?
32. Write equations for the formation of three different esters, starting with an acid and an alcohol in each case. Name all compounds.
33. Write equations for the formation of three different esters, starting with a different acid chloride and a different alcohol in each case. Name all compounds.

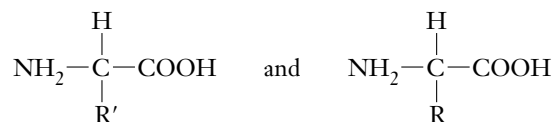
34. Write equations for the hydrolysis of (a) methyl acetate, (b) ethyl formate, (c) butyl acetate, and (d) octyl acetate. Name all products.
35. (a) What is saponification? (b) Why is this kind of reaction called saponification?

Biopolymers

36. What is necessary if a molecule is to be capable of polymerization? Name three types of molecules that can polymerize.
37. A cellulose polymer has a molecular weight of 750,000. Estimate the number of units of the monomer, β -glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in this polymer. This polymerization reaction can be represented as

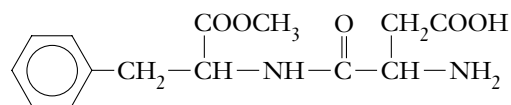


38. Write structural formulas of two monosaccharides that contain six carbon atoms.
39. Write the structural formula of a trisaccharide containing only α -1,4-linked glucose units.
40. Write two structural formulas of fructose, one in its cyclic form and one in its straight-chain form.
41. Describe the structure of a natural amino acid molecule. What kind of isomerism do most amino acids exhibit? Why?
42. How are the amino acid units in a polypeptide joined together? What are the links called?
43. Consider only two amino acids:



Write the structural formulas for the dipeptides that could be formed containing one molecule of each amino acid.

- *44. How many different dipeptides can be formed from the three amino acids A, B, and C? Write the sequence of amino acids in each. Assume that an amino acid could occur more than once in each dipeptide.
- *45. How many different tripeptides can be formed from the three amino acids A, B, and C? Write the sequence of amino acids in each. Assume that an amino acid could occur more than once in each tripeptide.
46. Aspartame (trade name NutraSweet) is a methyl ester of a dipeptide:

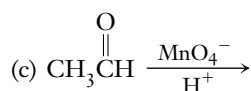
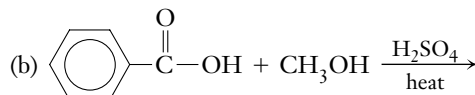
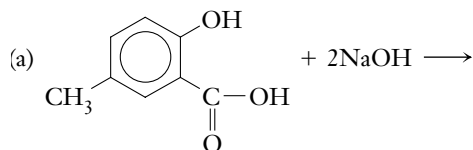


Write the structural formulas of the two amino acids that are combined to make aspartame (ignoring optical isomerism).

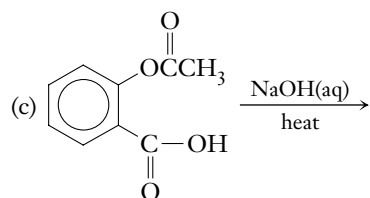
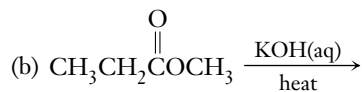
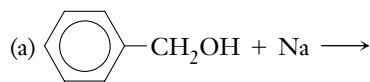
47. Write the structural formula of the carbohydrate found in deoxyribonucleic acid (DNA). How does this carbohydrate differ from the one found in ribonucleic acid (RNA)?
48. Write structural formulas of the four bases found in DNA. Circle at least one functional group on each that gives the compound its base properties.
49. Draw a short segment of the DNA biopolymer that contains three each of the phosphate, carbohydrate, and base groups.
50. In the double-strand form of DNA the base groups are paired. What base is found paired (hydrogen bonded) with thymine?
55. (a) Name three biopolymers found in animals. (b) Name at least one biopolymer that is composed of identical monomers.
56. Name the three types of monomers that are found in DNA. Give a structural formula of an example of each.

Mixed Exercises

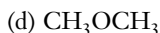
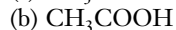
51. Identify the major products of each reaction.



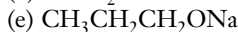
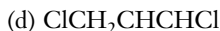
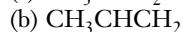
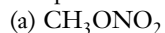
52. Identify the major products of each reaction.



53. Write a structural formula for each of the following compounds:



54. Write a structural formula for each of the following compounds:

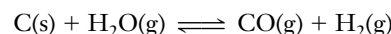


CONCEPTUAL EXERCISES

57. Nylon is decomposed by acids, but polyethylene is not. Suggest an explanation for this difference in behavior.
58. How does the heat of combustion of ethyl alcohol compare with the heats of combustion of low-molecular-weight saturated hydrocarbons on a per-mole basis and on a per-gram basis?

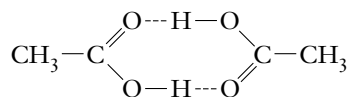
BUILDING YOUR KNOWLEDGE

59. A laboratory procedure calls for oxidizing 2-propanol to acetone using an *acidic* solution of K₂Cr₂O₇. An insufficient amount of K₂Cr₂O₇ is on hand, however, so the laboratory instructor decides to use an acidic solution of KMnO₄ instead. What mass of KMnO₄ is required to carry out the same amount of oxidation as 1.00 g of K₂Cr₂O₇?
60. The chemical equation for the water gas reaction is



At 1000 K, the value of K_p for this reaction is 3.2. When we treat carbon with steam and allow the reaction to reach equilibrium, the partial pressure of water vapor is observed to be 15.6 atm. What are the partial pressures of CO and H₂ under these conditions?

61. (a) In aqueous solution, acetic acid exists mainly in the molecular form ($K_a = 1.8 \times 10^{-5}$). Calculate the freezing point depression for a 0.10 molal aqueous solution of acetic acid, ignoring any ionization of the acid. $K_f = 1.86^\circ\text{C/molal}$ for water. (b) In nonpolar solvents such as benzene, acetic acid exists mainly as dimers



as a result of hydrogen bonding. Calculate the freezing point depression for a 0.10 molal solution of acetic acid in benzene. $K_f = 5.12^\circ\text{C/molal}$ for benzene. Assume complete dimer formation.

62. What is the pH of a 0.10 M solution of sodium benzoate? $K_a = 6.3 \times 10^{-5}$ for benzoic acid, C₆H₅COOH. Would this solution be more or less acidic than a 0.10 M solution of sodium acetate? $K_a = 1.8 \times 10^{-5}$ for acetic acid, CH₃COOH.