

Organic Chemistry I: Formulas, Names, and Properties

27





Waxes are high-molecular-weight straight-chain alkanes, alcohols, and carboxylic acids.

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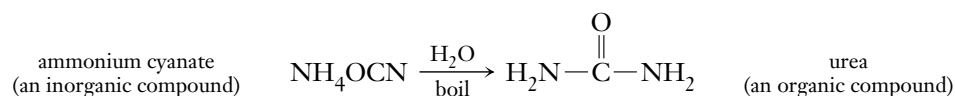
OBJECTIVES

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

- Describe saturated hydrocarbons (alkanes and cycloalkanes)—their structures and their nomenclature
- Describe unsaturated hydrocarbons (alkenes and alkynes)—their structures and their nomenclature
- Draw and name constitutional isomers of alkanes
- Draw and name constitutional and geometric isomers of alkenes
- Describe and name some aromatic hydrocarbons—benzene, condensed aromatics, and substituted aromatic compounds
- Describe some common functional groups and name compounds from the following classes
 - halides*
 - alcohols and phenols*
 - ethers*
 - aldehydes and ketones*
 - amines*
 - carboxylic acids and some of their derivatives*
- Recognize examples of the three fundamental classes of organic reactions: substitution, addition, and elimination
- Recall some uses of three fundamental classes of organic reactions and some compounds that are prepared by each class of reaction
- Recognize some common polymers and the reactions by which they are formed; identify the monomers from which they are formed

Organic chemistry is the chemistry of compounds that contain C—C or C—H bonds. Why is one entire branch of chemistry devoted to the behavior of the compounds of just one element? The answer is twofold: (1) There are many more compounds that contain carbon than there are compounds that do not (more than 11 million organic compounds have been identified), and (2) the molecules containing carbon can be so much larger and more complex (a methane molecule contains five atoms per molecule and DNA contains tens of billions of atoms per molecule).

Originally the term “organic” was used to describe compounds of plant or animal origin. “Inorganic” was used to describe compounds from minerals. In 1828, Friedrich Wöhler (1800–1882) synthesized urea by boiling ammonium cyanate with water.



This disproved the theory that held that organic compounds could be made only by living things. Today many organic compounds are manufactured from inorganic materials.

We encounter organic chemistry in every aspect of our lives. All life is based on a complex interrelationship of thousands of organic substances—from simple compounds such as sugars, amino acids, and fats to vastly more complex ones such as the enzymes that catalyze life’s chemical reactions and the huge DNA molecules that carry genetic information from one generation to the next. The food we eat (including many additives); the clothes we wear; the plastics and polymers that are everywhere; our life-saving medicines; the paper on which we write; our fuels; many of our poisons, pesticides, dyes, soaps and detergents—all involve organic chemistry.

We normally think of petroleum and natural gas as fuel sources, but most synthetic organic materials are also derived from these two sources. More than half of the top 50 commercial chemicals are organic compounds derived in this way. Indeed, petroleum and natural gas may one day be more valuable as raw materials for organic synthesis than as fuel sources. If so, we may greatly regret our delay in developing alternative energy sources while burning up vast amounts of our petroleum and natural gas deposits as fuels.

A carbon atom has four electrons in its outermost shell with ground state configuration $1s^2 2s^2 2p^2$. The C atom can attain a stable configuration by forming four covalent bonds. As we saw in Chapter 8, each C atom can form single, double, or triple bonds by utilizing various hybridizations. The bonding of carbon is summarized in Table 27-1 using examples that we saw in Chapters 7 and 8. Carbon is unique among the elements in the extent to which it forms bonds between like atoms and in the diversity of compounds that are formed. Bonds between atoms of the same element rarely occur for any element except carbon. Carbon atoms form long chains, branched chains, and rings that may also have chains attached to them. A tremendous variety of carbon-containing compounds is known.

Although millions of organic compounds are known, the elements they contain are very few: C and H; often N, O, S, P, or a halogen; and sometimes another element. The great number and variety of organic compounds are a result of the many different arrangements of atoms, or *structures*, that are possible. The chemical and physical properties of organic compounds are related to the structures of their molecules. Thus, the basis for organizing and understanding organic chemistry is our understanding of structure and bonding.

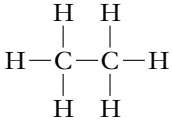
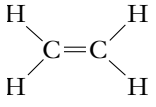
In this text we shall give only an introduction to organic chemistry. In this chapter we organize organic compounds into the most common classes or “families” according to their structural features and learn to name various types of compounds. In this chapter and the next, we will present a few typical reactions that organic substances undergo.

Urea, $\text{H}_2\text{N}-\text{CO}-\text{NH}_2$, is the principal end product of metabolism of nitrogen-containing compounds in mammals. It is eliminated in the urine. An adult man excretes about 30 grams of urea in 24 hours.




See the *Saunders Interactive General Chemistry CD-ROM*, Screen 11.2, Carbon–Carbon Bonds.

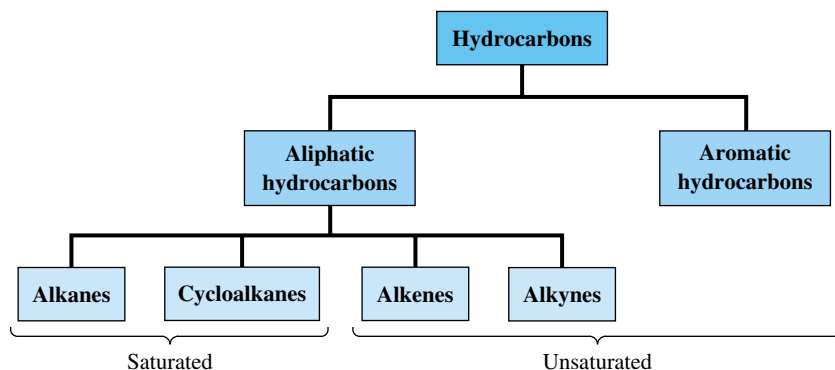
TABLE 27-1 Hybridization of Carbon in Covalent Bond Formation

Hybridization and Resulting Geometry	Orbitals Used by Each C Atom	Bonds Formed by Each C Atom	Example
sp^3 , tetrahedral	four sp^3 hybrids	four σ bonds	ethane 
sp^2 , trigonal planar	three sp^2 hybrids, one p orbital	three σ bonds, one π bond	ethylene 
sp , linear	two sp hybrids, two p orbitals	two σ bonds, two π bonds	acetylene $H-C\equiv C-H$

Organic molecules are based on a framework of carbon–carbon and carbon–hydrogen bonds. Many compounds contain *only* the two elements C and H; they are called **hydrocarbons**. Hydrocarbons that contain a delocalized ring of pi bonds such as the benzene ring (Section 9-6) are called **aromatic hydrocarbons**. Those that do not contain such delocalized systems are called **aliphatic hydrocarbons**. Aliphatic hydrocarbons that contain only sigma (σ) bonds (i.e., only single bonds) are called **saturated hydrocarbons**. Those that contain both sigma and pi (π) bonds (i.e., double, triple, or delocalized bonds) are called **unsaturated hydrocarbons**. These classifications are diagrammed in Figure 27-1. The first seven sections of this chapter are devoted to the study of hydrocarbons.

A **functional group** is a special arrangement of atoms within an organic molecule that is responsible for some characteristic chemical behavior of the compound. Different molecules that contain the same functional groups have similar chemical behavior. We shall follow the study of hydrocarbons with a presentation of some important characteristic functional groups.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 11.3, Hydrocarbons.

**Figure 27-1** Classification of hydrocarbons.

SATURATED HYDROCARBONS

27-1 ALKANES AND CYCLOALKANES

The *saturated hydrocarbons*, or **alkanes**, are compounds in which each carbon atom is bonded to four other atoms. **Cycloalkanes** are saturated hydrocarbons that contain carbon atoms joined to form a ring.

The term *saturated* comes from early studies in which chemists tried to add hydrogen to various organic substances. Those to which no more hydrogen could be added were called saturated, by analogy with saturated solutions.

Alkanes

Each H atom in a saturated hydrocarbon is bonded to only one C atom. Saturated hydrocarbons contain only single bonds. Petroleum and natural gas are composed mostly of saturated hydrocarbons.

In Section 8-7 we examined the structure of the simplest alkane, *methane*, CH_4 . We saw that methane molecules are tetrahedral with sp^3 hybridization at carbon (Figure 27-2).

Ethane, C_2H_6 , is the next simplest saturated hydrocarbon. Its structure is quite similar to that of methane. Two carbon atoms share a pair of electrons. Each carbon atom also shares an electron pair with each of three hydrogen atoms. Both carbon atoms are sp^3 hybridized (Figure 27-3). *Propane*, C_3H_8 , is the next member of the family (Figure 27-4).

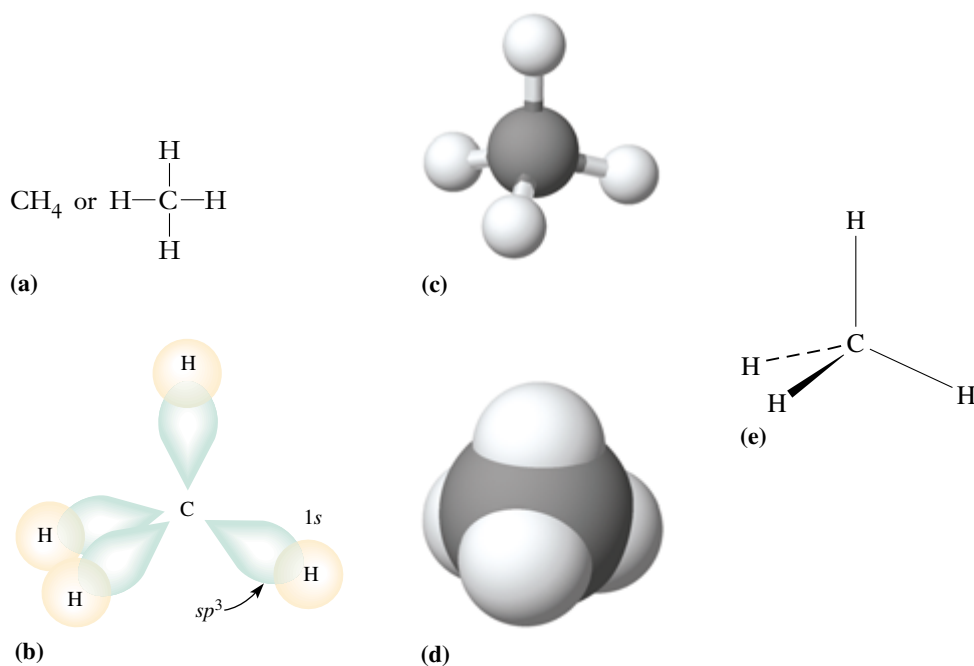


Figure 27-2 Representations of a molecule of methane, CH_4 . (a) The condensed and Lewis formulas for methane. (b) The overlap of the four sp^3 carbon orbitals with the s orbitals of four hydrogen atoms forms a tetrahedral molecule. (c) A ball-and-stick model, (d) a space-filling model of methane, and (e) a three-dimensional representation that uses the wedged line to indicate a bond coming forward and a dashed line to represent a bond projecting backward.

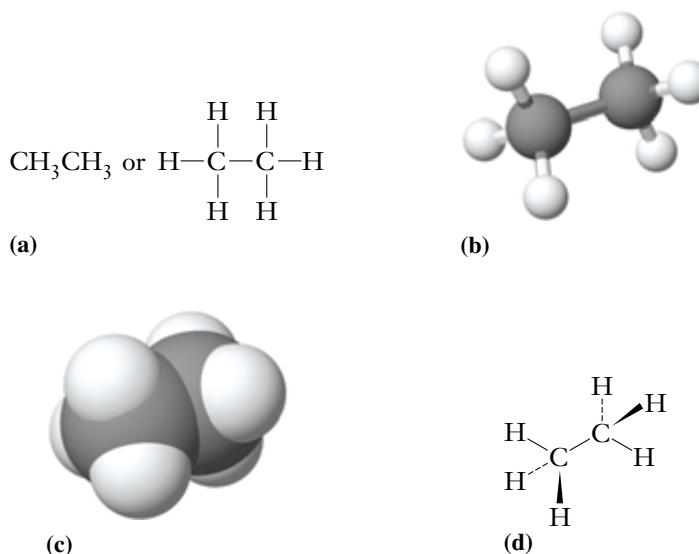


Figure 27-3 Models of ethane, C_2H_6 . (a) The condensed and Lewis formulas for ethane. (b) A ball-and-stick model, (c) a space-filling model of ethane, and (d) a 3-D representation.

Iso = “same”; *mer* = “part.” As we saw in Sections 25-6 and 25-7, isomers are substances that have the same numbers and kinds of atoms arranged differently. Isomerism in organic compounds is discussed more systematically in Chapter 28.

Two different compounds have the formula C_4H_{10} but different structures and, hence, different properties. Such *isomers* result when two molecules contain the same atoms bonded together in different orders. The structures of these two isomeric C_4H_{10} alkanes are shown in Figure 27-5. These two structures correspond to the two ways in which a hydrogen atom can be removed from a propane molecule and replaced by a $-\text{CH}_3$ group. If a $-\text{CH}_3$ replaces an H on either of the end carbon atoms, the result is butane. It is considered to be a straight-chain hydrocarbon because there is no branching. Though somewhat misleading, the term “straight chain” is widely used. The carbon chains are linear only in the structural formulas that we write. They are actually zigzag due to the tetrahedral bond angles at each carbon and are sometimes further kinked or twisted. Think of such a chain of carbon atoms as *continuous*. We can trace a single path from one terminal carbon to the other and pass through every other C atom *without backtracking*.

If the $-\text{CH}_3$ group replaces an H from the central carbon atom of propane, the result is the *branched-chain hydrocarbon* 2-methylpropane, or *isobutane*. This is the simplest branched-chain hydrocarbon.

The formulas of the alkanes can be written in general terms as $\text{C}_n\text{H}_{2n+2}$, where n is the number of carbon atoms per molecule. The first five members of the series are

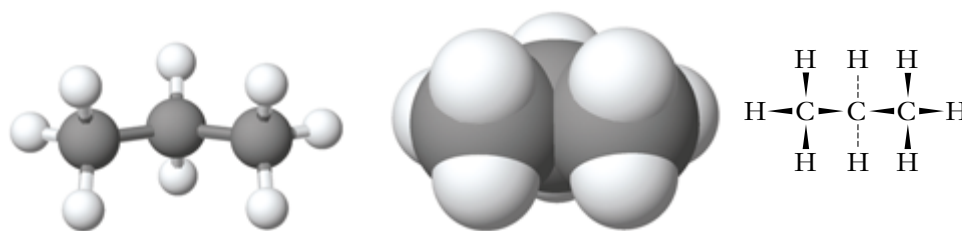


Figure 27-4 Ball-and-stick and space-filling models and a three-dimensional representation of propane, C_3H_8 .

	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂
Number of C atoms = n	= 1	2	3	4	5
Number of H atoms = $2n + 2$	= 4	6	8	10	12

The formula of each alkane differs from the next by CH₂, a *methylene group*.

A series of compounds in which each member differs from the next by a specific number and kind of atoms is called a **homologous series**. The properties of members of such a series are closely related. The boiling points of the lighter members of the straight-chain saturated hydrocarbon series are shown in Figure 27-6. As the molecular weights of the straight-chain hydrocarbons increase, their boiling points also increase regularly. Properties such as boiling point depend on the forces between molecules (Chapter 13). Carbon-carbon and carbon-hydrogen bonds are essentially nonpolar and are arranged tetrahedrally around each C atom. As a result, saturated hydrocarbons are nonpolar molecules, and the only significant intermolecular forces are dispersion forces (Section 13-2). These forces, which are due to induced dipoles, become stronger as the sizes of the molecules and the number of electrons in each molecule increase. Thus, trends such as those depicted in Figure 27-6 are due to the increase in effectiveness of dispersion forces.

Some systematic method for naming compounds is necessary. The system in use today is prescribed by the International Union of Pure and Applied Chemistry (IUPAC). The names of the first 20 straight-chain alkanes are listed in Table 27-2. You should become familiar with at least the first ten. The names of the alkanes starting with pentane have prefixes (from Greek) that give the number of carbon atoms in the molecules. All alkane names have the *-ane* ending.

Constitutional isomers (structured isomers) have the same molecular formula but differ in the order in which their atoms are attached.

We have seen that there are two saturated C₄H₁₀ hydrocarbons. For the C₅ hydrocarbons, there are three possible arrangements of the atoms. These three different C₅H₁₂ alkanes are examples of constitutional isomers.

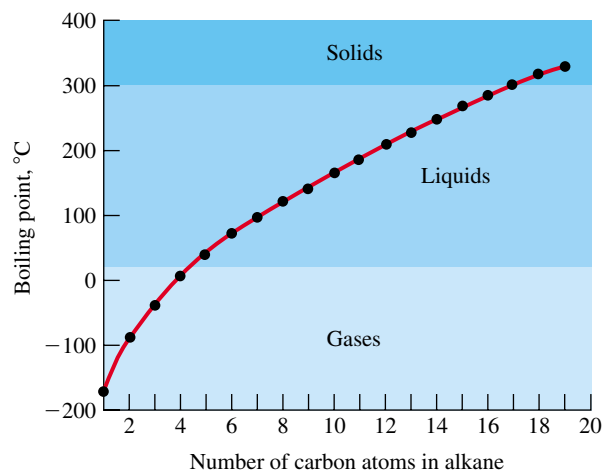


Figure 27-6 A plot of normal boiling point versus the number of carbon atoms in straight-chain, saturated hydrocarbons.

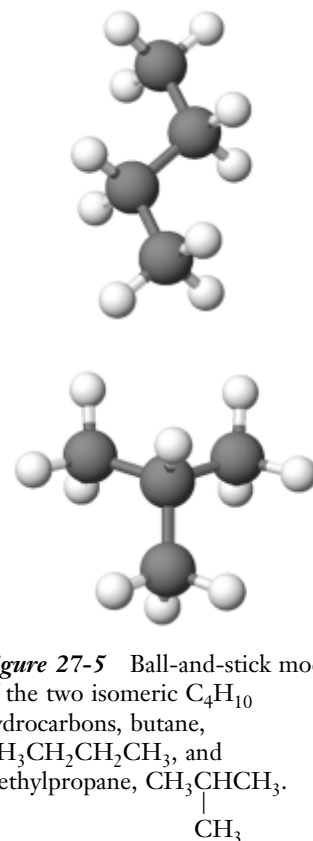


Figure 27-5 Ball-and-stick models of the two isomeric C₄H₁₀ hydrocarbons, butane, CH₃CH₂CH₂CH₃, and methylpropane, CH₃CH(CH₃)₂.

TABLE 27-2 *Some Straight-Chain Hydrocarbons (Alkanes)*

Molecular Formula	IUPAC Name	Normal bp (°C)	Normal mp (°C)	State at Room Temperature
CH ₄	methane	-161	-184	gas
C ₂ H ₆	ethane	-88	-183	
C ₃ H ₈	propane	-42	-188	
C ₄ H ₁₀	butane	+0.6	-138	
C ₅ H ₁₂	pentane	36	-130	liquid
C ₆ H ₁₄	hexane	69	-94	
C ₇ H ₁₆	heptane	98	-91	
C ₈ H ₁₈	octane	126	-57	
C ₉ H ₂₀	nonane	150	-54	
C ₁₀ H ₂₂	decane	174	-30	
C ₁₁ H ₂₄	undecane	194.5	-25.6	
C ₁₂ H ₂₆	dodecane	214.5	-9.6	
C ₁₃ H ₂₈	tridecane	234	-6.2	
C ₁₄ H ₃₀	tetradecane	252.5	+5.5	
C ₁₅ H ₃₂	pentadecane	270.5	10	
C ₁₆ H ₃₄	hexadecane	287.5	18	
C ₁₇ H ₃₆	heptadecane	303	22.5	solid
C ₁₈ H ₃₈	octadecane	317	28	
C ₁₉ H ₄₀	nonadecane	330	32	
C ₂₀ H ₄₂	eicosane	205 (at 15 torr)	36.7	

The number of constitutional isomers increases rapidly as the number of carbon atoms in saturated hydrocarbons increases. There are five isomeric C₆H₁₄ alkanes (Table 27-3). Table 27-4 displays the number of isomers of some saturated hydrocarbons (alkanes). Most of the isomers have not been prepared or isolated. They probably never will be.

As the degree of branching increases for a series of molecules of the same molecular weight, the molecules become more compact. A compact molecule can have fewer points of contact with its neighbors than more extended molecules do. As a result, the total induced dipole forces (dispersion forces) are weaker for branched molecules, and the boiling points of such compounds are lower. This pattern can be seen in the data in Table 27-3 and in Example 27-1.

EXAMPLE 27-1 *Isomeric Alkanes*

Write the Lewis formula of each of the three isomers having the molecular formula of C₅H₁₂. The boiling points of the three isomers are 9.5°C, 27.9°C, and 36.1°C. Match each compound with its boiling point.

Plan

We first write the carbon skeleton of the straight-chain isomer (no branching). Then we remove one carbon from the straight-chain structure and reposition it to form the skeleton for a branched isomer. We check to see whether branching is possible at other carbon atoms. Then

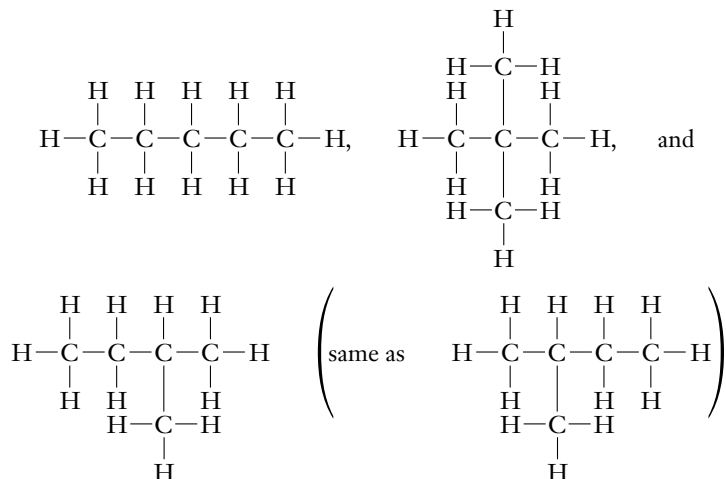
TABLE 27-3 *Isomeric C₆H₁₄ Alkanes*

IUPAC Name	Formula	Normal bp (°C)
hexane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	68.7
2-methylpentane	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3 \\ \\ \text{CH}_3 \end{array}$	60.3
3-methylpentane	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	63.3
2,2-dimethylbutane	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{CCH}_3 \\ \\ \text{CH}_3 \end{array}$	49.7
2,3-dimethylbutane	$\begin{array}{c} \text{CH}_3\text{CH}-\text{CHCH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	58.0

we remove a second carbon from the unbranched isomer and, if possible, form additional branching, and so on. Finally, we add hydrogen atoms to each skeleton to complete the structure.

Solution

The three compounds are:



The compound with the most branching would be expected to be the one with the lowest boiling point, and the straight-chain isomer would be expected to have the highest boiling point.

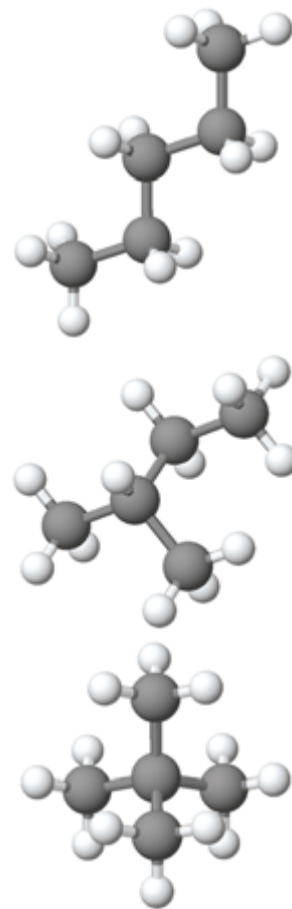
CH₃C(CH₃)₃, bp = 9.5°C; CH₃CH₂CH(CH₃)₂, bp = 27.9°C;
and CH₃CH₂CH₂CH₂CH₃, bp = 36.1°C.

(Models of these compounds are shown in the margin.)

You should now work Exercise 15.

TABLE 27-4 *Numbers of Possible Constitutional Isomers of Alkanes*

Formula	Isomers
C ₇ H ₁₆	9
C ₈ H ₁₈	18
C ₉ H ₂₀	35
C ₁₀ H ₂₂	75
C ₁₁ H ₂₄	159
C ₁₂ H ₂₆	355
C ₁₃ H ₂₈	802
C ₁₄ H ₃₀	1,858
C ₁₅ H ₃₂	4,347
C ₂₀ H ₄₂	366,319
C ₂₅ H ₅₂	36,797,588
C ₃₀ H ₆₂	4,111,846,763

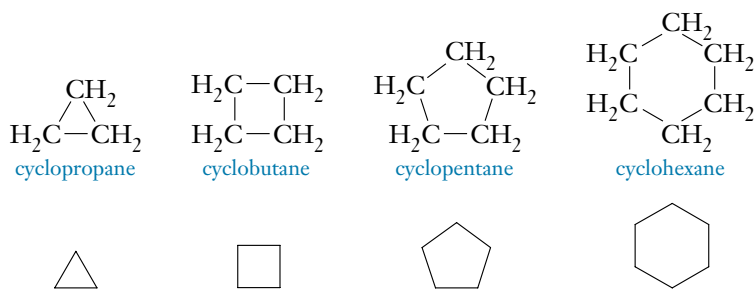


CH₃CH₂CH₂CH₂CH₃, CH₃CH₂CH(CH₃)₂,
and CH₃C(CH₃)₃.

Cycloalkanes

Noncyclic compounds are sometimes referred to as acyclic compounds.

The cyclic saturated hydrocarbons, or *cycloalkanes*, have the general formula C_nH_{2n} . The cycloalkanes (and other ring compounds that we will encounter later) are often shown in simplified skeletal form in which each intersection of two lines represents a C atom; we mentally add enough H atoms to give each carbon atom four bonds. The first four unsubstituted cycloalkanes and their simplified representations are



In skeletal representations, each intersection represents a carbon with any attached hydrogens. (See Section 27-3 for more details on writing skeletal representations.)

In some of these structures, the bond angles are somewhat distorted from the ideal tetrahedral angle of 109.5° , the most severe distortions being 60° in cyclopropane and 90° in cyclobutane. As a result, these rings are said to be “strained,” and these two compounds are unusually reactive for saturated hydrocarbons. Cyclopentane is stable with a nearly flat ring, because the bond angles in a regular pentagon (108°) are near the tetrahedral angle (109.5°).

Cyclohexane is not stable as a flat ring. The bond angles of the flat ring would be 120° , not the 109.5° , of an sp^3 -hybridized carbon. To avoid the strain, the ring “puckers” and becomes nonplanar (Figures 27-7 and 27-8).

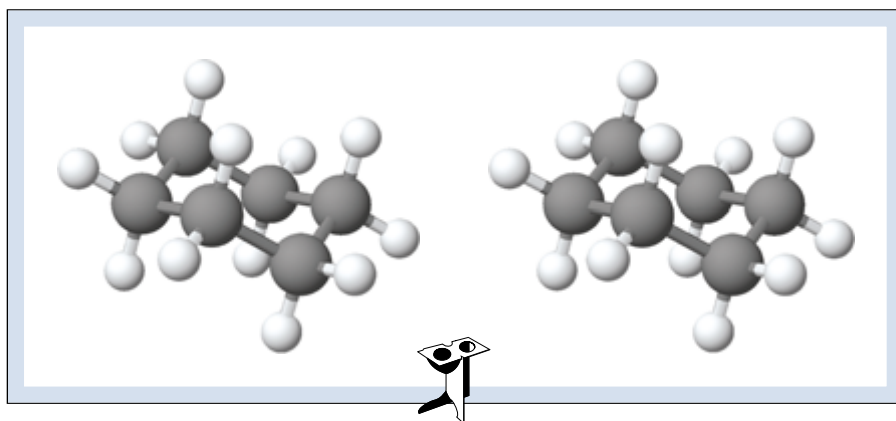


Figure 27-7 Stereoview of a nonplanar form of cyclohexane.

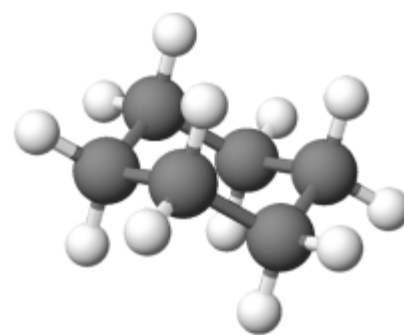
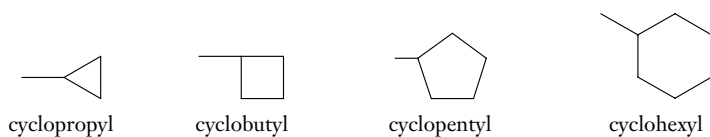


Figure 27-8 A model showing a nonplanar arrangement of cyclohexane.

27-2 NAMING SATURATED HYDROCARBONS

It is important to realize that many compounds (and their names) were so familiar to chemists before the development of the IUPAC system (beginning about 1890) that they continued to be called by their common, or “trivial,” names. In this and the next chapter, IUPAC names of compounds appear in blue type, and their common alternative names are shown in black type.

The IUPAC naming system is based on the names of the unbranched hydrocarbons given in Table 27-2 and their higher homologues. To name a branched-chain hydrocarbon, we first find the longest chain of carbon atoms and use the root name that corresponds to that hydrocarbon. We then indicate the positions and kinds of *substituents* attached to the chain. **Alkyl group** substituents attached to the longest chain are thought of as fragments of hydrocarbon molecules obtained by the removal of one hydrogen atom. We give them names related to the parent hydrocarbons from which they are derived. Other alkyl groups are named similarly (Table 27-5). We use the general symbol R to represent any alkyl group. The cycloalkyl groups derived from the first four cycloalkanes are called cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl, respectively.


TABLE 27-5 Some Alkanes and the Related Alkyl Groups

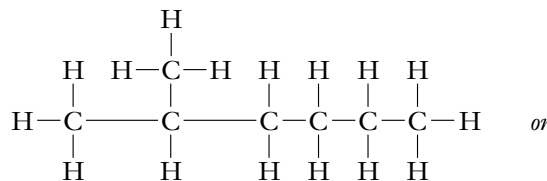
Parent Hydrocarbon	Alkyl group, —R	
CH_4 , methane $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array} \text{ or } \text{CH}_4$	$-\text{CH}_3$, methyl $\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{H} \\ \\ \text{H} \end{array} \text{ or } -\text{CH}_3$	
C_2H_6 , ethane $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} \text{ or } \text{CH}_3\text{CH}_3$	$-\text{C}_2\text{H}_5$, ethyl $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} \text{ or } -\text{CH}_2\text{CH}_3$	
C_3H_8 , propane $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} \text{ or } \text{CH}_3\text{CH}_2\text{CH}_3$	$-\text{C}_3\text{H}_7$, propyl $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ -\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array} \text{ or } -\text{CH}_2\text{CH}_2\text{CH}_3$	$-\text{C}_3\text{H}_7$, isopropyl $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{array}$
C_4H_{10} , butane $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array} \text{ or } \text{CH}_3(\text{CH}_2)_2\text{CH}_3$	$-\text{C}_4\text{H}_9$, butyl $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ -\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array} \text{ or } -\text{CH}_2(\text{CH}_2)_2\text{CH}_3$	$-\text{C}_4\text{H}_9$, <i>sec</i> -butyl (read as “secondary butyl”) $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \\ \text{H} \quad \quad \text{H} \quad \text{H} \end{array}$
C_4H_{10} , methylpropane (common name, isobutane) $\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \text{ or } \text{CH}(\text{CH}_3)_3$	$-\text{C}_4\text{H}_9$, <i>t</i> -butyl (read as “tertiary butyl”) $\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \text{ or } -\text{C}(\text{CH}_3)_3$	$-\text{C}_4\text{H}_9$, isobutyl $\begin{array}{c} -\text{CH}_2 \\ \\ \text{H}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$

Formerly the rule was to name the substituents in order of increasing complexity. This was sometimes difficult to determine. With the use of computers in literature searches, it became necessary to adopt the more definitive alphabetization of the names of substituents.

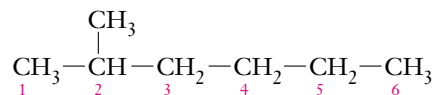
Summary of IUPAC Rules for Naming Alkanes

1. Find the longest chain of C atoms. Choose the base name that describes the number of C atoms in this chain, with the ending *-ane* (see Table 27-2). The longest chain may not be obvious at first if branches of different sizes are present.
2. Number the C atoms in this longest chain beginning at the end nearest the first branching. If necessary, go to the second branch closest to an end, and so on, until a difference is located. If there is branching at equal distances from both ends of the longest chain, begin numbering at the end nearest the branch that is first in alphabetical order.
3. Assign the name and position number to each substituent. Arrange the substituents in alphabetical order. Hyphenated prefixes, such as *tert-* and *sec-*, are not used in alphabetization of the substituents.
4. Use the appropriate prefix to group like substituents: *di-* = 2, *tri-* = 3, *tetra-* = 4, *penta-* = 5, and so on. Don't consider these prefixes when alphabetizing attached groups.
5. Write the name as a single word. Use hyphens to separate numbers and letters (plus some hyphenated prefixes) and commas to separate numbers. Don't leave any spaces.

Let us name the following compound.



We follow Rules 1 and 2 to number the carbon atoms in the longest chain.

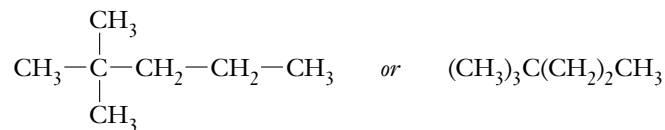


The methyl group is attached to the *second* carbon atom in a *six-carbon* chain, so the compound is named 2-methylhexane.

The following examples further illustrate the rules of nomenclature.

EXAMPLE 27-2 Naming Alkanes

Give the IUPAC name of the compound represented by the structural formula



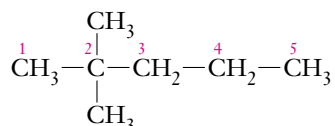
Parentheses are used to conserve space. Formulas written with parentheses must indicate unambiguously the structure of the compound. The parentheses here indicate that the CH_3 group is attached to the C next to it.

It is incorrect to name the compound 5-methylhexane because that violates Rule 2.

Remember that the (dash) formulas indicate which atoms are bonded to each other. They do *not* show molecular geometry. In this molecule, each C atom is tetrahedrally bonded to four other atoms.

Plan

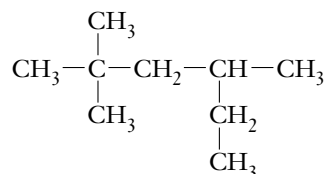
We first find the longest carbon chain and number it to give the substituent encountered first the smallest possible number. Then we name the substituents as in Table 27-5 and specify the number of each as indicated in Rule 4.

Solution

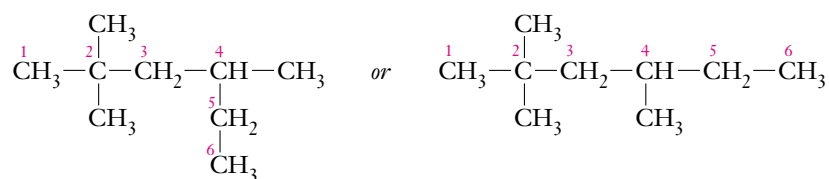
The longest chain contains five carbons, so this compound is named as a derivative of pentane. There are two methyl groups, both at carbon number 2. The IUPAC name of this compound is **2,2-dimethylpentane**.

EXAMPLE 27-3 Naming Alkanes

Give the IUPAC name of the compound represented by the structural formula

**Plan**

The approach is the same as in Example 27-2. We should be aware that the longest carbon chain might not be *written* in a straight line.

Solution

(rewritten to emphasize the six-C chain)

The longest chain contains six carbons, so this compound is named as a derivative of hexane. There are three methyl substituents: two at carbon number 2 and one at carbon number 4. The IUPAC name of this compound is **2,2,4-trimethylhexane**.

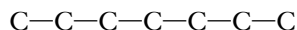
You should now work Exercises 13 and 14.

EXAMPLE 27-4 Writing Formulas from Names

Write the structure for 4-*tert*-butyl-2,5-dimethylheptane.

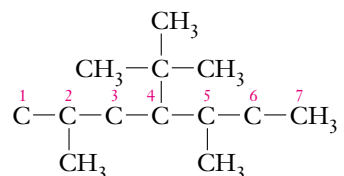
Plan

The root name “heptane” indicates that there is a seven-carbon chain.

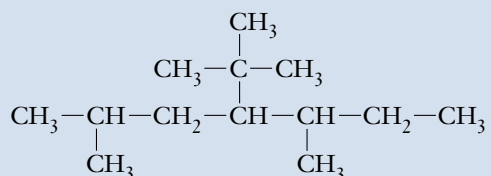


The names and numbers of the substituents tell us where to attach the alkyl groups.

Solution



Then we fill in enough hydrogens to saturate each C atom and arrive at the structure

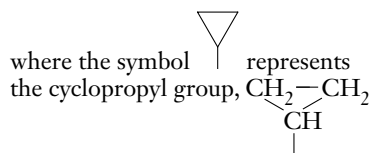
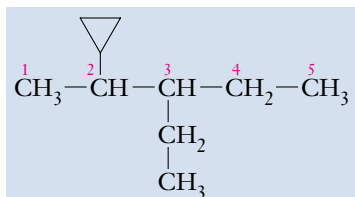
**EXAMPLE 27-5** Writing Formulas from Names

Write the structure for the compound 2-cyclopropyl-3-ethylpentane.

Plan

The root name “pentane” tells us that the structure is based on a five-carbon chain. We place the substituents at the positions indicated by the numbers in the name.

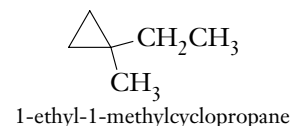
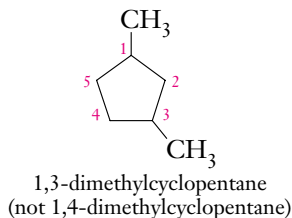
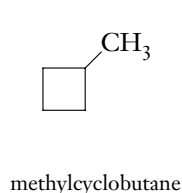
Solution



You should now work Exercise 16.

The names of substituted cycloalkanes are derived analogously to those of alkanes. (1) The base name is determined by the number of carbon atoms in the ring using the same base name as the alkane with the addition of cyclo in front. (2) If only one substituent is attached to the ring, no “location number” is required because all positions in a cycloalkane are equivalent. (3) Two or more functional groups on the ring are identified by location numbers, which should be assigned sequentially to the ring carbons in the order that gives the *smallest sum* of location numbers.

1,3-dimethylcyclopentane can exist as two different isomers; one with both methyl groups on the same side of the ring (*cis*-), another with the methyl groups on opposite sides of the plane of the ring (*trans*-). (See Section 27-3.)



UNSATURATED HYDROCARBONS

There are three classes of unsaturated hydrocarbons: (1) the alkenes and their cyclic counterparts, the cycloalkenes; (2) the alkynes and the cycloalkynes; and (3) the aromatic hydrocarbons.

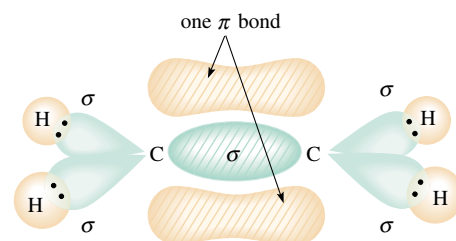
27-3 ALKENES

The simplest **alkenes** contain one carbon–carbon double bond, $C=C$, per molecule. The general formula for noncyclic alkenes is C_nH_{2n} . The simplest alkene is C_2H_4 , ethene, which is usually called by its common name, ethylene.

The bonding in ethylene was described in Section 8-13. The hybridization (sp^2) and bonding at other double-bonded carbon atoms are similar. Both carbon atoms in C_2H_4 are located at the centers of trigonal planes. Rotation about $C=C$ double bonds does not occur significantly at room temperature. Compounds that have the general formula $(XY)C=C(XY)$ therefore exist as a pair of *cis-trans* isomers. Figure 27-9 shows the *cis-trans* isomers of 1,2-dichloroethene. The existence of compounds with different arrangements of groups on the opposite sides of a bond with restricted rotation is called **geometric isomerism**. This *cis-trans* isomerism can occur across double bonds in alkenes and across single bonds in rings.

Two shared electron pairs draw the atoms closer together than a single electron pair does. Thus, carbon–carbon double bonds are shorter than $C-C$ single bonds, 1.34 Å versus 1.54 Å. The physical properties of the alkenes are similar to those of the alkanes, but their chemical properties are quite different.

The root for the name of each alkene is derived from the alkane having the same number of C atoms as the longest chain containing the double bond. In the trivial (common) system of nomenclature, the suffix *-ylene* is added to the characteristic root. In systematic (IUPAC) nomenclature, the suffix *-ene* is added to the characteristic root.



Four $C-H$ σ bonds, one $C-C$ σ bond (*green, hatched*), and one $C-C$ π bond (*tan, hatched*) in the planar C_2H_4 molecule.

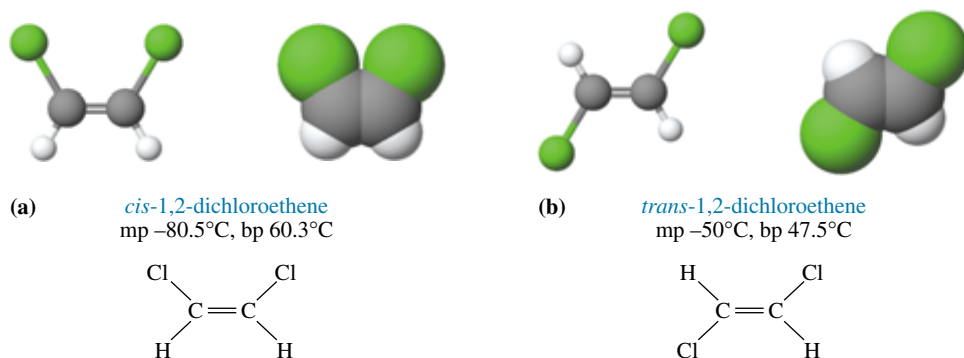


Figure 27-9 Two isomers of 1,2-dichloroethene are possible because rotation about the double bond is restricted. This is an example of *geometric isomerism*. A ball-and-stick model and a space-filling model are shown for each isomer. (a) The *cis* isomer. (b) The *trans* isomer.

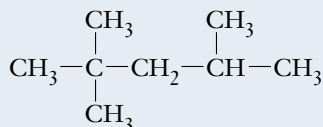


Petroleum

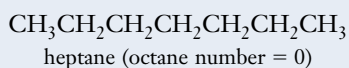
Petroleum, or crude oil, was discovered in the United States (Pennsylvania) in 1859 and in the Middle East (Iran) in 1908. It has been found in many other locations since these initial discoveries and is now pumped from the ground in many parts of the world. Petroleum consists mainly of hydrocarbons. Small amounts of organic compounds containing nitrogen, sulfur, and oxygen are also present. Each oil field produces petroleum with a particular set of characteristics. Distillation of petroleum produces several fractions.

Gasoline is much in demand, so higher hydrocarbons (C_{12} and up) are “cracked” to increase the amount of gasoline that can be made from a barrel of petroleum. The hydrocarbons are heated, in the absence of air and in the presence of a catalyst, to produce a mixture of smaller alkanes that can be used in gasoline. This process is called *catalytic cracking*.

The **octane number** (rating) of a gasoline indicates how smoothly it burns and how much engine “knock” it produces. (Engine knock is caused by premature detonation of fuel in the combustion chamber.) 2,2,4-trimethylpentane, isooctane, has excellent combustion properties and was arbitrarily assigned an octane number of 100. Heptane, $CH_3(CH_2)_5CH_3$, has very poor combustion properties and was assigned an octane number of zero.

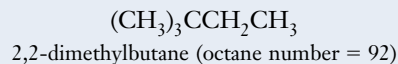
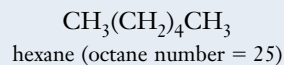


isooctane (octane number = 100)



Petroleum refinery towers.

Mixtures of these two were prepared and burned in test engines to establish the octane scale. The octane number of such a mixture is the percentage of isooctane in it. Gasolines burned in standard test engines are assigned octane numbers based on the compression ratio at which they begin to knock. A 90-octane fuel produces the same amount of knock as the 90% isooctane/10% heptane mixture. Branched-chain compounds produce less knock than straight-chain compounds. The octane numbers of two isomeric hexanes are



Petroleum Fractions

Fraction*	Principal Composition	Distillation Range (°C)
natural gas	$C_1 - C_4$	below 20
bottled gas	$C_5 - C_6$	20–60
gasoline	$C_4 - C_{12}$	40–200
kerosene	$C_{10} - C_{16}$	175–275
fuel oil, diesel oil	$C_{15} - C_{20}$	250–400
lubricating oils	$C_{18} - C_{22}$	above 300
paraffin	$C_{23} - C_{29}$	mp 50–60
asphalt	—	viscous liquid (“bottoms fraction”)
coke	—	solid

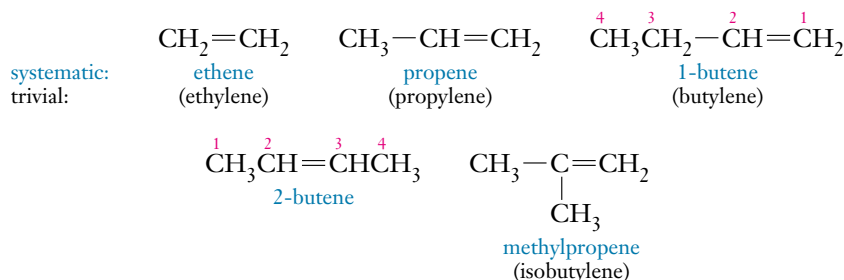
*Other descriptions and distillation ranges have been used, but all are similar.

Summary of IUPAC Rules for Naming Alkenes and Cycloalkenes

1. Locate the C atoms in the *longest C chain that contains the double bond*. Use the base name prefix with the ending *-ene*.
2. Number the C atoms of this chain sequentially *beginning at the end nearer the double bond*. Insert the number describing the position of the double bond (indicated by its *first* carbon location) before the base name. (This is necessary only for chains of four or more C atoms, because only one position is possible for a double bond in a chain of two or three carbon atoms.)
3. In naming alkenes, the double bond takes positional precedence over substituents on the carbon chain. The double bond is assigned the lowest possible number.
4. To name compounds with possible geometric isomers, consider the two largest groups within the carbon chain that contains the double bond—these are indicated as part of the base name. The isomer in which the largest groups at each end of the C=C are located on opposite sides is called *trans*. If the largest groups are on the same side, the molecule is referred to as *cis*. Insert the prefix *cis-* or *trans-* just before the number of the double bond to indicate whether the largest groups are on the same or opposite sides, respectively, of the double bond.
5. For cycloalkenes, the double bond is assumed to be between C atoms 1 and 2, so no position number is needed to describe it.

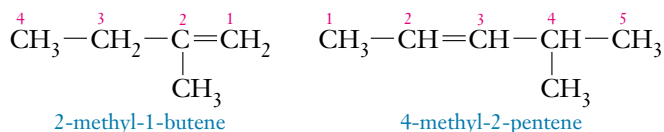
The prefix *trans-* means “across” or “on the other side of.” As a reminder of this terminology, think of words such as “transatlantic.”

Some illustrations of this naming system follow.

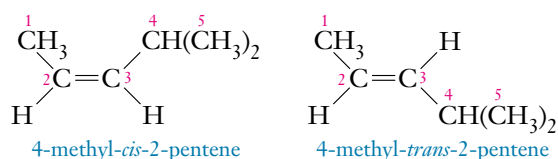


There are two isomers of 2-butene, *cis*-2-butene and *trans*-2-butene.

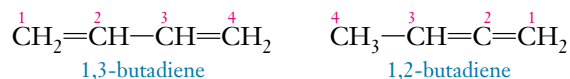
The following two names illustrate the application of Rule 3.



4-Methyl-2-pentene can exist as either of two isomers. Their names illustrate the application of Rule 4.



Some alkenes, called **polyenes**, have two or more carbon–carbon double bonds per molecule. The suffixes *-adiene*, *-atriene*, and so on are used to indicate the number of (C=C) double bonds in a molecule.

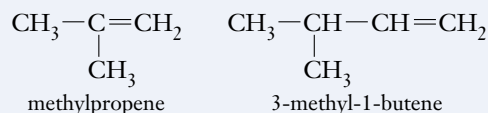


1,3-Butadiene and similar molecules that contain *alternating* single and double bonds are described as having **conjugated double bonds**. Such compounds are of special interest because of their polymerization reactions (Section 27-19).



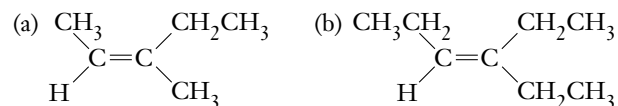
Problem-Solving Tip: *When Is the Location of a Substituent or a Multiple Bond Not Included in an IUPAC Name?*

If only one location is possible for a substituent or double bond, the number that indicates the location can be left out of the compound's name. If there is doubt, put the number in the name. For example, "2-methyl-1-propene" is named simply methylpropene. There are no other locations possible for the substituent or the double bond. The name without the numbers is the correct name. Both numbers are necessary to name 3-methyl-1-butene, however.



EXAMPLE 27-6 Naming Alkenes

Give the IUPAC names of the following two alkenes.

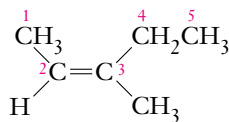


Plan

For each compound, we first find the longest chain that includes the double bond, and then number it beginning at the end nearer the double bond (Rules 1 and 2). Then we specify the identities and positions of substituents in the same way we did for alkanes. In (a) we specify the geometric isomer by locating the two largest groups attached to the double-bonded carbons and then describing their relationship using the *cis-trans* terminology.

Solution

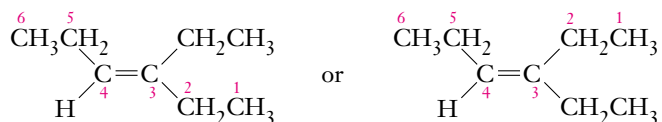
(a)



The longest such chain contains five atoms and has a double bond beginning at atom 2; thus, the compound is named as a derivative of 2-pentene. Now we must apply Rule 4. The two

largest groups in the chain are the terminal —CH_3 (carbon 1) and the $\text{—CH}_2\text{CH}_3$ (carbons 4 and 5); these are on the *same side* of the double bond, so we name the compound as a derivative of *cis*-2-pentene. The only substituent is the methyl group at carbon 3. The full name of the compound is **3-methyl-*cis*-2-pentene**.

(b) There are two choices for the longest chain, and either one would have an ethyl substituent.

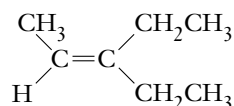


We could number either chain from the other end and still have the double bond starting at carbon 3; we number from the end that gives the carbon bearing the ethyl group the lowest possible position number, 3. Carbon 3 has two equivalent substituents, so geometric isomerism is not possible, and we do not use the *cis-trans* terminology. The name is **3-ethyl-3-hexene**.

You should now work Exercise 20.

EXAMPLE 27-7 Naming Alkenes

Name the following alkene.

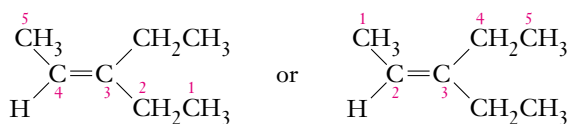


Plan

As we did in Example 27-6(b), we first find the longest chain that includes the double bond, and then number it beginning at the end nearer the double bond (Rules 1 and 2). Then we specify the identities and positions of substituents in the same way we did for alkanes.

Solution

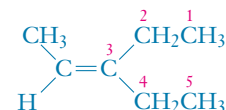
There are two choices for the longest chain, and either one would have an ethyl substituent.



Carbon 3 has two equivalent substituents, so geometric isomerism is not possible, and we do not use the *cis-trans* terminology. The name is **3-ethyl-2-pentene**.

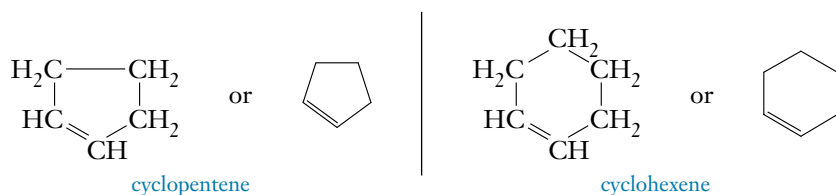
You should now work Exercise 22.


One would not number the carbons as:



Rule 1 requires that we use the longest chain that includes both carbons of the double bond.

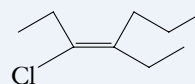
The cycloalkenes are represented by the general formula $\text{C}_n\text{H}_{2n-2}$. Two cycloalkenes and their skeletal representations are



 **Problem-Solving Tip: How to Draw Skeletal Representations**

The rules for drawing skeletal representations follow.

1. A carbon atom is assumed to be at each intersection of two lines and at the end of each line. All carbon–carbon bonds are shown as lines. A carbon atom might be shown for clarity.
2. Because carbon has four bonds, we mentally supply hydrogens to give each carbon its four bonds.
3. Atoms other than hydrogen and carbon are shown. The following skeletal representation is that of 3-chloro-4-ethyl-*cis*-3-heptene.



and its formula is $C_9H_{17}Cl$.

EXAMPLE 27-8 Cycloalkenes

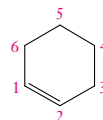
Write the skeletal representation of 3-methylcyclohexene.

Plan

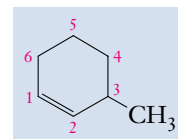
We draw the ring of the specified size with one double bond in the ring. We number the ring so the double bond is between atoms 1 and 2. Then we add the designated substituents at the indicated positions.

Solution

We number the six-membered ring so that the double bond is between atoms 1 and 2.



A methyl group is attached at carbon 3; the correct structure is



Remember that each intersection of two lines represents a carbon atom; there are enough H atoms at each C atom to make a total of four bonds to carbon.

You should now work Exercise 21.

27-4 ALKYNES

The **alkynes**, or acetylenic hydrocarbons, contain one or more carbon–carbon triple bonds, $-C\equiv C-$. The noncyclic alkynes with one triple bond per molecule have the general formula C_nH_{2n-2} . The bonding in all alkynes is similar to that in acetylene (Section

8-14). Triply bonded carbon atoms are *sp*-hybridized. The triply bonded atoms and their adjacent atoms lie on a straight line (Figure 27-10).

Alkynes are named like the alkenes except that the suffix *-yne* is added to the characteristic root. The first member of the series is commonly called acetylene. Its molecular formula is C_2H_2 . It is thermodynamically unstable, decomposing explosively to $C(s)$ and $H_2(g)$ at high pressures. It may be converted into ethene (also known as ethylene) and then to ethane by the addition of hydrogen. The condensed formulas for several small alkynes are

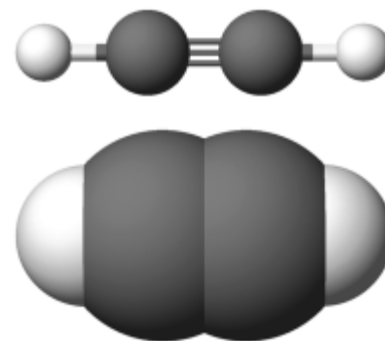
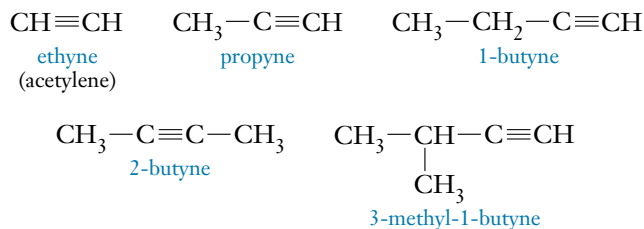


Figure 27-10 Models of acetylene, $H-C \equiv C-H$.

The triple bond takes positional precedence over substituents on the carbon chain. It is assigned the lowest possible number in naming.

Summary of IUPAC Rules for Naming Alkynes

Alkynes are named like the alkenes except for the following two points.

1. The suffix *-yne* is added to the characteristic root.
2. Because the linear arrangement about the triple bond does not lead to geometric isomerism, the prefixes *cis*- and *trans*- are not used.

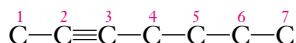
EXAMPLE 27-9 Alkynes

Write the structural formula of 5,5-dimethyl-2-heptyne.

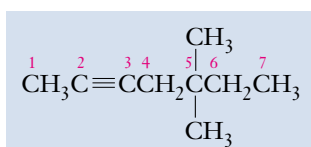
Plan

The structure is based on a seven-carbon chain with a triple bond beginning at carbon 2. We add methyl groups at the positions indicated.

Solution



Two methyl groups are attached to carbon 5, and sufficient hydrogens are added to complete the bonding at each C atom.

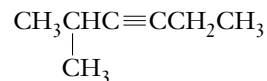


The carbon chain is numbered to give the triple bond the lowest possible numbers even though that results in higher position numbers for the methyl substituents.

You should now work Exercise 28.

EXAMPLE 27-10 Naming Alkynes

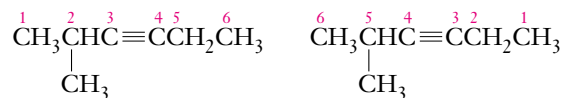
Give the IUPAC name of the compound

**Plan**

We find the longest chain and number it to give the triple bond the lowest possible number. Then we specify the substituent(s) by name and position number.

Solution

The longest continuous carbon chain that includes the triple bond has six C atoms. There are two ways in which we could choose and number such a chain, and in both the triple bond would be between C atoms 3 and 4.



Because we also want the methyl substituent to have the lowest possible number, we choose the first possibility. The name of the compound is **2-methyl-3-hexyne**.

You should now work Exercise 30.

AROMATIC HYDROCARBONS

Originally the word “**aromatic**” was applied to pleasant-smelling substances. The word now describes benzene, its derivatives, and certain other compounds that exhibit similar chemical properties. Some have very foul odors because of substituents on the benzene ring. On the other hand, many fragrant compounds do not contain benzene rings.

Steel production at one time required large amounts of coke. This was prepared by heating bituminous coal to high temperatures in the absence of air. This process also favors production of *coal gas* and *coal tar*. Because of the enormous amount of coal converted to coke, coal tar was produced in large quantities. It served as a source of aromatic compounds. For each ton of coal converted to coke, about 5 kg of aromatic compounds were obtained. Today petroleum refining is the major source of aromatic hydrocarbons.

Early research on the reactions of the aromatic hydrocarbons led to methods for preparing a great variety of dyes, drugs, flavors, perfumes, and explosives. More recently, large numbers of polymeric materials, such as plastics and fabrics, have been prepared from these compounds.

27-5 BENZENE

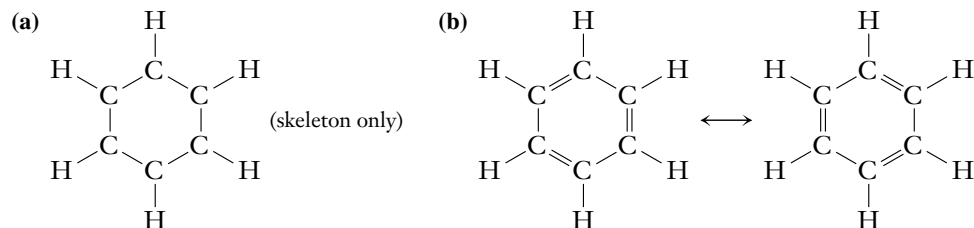
Benzene is the simplest aromatic hydrocarbon. By studying its reactions, we can learn a great deal about aromatic hydrocarbons. Benzene was discovered in 1825 by Michael Faraday when he fractionally distilled a by-product oil obtained in the manufacture of illuminating gas from whale oil.

The main components of coal gas are hydrogen ($\approx 50\%$) and methane ($\approx 30\%$).

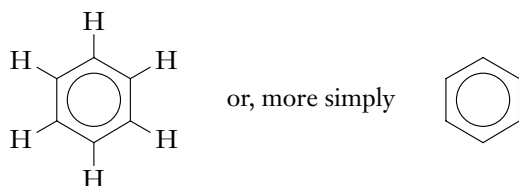
Distillation of coal tar produces a variety of aromatic compounds.

Elemental analysis and determination of its molecular weight showed that the molecular formula for benzene is C_6H_6 . The formula suggests that it is highly unsaturated. But its properties are quite different from those of alkenes and alkynes.

The facts that only one monosubstitution product is obtained in many reactions and that no addition products can be prepared show conclusively that benzene has a *symmetrical ring structure*. Stated differently, every H atom is equivalent to every other H atom, and this is possible only in a symmetrical ring structure (a).



The debate over the structure and bonding in benzene raged for at least 30 years. In 1865, Friedrich Kekulé (1829–1896) suggested that the structure of benzene was intermediate between two structures [part (b) of the preceding structures] that we now call resonance structures. We often represent benzene as



All 12 atoms in a benzene molecule lie in a plane. This suggests sp^2 hybridization of each carbon. The six sp^2 -hybridized C atoms lie in a plane, and the unhybridized p orbitals extend above and below the plane. Side-by-side overlap of the p orbitals forms pi orbitals (Figure 9-11). The electrons associated with the pi bonds are *delocalized* over the entire benzene ring (Figure 27-11a,b).

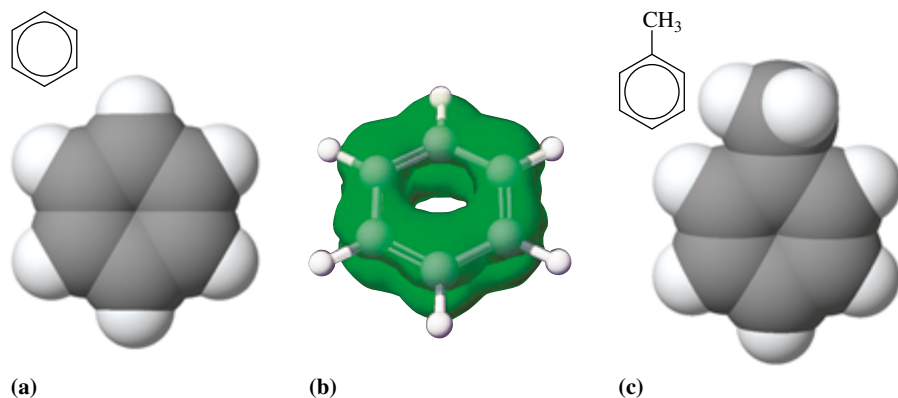
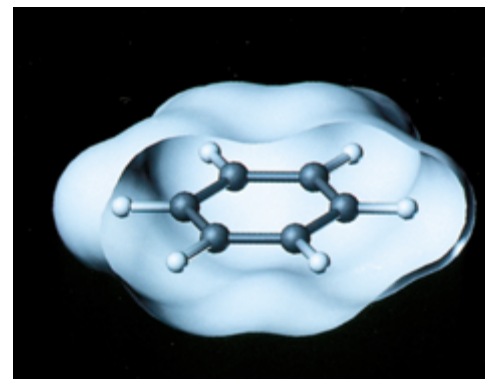


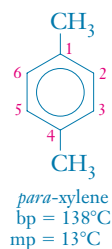
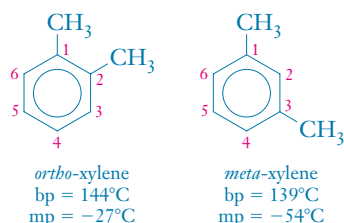
Figure 27-11 (a) A model of the benzene molecule, C_6H_6 , and (b) its electron distribution. (c) A model of toluene, $C_6H_5CH_3$. This is a derivative of benzene in which one H atom has been replaced by an alkyl group.



A computer-generated model of a molecule of benzene, C_6H_6 . A ball-and-stick model is shown inside a representation of the molecular surface.

The structure of benzene is described in detail in Section 9-6 in terms of MO theory.

27-6 OTHER AROMATIC HYDROCARBONS



Benzene molecules bearing alkyl substituents are called **alkylbenzenes**. The simplest of these is methylbenzene (common name, toluene), shown in Figure 27-11c. The dimethylbenzenes are called xylenes. Three different compounds (Table 27-6) have the formula $C_6H_4(CH_3)_2$ (see margin). These three xylenes are *constitutional isomers*. In naming these (as well as other disubstituted benzenes), we use prefixes *ortho*- (abbreviated *o*-), *meta*- (*m*-), or *para*- (*p*-) to refer to relative positions of substituents on the benzene ring. The *ortho*- prefix refers to two substituents located on *adjacent* carbon atoms; for example, 1,2-dimethylbenzene is *o*-xylene. The *meta*- prefix identifies substituents on C atoms 1 and 3, so 1,3-dimethylbenzene is *m*-xylene. The *para*- prefix refers to substituents on C atoms 1 and 4, so 1,4-dimethylbenzene is *p*-xylene.

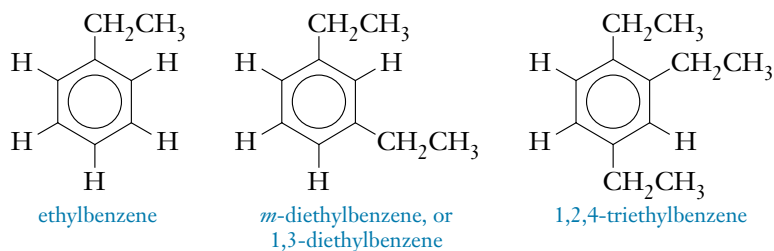
Summary of Rules for Naming Derivatives of Benzene

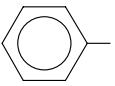
1. If there is only one group on the ring, no number is needed to designate its position.
2. If there are two groups on the ring, we use the traditional designations.

ortho- or *o*- for 1,2-disubstitution
meta- or *m*- for 1,3-disubstitution
para- or *p*- for 1,4-disubstitution

3. If there are three or more groups on the ring, location numbers are assigned to give the *minimum sum* of numbers.

Examples are



When an H atom is removed from a benzene molecule, C_6H_6 , the resulting group, C_6H_5- or , is called “phenyl.” Sometimes we name mixed alkyl-aromatic hydrocarbons on that basis.

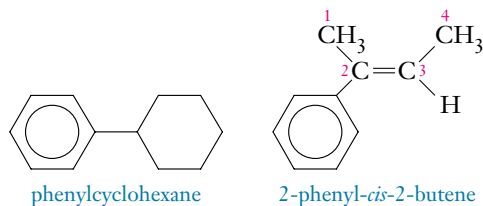
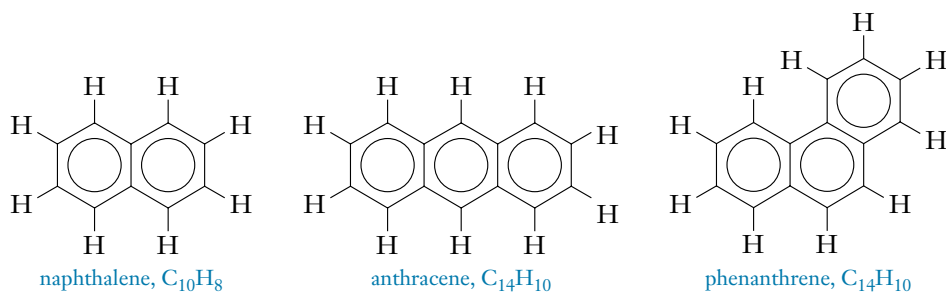


TABLE 27-6 *Aromatic Hydrocarbons from Coal Tar*

Name	Formula	Normal bp (°C)	Normal mp (°C)	Solubility
benzene	C ₆ H ₆	80	+6	
toluene	C ₆ H ₅ CH ₃	111	-95	
<i>o</i> -xylene	C ₆ H ₄ (CH ₃) ₂	144	-27	
<i>m</i> -xylene	C ₆ H ₄ (CH ₃) ₂	139	-54	All insoluble
<i>p</i> -xylene	C ₆ H ₄ (CH ₃) ₂	138	+13	in water
naphthalene	C ₁₀ H ₈	218	+80	
anthracene	C ₁₄ H ₁₀	342	+218	
phenanthrene	C ₁₄ H ₁₀	340	+101	

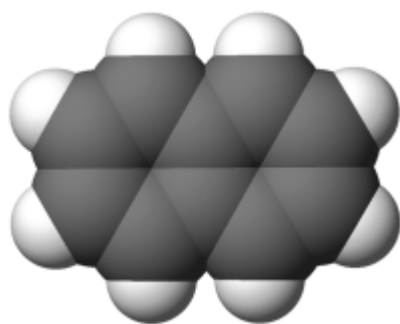
Another class of aromatic hydrocarbons consists of “condensed” or “fused-ring” aromatic systems. The simplest of these are naphthalene, anthracene, and phenanthrene.



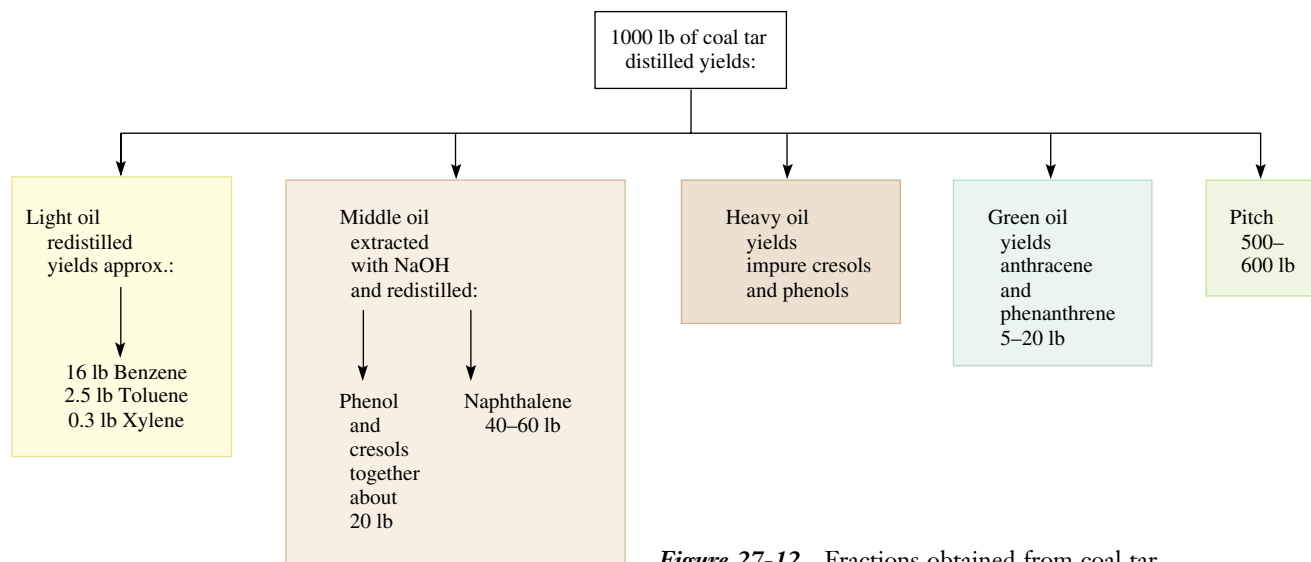
No hydrogen atoms are attached to the carbon atoms that are involved in fusion of aromatic rings, that is, carbon atoms that are members of two or more aromatic rings.

The traditional name is often used as part of the base name in naming an aromatic hydrocarbon and its derivatives. You should know the names and structures of the aromatic hydrocarbons discussed thus far: benzene, toluene, the three xylenes, naphthalene, anthracene, and phenanthrene.

Distillation of coal tar provides four volatile fractions as well as the pitch that is used for surfacing roads and in the manufacture of “asphalt” roofing (Figure 27-12). Eight aromatic hydrocarbons obtained in significant amounts by efficient fractional distillation of the “light oil” fraction are those in Table 27-6.



Naphthalene.



27-7 HYDROCARBONS: A SUMMARY

Hydrocarbons contain only carbon and hydrogen. They can be subdivided into various groups. To assist you in organizing what you have studied so far in this chapter, take a few minutes and study Figure 27-13.

FUNCTIONAL GROUPS

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 11.5, Functional Groups.

As you study the following sections, you may wish to refer to the summary in Section 27-15.

The study of organic chemistry is greatly simplified by considering hydrocarbons as parent compounds and describing other compounds as derived from them. In general, an organic molecule consists of a skeleton of carbon atoms with special groups of atoms attached to that skeleton. These special groups of atoms are often called **functional groups** because they represent the most common sites of chemical reactivity (function). The only functional groups that are possible in hydrocarbons are double and triple (i.e., pi) bonds. Atoms other than C and H are called **heteroatoms**, the most common being O, N, S, P, and the halogens. Most functional groups contain one or more heteroatoms.

In the next several sections we will introduce some common functional groups that contain heteroatoms and learn a little about the resulting classes of compounds. We will continue to represent alkyl groups with the symbol R—. We commonly use that symbol to represent either an aliphatic (e.g., alkyl) or an aromatic (e.g., an aryl such as phenyl) group. When we specifically mean an aryl group, we will use the symbol Ar—.

27-8 ORGANIC HALIDES

Almost any hydrogen atom in a hydrocarbon can be replaced by a halogen atom to give a stable compound. Table 27-7 shows some organic halides and their names.

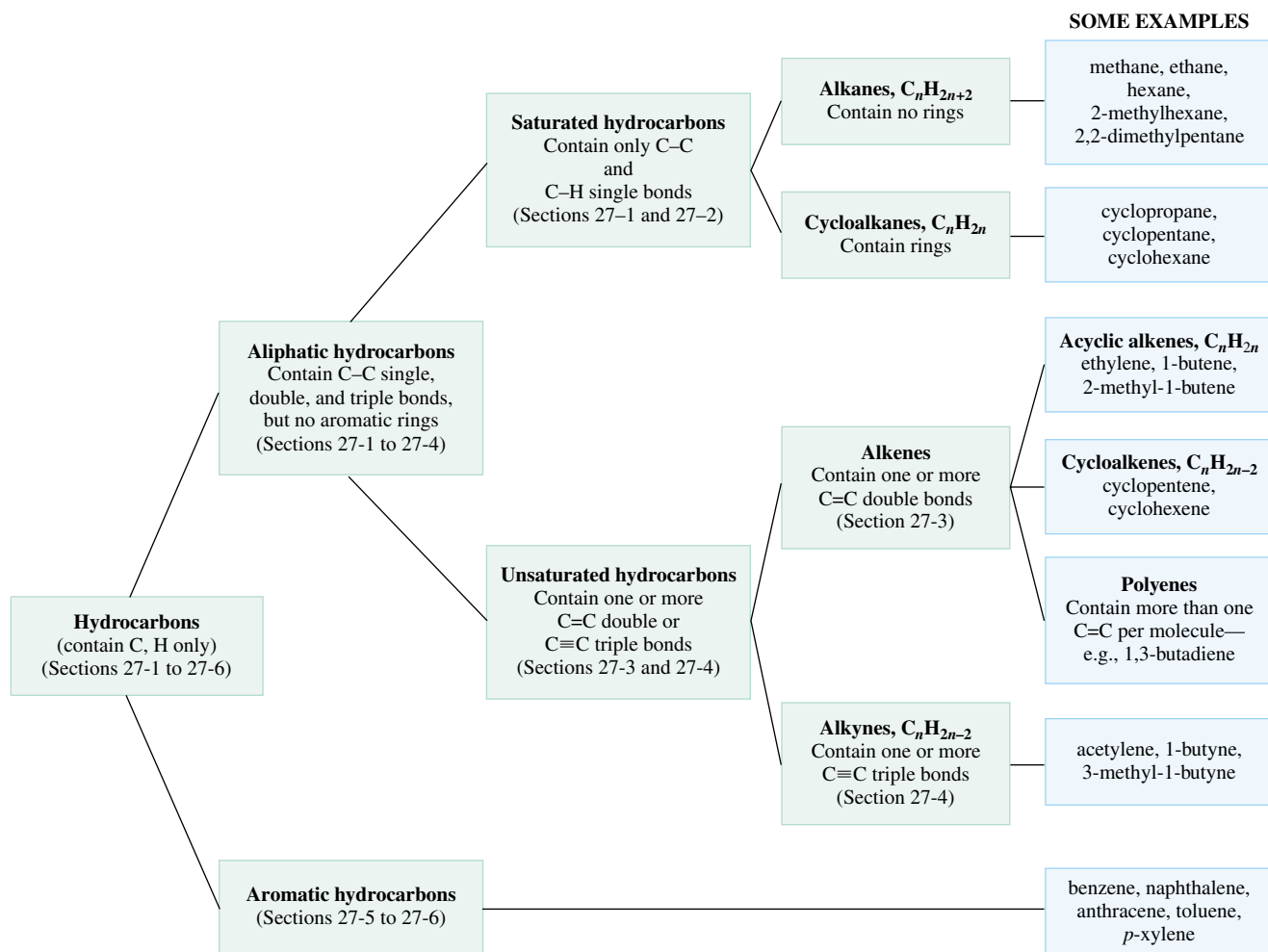


Figure 27-13 A classification of hydrocarbons.

In the IUPAC naming system, the organic halides are named as *halo-* derivatives of the parent hydrocarbons. The prefix *halo-* can be *fluoro-*, *chloro-*, *bromo-*, or *iodo-*. Simple alkyl chlorides are sometimes given common names as alkyl derivatives of the hydrogen halides. For instance, the IUPAC name for CH_3CH_2-Cl is chloroethane; it is commonly called ethyl chloride by analogy to $H-Cl$, hydrogen chloride.

A carbon atom can be bonded to as many as four halogen atoms, so an enormous number of organic halides can exist. Completely fluorinated compounds are known as **fluorocarbons** or sometimes *perfluorocarbons*. The fluorocarbons are even less reactive than hydrocarbons. Saturated compounds in which all H atoms have been replaced by some combination of Cl and F atoms are called *chlorofluorocarbons* or sometimes **freons**. These compounds were widely used as refrigerants and as propellants in aerosol cans. However, the release of chlorofluorocarbons into the atmosphere has been shown to be quite damaging to the earth's ozone layer. Since January 1978, the use of chlorofluorocarbons in aerosol cans in the United States has been banned, and efforts to develop both controls for existing chlorofluorocarbons and suitable replacements continue. The production and sale of freons have been banned in many countries.

Freon is a DuPont trademark for certain chlorofluorocarbons; other companies' related products are known by other names. Typical freons are trichlorofluoromethane, $CFCl_3$ (called Freon-11), and dichlorodifluoromethane, CF_2Cl_2 (called Freon-12).

TABLE 27-7 Some Organic Halides

Formula	Structural Formula	Normal bp (°C)	IUPAC Name	Common Name
CH ₃ Cl	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{H} \end{array}$	-23.8	chloromethane	methyl chloride
CH ₂ Cl ₂	$\begin{array}{c} \text{Cl} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{H} \end{array}$	40.2	dichloromethane	methylene chloride
CHCl ₃	$\begin{array}{c} \text{Cl} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array}$	61	trichloromethane	chloroform
CCl ₄	$\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array}$	76.8	tetrachloromethane	carbon tetrachloride
CHCl ₂ Br	$\begin{array}{c} \text{Cl} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{Br} \end{array}$	90	bromodichloromethane	—

27-9 ALCOHOLS AND PHENOLS

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 11.6, Reactions of Alcohols.

Alcohols and phenols contain the hydroxyl group ($-\text{O}-\text{H}$) as their functional group. **Alcohols** may be considered to be derived from saturated or unsaturated hydrocarbons by the replacement of at least one H atom by a hydroxyl group. The properties of alcohols result from a hydroxyl group attached to an *aliphatic* carbon atom, $-\text{C}-\text{O}-\text{H}$. Ethanol (ethyl alcohol) is the most common example (Figure 27-14).

When a hydrogen atom on an aromatic ring is replaced by a hydroxyl group (Figure 27-15), the resulting compound is known as a **phenol**. Such compounds behave more like acids than alcohols. Alternatively, we may view alcohols and phenols as derivatives of water in which one H atom has been replaced by an organic group.

The simplest phenol is called phenol. The most common member of a class of compounds is often called by the class name. Salt, sugar, alcohol, and phenol are examples.

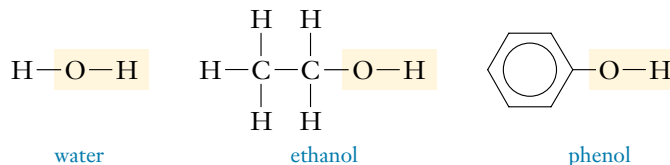
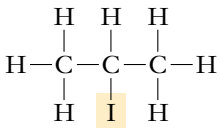
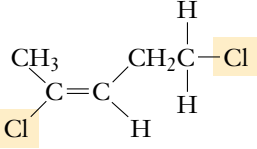
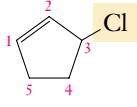
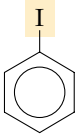
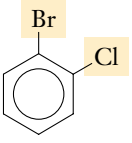
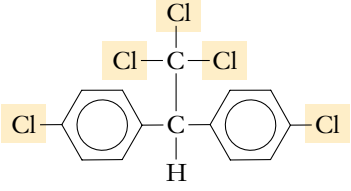


TABLE 27-7 (continued)

Formula	Structural Formula	Normal bp (°C)	IUPAC Name	Common Name
$(\text{CH}_3)_2\text{CHI}$		89.5	2-iodopropane	isopropyl iodide
$\text{CH}_3\text{ClC}=\text{CHCH}_2\text{CH}_2\text{Cl}$		40	2,5-dichloro- <i>cis</i> -2-pentene; <i>trans</i> isomer is also possible	—
$\text{C}_5\text{H}_7\text{Cl}$		25	3-chlorocyclopentene is shown; other isomers are also possible	—
$\text{C}_6\text{H}_5\text{I}$		118	iodobenzene	phenyl iodide
$\text{C}_6\text{H}_4\text{ClBr}$		204	1-bromo-2-chlorobenzene is shown; other isomers are also possible	<i>o</i> -bromochlorobenzene
$\text{C}_{14}\text{H}_9\text{Cl}_5$			1,1,1-trichloro-2,2-bis(<i>p</i> -chlorophenyl)ethane	DDT

Indeed, this is a better view. The structure of water was discussed in Section 8-9. The hydroxyl group in an alcohol or a phenol is covalently bonded to a carbon atom, but the O—H bond is quite polar. The oxygen atom has two unshared electron pairs, and the C—O—H bond angle is nearly 104.5°.

The presence of a bonded alkyl or aryl group changes the properties of the —OH group. *Alcohols* are so very weakly acidic that they are thought of as neutral compounds. *Phenols* are weakly acidic.

Many properties of alcohols depend on whether the hydroxyl group is attached to a carbon that is bonded to *one*, *two*, or *three* other carbon atoms.

Primary alcohols contain one R group; **secondary alcohols** contain two R groups; and **tertiary alcohols** contain three R groups bonded to the carbon atom to which the —OH group is attached.

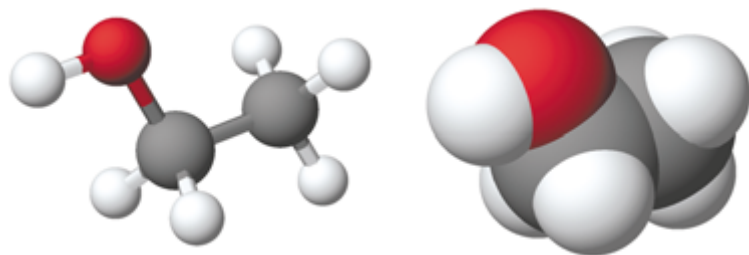


Figure 27-14 Models of ethanol (also called ethyl alcohol or grain alcohol), $\text{CH}_3\text{CH}_2\text{OH}$.

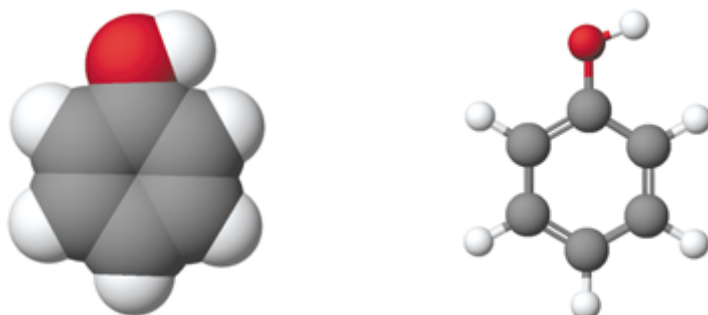
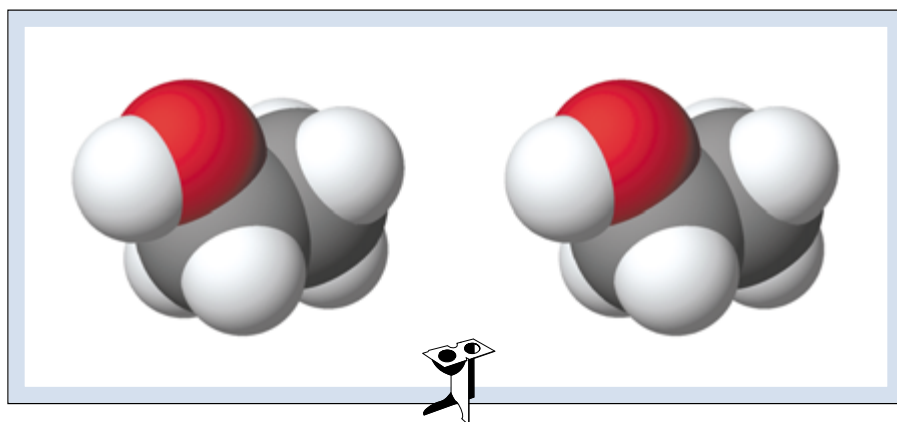
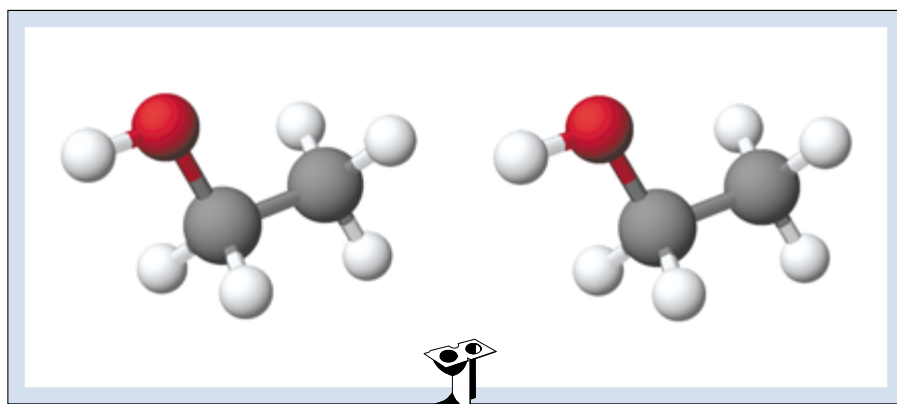
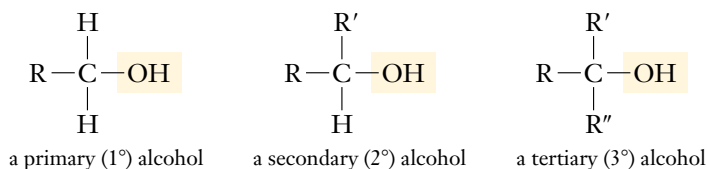


Figure 27-15 Models of phenol, $\text{C}_6\text{H}_5\text{OH}$.

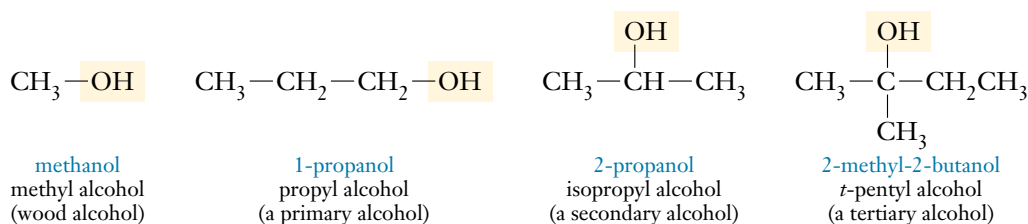
Representing alkyl groups as R, we can illustrate the three classes of alcohols. The R groups may be the same or different.



In writing organic structures, we often use primes when we wish to specify that the alkyl groups might be different, for example, R, R', R''.

Nomenclature

The systematic name of an alcohol consists of the root name plus an *-ol* ending. A numeric prefix indicates the position of the —OH group on a chain of three or more carbon atoms.



EXAMPLE 27-11 Formulas of Alcohols

There are four constitutional isomers of the saturated acyclic four-carbon alcohols with one —OH per molecule. Write the structural formula of each, and identify each as primary, secondary, or tertiary. Name each isomer.

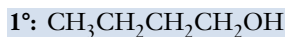
Acyclic compounds contain no rings.

Plan

The carbon skeleton can be either a straight chain, C—C—C—C, or branched, C—C—C.

Each skeleton has two different types of carbons to which the —OH group can be attached.

Solution



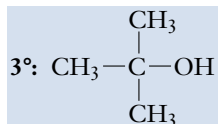
1-butanol
butyl alcohol



2-butanol
secondary butyl alcohol



2-methyl-1-propanol
isobutyl alcohol



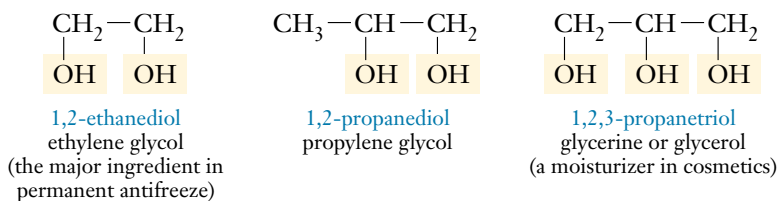
2-methyl-2-propanol
tertiary butyl alcohol

You should now work Exercise 46.

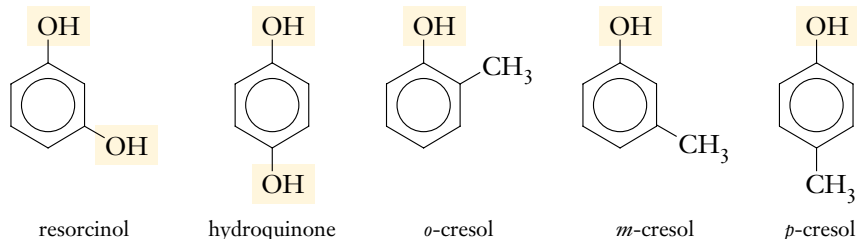


The **polyhydric alcohols** contain more than one —OH group per molecule. Those containing two OH groups per molecule are called **glycols**. Important examples of polyhydric alcohols include

Polyhydric alcohols are used in permanent antifreeze and in cosmetics.



Phenols are usually referred to by their common names. Examples are

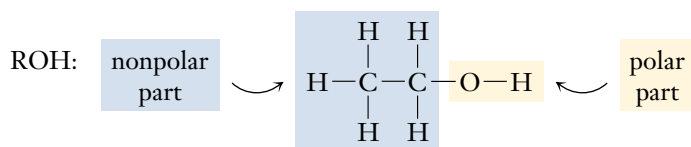


The *o*-, *m*-, and *p*- notation was introduced in Section 27-6.

As you might guess, cresols occur in “creosote,” a wood preservative.

Physical Properties

The hydroxyl group, —OH, is quite polar, whereas alkyl groups, R, are nonpolar. The properties of alcohols depend on two factors: (1) the number of hydroxyl groups per molecule and (2) the size of the nonpolar portion of the molecule.



The low-molecular-weight alcohols are soluble in water in all proportions (miscible). Beginning with the four butyl alcohols, solubility in water decreases rapidly with increasing molecular weight. This is because the nonpolar parts of such molecules are much larger than the polar parts. Many polyhydric alcohols are very soluble in water because they contain two or more polar —OH groups per molecule.

Table 27-8 shows that the boiling points of unbranched primary alcohols increase, and their solubilities in water decrease, with increasing molecular weight. The boiling points

TABLE 27-8 Physical Properties of Primary Alcohols

Name	Formula	Normal bp (°C)	Solubility in H ₂ O (g/100 g at 20°C)
methanol	CH ₃ OH	65	miscible
ethanol	CH ₃ CH ₂ OH	78.5	miscible
1-propanol	CH ₃ CH ₂ CH ₂ OH	97	miscible
1-butanol	CH ₃ CH ₂ CH ₂ CH ₂ OH	117.7	7.9
1-pentanol	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH	137.9	2.7
1-hexanol	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ OH	155.8	0.59

of alcohols are much higher than those of the corresponding alkanes (see Table 27-2) because of the hydrogen bonding of the hydroxyl groups.

Most phenols are solids at 25°C. Phenols are only slightly soluble in water unless they contain other functional groups that interact with water.

Uses

Many alcohols and phenols have considerable commercial importance. Methanol, CH_3OH , was formerly produced by the destructive distillation of wood and is sometimes called wood alcohol. It is now produced in large quantities from carbon monoxide and hydrogen. It is very toxic and causes permanent blindness when taken internally.

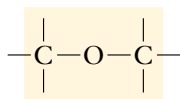
Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, also known as ethyl alcohol or grain alcohol, can be prepared by fermentation of sugar. The most ancient written literature refers to beverages that were obviously alcoholic!

Many simple alcohols are important raw materials in the industrial synthesis of polymers, fibers, explosives, plastics, and pharmaceutical products. Phenols are widely used in the preparation of plastics and dyes. Solutions of phenols are used as antiseptics and disinfectants. Some uses of polyhydric alcohols depend on their relatively high boiling points. For instance, glycerine is used as a wetting agent in cosmetic preparations. Ethylene glycol (bp 197°C), which is miscible with water, is used in commercial permanent antifreeze.

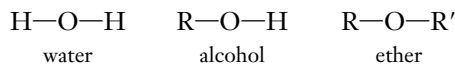
Fermentation is an enzymatic process carried out by certain kinds of bacteria.

27-10 ETHERS

When the word “ether” is mentioned, most people think of the well-known anesthetic, diethyl ether. There are many ethers. Their uses range from artificial flavorings to refrigerants and solvents. An **ether** is a compound in which an O atom is bonded to two organic groups.

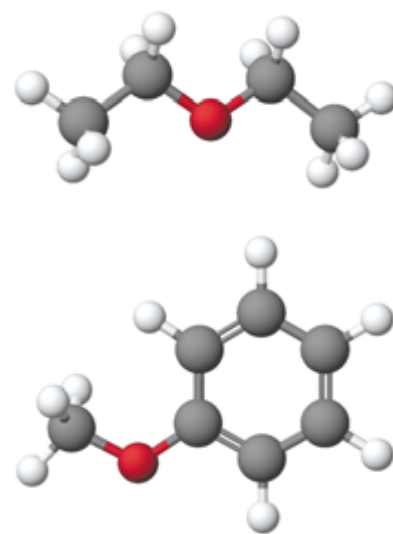


Alcohols are considered derivatives of water in which one H atom has been replaced by an organic group. Ethers may be considered derivatives of water in which both H atoms have been replaced by organic groups.

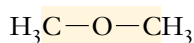


The similarity is only structural, however, because ethers are only slightly polar and are chemically rather unreactive. In fact, their physical properties are similar to those of the corresponding alkanes; for example, CH_3OCH_3 is like $\text{CH}_3\text{CH}_2\text{CH}_3$.

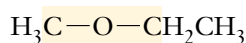
Three kinds of ethers are known: (1) aliphatic, (2) aromatic, and (3) mixed. Common names are used for ethers in most cases.



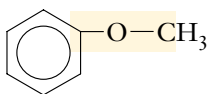
Models of diethyl ether (*top*) and methyl phenyl ether (*bottom*).



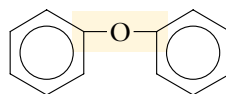
methoxymethane
dimethyl ether
(an aliphatic ether)



methoxyethane
methyl ethyl ether
(an aliphatic ether)



methoxybenzene
methyl phenyl ether
anisole
(a mixed ether)



phenoxybenzene
diphenyl ether
(an aromatic ether)

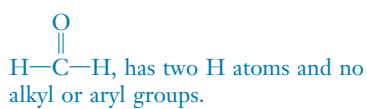
When the benzene ring is a substituent, it is called a phenyl group ($-\text{C}_6\text{H}_5$).

Diethyl ether is a very low boiling liquid (bp 35°C). Dimethyl ether is a gas that is used as a refrigerant. The aliphatic ethers of higher molecular weights are liquids, and the aromatic ethers are liquids and solids.

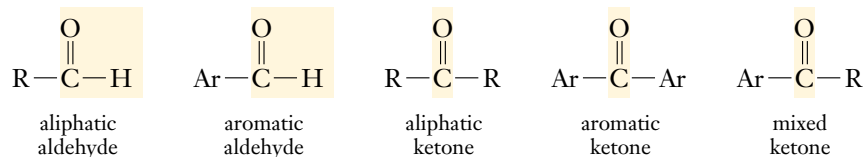
Even ethers of low molecular weight are only slightly soluble in water. Diethyl ether is an excellent solvent for organic compounds. It is widely used to extract organic compounds from plants and other natural sources.

27-11 ALDEHYDES AND KETONES

The simplest aldehyde, formaldehyde,



Aldehydes and ketones contain the carbonyl group, >C=O . In **aldehydes**, at least one H atom is bonded to the carbonyl group. **Ketones** have two carbon atoms bonded to a carbonyl group. Models of formaldehyde (the simplest aldehyde) and acetone (the simplest ketone) are shown in Figure 27-16.



Aldehydes are usually called by their common names. These are derived from the name of the acid with the same number of C atoms (Table 27-9). The systematic (IUPAC) name is derived from the name of the parent hydrocarbon. The suffix *-al* is added to the characteristic stem. The carbonyl group takes positional precedence over most other substituents.

Formaldehyde has long been used as a disinfectant and as a preservative (including embalming fluid) for biological specimens. Its main use is in the production of certain plastics and in binders for plywood. Many important natural substances are aldehydes and ketones. Examples include sex hormones, some vitamins, camphor, and the flavorings extracted from almonds and cinnamon. Aldehydes contain a carbon–oxygen double bond, so they are very reactive compounds. As a result, they are valuable in organic synthesis, particularly in the construction of carbon chains.

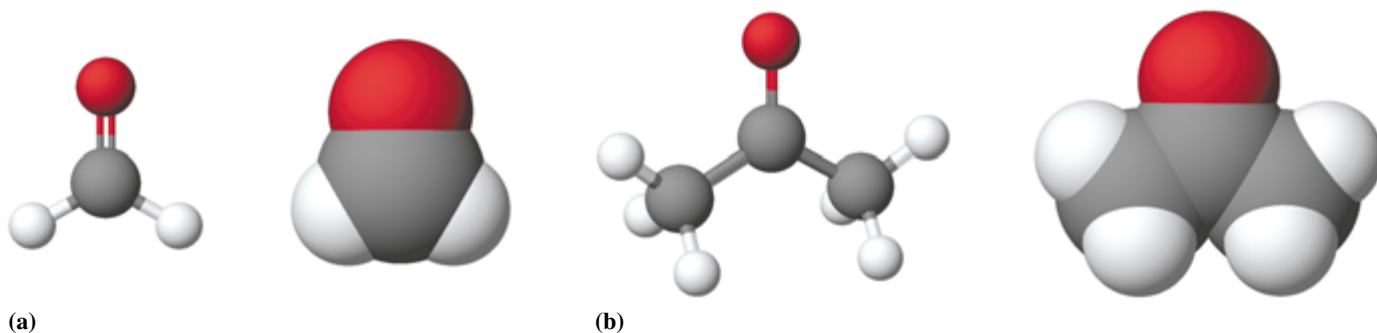
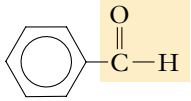
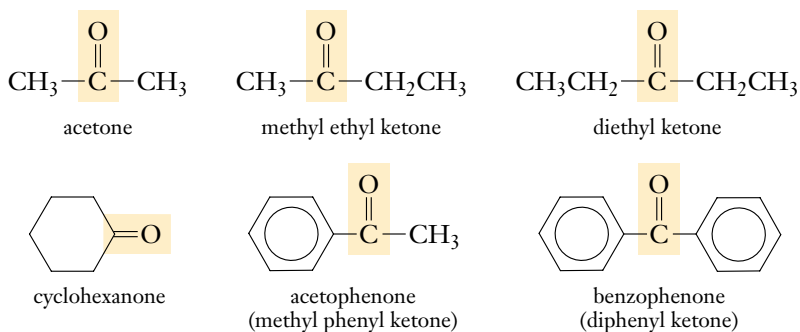


Figure 27-16 (a) Models of formaldehyde, HCHO, the simplest aldehyde. (b) Models of acetone, CH₃–CO–CH₃, the simplest ketone.

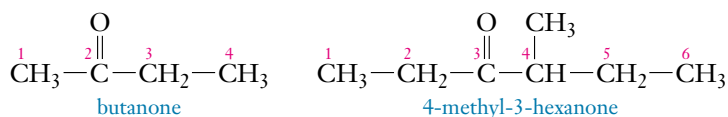
TABLE 27-9 Properties of Some Simple Aldehydes

Common Name	Formula	Normal bp (°C)
formaldehyde (methanal)	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	-21
acetaldehyde (ethanal)	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	20.2
propionaldehyde (propanal)	$\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	48.8
benzaldehyde		179.5

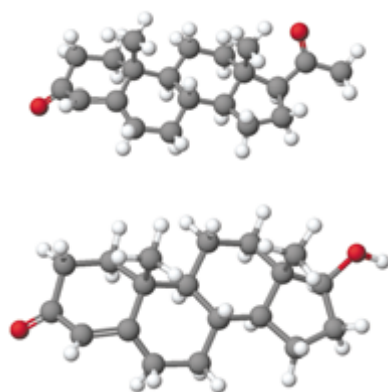
The simplest ketone is called acetone. Other simple, commonly encountered ketones are usually called by their common names. These are derived by naming the alkyl or aryl groups attached to the carbonyl group.



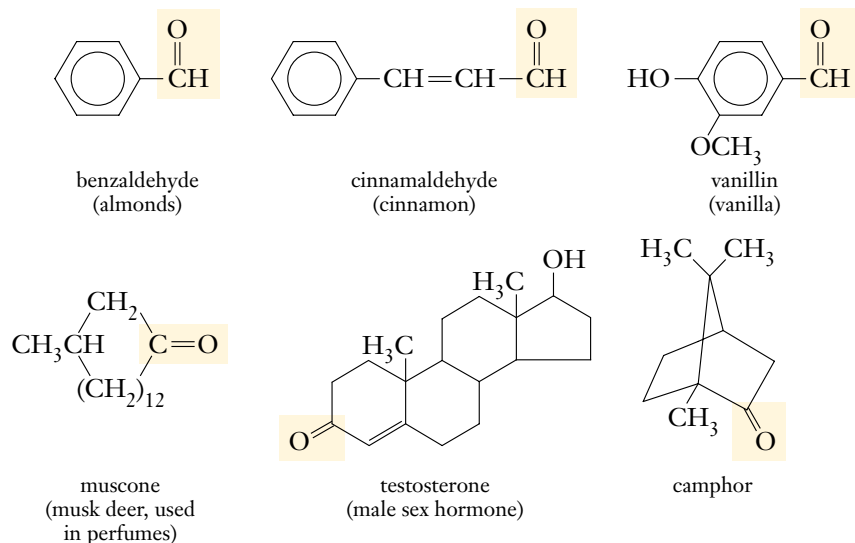
The systematic names for ketones are derived from their parent hydrocarbons. The suffix *-one* is added to the characteristic stem.



The ketones are excellent solvents. Acetone is very useful because it dissolves most organic compounds yet is miscible with water. Acetone is widely used as a solvent in the manufacture of lacquers, paint removers, explosives, plastics, drugs, and disinfectants. Some ketones of high molecular weight are used extensively in blending perfumes. Structures of some naturally occurring aldehydes and ketones are



Steroid molecules have similar molecular shapes but different biochemical functions. Progesterone (*top*), a female sex hormone, and testosterone (*bottom*), a male sex hormone. Both are ketones.



27-12 AMINES

The **amines** are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. Many low-molecular-weight amines are gases or low-boiling liquids (Table 27-10). Amines are basic compounds (Table 18-6, Section 28-4). The aliphatic amines of low molecular weight are soluble in water. Aliphatic diamines of fairly high molecular weight are soluble in water because each molecule contains two highly polar —NH_2 groups that form hydrogen bonds with water.

The odors of amines are quite unpleasant; many of the malodorous compounds that are released as fish decay are low-molecular-weight amines. Amines of high molecular weight are nonvolatile, so they have little odor. One of the materials used to manufacture nylon, hexamethylenediamine, is an aliphatic amine. Many aromatic amines are used to prepare organic dyes that are widely used in industrial societies. Amines are also used to produce many medicinal products, including local anesthetics and sulfa drugs.

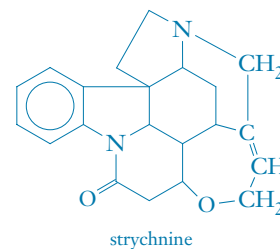
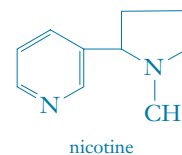
Amines are widely distributed in nature in the form of amino acids and proteins, which are found in all higher animal forms, and in alkaloids, which are found in most plants.

TABLE 27-10 Boiling Points of Ammonia and Some Amines

Name	Formula	Boiling Point (°C)
ammonia	NH_3	-33.4
methylamine	CH_3NH_2	-6.5
dimethylamine	$(\text{CH}_3)_2\text{NH}$	7.4
trimethylamine	$(\text{CH}_3)_3\text{N}$	3.5
ethylamine	$\text{CH}_3\text{CH}_2\text{NH}_2$	16.6
aniline	$\text{C}_6\text{H}_5\text{NH}_2$	184
ethylenediamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	116.5
pyridine	$\text{C}_5\text{H}_5\text{N}$	115.3
pyrrole	$\text{C}_4\text{H}_5\text{N}$	129.8

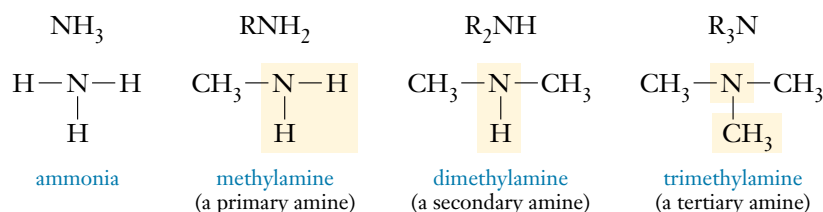
Ammonia acts as a Lewis base because there is one unshared pair of electrons on the N atom (Section 10-10).

Some of these substances are fundamental building blocks of animal tissue, and minute amounts of others have dramatic physiological effects, both harmful and beneficial. Countless other biologically important substances, including many vitamins, antibiotics, and other drugs, contain amino groups, —NR_2 (where R can represent an H, alkyl, or aryl group).

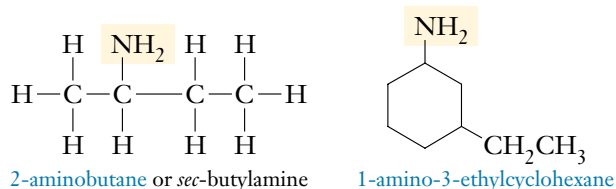


Structure and Nomenclature

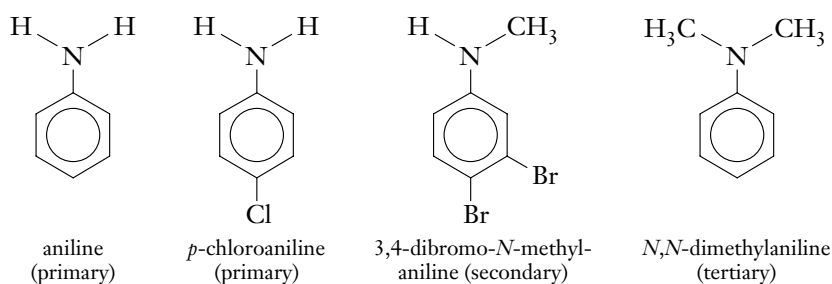
There are three classes of amines, depending on whether one, two, or three hydrogen atoms have been replaced by organic groups. They are called primary, secondary, and tertiary amines, respectively.



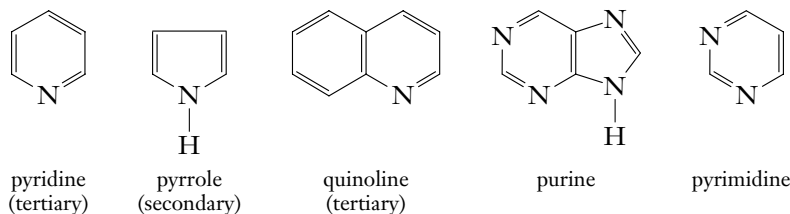
The systematic names of amines are based on consideration of the compounds as derivatives of ammonia. Amines of more complex structure are sometimes named as derivatives of the parent hydrocarbon with the term *amino-* used as a prefix to describe —NH_2 .

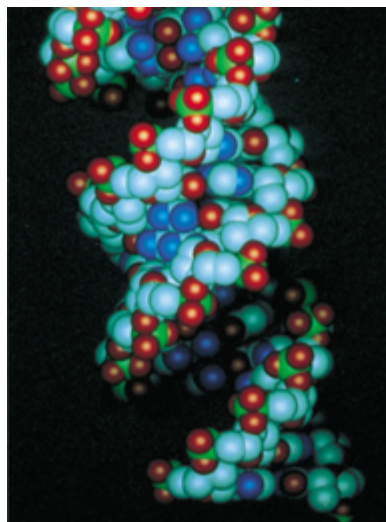


Aniline is the simplest aromatic amine. Many aromatic amines are named as derivatives of aniline.



Heterocyclic amines contain nitrogen as a part of the ring, bound to two carbon atoms. Many of these amines are found in coal tar and a variety of natural products. Some aromatic and heterocyclic amines are called by their common names.





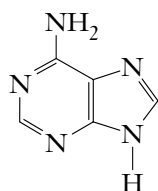
A space-filling model of a portion of the DNA double helical structure.

In the general formulas for alcohols and ethers, R cannot be H. In carboxylic acids, R can be H.

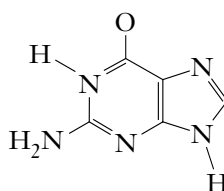
Aliphatic carboxylic acids are sometimes referred to as *fatty acids* because many have been obtained from animal fats.

Formic acid was obtained by distillation of ants (*L. formica*, “ant”); acetic acid occurs in vinegar (*L. acetum*, “vinegar”); butyric acid in rancid butter (*L. butyrum*, “butter”); and stearic acid in animal fats (Gr. *stear*, “beef suet”). Caproic acid is one of the so-called “goat acids.” Its odor is responsible for the name.

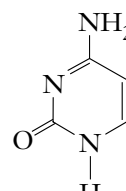
Genes, the units of chromosomes that carry hereditary characteristics, are long stretches of double helical deoxyribonucleic acid, or DNA. DNA is composed of four *nucleotide bases*: adenine, guanine, cytosine, and thymine. The first two are modified purines, and the latter two are modified pyrimidines. The sequence of these building blocks in DNA acts as a code for the order of amino acids in the proteins of an organism. The DNA in each cell of an organism contains the instructions for making the complete organism (see Section 28-10).



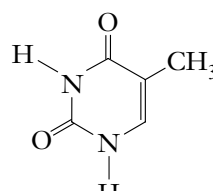
adenine



guanine



cytosine



thymine

27-13 CARBOXYLIC ACIDS

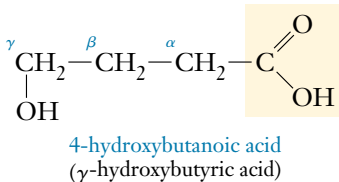
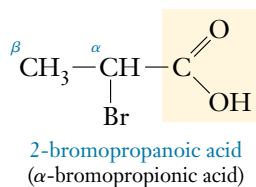
Compounds that contain the **carboxyl group**, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{H} \end{array}$, are acidic. They are called **carboxylic acids**. Their general formula is $\text{R}-\text{COOH}$. Most are *weak acids*. They are much stronger acids than most phenols, however. Carboxylic acids are named systematically by dropping the terminal *-e* from the name of the parent hydrocarbon and adding *-oic acid* (Table 27-11). Many older names survive, however, and organic acids are often called by common names. In aromatic acids the carboxyl group is attached to an aromatic ring (Figure 27-17).

Organic acids occur widely in natural products, and many have been known since ancient times. Their common (trivial) names are often derived from a Greek or Latin word that indicates the original source (see Table 27-11).

The names of modified carboxylic acids are often derived from the trivial names of the acids. Positions of substituents are sometimes indicated by lowercase Greek letters, beginning with the carbon *adjacent* to the carboxyl carbon, rather than by numbering the carbon chain.

TABLE 27-11 Some Aliphatic Carboxylic Acids

Formula	Common Name	IUPAC Name
HCOOH	formic acid	methanoic acid
CH ₃ COOH	acetic acid	ethanoic acid
CH ₃ CH ₂ COOH	propionic acid	propanoic acid
CH ₃ CH ₂ CH ₂ COOH	butyric acid	butanoic acid
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ COOH	caproic acid	hexanoic acid
CH ₃ (CH ₂) ₁₀ COOH	lauric acid	dodecanoic acid
CH ₃ (CH ₂) ₁₄ COOH	palmitic acid	hexadecanoic acid
CH ₃ (CH ₂) ₁₆ COOH	stearic acid	octadecanoic acid



Derivatives of α -hydroxy carboxylic acids are currently used in some cosmetic preparations.

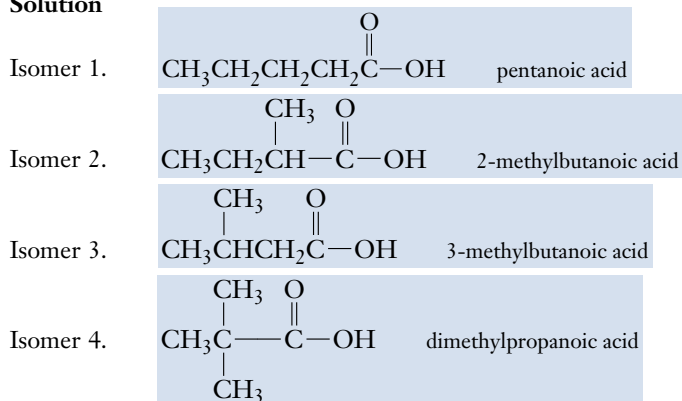
EXAMPLE 27-12 Isomeric Carboxylic Acids

Write the structural formula of each of the four carboxylic acids having the molecular formula of $\text{C}_5\text{H}_{10}\text{O}_2$. Give the IUPAC name of each.

Plan

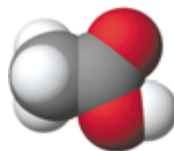
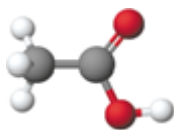
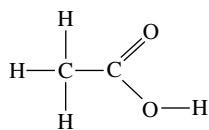
We first write the structural formula of the carboxylic acid that does not have branching. Then we remove one carbon from the straight-chain structure and reposition it to form branched isomers. We check to see whether branching is possible at more than one location. We find that branching is possible at two different locations. Remove a second carbon from the unbranched isomer and, if possible, from additional branching. The two removed carbons can be added as methyl branches. Each isomer is named by naming the longest chain that contains the carboxylic acid group. The final *-e* of the name is changed to *-oic acid*. Names for branches appear at the beginning of the name.

Solution



You should now work Exercise 72a, b.

- (a) acetic acid
(an aliphatic acid)



- (b) benzoic acid
(an aromatic acid)

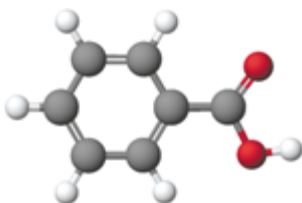
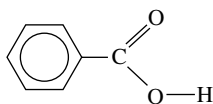
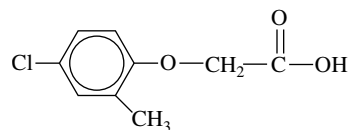
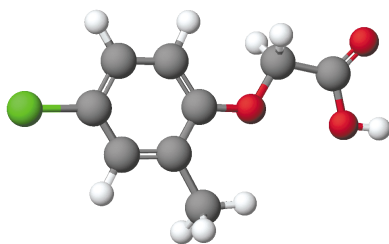
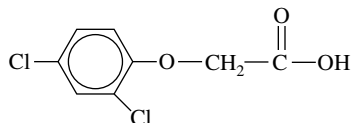
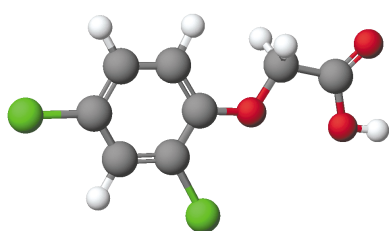


Figure 27-17 (a) Models of acetic acid. (b) Models of benzoic acid.

TABLE 27-12 Some Naturally Occurring Organic Acids

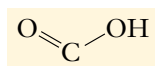
	Name	Source
acetic acid	$\text{CH}_3\text{—COOH}$	vinegar
citric acid	$\begin{array}{c} \text{OH} \\ \\ \text{HOOC—CH}_2\text{—C—CH}_2\text{—COOH} \\ \\ \text{COOH} \end{array}$	citrus fruits
lactic acid	$\begin{array}{c} \text{CH}_3\text{—CH—COOH} \\ \\ \text{OH} \end{array}$	sour milk
malic acid	$\begin{array}{c} \text{HOOC—CH}_2\text{—CH—COOH} \\ \\ \text{OH} \end{array}$	apples, watermelons, grape juice, wine
oxalic acid	$\begin{array}{c} \text{HOOC—COOH} \\ \quad \\ \text{H} \quad \text{OH} \\ \quad \\ \text{H—C—CH}_2\text{—COOH} \\ \quad \\ \text{C} \quad \text{C} \\ \quad \\ \text{HO—C—CH}_2\text{—OH} \\ \quad \\ \text{H} \quad \text{OH} \end{array}$	rhubarb, spinach, tomatoes
quinic acid	$\begin{array}{c} \text{H} \quad \text{OH} \\ \quad \\ \text{H—C—CH}_2\text{—COOH} \\ \quad \\ \text{C} \quad \text{C} \\ \quad \\ \text{HO—C—CH}_2\text{—OH} \\ \quad \\ \text{H} \quad \text{OH} \end{array}$	cranberries
tartaric acid	$\begin{array}{c} \text{HOOC—CH—CH—COOH} \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	grape juice, wine



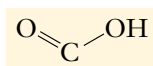
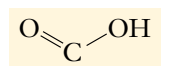
These two derivatives of acetic acids act as herbicides (weed killers) by overstimulating the plant's growth system.

Some carboxylic acid molecules contain more than one —COOH group (Table 27-12). These acids are nearly always called by their common names. For example, oxalic acid, found in rhubarb, spinach, and tomatoes, is a dicarboxylic acid; citric acid, found in citrus fruits, is a tricarboxylic acid.

Aromatic acids are called by their common names or named as derivatives of benzoic acid, which is considered the “parent” aromatic acid.

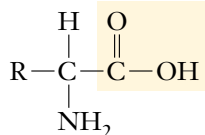


benzoic acid

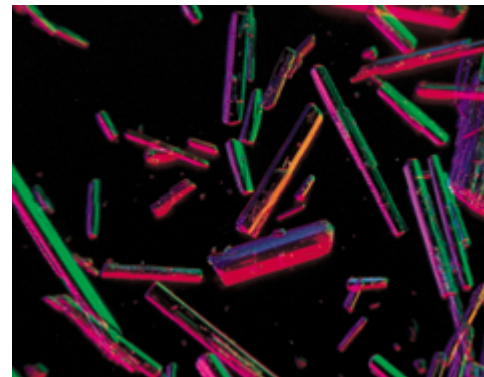
*p*-chlorobenzoic acid

2,4-dimethylbenzoic acid

Although many carboxylic acids occur in the free state in nature, many occur as amides or esters (Section 27-14). α -Amino acids are substituted carboxylic acids with the general structure



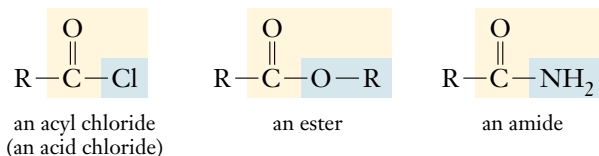
where R can be either an alkyl or an aryl group. α -Amino acids are the components of proteins, which make up the muscle and tissue of animals. Many other acids are important in the metabolism and synthesis of fats by enzyme systems. Acetic acid (the acid in vinegar) is the end product in the fermentation of most agricultural products. It is the fundamental unit used by living organisms in the biosynthesis of such widely diverse classes of natural products as long-chain fatty acids, natural rubber, and steroid hormones.



Crystals of glycine viewed under polarized light. Glycine, the simplest amino acid, has the structure shown in the text, with R = H.

27-14 SOME DERIVATIVES OF CARBOXYLIC ACIDS

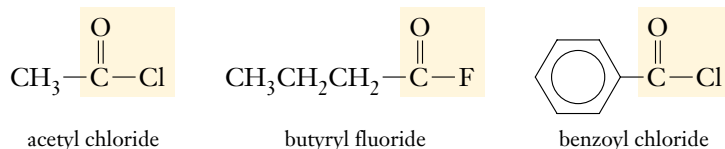
Three important classes of acid derivatives are formed by the replacement of the hydroxyl group by another atom or group of atoms. Each of these derivatives contains an acyl group.



Aromatic compounds of these types (with R = aryl groups) are also encountered frequently.

Acyl Halides (Acid Halides)

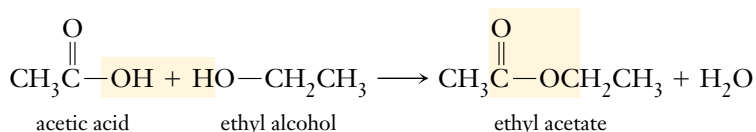
The **acyl halides**, sometimes called **acid halides**, are structurally related to carboxylic acids by the replacement of the $-\text{OH}$ group by a halogen, most often $-\text{Cl}$. They are usually named by combining the stems of the common names of the carboxylic acids with the suffix *-yl* and then adding the name of the halide ion. Examples are



Acid halides are very reactive and have not been observed in nature.

Esters

Esters can be thought of as the result of removing one molecule of water from a carboxylic acid and an alcohol. Removing a molecule of water from acetic acid and ethyl alcohol gives ethyl acetate.



As we will see in Section 28-6, one method of forming esters involves acid-catalyzed reaction of an alcohol with a carboxylic acid.

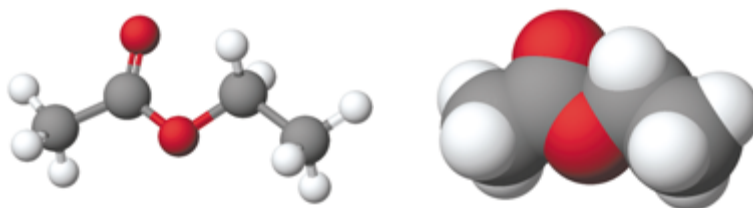
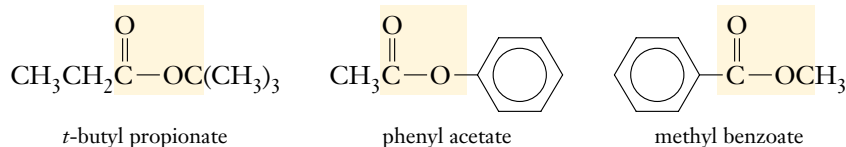


Figure 27-18 Models of ethyl acetate, $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—O—CH}_2\text{CH}_3$, an ester.

The $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—}$ fragment is derived from acetic acid, the parent acid; the $\text{O—CH}_2\text{CH}_3$ fragment is derived from ethanol, the parent alcohol. Models of ethyl acetate, an ester, are shown in Figure 27-18.


Esters are nearly always called by their common names. These consist of, first, the name of the alkyl group in the alcohol, and then the name of the anion derived from the acid.



Because of their inability to form hydrogen bonds, esters tend to be liquids with boiling points much lower than those of carboxylic acids of similar molecular weights.

Most simple esters are pleasant-smelling substances. They are responsible for the flavors and fragrances of most fruits and flowers and many of the artificial fruit flavorings that are used in cakes, candies, and ice cream (Table 27-13). Esters of low molecular weight are excellent solvents for nonpolar compounds. Ethyl acetate is an excellent solvent that gives many nail polish removers their characteristic odor.

Fats (solids) and **oils** (liquids) are esters of glycerol and aliphatic acids of high molecular weight. “Fatty acids” are all organic acids whose esters occur in fats and oils. Fats and oils have the general formula

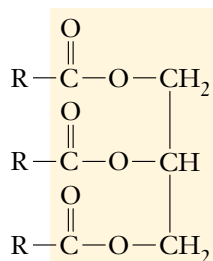
 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 11.7, Fats and Oils.



Apple blossoms.

TABLE 27-13 Some Common Esters

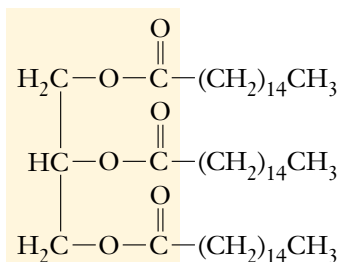
Ester	Formula	Odor of
isoamyl acetate	$\text{CH}_3\text{COOC}_5\text{H}_{11}$	bananas
ethyl butyrate	$\text{C}_3\text{H}_7\text{COOC}_2\text{H}_5$	pineapples
amyl butyrate	$\text{C}_3\text{H}_7\text{COOC}_5\text{H}_{11}$	apricots
octyl acetate	$\text{CH}_3\text{COOC}_8\text{H}_{17}$	oranges
isoamyl isovalerate	$\text{C}_4\text{H}_9\text{COOC}_5\text{H}_{11}$	apples
methyl salicylate	$\text{C}_6\text{H}_4(\text{OH})(\text{COOCH}_3)$	oil of wintergreen
methyl anthranilate	$\text{C}_6\text{H}_4(\text{NH}_2)(\text{COOCH}_3)$	grapes



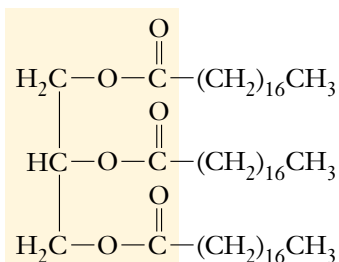
The fatty acid portions, $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-$, may be saturated or unsaturated. The R's may be in the same or different groups.

Naturally occurring fats and oils are mixtures of many different esters. Milk fat, lard, and tallow are familiar, important fats. Soybean oil, cottonseed oil, linseed oil, palm oil, and coconut oil are examples of important oils.

The triesters of glycerol are called glycerides. *Simple glycerides* are esters in which all three R groups are identical. Two examples are



glyceryl tripalmitate
(palmitin)



glyceryl tristearate
(stearin)

Waxes are esters of fatty acids and alcohols other than glycerol. Most are derived from long-chain fatty acids and long-chain monohydric alcohols. Both usually contain even numbers of carbon atoms. Beeswax is largely $\text{C}_{15}\text{H}_{31}\text{COOC}_{30}\text{H}_{61}$; carnauba wax contains $\text{C}_{25}\text{H}_{51}\text{COOC}_{30}\text{H}_{61}$. Both are esters of myricyl alcohol, $\text{C}_{30}\text{H}_{61}\text{OH}$.

Fats are solid esters of glycerol and (mostly) saturated acids. Oils are liquid esters that are derived primarily from unsaturated acids and glycerol. The acid portion of a fat usually contains an even number of carbon atoms, often 16 or 18. Some acids that occur frequently in fats and oils are

butyric	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
lauric	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
myristic	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
palmitic	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
stearic	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
oleic	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
linolenic	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
ricinoleic	$\text{CH}_3(\text{CH}_2)_5\text{CHOHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

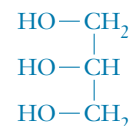
Figure 27-19a shows a model of stearic acid, a long-chain saturated fatty acid.

Amides

Amides are thought of as derivatives of organic acids and ammonia, primary amines, or

secondary amines. Amides contain the $-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}<$ functional group. They are named as

Glycerol is

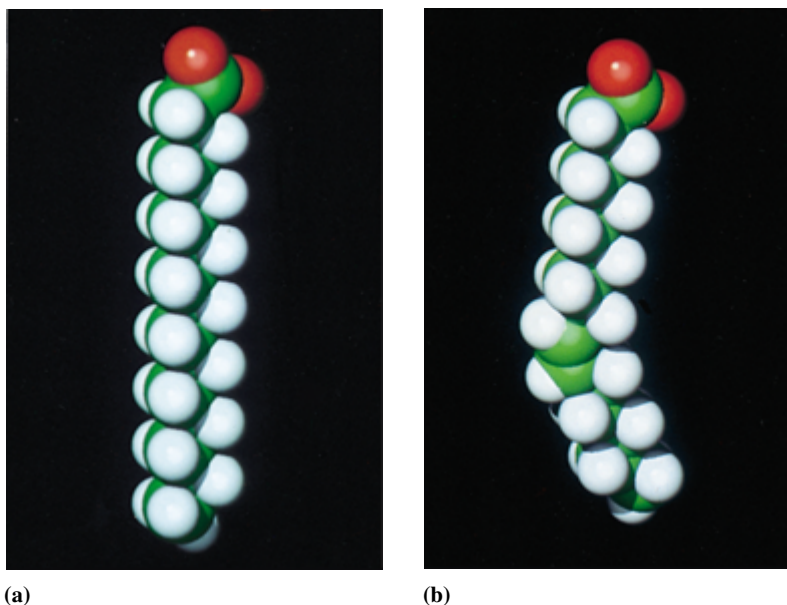


Most natural fatty acids contain even numbers of carbon atoms because they are synthesized in the body from two-carbon acetyl groups.

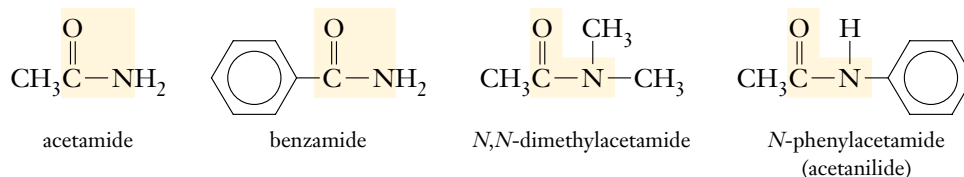



Honeybees produce the wax to build their honeycombs.

Figure 27-19 Models of long-chain fatty acids. The saturated fatty acids (a) are linear and tend to pack like sticks of wood to form solid masses in blood vessels, thereby constricting them. The *trans* unsaturated fatty acids have a slight Z-shaped kink in the chain, but are also essentially linear molecules. By contrast, *cis* unsaturated fatty acids are bent and so do not pack as well as linear structures and do not collect in blood vessels as readily. Many natural vegetable fats and oils contain esters of *cis* unsaturated fatty acids, or polyunsaturated fatty acids. Health problems associated with saturated fatty acids can be decreased by eating less animal fat, butter, and lard. Problems due to *trans* fatty acids are reduced by avoiding processed vegetable fats.



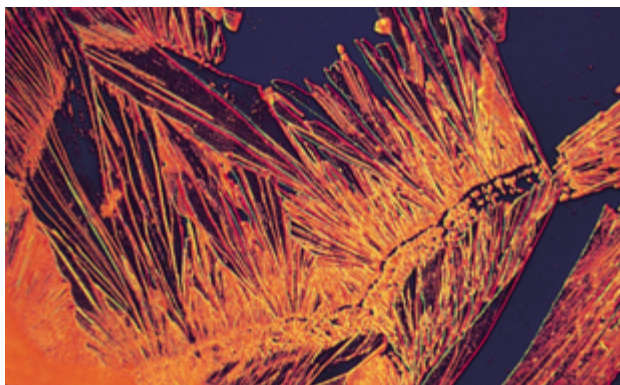
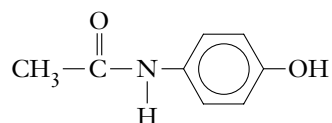
derivatives of the corresponding carboxylic acids, the suffix *-amide* being substituted for *-ic acid* or *-oic acid* in the name of the parent acid. The presence of alkyl or aryl substituents attached to nitrogen is designated by prefixing the letter *N* and the name of the substituent to the name of the unsubstituted amide.



 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 11.8, Amino Acids and Proteins.

Proteins are complex amides of high molecular weight. Some synthetic fibers are also polyamides (Sections 27-19 and 28-9).

Crystals of the amide known as acetaminophen (Tylenol) viewed under polarized light. The structure of acetaminophen is





Our Daily Lives

Butter, Margarine, and *trans* Fats

Humans had consumed butter for thousands of years before France introduced the world to margarine in the late 1860s; by 1874, margarine had reached the United States. Margarine consumption has increased rapidly, due in part to an increased risk of heart disease that has been associated with consumption of butter.

Both butter and margarine are primarily fats, but they contain different kinds of fats. The main ingredient in butter is cream, the concentrated fat from milk, whereas the main ingredient in margarine is vegetable oil, the concentrated fat from plants. Although it is widely accepted that animal fats pose a greater risk for heart disease than vegetable oils, most vegetable oils used in margarine and processed foods are modified by hydrogenation.

The hydrogenation process adds hydrogen atoms to unsaturated vegetable oils; this causes vegetable oils to solidify, which makes them creamier and prolongs their shelf life. Unfortunately, the hydrogenation process changes about 40% of the naturally occurring *cis* molecules of vegetable oil into *trans* isomers; the resulting fat molecules are referred to as *trans* fats. Oils produced in nature contain only *cis* isomers and are considered healthful, but the *trans* fats have been linked to many thousands of deaths due to heart disease. Diets high in hydrogenated vegetable oil may be as unhealthy as those high in saturated animal fats.

To understand the different effects produced by animal fats, vegetable oils, and *trans* fats, we need to know a little about blood cholesterol. Medical specialists recognize several types of cholesterol, two of which are HDL (high-density lipoproteins) and LDL (low-density lipoproteins). Because high levels of HDL reduce the risk of heart disease, HDL has become known as “good” cholesterol; because high levels of LDL increase the risk for heart disease, LDL has become known as “bad” cholesterol. In the average U.S. adult, the total amount of cholesterol (including HDL and LDL) circulating in the blood is about 200 mg per 100 mL of serum.

A diet high in animal fats usually increases blood cholesterol levels beyond 200 mg per 100 mL of serum, thereby increasing the risk for heart disease. When animal fats increase the total blood cholesterol level, however, they increase the levels of both HDL and LDL. In contrast, vegetable oils decrease the total blood cholesterol level, which



Blood pressure check.

makes them healthier foods than other fats. *Trans* fats (from hydrogenated vegetable oils) also decrease the total blood cholesterol level, giving the appearance of being healthy, but unfortunately they accomplish this reduction by simultaneously reducing the desirable HDL levels and increasing the undesirable LDL levels.

The damage done by hydrogenated vegetable oils is particularly disturbing because margarine is one of the largest sources of calories in the U.S. diet; approximately 40% of margarine fat is the *trans* isomer. Hydrogenated vegetable oils are widely used in shortening, cookies, crackers, chips, and other processed foods. Ironically, most of these foods are touted as being healthy because they contain no cholesterol or saturated fats.

What can we do to protect our health? For many years, nutritionists have been telling us what appears to be the “best solution”: reduce your total fat intake to 20% of your daily calories, and reduce your consumption of animal fats by substituting vegetable oils. Whenever possible, use vegetable oils that have not been hydrogenated.

Ronald DeLorenzo
Middle Georgia College

	FUNCTIONAL GROUP	CLASS OF COMPOUNDS	SOME EXAMPLES
Organic compounds with functional groups		Alkenes (Section 27-3)	ethylene, butene, cyclohexene
		Alkynes (Section 27-4)	acetylene, propyne
		Organic halides (Section 27-8)	methyl chloride, chloroform
		Alcohols, R—OH (Section 27-9)	ethyl alcohol, methyl alcohol, 2-butanol
		Phenols, Ar—OH (Section 27-9)	phenol, m-cresol,
		Ethers (Section 27-10)	diethyl ether, methyl phenyl ether, diphenyl ether
		Amines (Section 27-12)	methylamine, aniline, dimethylamine, pyridene
		Carboxylic acids (Section 27-13)	formic acid, acetic acid benzoic acid
		Acyl halides (Section 27-14)	acetyl chloride
		Esters (Section 27-14)	ethyl acetate, glyceryl tristearate
		Amides (Section 27-14)	N-methylacetamide, acetanilide, various polyamides
	Aldehydes (Y = H) (Section 27-11)	formaldehyde, acetaldehyde benzaldehyde	
	Ketones (Y = R or Ar) (Section 27-11)	acetone, cyclohexanone, camphor	

Figure 27-20 Summary of some functional groups and classes of organic compounds.

27-15 SUMMARY OF FUNCTIONAL GROUPS

Some important functional groups and the corresponding classes of related compounds are summarized in Figure 27-20.

FUNDAMENTAL CLASSES OF ORGANIC REACTIONS

Organic compounds display very different abilities to react, ranging from the limited reactivity of hydrocarbons and fluorocarbons to the great variety of reactions undergone by the millions 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. But the electronic and structural features that are *near* a functional group can also affect its reactivity. One of the fascinations of organic chemistry is our ability to “fine-tune” both physical and chemical properties by making small changes in structure. The successes of this approach are innumerable, including the development of fuels and their additives or alternatives, the improvement of pharmaceuticals to enhance their effectiveness and minimize their ill effects, and the development of polymers and plastics with an incredible variety of properties and uses.

In the following sections of this chapter we will present a few of the kinds of reactions that organic compounds undergo. A topic of such vast scope as reactivity of organic compounds can be made manageable only if we divide our study of this field into subtopics. Nearly all organic transformations involve at least one of three fundamental classes of reactions. The following three sections will address substitution, addition, and elimination reactions. We will also look at some reaction sequences that combine reaction steps from more than one of the fundamental classes.

27-16 SUBSTITUTION REACTIONS

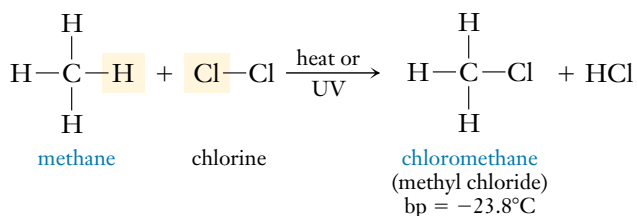
In a **substitution reaction** an atom or a group of atoms attached to a carbon atom is removed, and another atom or group of atoms takes its place. No change occurs in the degree of saturation at the reactive carbon atom.

The saturated hydrocarbons (alkanes and cycloalkanes) are chemically rather inert materials. For many years they were known as *paraffins* because they undergo few reactions. They do not react with such powerful oxidizing agents as potassium permanganate and potassium dichromate. They do react with the halogens, however, with oxygen when ignited, and with concentrated nitric acid. As expected, members of a homologous series (see Section 27-1) have similar chemical properties. If we study the chemistry of one of these compounds, we can make predictions about the others with a fair degree of certainty.

The saturated hydrocarbons can react without a big disruption of the molecular structure only by *displacement*, or *substitution of one atom for another*. At room temperature, chlorine and bromine react very slowly with saturated straight-chain hydrocarbons. At

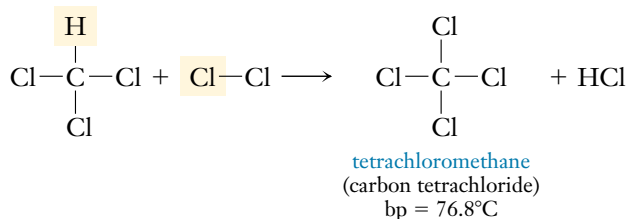
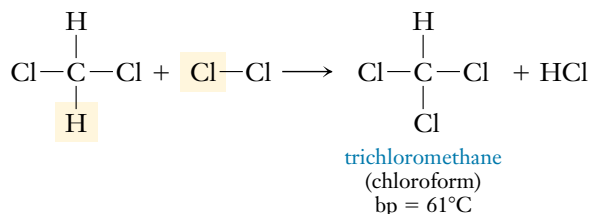
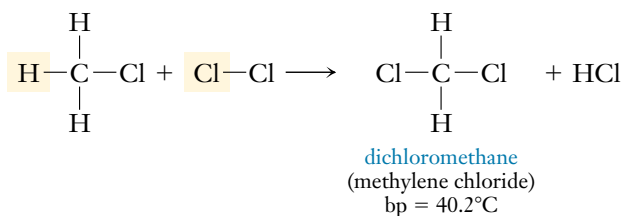
higher temperatures, or in the presence of sunlight or other sources of ultraviolet light, H atoms in the hydrocarbon can be replaced easily by halogen atoms. These substitution reactions are called **halogenation** reactions.

The reaction is represented as

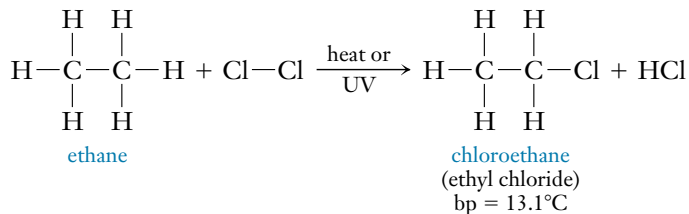


Note that only one half of the chlorine atoms occur in the organic product. The other half form hydrogen chloride, a commercially valuable compound.

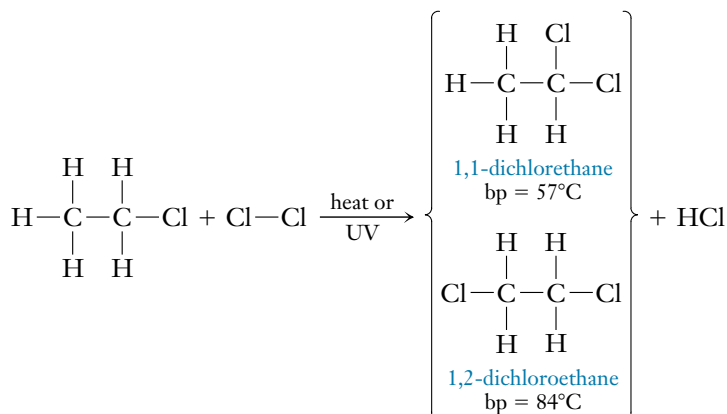
Many organic reactions produce more than a single product. For example, the chlorination of CH_4 may produce several other products in addition to CH_3Cl , as the following equations show.



When a hydrocarbon has more than one C atom, its reaction with Cl_2 is more complex. The first step in the chlorination of ethane gives the product that contains one Cl atom per molecule.

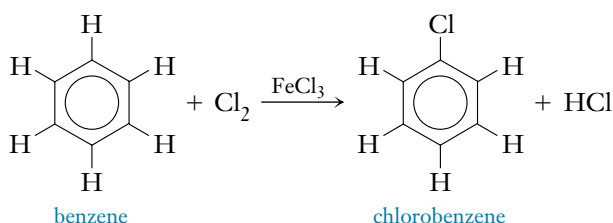


When a second hydrogen atom is replaced, a mixture of the two possible products is obtained.



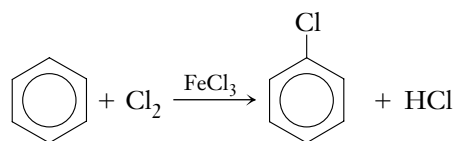
The product mixture does not contain equal numbers of moles of the dichloroethanes so we do not show a stoichiometrically balanced equation. Because reactions of saturated hydrocarbons with chlorine can produce many products, the reactions are not always as useful as might be desired.

Substitution is the most common kind of reaction of an aromatic ring. Halogenation, with chlorine or bromine, occurs readily in the presence of iron or anhydrous iron(III) chloride (a Lewis acid) catalyst.

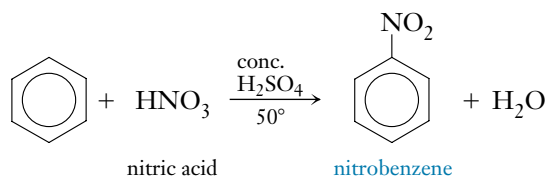


When iron is added as a catalyst, it reacts with chlorine to form iron(III) chloride, which is the true catalyst.

The equation is usually written in condensed form as

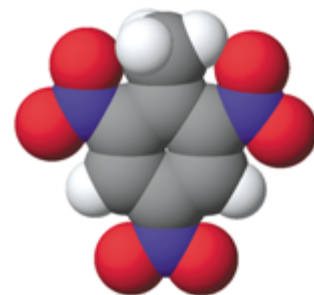
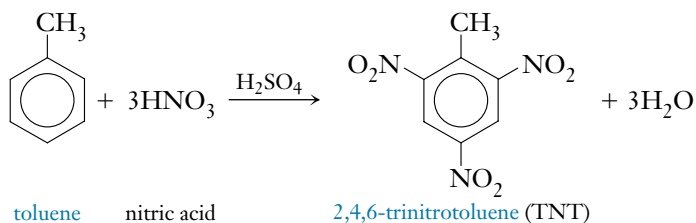


Aromatic rings can undergo *nitration*, substitution of the *nitro* group $-\text{NO}_2$, in a mixture of concentrated nitric and sulfuric acids at moderate temperatures.



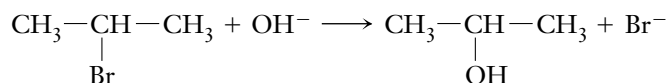
The H_2SO_4 is both a catalyst and a dehydrating agent. The H in the product H_2O comes from the hydrocarbon; the OH comes from HNO_3 .

The explosive TNT (2,4,6-trinitrotoluene) is manufactured by the nitration of toluene in three steps.



A model of a molecule of TNT.

Groups other than hydrogen can be substituted by other atoms or groups of atoms. For example, the bromine atom of an alkyl bromide can be replaced with a hydroxyl group to form an alcohol. The mechanism of this type of reaction is often studied in introductory organic chemistry courses.

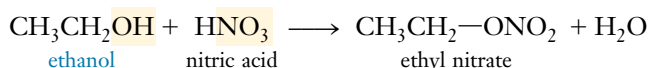


Simple inorganic esters may be thought of as compounds that contain one or more alkyl groups covalently bonded to the anion of a *ternary* inorganic acid. Unless indicated, the term “ester” refers to organic esters.

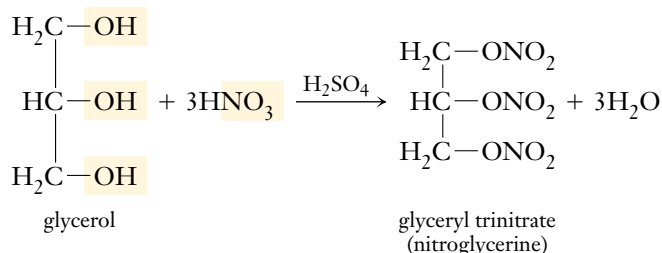
Nobel's brother had been killed and his father physically disabled in a nitroglycerine explosion in 1864. Nobel willed \$9.2 million to establish a fund for annual prizes in physics, chemistry, medicine, literature, and peace. The prizes were first awarded in 1901.

Interestingly, nitroglycerine (“nitro”) is taken by some who have heart disease. It acts as a vasodilator (dilates the blood vessels) to decrease arterial tension.

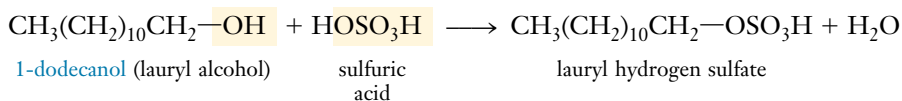
Alcohols react with common inorganic oxyacids to produce **inorganic esters**. For instance, nitric acid reacts with alcohols to produce nitrates by substitution of nitrate, $-\text{ONO}_2$, for hydroxyl, $-\text{OH}$.



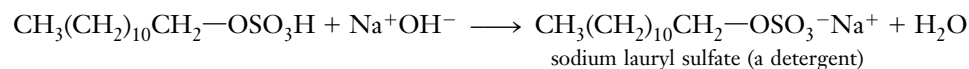
The substitution reaction of nitric acid with glycerol produces the explosive nitroglycerine. Alfred Nobel's (1833–1896) discovery in 1866 that this very sensitive material could be made into a “safe” explosive by absorbing it into diatomaceous earth or wood meal led to his development of dynamite.



Cold, concentrated H_2SO_4 reacts with alcohols to form **alkyl hydrogen sulfates**. The reaction with lauryl alcohol is an important industrial reaction.



The neutralization reaction of an alkyl hydrogen sulfate with NaOH then produces the sodium salt of the alkyl hydrogen sulfate.

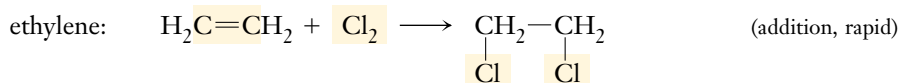
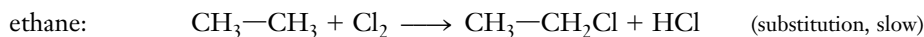


Sodium salts of the alkyl hydrogen sulfates that contain about 12 carbon atoms are excellent detergents. They are also biodegradable. (Soaps and detergents were discussed in Section 14-18.)

27-17 ADDITION REACTIONS

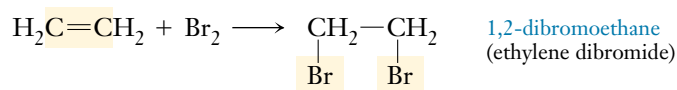
An **addition reaction** involves an *increase* in the number of atoms or groups attached to carbon. The molecule becomes more nearly saturated.

The principal reactions of alkenes and alkynes are addition reactions rather than substitution reactions. For example, contrast the reactions of ethane and ethylene with Cl_2 .



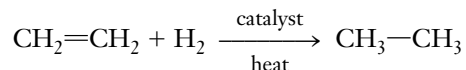
Carbon–carbon double bonds are *reaction sites* and so represent *functional groups*. Most addition reactions involving alkenes and alkynes proceed rapidly at room temperature. By contrast, many substitution reactions of the alkanes require catalysts and high temperatures.

Bromine adds readily to the alkenes to give dibromides. The reaction with ethylene is

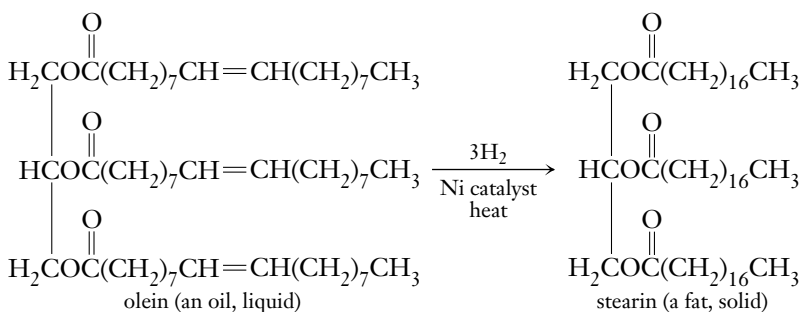


The addition of Br_2 to alkenes is used as a simple qualitative test for unsaturation. Bromine, a dark red liquid, is dissolved in a nonpolar solvent. When an alkene is added, the solution becomes colorless as the Br_2 reacts with the alkene to form a colorless compound. This reaction may be used to distinguish between alkanes and alkenes.

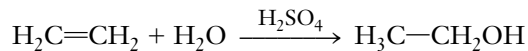
Hydrogenation is an extremely important addition reaction of the alkenes. Hydrogen adds across double bonds at elevated temperatures, under high pressures, and in the presence of an appropriate catalyst (finely divided Pt, Pd, or Ni).



Some unsaturated hydrocarbons are converted to saturated hydrocarbons in the manufacture of high-octane gasoline and aviation fuels. Unsaturated vegetable oils can also be converted to solid cooking fats (shortening) by hydrogenation of most of the carbon–carbon double bonds present (Figure 27-21). Most of the double bonds that remain are the *trans*- isomer.



The *hydration reaction* (addition of water) is another very important addition reaction of alkenes. It is used commercially for the preparation of a wide variety of alcohols from petroleum by-products. Ethanol, the most important industrial alcohol, is produced industrially by the hydration of ethylene from petroleum, using H_2SO_4 as a catalyst.




 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 11.4, Hydrocarbons and Addition Reactions.

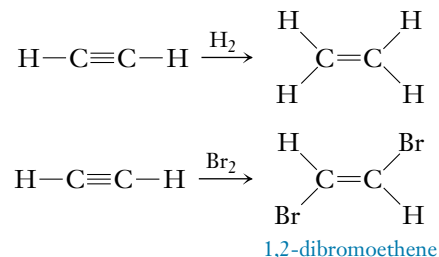


Figure 27-21 Hydrogenation of the olefinic double bonds in vegetable oil converts it to solid fat.

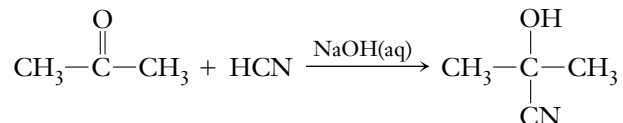
Think of H_2O as HOH.

One of the commercially most important addition reactions of the alkenes forms *polymers*. This reaction will be discussed in Section 27-19.

The alkynes contain two pi bonds, both of which are sources of electrons, and they are more reactive than the alkenes. The most common reaction of the alkynes is addition across the triple bond. The reactions with hydrogen and with bromine are typical.



Other unsaturated bonds can also undergo addition reactions. Probably the most important example is the carbonyl group, $\text{C}=\text{O}$. Because of the availability of unshared pairs of electrons on the oxygen atom, the products can undergo a wide variety of subsequent reactions. For example, HCN adds to the C=O bond of acetone.

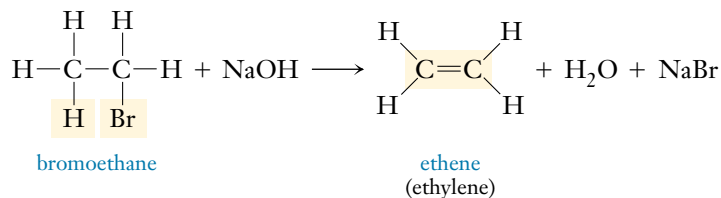


This reaction is a key early step in the production of the transparent plastic known as Plexiglas or Lucite.

27-18 ELIMINATION REACTIONS

An **elimination reaction** involves a *decrease* in the number of atoms or groups attached to carbon. The degree of unsaturation increases.

An elimination reaction, **dehydrohalogenation**, can occur for chloro-, bromo- and iodoalkanes. In such a reaction, the halogen, X, from one C atom and a hydrogen from an adjacent C atom are eliminated. A double bond between two carbon atoms is formed; the molecule becomes *more unsaturated*. The net reaction is the transformation of an alkyl halide (or haloalkane) into an alkene. Dehydrohalogenation reactions usually require a strong base such as sodium hydroxide, NaOH.





Concentrated sulfuric acid is an excellent dehydrating agent. Here it removes water from sucrose, a sugar with the formula $C_{12}H_{22}O_{11}$. Dehydration of sucrose produces (mostly) carbon.

A related reaction is **dehydration**, in which an alcohol is converted into an alkene and water by the elimination of $H-$ and $-OH$ from adjacent carbon atoms. The dehydration of an alcohol to form an alkene can be considered the reverse of the hydration of an alkene to form an alcohol (Section 27-17). Dehydration reactions are catalyzed by acids.

Such simple elimination reactions are relatively rare. Elimination reactions, however, frequently occur as individual steps in more complex reaction sequences. Many more elimination reactions are encountered in courses in organic chemistry.


27-19 POLYMERIZATION REACTIONS

A **polymer** is a large molecule that is a high-molecular-weight chain of small molecules. The small molecules that are linked to form polymers are called **monomers**. Typical polymers consist of hundreds or thousands of monomer units and have molecular weights up to thousands or millions.

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

The word fragment *-mer* means “part.” Recall that *isomers* are compounds that are composed of the same (*iso*) parts (*mers*). A *monomer* is a “single part”; a large number of monomers combine to form a *polymer*; “many parts.”

Polymers are divided into two classes: natural and synthetic. Important biological molecules such as proteins, nucleic acids, and polysaccharides (starches and the cellulose in wood and cotton) are natural polymers. Natural rubber and natural fibers such as silk and wool are also natural polymers. Familiar examples of synthetic polymers include plastics such as polyethylene, Teflon, and Lucite (Plexiglas) and synthetic fibers such as nylon, Orlon, and Dacron. In this section we will describe some processes by which polymers are formed from organic compounds.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 11.9, Addition Polymerization.

Teflon is a trade name owned by DuPont, a company that has developed and manufactured many fluorinated polymers.

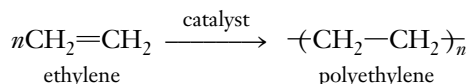


Many cooking utensils with “nonstick” surfaces are coated with a polymer such as Teflon.

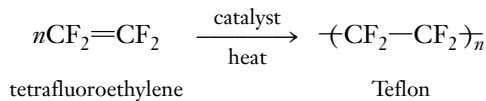
Numerous other polymers are elastic enough to be called by the generic name “rubber.”

Addition Polymerization

Polymerization is an important addition reaction (Section 27-17) of the alkenes. Polymers formed by this kind of reaction are called **addition polymers**. The formation of polyethylene is an important example. In the presence of appropriate catalysts (a mixture of aluminum trialkyls, R_3Al , and titanium tetrachloride, $TiCl_4$), ethylene polymerizes into chains containing 800 or more carbon atoms.

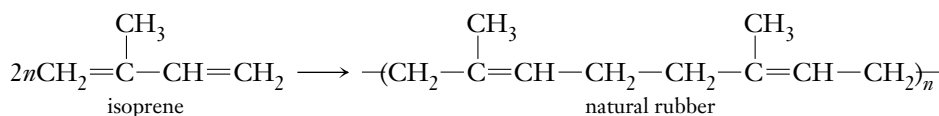


The polymer may be represented as $\text{CH}_3(\text{CH}_2\text{-CH}_2)_n\text{CH}_3$, where n is approximately 400. Polyethylene is a tough, flexible plastic. It is widely used as an electrical insulator and for the fabrication of such items as unbreakable refrigerator dishes, plastic cups, and squeeze bottles. Polypropylene is made by polymerizing propylene, $\text{CH}_3\text{-CH=CH}_2$, in much the same way. Teflon is made by polymerizing tetrafluoroethylene in a similar reaction.



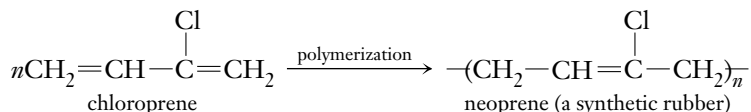
The molecular weight of Teflon is about 2×10^6 . Approximately 20,000 $\text{CF}_2=\text{CF}_2$ molecules polymerize to form a single giant molecule. Teflon is a very useful polymer. It does *not* react with concentrated acids and bases or with most oxidizing agents. It does not dissolve in most organic solvents.

Natural rubber is obtained from the sap of the rubber tree, a sticky liquid called latex. Rubber is a polymeric hydrocarbon formed in the sap by the combination of about 2000 molecules of 2-methyl-1,3-butadiene, commonly called isoprene. The molecular weight of rubber is about 136,000.



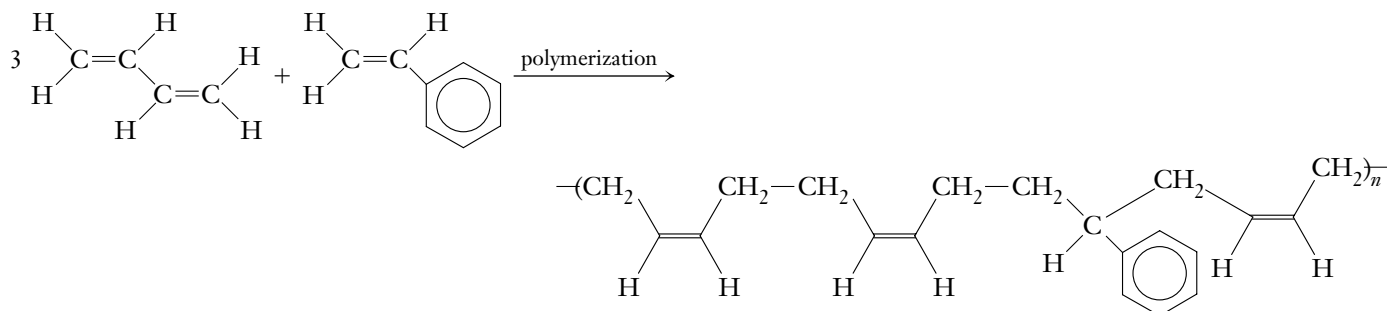
When natural rubber is warmed, it flows and becomes sticky. To eliminate this problem, **vulcanization** is used. This is a process in which sulfur is added to rubber and the mixture is heated to approximately 140°C . Sulfur atoms combine with some of the double bonds in the linear polymer molecules to form bridges that bond one rubber molecule to another. This cross-linking by sulfur atoms converts the linear polymer into a three-dimensional polymer. Fillers and reinforcing agents are added during the mixing process to increase the durability of rubber and to form colored rubber. Carbon black is the most common reinforcing agent. Zinc oxide, barium sulfate, titanium dioxide, and antimony(V) sulfide are common fillers.

Some synthetic rubbers are superior to natural rubber in some ways. Neoprene is a synthetic elastomer (an elastic polymer) with properties quite similar to those of natural rubber. The basic structural unit is 2-chloro-1,3-butadiene, commonly called chloroprene, which differs from isoprene in having a chlorine atom rather than a methyl group at carbon 2 of the 1,3-butadiene chain.



Neoprene is less affected by gasoline and oil and is more elastic than natural rubber. It resists abrasion well and is not swollen or dissolved by hydrocarbons. It is widely used to make hoses for oil and gasoline, electrical insulation, and automobile and refrigerator parts.

When two different monomers are mixed and then polymerized, **copolymers** are formed. Depending on the ratio of the two monomers and the reaction conditions, the order of the units can range from quite regular (e.g., alternating) to completely random. In this way, polymers with a wide variety of properties can be produced. The most important rubber produced in the largest amount in the United States is styrene butadiene rubber (SBR), a polymer of styrene with butadiene in a 1:3 molecular ratio.




The double bonds in SBR can be cross-linked by vulcanization as described for natural rubber. SBR is used primarily for making tires. Other copolymers are used to make car bumpers, body and chassis parts, wire insulation, sporting goods, sealants, and caulking compounds.

Some addition polymers and their uses are listed in Table 27-14.

Condensation Polymerization

Some polymerization reactions are based on *condensation reactions*, in which two molecules combine by splitting out or eliminating a small molecule. For such a polymer to be formed, each monomer must have two functional groups, one on each end. A polymer formed in this way is called a **condensation polymer**. There are many useful condensation polymers, based on a wide variety of bifunctional molecules.

Polyesters (short for “*polymeric esters*”) are condensation polymers that are formed when *dihydric alcohols* react with *dicarboxylic acids*. An ester linkage is formed at each end of each monomer molecule to build up large molecules. A useful polyester is prepared from terephthalic acid and ethylene glycol.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 11.10, Condensation Polymerization.

Dihydric alcohols contain two —OH groups per molecule. They are often called glycols.

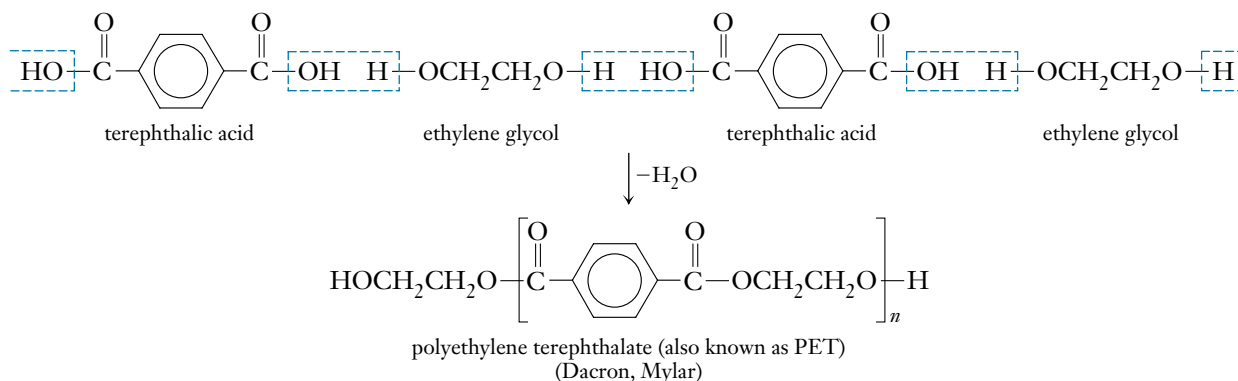
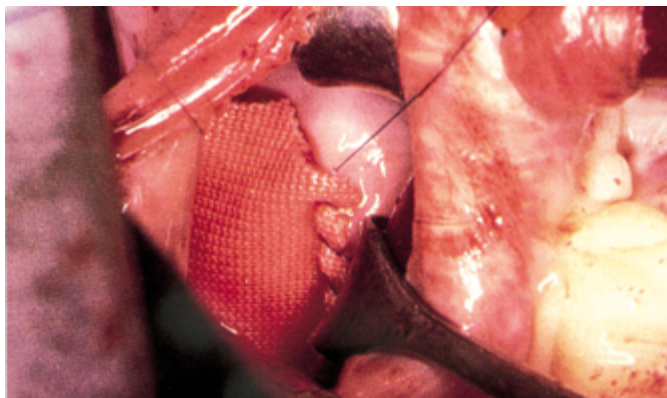
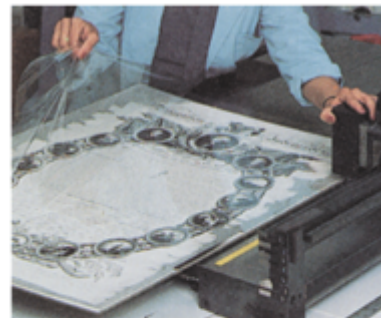


TABLE 27-14 *Some Important Addition Polymers*

Polymer Name (some trade names)	Some Uses	Polymer Production, Tons/Year in United States	Monomer Name	Monomer Formula
polyethylene (Polythene)	electrical insulation; toys and molded objects; bags; squeeze bottles	14 million	ethylene	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$
polypropylene (Herculon, Vectra)	bottles; films; lab equipment, toys; packaging film; filament for rope, webbing, carpeting; molded auto and appliance parts	6.7 million	propylene	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{CH}_3 \end{array}$
polyvinyl chloride (PVC)	pipe, siding, gutters; floor tiles	7.4 million	vinyl chloride	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{Cl} \end{array}$
polyacrylonitrile (Orlon, Acrilan)	acrylic fibers for carpets, clothing, knitwear	95,000	acrylonitrile	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{CN} \end{array}$
polystyrene (Styrene, Styrofoam, Styron)	molded toys, dishes, kitchen equipment; insulating foam, e.g., ice chests; rigid foam packaging	3.3 million	styrene	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{C}_6\text{H}_5 \end{array}$
poly(methyl meth- acrylate) (Plexiglas, Lucite)	high-quality transparent objects; water- based paints; contact lenses	507,000	methyl methacrylate	$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{C}=\text{O} \\ & & \\ & & \text{OCH}_3 \end{array}$
polybutadiene	automotive tire tread, hoses, belts; metal can coatings	610,000	1,3-butadiene	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{C}=\text{C} \\ & & / \quad \backslash \\ & & \text{H} \quad \text{H} \end{array}$
ethylene-propylene copolymer	appliance parts; auto hoses, bumpers, body and chassis parts; coated fabrics	324,000	ethylene, propylene	formulas given above
SBR copolymer	tires	1 million	styrene, 1,3-butadiene	formulas given above



A patch made of Dacron polymer is used to close a defect in a human heart.

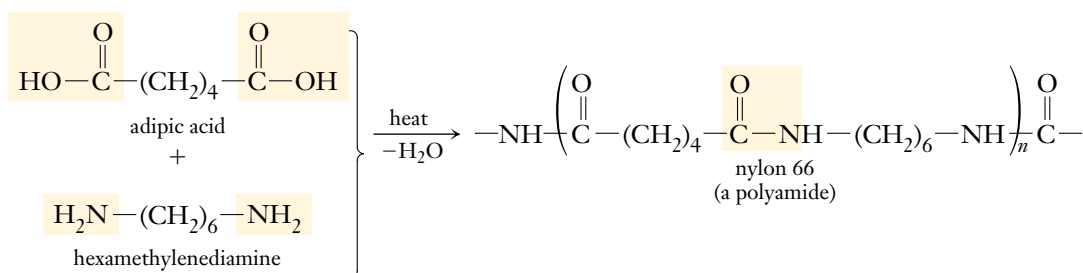


More than 2 million tons of this polymer is produced annually in the United States. Dacron, the fiber produced from this polyester, accounts for approximately 50% of all synthetic fibers. It absorbs very little moisture, and its properties are nearly the same whether it is wet or dry. Additionally, it possesses exceptional elastic recovery properties so it is used to make “permanent-press” fabrics. This polyester can also be made into films of great strength (e.g., Mylar), which can be rolled into sheets 1/30 the thickness of a human hair. Such films can be magnetically coated to make audio- and videotapes.

The polymeric amides, **polyamides**, are an especially important class of condensation polymers. **Nylon** is the best known polyamide. It is prepared by heating anhydrous hexamethylenediamine with anhydrous adipic acid, a dicarboxylic acid. This substance is often called nylon 66 because the parent diamine and dicarboxylic acid each contain six carbon atoms.

Polymers have a wide range of properties and uses. Mylar sheet polymer (another polyethylene terephthalate) is used to protect documents, such as this photocopy of a later version of the Declaration of Independence (*top*). Another kind of polymer coating is used to make shatterproof covers on glass items such as fluorescent light bulbs (*bottom*).

The molecular weight of the polymer varies from about 10,000 to about 25,000. It melts at about 260–270°C.



Molten nylon is drawn into threads (Figure 27-22). After cooling to room temperature, these can be stretched to about four times their original length. The “cold drawing” process orients the polymer molecules so that their long axes are parallel to the fiber axis. At regular intervals there are N—H---O hydrogen bonds that *cross-link* adjacent chains to give strength to the fiber.

Petroleum is the ultimate source of both adipic acid and hexamethylenediamine. We do not mean that these compounds are present in petroleum, only that they are made from it. The same is true for many other industrial chemicals. The cost of petroleum is an important factor in our economy because so many products are derived from petroleum.



Nylon is formed at the interface where hexamethylenediamine (in the lower water layer) and adipyl chloride (a derivative of adipic acid, in the upper hexane layer) react. The nylon can be drawn out and wound on a stirring rod. In industry, adipic acid is used in place of adipyl chloride.

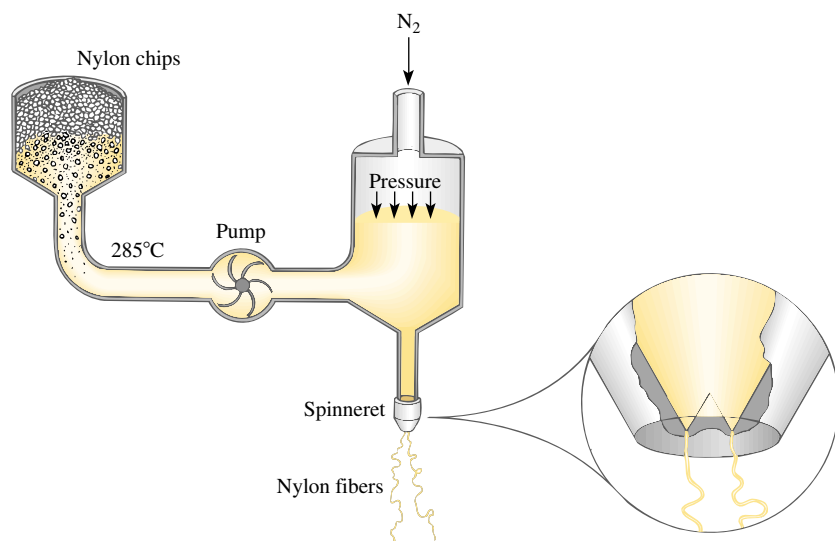
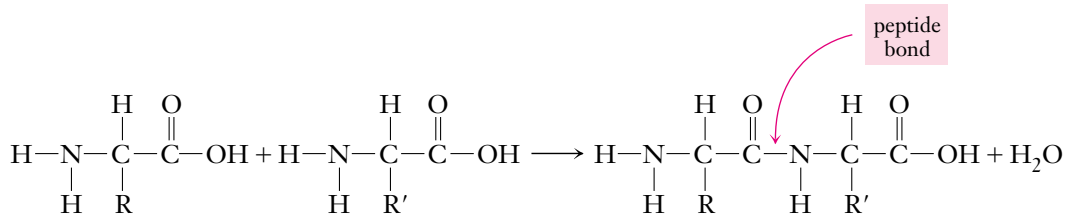
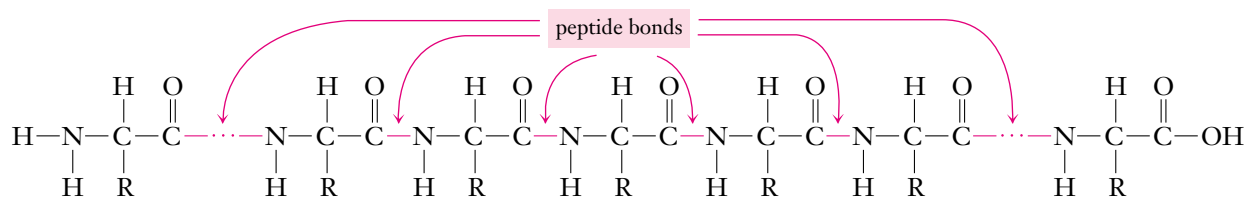


Figure 27-22 Fibers of synthetic polymers are made by extrusion of the molten material through tiny holes, called *spinnerets*. After cooling, nylon fibers are stretched to about four times their original length to orient the polymer molecules.

Some types of natural condensation polymers play crucial roles in living systems. **Proteins** (Section 28-9) are polymeric chains of *L-amino acids* linked by peptide bonds. A **peptide bond** is formed by the elimination of a molecule of water between the amino group of one amino acid and the carboxylic acid group of another.



When this process is carried out repeatedly, a large molecule called a **polypeptide** is formed.



Proteins are discussed in greater detail in Section 28-9.

Key Terms

Acid halide See *Acyl halide*.

Acyl group The group of atoms remaining after removal of an —OH group of a carboxylic acid.

Acyl halide A compound derived from a carboxylic acid by replacing the —OH group with a halogen (X), usually —Cl;

general formula is $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}$; also called acid halide.

Addition reaction A reaction in which two atoms or groups of atoms are added to a molecule, one on each side of a double or triple bond. The number of groups attached to carbon *increases*, and the molecule becomes more nearly saturated.

Alcohol A hydrocarbon derivative in which an H attached to a carbon atom not part of an aromatic ring has been replaced by an —OH group.

Aldehyde A compound in which an alkyl or aryl group and a hydrogen atom are attached to a carbonyl group; general

formula is $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$; R may be H.

Aliphatic hydrocarbons Hydrocarbons that do not contain aromatic rings.

Alkanes See *Saturated hydrocarbons*.

Alkenes Unsaturated hydrocarbons that contain a carbon-carbon double bond.

Alkyl group A group of atoms derived from an alkane by the removal of one hydrogen atom.

Alkylbenzene A compound containing an alkyl group bonded to a benzene ring.

Alkynes Unsaturated hydrocarbons that contain a carbon-carbon triple bond.

Amide A compound containing the $-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}$ group.

Amine A compound that can be considered a derivative of ammonia, in which one or more hydrogens are replaced by alkyl or aryl groups.

Amino acid A compound containing both an amino group and a carboxylic acid group.

Amino group The —NH₂ group.

Aromatic hydrocarbons Benzene and similar condensed ring compounds; contain delocalized rings of electrons.

Aryl group The group of atoms remaining after a hydrogen atom is removed from an aromatic system.

Carbonyl group The $-\overset{\text{O}}{\parallel}{\text{C}}-$ group.

Carboxylic acid A compound containing a $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$ group.

Condensation polymer A polymer that is formed by a condensation reaction.

Condensation reaction A reaction in which a small molecule, such as water or hydrogen chloride, is eliminated and two molecules are joined.

Conjugated double bonds Double bonds that are separated from each other by one single bond, as in $\text{C}=\text{C}-\text{C}=\text{C}$.

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

Copolymer A polymer formed from two different compounds (monomers).

Cycloalkanes Cyclic saturated hydrocarbons.

Dehydration The reaction in which H— and —OH are eliminated from adjacent carbon atoms to form water and a more unsaturated bond.

Dehydrohalogenation An elimination reaction in which a hydrogen halide, HX (X = Cl, Br, I), is eliminated from a haloalkane. A C=C double bond is formed.

Elimination reaction A reaction in which the number of groups attached to carbon *decreases*. The degree of unsaturation in the molecule increases.

Ester A compound of the general formula $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}'$, where R and R' may be the same or different and may be either aliphatic or aromatic. R may be H. R' cannot be H.

Ether A compound in which an oxygen atom is bonded to two alkyl or two aryl groups, or one alkyl and one aryl group.

Fat A solid triester of glycerol and (mostly) saturated fatty acids.

Fatty acid A long-chain aliphatic acid; many can be obtained from animal fats.

Functional group A group of atoms that represents a potential reaction site in an organic compound.

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

Glyceride A triester of glycerol.

Heterocyclic amine An amine in which nitrogen is part of a ring.

Homologous series A series of compounds in which each member differs from the next by a specific number and kind of atoms.

Hydration reaction A reaction in which the elements of water, H and OH, add across a double or triple bond.

Hydrocarbon A compound that contains only carbon and hydrogen.

Hydrogenation The reaction in which hydrogen adds across a double or triple bond.

Isomers Different compounds that have the same molecular formula.

Ketone A compound in which a carbonyl group is bound to two alkyl or two aryl groups, or to one alkyl and one aryl group.

Oil A liquid triester of glycerol and unsaturated fatty acids.

Organic chemistry The chemistry of substances that contain carbon-carbon or carbon-hydrogen bonds.

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.

Phenol A hydrocarbon derivative that contains an —OH group bound to an aromatic ring.

Pi bond A chemical bond formed by the side-to-side overlap of atomic orbitals.

Polyamide A polymeric amide.

Polyene A compound that contains more than one double bond per molecule.

Polyester A polymeric ester.

Polyhydric alcohol An alcohol that contains more than one —OH group.

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.

Primary alcohol An alcohol with no or one R group bonded to the carbon bearing the —OH group.

Primary amine An amine in which one H atom of ammonia has been replaced by an organic group.

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

Saturated hydrocarbons Hydrocarbons that contain only single bonds. They are also called *alkanes* or *paraffin hydrocarbons*.

Secondary alcohol An alcohol with two R groups bonded to the carbon bearing the —OH group.

Secondary amine An amine in which two H atoms of ammonia have been replaced by organic groups.

Sigma bond A chemical bond formed by the end-to-end overlap of atomic orbitals.

Structural isomers See *Constitutional isomers*.

Substitution reaction A reaction in which an atom or a group of atoms attached to a carbon atom is replaced by another atom or group of atoms. No change occurs in the degree of saturation at the reactive carbon.

Tertiary alcohol An alcohol with three R groups bonded to the carbon bearing the —OH group.

Tertiary amine An amine in which three H atoms of ammonia have been replaced by organic groups.

Unsaturated hydrocarbons Hydrocarbons that contain double or triple carbon-carbon bonds.

Vulcanization The process in which sulfur is added to rubber and heated to 140°C, to cross-link the linear rubber polymer into a three-dimensional polymer.

Exercises

Basic Ideas

- (a) Give a brief definition of *organic chemistry*. (b) Can life, as currently known, exist without organic compounds? (c) What happened to the “vital force” theory?
- How is carbon’s tendency to bond to other carbon atoms unique among the elements?
- (a) Why do many organic compounds have low melting and boiling points? (b) Some organic compounds, like table sugar, do not have a boiling point. Suggest a reason why.
- (a) What are the principal sources of organic compounds? (b) Some chemists argue that the ultimate source of all natural occurring organic compounds is carbon dioxide. Could this be possible? *Hint*: Think about the origins of coal, natural gas, and petroleum.
- List 10 “everyday” uses of organic compounds. Choose examples from at least five different classes of compounds.

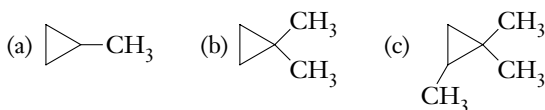
Aliphatic Hydrocarbons

- (a) Define and compare the structures of alkanes, alkenes, and alkynes. (b) Write the general formula of each of these hydrocarbon families. (c) What is a saturated hydrocarbon?

- (a) What are hydrocarbons? (b) What are the cycloalkanes? (c) Write the general formula for acyclic alkanes.
- Describe the bonding in and the geometry of molecules of the following alkanes: (a) methane; (b) ethane; (c) propane; (d) butane. How are the formulas for these compounds similar? How are they different?
- (a) What are straight-chain hydrocarbons? (b) What are branched-chain hydrocarbons? (c) Cite three examples of each.
- (a) What is a homologous series? (b) Provide specific examples of compounds that are members of a homologous series. (c) What is a methylene group? (d) How does each member of a homologous series differ from compounds that come before and after it in the series? (e) Name three homologous series that are also aliphatic hydrocarbons.
- (a) What are alkyl groups? (b) Draw structures for and write the names of the first five straight-chain alkyl groups. (c) What is the origin of the names for alkyl groups?
- Could a substance with the molecular formula C_3H_8 be a cycloalkane? Could C_3H_8 be a branched alkane having

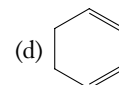
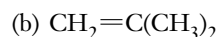
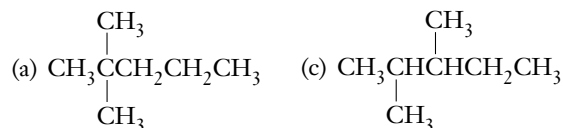
a methyl group as a substituent attached to the longest chain?

13. Name the following compound by the IUPAC system: $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$. Draw a constitutional isomer of this compound, and give its correct IUPAC name.
14. Give the IUPAC name of each of the following compounds.
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$
 - $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$
15. Write structural formulas for the isomeric saturated hydrocarbons having the molecular formula C_6H_{14} . Which one would have the highest boiling point?
16. Write structural formulas for four constitutional isomers of C_7H_{14} that contain a cyclopropyl substituent. Name each by the IUPAC system.
17. Write the structural formula for 2,2-dimethylpropane.
18. Write the IUPAC name for each of the following.

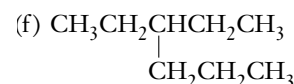
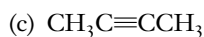
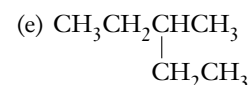
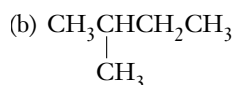
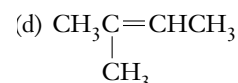
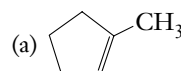


19. Write structural formulas for 1,1,2-trimethylcyclohexane, isopropylcyclobutane, and *sec*-butylcyclohexane.
20. (a) How does the general formula for the alkenes differ from the general formula for the alkanes? (b) Why are the general formulas identical for alkenes and cycloalkanes that contain the same number of carbon atoms?
21. (a) What are cycloalkenes? (b) What is their general formula? (c) Provide the structural formulas and names of three examples.
22. Describe the bonding at each carbon atom in (a) ethene, (b) propene, (c) 1-butene, and (d) 2-methyl-2-butene.
23. (a) What are geometric isomers? (b) Why is rotation around a double bond not possible at room temperature? (c) What do *cis* and *trans* mean? (d) Draw structures for *cis*- and *trans*-3-methyl-3-hexene. How should their melting and boiling points compare?
24. How do carbon-carbon single bond lengths and carbon-carbon double bond lengths compare? Why?
25. (a) What are alkynes? (b) What other name is used to describe them? (c) What is the general formula for alkynes? (d) How does the general formula for alkynes compare with the general formula for cycloalkenes? Why?
26. Describe the bonding and geometry associated with the triple bond of alkynes.
27. Write the structural formulas of the following compounds: (a) 1-butyne; (b) 2-methylpropene; (c) 2-ethyl-3-methyl-1-butene; (d) 3-methyl-1-butyne.

28. Write the structural formulas of the following compounds: (a) 3-hexyne; (b) 1,3-pentadiene; (c) 3,3-dimethylcyclobutene; (d) 3,4-diethyl-1-hexyne.
29. Write the IUPAC names for the following compounds.



30. Repeat Exercise 29 for

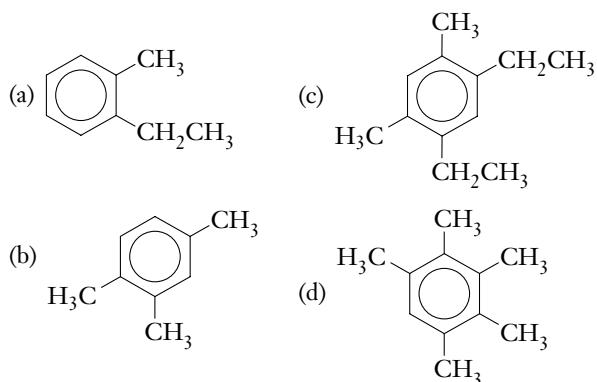


31. Each of the hydrocarbon families has members that are cyclic hydrocarbons. (a) What is a cyclic hydrocarbon? (b) Write the structural formula of one example of each of the following: (i) cycloalkene; (ii) cycloalkane; and (iii) cycloalkyne.

Aromatic Hydrocarbons

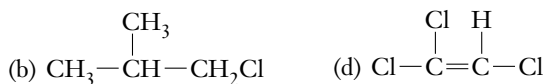
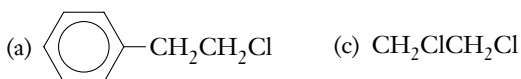
32. (a) What distinguishes an aromatic compound from other cyclic compounds? (b) What is the principal source of aromatic hydrocarbons?
33. (a) The structure for benzene is sometimes drawn as a hexagon enclosing a circle; what is the meaning of the circle? (b) Write the structural formulas of the three most common aromatic hydrocarbons.
34. (a) What is a phenyl group? (b) How many isomeric monophenylnaphthalenes are possible?
35. There are only three isomeric trimethylbenzenes. Write their structural formulas, and name them.
36. (a) How many isomeric dibromobenzenes are possible? (b) What names are used to designate these isomers?
37. Write the structural formulas for the following compounds: (a) *p*-difluorobenzene; (b) ethylbenzene; (c) 1,3,5-tribromobenzene; (d) 1,3-diphenylbutane; (e) *p*-chlorotoluene.

38. Write the IUPAC names for the following compounds.

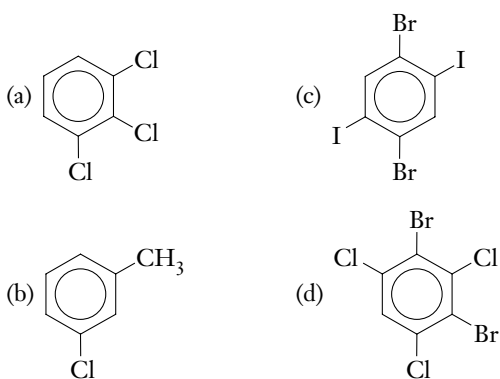


Alkyl and Aryl Halides

39. (a) Write the general representation for the formula of an alkyl halide. (b) How does this differ from the representation for the formula of an aryl halide?
40. Write the IUPAC names for the following halides.



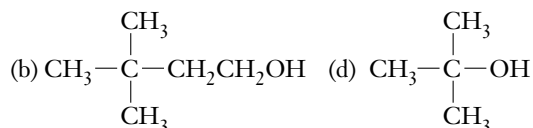
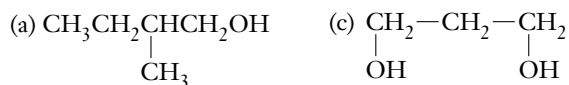
41. Write the structural formulas for the following: (a) 2,2-dichloropentane; (b) 3-bromo-1-butene; (c) 1,2-dichloro-2-fluoropropane; (d) *p*-dichlorobenzene.
42. Name the following.



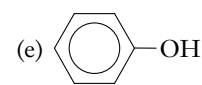
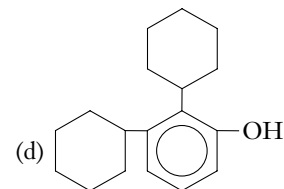
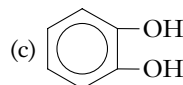
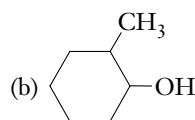
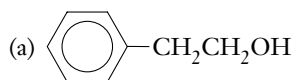
43. The compound 1,2-dibromo-3-chloropropane (DBCP) was used as a pesticide in the 1970s. Recently, agricultural workers have claimed that exposure to DBCP made them sterile. Write the structural formula for this compound.

Alcohols and Phenols

44. (a) What are alcohols and phenols? (b) How do they differ? (c) Why can alcohols and phenols be viewed as derivatives of hydrocarbons? as derivatives of water?
45. (a) Distinguish among primary, secondary, and tertiary alcohols. (b) Write names and formulas for three alcohols of each type.
46. Write structural formulas for and write the IUPAC names of the eight (saturated) alcohols that contain five carbon atoms and one —OH group per molecule. Which ones may be classified as primary alcohols? secondary alcohols? tertiary alcohols?
47. (a) What are glycols? (b) Write the structural formula of three examples. (c) Why are glycols more soluble in water than monohydric alcohols that contain the same number of carbon atoms?
48. Refer to Table 27-8, and explain the trends in boiling points and solubilities of alcohols in water.
49. Why are methyl alcohol and ethyl alcohol called wood alcohol and grain alcohol, respectively?
50. Why are most phenols only slightly soluble in water?
51. Write the structural formula for each of the following compounds: (a) 2-butanol; (b) cyclohexanol; (c) 1,4-butanediol.
52. Give the IUPAC name for each of the following compounds.

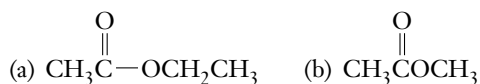


53. Which of the following compounds are phenols? Give the IUPAC name for each compound.

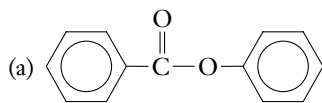


54. Write the structural formulas for the following: (a) *p*-iodophenol; (b) 4-nitrophenol (the nitro group is —NO₂); (c) *m*-nitrophenol.

77. Give the IUPAC names for the following esters.



78. Name the following esters.

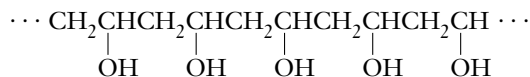


Reactions of Organic Molecules

79. (a) When an addition reaction occurs, the molecule becomes more nearly saturated. Explain. (b) When an elimination reaction occurs, the molecule becomes more unsaturated. Explain.
80. (a) What is a substitution reaction? (b) What is a halogenation reaction? (c) What is an addition reaction?
81. (a) Describe the reaction of methane with chlorine in ultraviolet light. (b) Write equations that show structural formulas for all compounds that can be formed by reaction (a). (c) Name all compounds in these equations. (d) Why are the halogenation reactions of the larger alkanes of limited value?
82. (a) Describe the reaction of ethane with chlorine in ultraviolet light. (b) Write equations that show structural formulas for all compounds that can be formed by reaction (a). (c) Give the IUPAC names for all compounds in these equations.
83. Which of the following compounds could undergo addition reactions? (a) propane; (b) 1,3-butadiene; (c) cyclopentene; (d) acetone.
84. Most reactions of the alkanes that do not disrupt the carbon skeleton are substitution reactions, whereas the alkenes are characterized by addition to the double bond. What does this statement mean?
85. How can bromination be used to distinguish between alkenes and alkanes?
86. Write equations for two reactions in which alkenes undergo addition reactions with halogens. Give the IUPAC names for all compounds.
87. When a substitution reaction occurs, there is no change in saturation. Explain.
88. (a) What is hydrogenation? (b) Why is it important? (c) Write equations for two reactions that involve hydrogenation of alkenes. (d) Give the IUPAC names for all compounds in part (c).
89. Describe two qualitative tests that can be used to distinguish between alkenes and alkanes. (b) Cite some specific examples. (c) What difference in reactivity is the basis for the qualitative distinction between alkanes and alkenes?
90. (a) Why are alkynes more reactive than alkenes? (b) What is the most common kind of reaction that alkynes undergo? (c) Write equations for three such reactions. (d) Give the IUPAC names for all compounds in part (c).
91. (a) What is the most common kind of reaction that the benzene ring undergoes? (b) Write equations for the reaction of benzene with chlorine in the presence of an iron catalyst and for the analogous reaction with bromine.
92. Write equations to illustrate both aromatic and aliphatic substitution reactions of toluene using (a) chlorine, (b) bromine, and (c) nitric acid.
93. Classify each reaction as substitution, addition, or elimination.
- (a) $\text{CH}_3\text{CH}_2\text{Br} + \text{CN}^- \longrightarrow \text{CH}_3\text{CH}_2\text{CN} + \text{Br}^-$
- (b) $\text{CH}_3\underset{\text{Br}}{\text{CH}}\text{CH}_2\text{Br} + \text{Zn} \longrightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{ZnBr}_2$
- (c) $\text{C}_6\text{H}_6 + \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$
94. Describe a simple test to distinguish between the two isomers 2-pentene and cyclopentane.

Polymers

95. (a) What is a polymer? (b) What is the term for the smaller molecule that serves as the repeating unit making up a polymer? (c) What are typical molecular weights of polymers?
96. (a) What is polymerization? (b) Write equations for three polymerization reactions.
97. (a) Give an example of a condensation reaction. (b) What is the essential feature of monomers used in condensation polymerizations?
- *98. The examples of condensation polymers given in the text are all copolymers, that is, they contain two different monomers. Is it possible for a single monomer to polymerize so as to form a condensation *homopolymer*? If so, suggest an example. If not, explain why not.
99. (a) What is a monomer? (b) Name three polymers commonly found in a classroom and their use or function.
100. (a) What is a copolymer? (b) What is a condensation polymer? (c) Name three polymers that are addition polymers.
101. Poly(vinyl alcohol) has a relatively high melting point, 258°C. How would you explain this behavior? A segment of the polymer is



102. What changes could be made in the structures of polymer molecules that would increase the rigidity of a polymer and raise its melting point?

103. Methyl vinyl ketone, $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}=\text{CH}_2$, can be polymerized by addition polymerization. The addition reaction involves only the $\text{C}=\text{C}$ bond. Write the structural formula of a four-unit segment of this polymer.

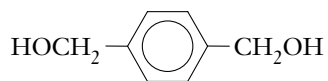
104. (a) What is rubber? (b) What is vulcanization? (c) What is the purpose of vulcanizing rubber? (d) What are fillers and reinforcing agents? (e) What is their purpose?

105. (a) What is an elastomer? (b) Cite a specific example. (c) What are some of the advantages of neoprene compared with natural rubber?

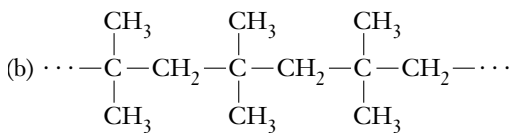
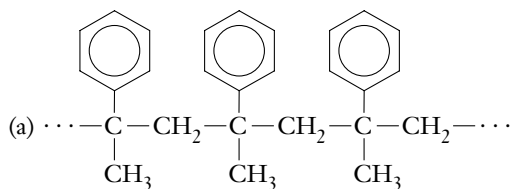
106. (a) What are polyamides? (b) What kind of reaction forms polyamides?

107. (a) What are polyesters? (b) What is Dacron? (c) How is Dacron prepared? (d) What is Mylar? (e) Is it reasonable to assume that a polyester can be made from propylene glycol and terephthalic acid? If so, sketch its structure.

108. Suppose the following glycol is used with terephthalic acid to form a polyester. Write the structure of the polymer, showing two repeating units.



109. Write the structural formula of the monomer used in preparation of each of the following polymers.



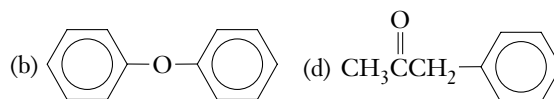
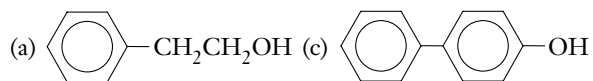
110. Is it possible to produce a copolymer by addition polymerization? If so, give an example. If not, explain why not.

111. (a) What is nylon? (b) How is it prepared?

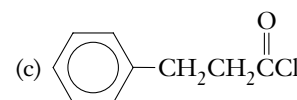
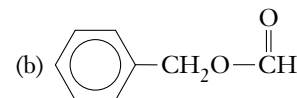
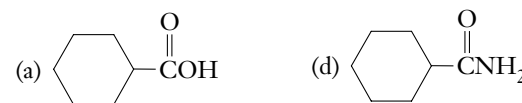
112. Common nylon is called nylon 66. (a) What does this mean? (b) Write formulas for two other possible nylons.

Mixed Exercises

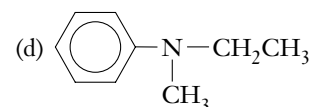
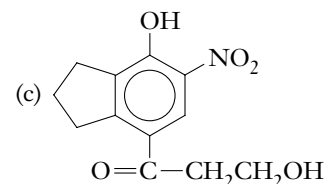
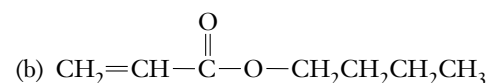
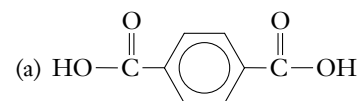
*113. Identify the class of organic compounds (ester, ether, ketone, and so on) to which each of the following belongs.



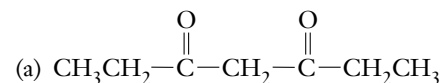
*114. Identify the class of organic compounds (ester, ether, ketone, etc.) to which each of the following belongs.

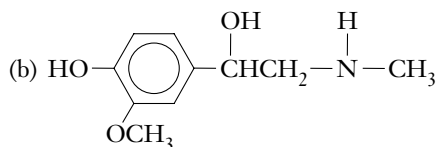


*115. Identify and name the functional groups in each of the following.

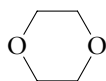


116. Identify and name the functional groups in the following.

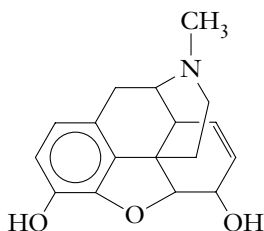




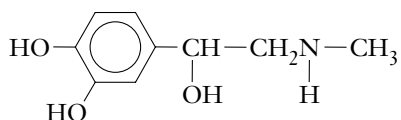
(c) dioxane (also known as 1,4-dioxin)



(d) morphine

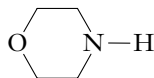


(e) epinephrine (adrenaline)

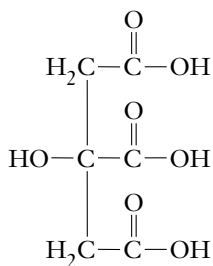


117. Identify and name the functional groups in each of the following.

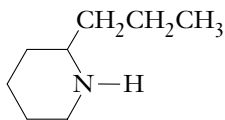
(a) morpholine



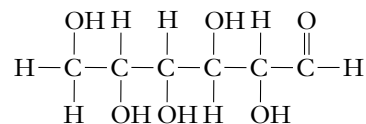
(b) citric acid



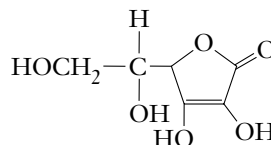
(c) coniine (from the hemlock plant; the poison that Socrates drank)



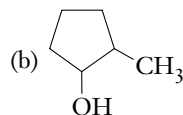
(d) glucose (a simple sugar, also known as dextrose)



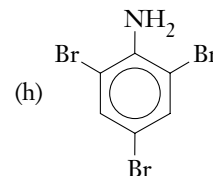
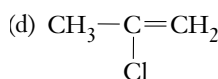
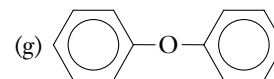
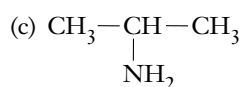
(e) vitamin C (also called ascorbic acid)



118. Name the following compounds.

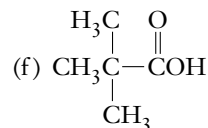
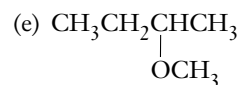
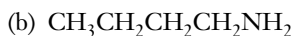
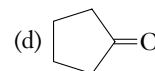
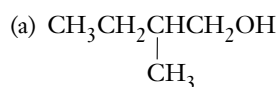


(f) $(\text{CH}_3\text{CH}_2)_3\text{N}$



119. Write the structural formulas for the following compounds: (a) *p*-bromotoluene; (b) cyclohexanol; (c) 2-methoxy-3-methylbutane; (d) diethylamine; (e) *o*-chlorophenol; (f) 1,4-butanediol.

120. Give the IUPAC names for the following compounds.



CONCEPTUAL EXERCISES

121. Suggest why the C_6 ring in cyclohexane is not planar.
 122. Can an aromatic compound also be a saturated compound?

BUILDING YOUR KNOWLEDGE

123. (a) How do the melting points and boiling points of the alkanes vary with molecular weight? (b) Do you expect them to vary in this order? (c) Why or why not? Use intermolecular forces to explain your answer.
 124. Write a Lewis formula for butanone.
 125. (a) What are resonance structures? (b) Draw resonance structures for benzene. (c) What do we mean when we

say that the electrons associated with the π bonds in benzene are delocalized over the entire ring?

126. Lidocaine has replaced Novocain (procaine) as the favored anesthetic in dentistry. What functional group do the two compounds have in common?

