

Organic Chemistry

The swimmer, fish and vegetation, and all other forms of life on this planet are based on the element carbon. The chemistry of carbon compounds is discussed in this chapter.



Setting the Stage

Perfectly positioned about 90 million miles from a medium-sized star and protected by a thick atmosphere, our planet glides majestically in space. Under these ideal conditions, the formation and stable existence of chemical bonds that compose living systems are possible. These living systems grow and reproduce on the Earth, move gracefully in the oceans, and float effortlessly in the air. All of these creatures and plants are composed of compounds that include the element carbon as the central character. We, of course, consider ourselves to be the very ultimate carbon-based life form. Could there be life forms based on other elements? Science fiction stories would have us think so, but it is actually quite unlikely, if not impossible. In this chapter, we will see how this unique element forms the types of molecules that are part of living systems.

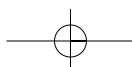
Traditionally, all chemical compounds have been relegated to two categories: organic and inorganic. **Organic compounds** include most of the compounds of carbon, especially those containing carbon–hydrogen bonds. However, much of the chemistry that we have discussed so far concerns compounds derived from minerals and other noncarbon compounds, and these are known as **inorganic compounds**. A few compounds of carbon such as CaCO_3 and LiCN are considered to be inorganic compounds since they are derived from minerals and do not contain C–H bonds. Originally, the division of compounds into the two categories was determined by whether they were derived from (or part of) a living system

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(organic) or from a mineral (inorganic). In fact, before 1828 it was thought that organic compounds and their decay products could be synthesized from inorganic compounds (e.g., H_2O , CO_2 , and NH_3) only by living matter (organisms). Only life had that magic ingredient of nature called the “vital force” that allowed the miracle of organic synthesis. In 1828, however, a German scientist named Friedrich Wöhler synthesized urea (H_2NCONH_2), which had been classified as organic, from the inorganic compound ammonium cyanate (NH_4CNO). Urea is a waste product of the metabolism of proteins and, until 1828, was thought to result only from this source. Although it was just one compound, the concept of the “vital force” was doomed. Since that time, millions of organic compounds have been synthesized from basic minerals in the laboratory.

Organic compounds are certainly central to our lives. Hydrocarbons (compounds composed only of carbon and hydrogen) are used as fuel to power our cars and to heat our homes. Our bodies are fueled with organic compounds obtained from the food we eat in the form of sugars (carbohydrates), fats, and proteins. This food is made more palatable by organic flavorings, is wrapped in organic plastic, and is kept from spoiling with organic preservatives. Our clothes are made of organic compounds, whether these compounds come from plant and animal sources (cotton and wool) or are synthetic (Nylon and Dacron). These fabrics are made colorful with organic dyes. When we are ill, we take drugs that may also be organic: aspirin relieves headaches, codeine suppresses coughs, and diazepam (Valium) calms nerves. These are only a few examples of how we use organic chemicals daily.

Formulating Some Questions

The introduction of such a large topic as organic chemistry in one chapter is not an easy task. The questions that we will address for each type of organic compound are: What is unique about its molecular structure? How is it named? What are its particular properties? How is it made or otherwise obtained? What use is made of the specific type of compound?

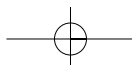
First, however, we will lay the groundwork by reviewing the bonding and general properties of the central and most important atom in organic compounds—carbon. In this endeavor, the discussions of Lewis structures, polarity of bonds, geometry, and polarity of molecules are important. These topics were all covered in Chapter 6.

Section A HYDROCARBONS

16-1 Bonding in Organic Compounds

Looking Ahead! It will serve us well to begin our discussions of organic compounds with a look back at some of the properties of carbon-hydrogen compounds. Of particular interest to the discussions that follow are the Lewis structures, polarity of bonds, geometry, and polarity of molecules.

Of the 114 elements in the periodic table, only one has properties that make it possible for the existence of large complex molecules on which living systems are based. This, of course, is carbon. There are two reasons for carbon’s unique properties.



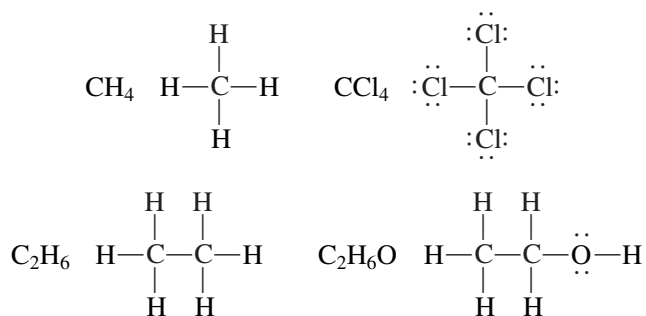
1. Carbon–carbon bonds are strong. This makes long chains of carbon atoms possible.
2. Carbon and hydrogen have similar electronegativities. This means that the C—H bond is nearly nonpolar. As a result, the C—H bond is not chemically reactive toward many compounds, such as water.

A science fiction writer may look at Group IVA in the periodic table and notice that silicon is immediately under carbon. Could the writer propose life based on silicon? In fact, such life forms are not likely. First, the silicon–silicon bond is much weaker than carbon–carbon bonds, so long chains of silicon atoms in a molecule do not occur. Second, the Si—H bond is polar, meaning that it is chemically reactive with other polar compounds. For example, silicon–hydrogen compounds react spontaneously with water (a polar compound) at room temperature. It is hard to imagine a life form based on small molecules that react with water. If such life existed on some distant planet, we would hope that it wouldn't get caught in the rain.

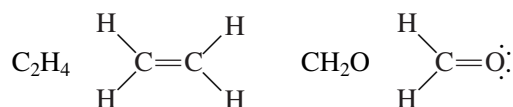
Most organic compounds are typical molecular compounds. That is, they are usually gases or liquids at room temperature or solids with low melting points. Since the C—H bond is nearly nonpolar, most organic molecules are nonpolar or, at most, have low polarity. This means that, in general, they have little solubility in water. Inorganic compounds, on the other hand, are likely to be high-melting solids and are more likely to be soluble in water.

Carbon (in Group IVA) has four valence electrons. In its compounds, carbon follows the octet rule, which means that it must form *four* bonds to have access to eight valence electrons. It may form (a) four single bonds to four different atoms, (b) a double bond to one atom and two single bonds to two others, or (c) a triple bond to one atom and one single bond to one other atom. Examples of each of these three cases are shown, written as Lewis structures.

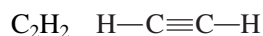
a. Single bonds



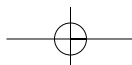
b. Double bonds



c. Triple bonds



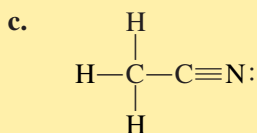
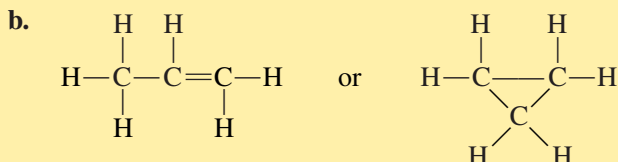
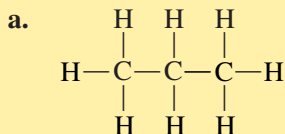
As we will see, organic compounds are classified according to the types of bonds in their molecules. Thus writing correct Lewis structures is an important endeavor and is reviewed in Example 16-1.



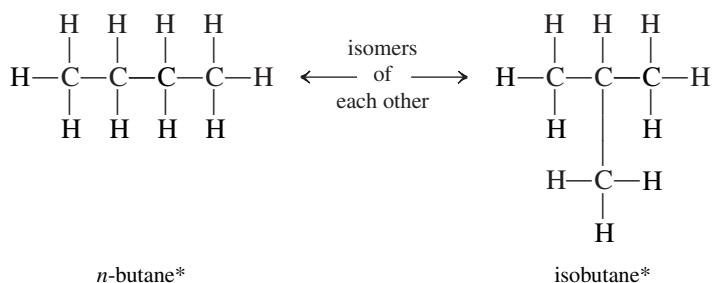
Example 16-1 Writing Lewis Structures of Some Organic Compounds**working it out**

Give Lewis structures for the following compounds.

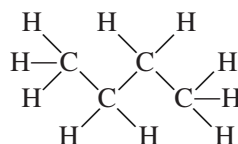
- a. C_3H_8 b. C_3H_6 c. H_3C_2N (all H's on one C)

Answers

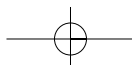
Many times we find that there is more than one Lewis structure for a given formula. Such is the case with butane, C_4H_{10} , since two correct structures can be drawn. *Compounds with different structures but the same molecular formula are called isomers.*



These Lewis structures represent the molecules as flat and two dimensional. In fact, when carbon is bonded to four other atoms, it lies in the center of a tetrahedron. In the actual three-dimensional structure, the $H-C-H$ bond angle is about 109° . A truer representation of the structure of *n*-butane is

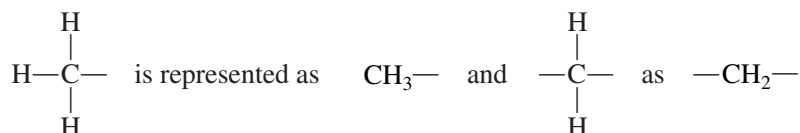


*The *n* is an abbreviation of normal and refers to the isomer in which all the carbons are bound consecutively in a continuous chain. The *iso* prefix refers to the isomer in which there is a branch involving three carbons attached to a carbon chain or another atom. For example,

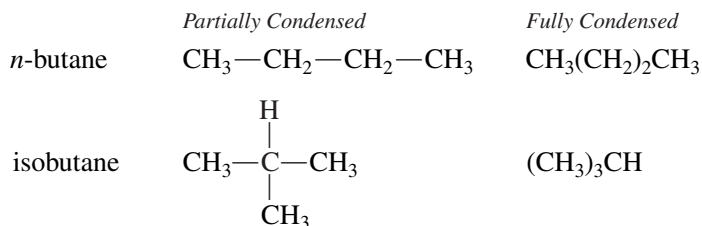


This representation is somewhat awkward, however, so long-chain structures are usually shown in a straight line even though they actually have a three-dimensional geometry. A true representation of the structure requires the use of molecular models. In Figure 16-1, the CH_4 , C_2H_6 , and C_3H_8 molecules are represented by “ball-and-stick” models. In a three-dimensional representation, we can see that all the hydrogens in the C_2H_6 molecule are identical.

Many of the compounds that we will mention in the following sections have several repeating units. Drawing these structures can become quite tedious if all hydrogens and carbons are written out. A **condensed formula** in which separate bonds are not written is helpful. For example,



Depending on what we are trying to show, the structure may be partially or fully condensed.



In a fully condensed structure, it is understood that the CH_2 's in parentheses are in a continuous chain and the CH_3 's in parentheses are attached to the same atom.

A few other compounds and their isomers are shown in Table 16-1. As you can see, the number of isomers increases as the number of carbons increases, and addition of a **hetero atom** (*any atom other than carbon or hydrogen*) also increases the number of isomers.

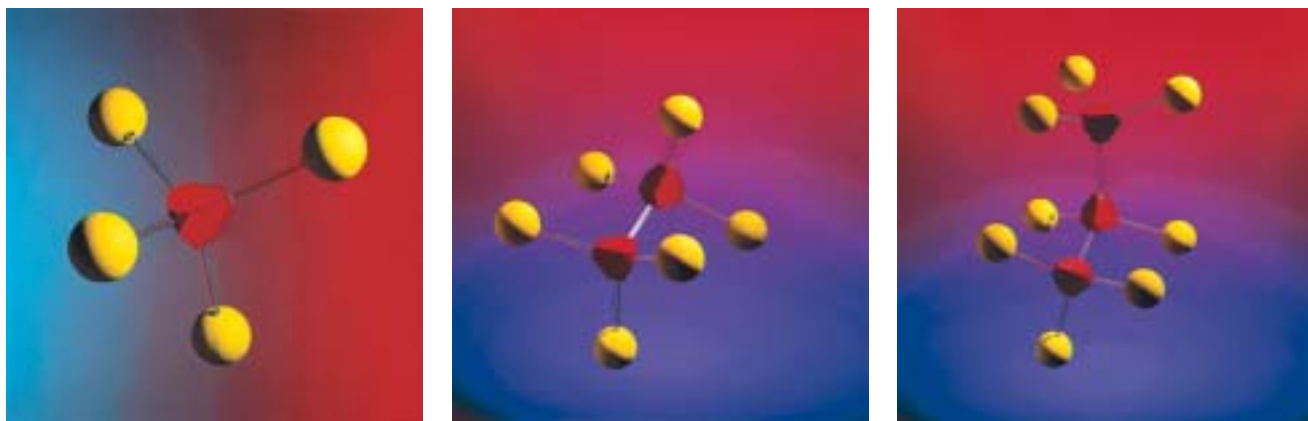


Figure 16-1 Geometry of CH_4 , C_2H_6 , and C_3H_8 In these hydrocarbons, each carbon is at the center of a tetrahedron.

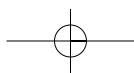


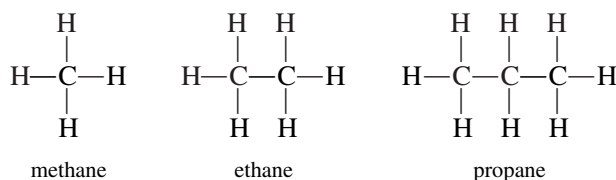
Table 16-1 Isomers

C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$ <i>n</i> -pentane	$CH_3CH_2\overset{\text{CH}_3}{\text{CH}}-CH_3$ isopentane	$CH_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-CH_3$ neopentane
C_3H_6	$H_2C=CHCH_3$ propene	$\begin{array}{ccc} H_2C & \text{---} & CH_3 \\ & \diagdown & / \\ & CH_2 & \end{array}$ cyclopropane	(Note that the carbons can also be arranged in a ring or <i>cyclic</i> structure.)
C_2H_6O	CH_3CH_2OH ethanol	$H_3C-O-CH_3$ dimethyl ether	
C_3H_6O	$CH_3CH_2\overset{\text{O}}{\parallel}{\text{C}}H$ propanal	$H_3C-\overset{\text{O}}{\parallel}{\text{C}}-CH_3$ propanone	$H_2C=CHCH_2OH$ allyl alcohol and others

16-2 Alkanes

Looking Ahead! In the next four sections, we will discuss organic compounds composed of only two elements (carbon and hydrogen). These compounds are classified into four categories based on the type of bonding in the molecules. In this section, we will investigate carbon-hydrogen compounds that contain only single covalent bonds.

Natural gas, gasoline, and candle wax are all composed of hydrocarbons. **Hydrocarbons** are compounds that contain only carbon and hydrogen. These particular hydrocarbons are also known as alkanes. **Alkanes** are hydrocarbons that contain only single covalent bonds. Since the carbons in these molecules bond to the maximum number of hydrogens, alkanes are known as **saturated** hydrocarbons. Alkanes can be described by the general formula C_nH_{2n+2} . This refers only to *open-chain alkanes*, meaning that the carbons do not form a ring. The simplest alkane ($n = 1$) is methane (CH_4), in which the carbon shares *four pairs of electrons* with four different hydrogen atoms. The next alkane ($n = 2$) is ethane (C_2H_6), and the third is propane (C_3H_8). These alkanes are members of a homologous series. In a **homologous series**, the next member differs from the previous one by a constant structure unit, which is one carbon and two hydrogens (CH_2).



The names in Table 16-2 are the basis for the names of all organic compounds. By altering them slightly, we can name other classes of organic compounds that are discussed later. Two systems of nomenclature are used in organic chemistry. The most systematic is the one devised by the International Union of Pure and Applied Chemistry (the IUPAC system). Although the rules for naming complex molecules can be

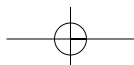


Table 16-2 Alkanes

Formula	Name	Formula	Name
CH ₄	<u>meth</u> ane	C ₆ H ₁₄	<u>hex</u> ane
C ₂ H ₆	<u>eth</u> ane	C ₇ H ₁₆	<u>hept</u> ane
C ₃ H ₈	<u>prop</u> ane	C ₈ H ₁₈	<u>oct</u> ane
C ₄ H ₁₀	<u>but</u> ane	C ₉ H ₂₀	<u>non</u> ane
C ₅ H ₁₂	<u>pent</u> ane	C ₁₀ H ₂₂	<u>dec</u> ane

extensive, we will be concerned with just the basic concepts. Compounds are also known by *common* or *trivial* names. Sometimes these names follow a pattern; sometimes they do not. They have been used for so many years that it is hard to break the habit of using them. When a chemical that is frequently known by its common name is encountered, that name is given in parentheses.

The name of a simple organic compound has two parts; the base of the name gives the number of carbons in the longest carbon chain, and the ending tells what kind of a compound it is. The underlined portions of the names in Table 16-2 are the basis of the names used for compounds containing 1 through 10 carbons in the longest chain; *meth-* stands for one carbon, *eth-* for two carbons, and so on. The ending used for alkanes is *-ane*. Therefore, the one-carbon alkane is methane, the two-carbon alkane is ethane, and so on.

Organic compounds can exist as unbranched compounds (all carbons bound to each other in a continuous chain) or as branched compounds (where at least one carbon is joined to three or four others). Previously, we indicated that *n*-butane is an unbranched alkane and that isobutane is a branched alkane. The IUPAC system bases its names on the longest carbon chain in the molecule, whereas the common names frequently include all of the carbons in the name (e.g., isobutane). The longest carbon chain in isobutane is three carbons long and is therefore considered a propane in the IUPAC system. Note that isobutane has a CH₃ group attached to a propane chain. In this system of nomenclature, the branches are named separately. *Since the branches can be considered as groups of atoms substituted for a hydrogen, the branches are called substituents. Substituents that contain one less hydrogen than an alkane are called alkyl groups.* Alkyl groups are not compounds by themselves; they must always be attached to some other group or atom. They are named by taking the alkane name, dropping the *-ane* ending, and substituting *-yl*. The most common alkyl groups are given in Table 16-3.

Thus the alkyl substituent in isobutane is a methyl group. The IUPAC name for isobutane is *methylpropane*.

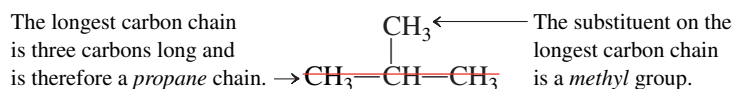
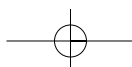


Table 16-3 Alkyl Groups (One to Four Carbons)

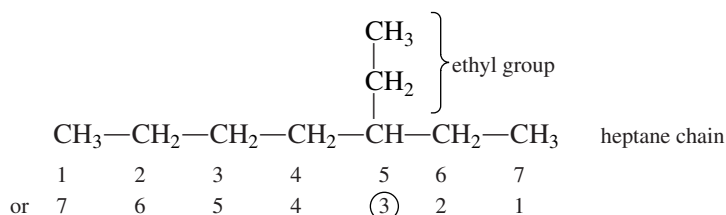
Alkyl Group ^a	Name	Alkyl Group	Name
CH ₃ —	methyl	CH ₃ CH ₂ CH ₂ CH ₂ —	<i>n</i> -butyl
CH ₃ CH ₂ —	ethyl	(CH ₃) ₂ CHCH ₂ —	isobutyl
CH ₃ CH ₂ CH ₂ —	<i>n</i> -propyl	CH ₃ CH ₂ CH(CH ₃)—	<i>sec</i> -butyl
(CH ₃) ₂ CH—	isopropyl	(CH ₃) ₃ C—	<i>tert</i> -butyl (or <i>t</i> -butyl)

^aThe dash (—) shows where the alkyl group is attached to a carbon chain or a hetero atom.

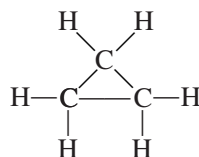


If the same group is substituted on either the same carbon or another carbon, the prefix *di-* is used to indicate two groups. If the same group is substituted on three carbons, the prefix *tri-* is used to indicate three groups. For example, the IUPAC name for neopentane (see Table 16-1) is *dimethylpropane*.

The location of the substituent on the longest chain is designated by a number. The carbons are numbered from the end that gives the substituent the lowest number. Thus the following compound is named 3-ethylheptane rather than 5-ethylheptane.



When the carbons form a ring, the name is prefixed with *cyclo-*. Therefore, the three-carbon ring compound



is called cyclopropane. Cycloalkanes have the general formula C_nH_{2n} .

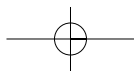
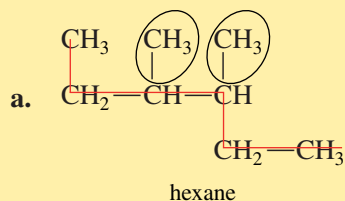
Example 16-2 Identification and the Name of the Longest Carbon Chain

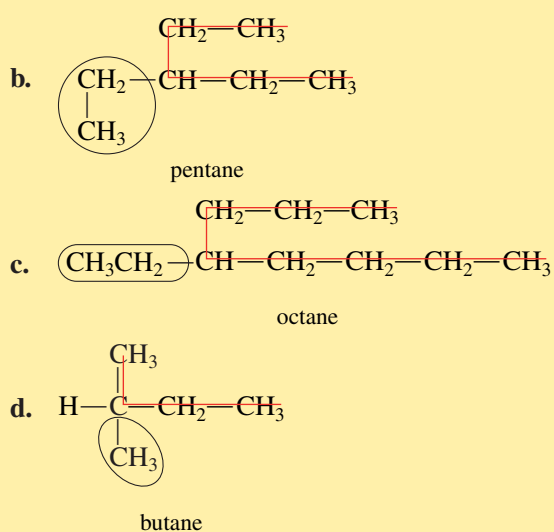
working it out

Draw a line through the longest carbon chain in the following compounds and circle the substituents. Name the longest chain.

- a.
$$\begin{array}{c}
 \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
 | \quad | \quad | \\
 \text{CH}_2 - \text{CH} - \text{CH} \\
 \quad \quad \quad | \\
 \quad \quad \quad \text{CH}_2 - \text{CH}_3
 \end{array}$$
- b.
$$\begin{array}{c}
 \text{CH}_2 - \text{CH}_3 \\
 | \\
 \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\
 | \\
 \text{CH}_3
 \end{array}$$
- c.
$$\begin{array}{c}
 \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\
 | \\
 \text{CH}_3\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3
 \end{array}$$
- d.
$$\begin{array}{c}
 \text{CH}_3 \\
 | \\
 \text{H} - \text{C} - \text{CH}_2 - \text{CH}_3 \\
 | \\
 \text{CH}_3
 \end{array}$$

Answers





Naming Compounds by the IUPAC Method

Name the compounds in Example 16-2 by the IUPAC method.

Answers

- 3,4-dimethylhexane
- 3-ethylpentane
- 4-ethyloctane
- methylbutane (no number necessary)

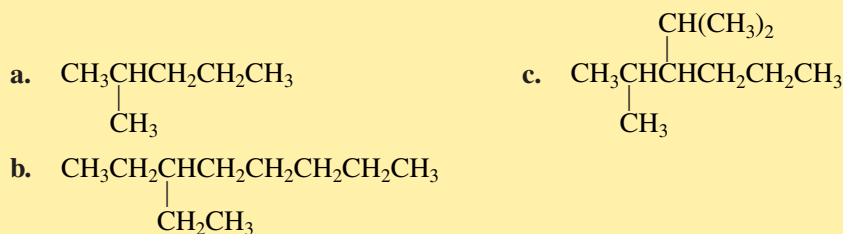
Example 16-3

Writing Condensed Structures from a Name

Write the condensed structures of the following.

- 2-methylpentane
- 3-ethyloctane
- 3-isopropyl-2-methylhexane (Substituent groups are listed in alphabetical order.)

Answers



Example 16-4

Since alkanes are essentially nonpolar compounds, the only intermolecular forces of attraction between molecules are London forces. These forces depend on the volume of the molecules. Since the molar mass is roughly proportional to the volume, we can state that the lighter the molecules, the less are the London forces. (See section 10-2.) As a result, the boiling points of alkanes are related to their molar masses. The lighter alkanes

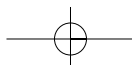




Figure 16-2 An Oil Refinery
The crude oil is processed in large refineries.

are the more volatile. **Volatility** refers to the tendency of a liquid to vaporize to the gaseous state and is related to its boiling point. Alkanes with four or fewer carbon atoms are all gases at room temperature. Those with five to eighteen carbons are liquids, whereas those with more than eighteen carbons are low-melting solids (resembling candle wax). All alkanes are odorless and colorless. They are also extremely flammable.

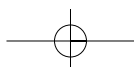
There are two major sources of alkanes, natural gas and crude oil (petroleum). Natural gas is mainly methane with smaller amounts of ethane, propane, and butanes. Unlike natural gas, petroleum contains hundreds of compounds, the majority of which are open-chain and cyclic alkanes. Before we can make use of petroleum, it must be separated into groups of compounds with similar properties. Further separation may or may not be carried out depending on the final use of the hydrocarbons.

Crude oil is separated into groups of compounds according to boiling points by distillation in a refinery. (See Figure 16-2.) In such a distillation, the liquid is boiled, and the gases move up a large column that becomes cooler and cooler toward the top. Compounds condense (become liquid) at different places in the column, depending on their boiling points. As the liquids condense, they are drawn off, providing a rough separation of the crude oil. Some of the material has too high a boiling point to vaporize and remains in the bottom of the column. A drawing showing this process and the various fractions obtained is shown in Figure 16-3. Note that the fewer the carbon atoms in the alkane, the lower the boiling point (the more volatile it is).

The composition of crude oil itself varies somewhat depending on where it is found. Certain crude oil, such as that found in Nigeria and Libya, is called light oil because it is especially rich in the hydrocarbons that are present in gasoline. Otherwise, one fraction can be converted into another by three processes: cracking, re-forming, and alkylation. **Cracking** changes large molecules into small molecules. **Re-forming** removes hydrogens from the carbons and/or changes unbranched hydrocarbons into branched hydrocarbons. (Branched hydrocarbons perform better in gasoline; that is, they have a higher octane rating.) **Alkylation** takes small molecules and puts them together to make larger molecules. In all of these processes, catalysts are used, but there is a different catalyst for each process.



Natural gas (methane) is stored in the gaseous state.



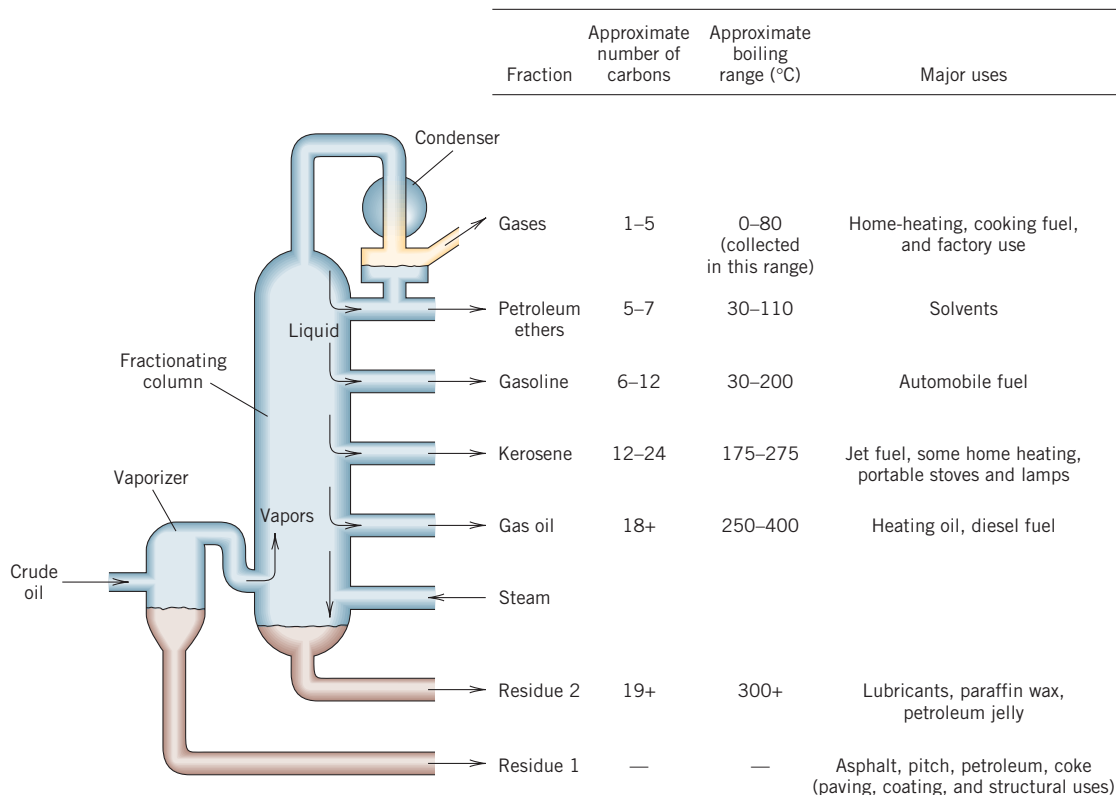
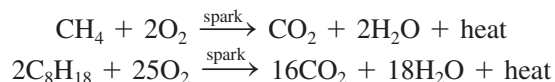


Figure 16-3 Refining of Petroleum Oil is separated into fractions according to boiling points.

About 96% of all oil and gas is burned as fuel, whereas only 4% is used to make other organic chemicals. As a fuel, hydrocarbons burn to give carbon dioxide, water, and a great deal of heat energy.

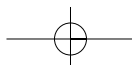
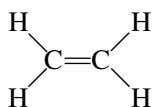


Industrially, most synthetic organic chemicals have their ultimate origin in *the alkanes obtained from crude oil*. These **petrochemicals** are put to a wide range of uses in the manufacture of fibers, plastics, coatings, adhesives, synthetic rubber, some flavorings, perfumes, and pharmaceuticals.

16-3 Alkenes

Looking Ahead! The second class of hydrocarbons we will discuss are those that contain a double bond somewhere in the carbon chain. These compounds are important in the production of many plastics.

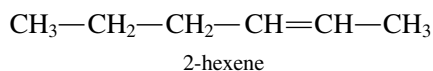
Alkenes are hydrocarbons that contain a double bond. Organic compounds with multiple bonds are said to be **unsaturated**. The general formula for an open-chain alkene with one double bond is C_2H_{2n} , which, you may recall, is also the formula of cyclic alkanes. The simplest alkene is ethene (common name ethylene), which has the structure



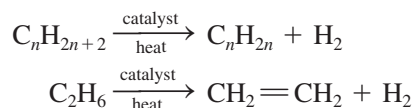


The plastic bag is made of polyethylene.

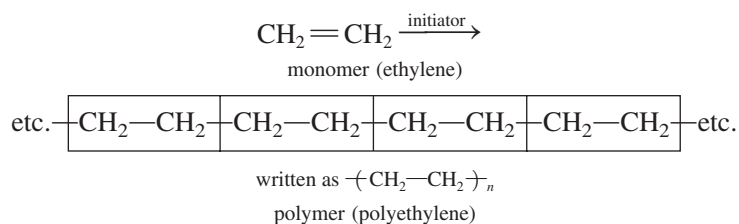
Alkenes are named by dropping the *-ane* ending of the corresponding alkane and substituting *-ene*. The location of the double bond is indicated by number in a manner similar to the naming of branched alkanes by the IUPAC method. The double bond is located by numbering the carbon-carbon bonds starting from the end closest to the double bond in the main hydrocarbon chain. The smallest number for a double bond takes precedence over the numbering of any substituents on the carbon chain.



Only small amounts of alkenes are found naturally in crude oil; the majority are made from alkanes by the re-forming process during the refining of crude oil. When alkanes are heated over a catalyst, hydrogen is lost from the molecule and alkenes together with hydrogen are formed



A large amount of alkenes are produced industrially to make polymers. When certain compounds called initiators are added to an alkene or a mixture of alkenes, the double bond is broken and the alkenes become joined to each other by single bonds. This produces a high-molar-mass molecule called a **polymer**, which has repeating units of the original alkene (called the monomer).



These types of polymers are named by adding *poly-* to the name of the alkene used to form the polymer. In the example shown above, the polymer was made from ethylene (usually common names are used for polymers), and so the polymer is called polyethylene. If the name of the polymer contains two words, the alkene name is enclosed in parentheses [e.g., poly(methyl methacrylate)]. This rule is not always followed in some well-known polymers such as polyvinyl chloride. When writing the condensed structure of a polymer, we abbreviate the structure by giving the repeating unit in parentheses along with a subscript *n* to indicate that the monomer is repeated many times. Groups attached to the double bond affect the properties of the polymer, and by varying the group, we can vary the uses for which the polymer is suited. (See Figure 16-4.) Some commonly used polymers and their uses are given in Table 16-4.

Chemicals can add to the double bond to form new single bonds and therefore new compounds. A test based on such a reaction, the addition of bromine to an alkene, is used to show the presence of alkenes. It is a very simple test to perform. The disappearance of the red color of bromine when it is added to a liquid means that multiple bonds are present (the dibromide formed is colorless). We will talk more about this test when we discuss aromatic compounds.

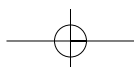
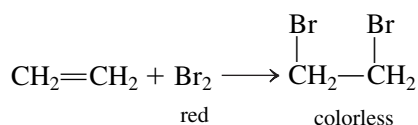






Figure 16-4 Polymers The frying pan is coated with Teflon, which gives it a “nonstick” surface. Polypropylene is used to make artificial turf, and polystyrene (Styrofoam) is used for insulation.

Table 16-4 Polymers

Monomer	Polymer	Some Common Trade Names	Uses
ethylene $\text{CH}_2=\text{CH}_2$	polyethylene $\text{-(CH}_2\text{-CH}_2\text{)}_n\text{-}$	Polyfilm ^a Marlex ^b	Electrical insulation, packaging (plastic bags), floor covering, plastic bottles, pipes, tubing
propylene $\text{CH}_2=\text{CH}$ CH_3	polypropylene $\text{-(CH}_2\text{-CH)}_n\text{-}$ CH_3	Herculon ^c	Pipes, carpeting, artificial turf, molded auto parts, fibers
vinyl chloride $\text{CH}_2=\text{CH}$ Cl	polyvinyl chloride (PVC) $\text{-(CH}_2\text{-CH)}_n\text{-}$ Cl	Tygon ^d	Wire and cable coverings, pipes, rainwear, shower curtains, tennis court playing surfaces
styrene $\text{CH}_2=\text{CH}$ 	polystyrene $\text{-(CH}_2\text{-CH)}_n\text{-}$ 	Styrofoam ^a Styron ^a	Molded objects (combs, toys, brush and pot handles), refrigerator parts, insulating material, phonograph records, clock and radio cabinets
tetrafluoroethylene $\text{CF}_2=\text{CF}_2$	polytetrafluoroethylene $\text{-(CF}_2\text{-CF}_2\text{)}_n\text{-}$	Teflon ^e Halon ^f	Gaskets, valves, tubing, coatings for cookware
methyl methacrylate $\text{CH}_2=\text{C}$ CH_3 CO_2CH_3	poly(methyl methacrylate) $\text{-(CH}_2\text{-C)}_n\text{-}$ CH_3 CO_2CH_3	Plexiglas ^g Lucite ^e	Glass substitute, lenses, aircraft glass, dental fillings, artificial eyes, braces
acrylonitrile $\text{CH}_2=\text{CH}$ CN	polyacrylonitrile $\text{-(CH}_2\text{-CH)}_n\text{-}$ CN	Orlon ^e Acrilan ^h	Fibers for clothing, carpeting

^aDow Chemical Co.

^bPhillips Petroleum Co.

^cHercules, Inc.

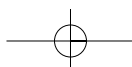
^dU.S. Stoneware Co.

^eE. I. du Pont de Nemours & Co.

^fAllied Chemical Corp.

^gRohm & Haas Co.

^hMonsanto Industrial Chemicals, Inc.

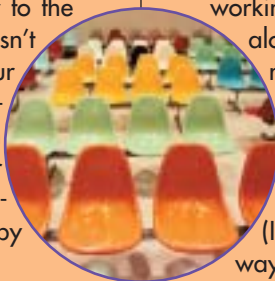


The Age of Plastics

In the classic movie of the late 1960s, *The Graduate*, Dustin Hoffman's character was informed that the key to the future involved one word—"Plastics." It wasn't wrong then and it still isn't. More and more of our infrastructure is changing from natural substances to the polymers we know as plastics. In this century we are on the cusp of even greater polymer discoveries that are just becoming imaginable today and will surely be followed by unimaginable discoveries tomorrow.

Actually plastics have been known for about 200 years. The first synthetic polymer was made by Schoenbein (UK) in the early 1800s and was known as *Colloidion*. It was a hard transparent film used in medicine and later in photography. In 1872 John Wesley Hyatt produced *Celluloid*, which was also used in photography and in combs and portable windows. In 1888, G. W. A. Kahlbaum (Switzerland) made a methacrylate polymer which was later used to make unbreakable beer glasses. In 1897 W. Krishe and A. Spitteler (Germany) made a condensation polymer that was a substitute for ivory. In 1910, L. H. Baekeland (U.S.) manufactured *Bakelite*, the first all-synthetic plastic, from phenol and formaldehyde. It had a high-temperature resistance, so it could be used in ashtrays and eventually in cabinets for radios and televisions.

The 1930s was an important decade for plastics, which included polyacrylics and polyesters (Julian Hill at DuPont Chemical Co.). Nylon (a polyamide) was first made



in 1934 by Donald Cofman, also at DuPont. Individuals working for large corporations rather than working alone were now making discoveries. We still know many of them by their trade names, such as Lucite and Plexiglas.

The explosion of plastics into our everyday lives actually began with an important discovery in the 1950s. Two scientists, Giulio Natta (Italy) and Karl Ziegler (Germany), discovered ways of using heterogeneous catalysts to polymerize ethylene to polyethylene. This new method produced polymers cheaper and easier than other methods. More importantly, the plastics produced by this procedure had much higher strengths and chemical resistance and thus many more applications.

One hundred years ago almost everything that we wore or used was made from natural substances such as wood, metal, or natural fibers. The space station, cell phones, laptop computers, eyeglasses, and many modern clothes are now synthetic. And we are not finished. Plastics that conduct electricity will soon be available and will probably replace metals in electrical wiring. Many new and exciting types of polymers are being studied. Carbon atoms arranged in tubes (called *nanotubes*) and polymers that extend outward from a central core (called *dendrimers*) give promise of applications we have yet to imagine.

*Submitted by Edward Tokas—
Carolina Reading and Learning*

Plastics are everywhere.

16-4 Alkynes

Looking Ahead! The third category of hydrocarbons has a triple bond somewhere in the carbon chain. This class of hydrocarbons is important in the production of alkenes, which are used to make polymers.

Alkynes are hydrocarbons that contain a triple bond. The general formula for an open-chain alkyne with one triple bond is C_nH_{2n-2} . The simplest alkyne is ethyne (acetylene), which has the structure

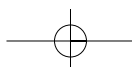
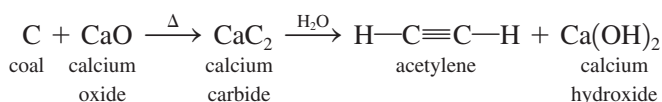


Alkynes are named just like alkenes except that *-yne* is substituted for the alkane ending instead of *-ene*. Thus,

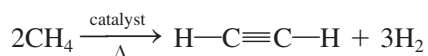


is named 3-octyne.

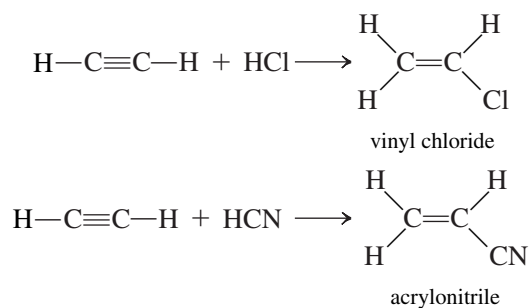
Alkynes are rare in nature, but they can be prepared synthetically. Acetylene can be made from coal by first reacting the coal with calcium oxide at high temperature and then treating the calcium carbide formed with water.



A more common method of making acetylene is the re-forming process. Methane is heated in the presence of a catalyst, forming acetylene and hydrogen.



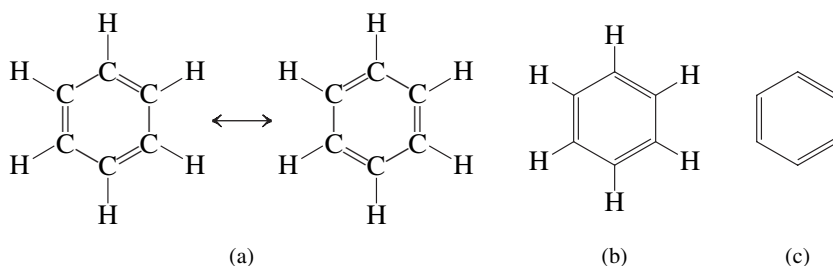
Although acetylene is used in oxyacetylene torches, its most important application is in the synthesis of specific alkenes for polymers. For example, acetylene reacts with hydrogen chloride to form vinyl chloride or with hydrogen cyanide to form acrylonitrile. These alkenes are then used to manufacture polyvinyl chloride and polyacrylonitrile, respectively.



16-5 Aromatic Compounds

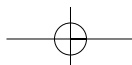
Looking Ahead! The final category of hydrocarbons involves cyclic compounds that are particularly stable. The most important member of this group involves a six-membered ring. These compounds are discussed in this section.

Benzene (C_6H_6) is a six-membered ring compound. Its Lewis structure can be written with alternating single and double bonds between adjacent carbons. In fact, two identical resonance structures can be written for benzene, which indicates that all six bonds are equivalent. The two resonance Lewis representations of benzene are shown below in (a). The Lewis representation in (b) is simplified by omitting the carbons. In (c), the structure is simplified further by omitting the hydrogens.

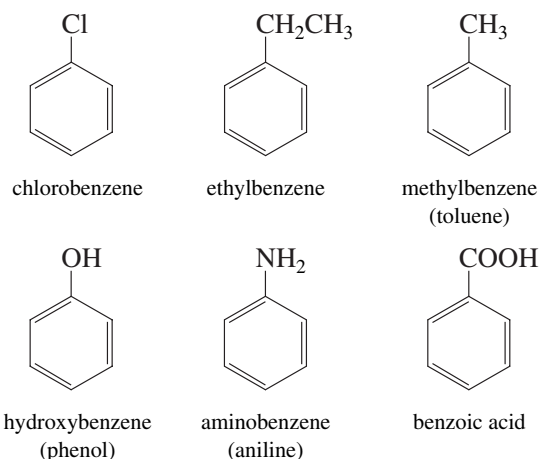


The benzene molecule is symmetrical and planar. It is also chemically unreactive compared to alkenes. For example, benzene does not “decolorize” a solution of bromine as do straight-chain alkenes (see page 494). It is this special stability that allows us to classify benzene among a unique class of ring hydrocarbons known as **aromatic compounds**.

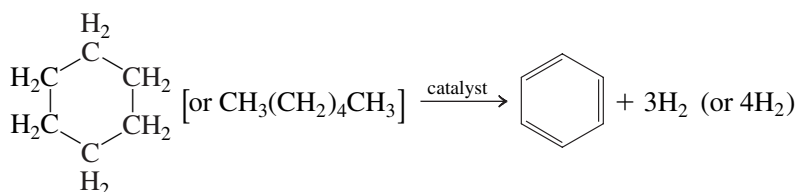
There are other ring hydrocarbons that are also aromatic and can be written with alternating single and double bonds, but we will confine our discussion to benzene and derivatives of benzene. A **derivative** of a compound is produced by the substitution of a group or hetero atom for a hydrogen on the molecules of the original compound. Compounds that contain the benzene ring can often be recognized by name because they are named as derivatives of benzene. Others have been given their own



distinctive name (shown in parentheses below). The following are the simplified structures and the names of some common derivatives of benzene.



Although some benzene and toluene are present in crude oil, additional quantities can be obtained by the re-forming process. When cyclohexane and/or hexane are heated with a catalyst, benzene is formed. Coal is another source of benzene. When coal is heated to high temperatures in the absence of air, some benzene is formed.



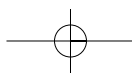
Benzene and toluene find application mainly as solvents and as starting materials to make other aromatic compounds. Benzene must be handled with care, however, because it has been found to be a potent carcinogen (it can cause cancer). Phenol and its derivatives are used as disinfectants and preservatives, and in the manufacture of dyes, explosives, drugs, and plastic.

Looking Back! Organic compounds form the basis of life processes. The central atom in the molecules of these compounds is the carbon atom, which can form bonds to other carbons in long chains, or to atoms of other elements. Carbon-hydrogen compounds (hydrocarbons) are classified as alkanes, alkenes, alkynes, or aromatics, based on the types of bonds or their molecular structure.

Learning Check A | checking it out

A-1. Fill in the blanks.

Lewis structures of organic compounds illustrate that carbon forms a total of _____ bonds to other atoms. Two different compounds that share the same formula are known as _____. A hydrocarbon that has only single bonds in its molecules is classified as an _____. The principal sources of this class of compounds are _____ gas and _____. The latter liquid is separated into component compounds in a _____. The separation is accomplished because light alkanes are more _____ than the heavier compounds. Alkenes are known as _____ hydrocarbons because they contain a _____ bond. An important use of these compounds is in the manufacture of _____. Alkynes contain a _____ bond. Benzene is the most important example of an _____ hydrocarbon. A _____ of benzene is formed by the replacement of a hydrogen with a hydrocarbon or hetero atom group.



- A-2. Represent all of the isomers of pentane. (Show as partially condensed structures.)
- A-3. Give the IUPAC names for each of the isomers in the previous problem.
- A-4. Show the partially condensed Lewis structures of
- 2-pentene
 - 4,4, dimethyl-1-pentyne
 - isopropylbenzene

Additional Examples: Exercises 16-3, 16-8, 16-18, 16-19, 16-25, 16-31, and 16-33.

Section B OTHER CLASSES OF ORGANIC COMPOUNDS

16-6 Organic Functional Groups

Looking Ahead! Organic chemistry is not limited to hydrocarbons. Many other elements, especially oxygen and nitrogen, can also be attached to a hydrocarbon group. When this happens, the presence of one or more of these atoms (known as *hetero atoms*) in a molecule may drastically change the properties of the compound. We begin our discussion of this area of organic chemistry with an overview of the effects of the presence of hetero atoms.

Methane (CH_4) boils at a very low -164°C and thus is a gas at room temperature. If one chlorine is substituted for a hydrogen on the carbon, the resulting compound, CH_3Cl (chloromethane), has properties very different from those of methane. Chloromethane is a polar compound with a higher molar mass than methane, so it boils at a much higher -24°C . The presence of the chlorine atom has a significant effect on the properties of the original compound. In most compounds, the nature and bonding of the hetero atom (or atoms) control the chemistry or the function of the molecule. *In an organic compound, the atom or group of atoms that determines the chemical nature of the molecule is known as the **functional group**.* Although no hetero atom is involved, the functional group of alkenes is the double bond and that of alkynes is the triple bond since those bonds account for several types of reactions that these compounds undergo. Each functional group has a strong influence on the chemistry of the compounds that contain it and thus establishes a specific class of compounds. In the following sections, we examine some of these classes of compounds that are determined by the presence of a particular functional group.

16-7 Alcohols ($\text{R}-\text{OH}$)*

Looking Ahead! In the next two sections, we will examine two classes of compounds that contain oxygen as a hetero atom where the oxygen forms bonds to two other atoms. The first is a familiar class of compounds known as alcohols.

Alcohol is most familiar to us as the active ingredient in alcoholic beverages. That is just one alcohol. Others are known to us as rubbing alcohol and wood alcohol. **Alcohols** are a class of organic compounds that contain the *OH* functional group (known as a **hydroxyl group**) in place of a hydrogen on a carbon chain.

*The R or R' represents a group such as an alkyl or an aromatic group.

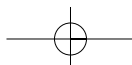
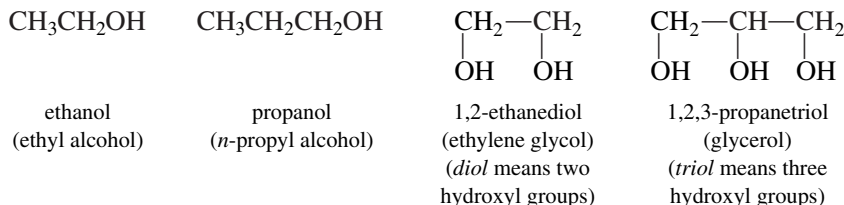


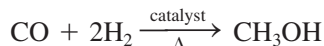


Figure 16-5 Alcohols
A major ingredient in each of these products is an alcohol.

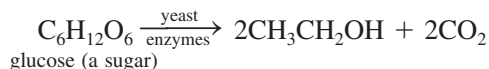
Alcohols are named by taking the alkane name, dropping the *-e*, and substituting *-ol*. Common names are obtained by just naming the alkyl group attached to the —OH followed by *alcohol*. Some familiar alcohols (see Figure 16-5) have more than one hydroxyl group. (In naming alcohols with more than one hydroxyl group, the *-e* in the alkane is not dropped.) Four examples of alcohols are



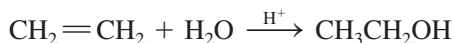
Methanol and ethanol can both be obtained from natural sources. Methanol can be prepared by heating wood in the absence of oxygen to about 400°C ; at such high temperatures, methanol, together with other organic compounds, is given off as a gas. Since methanol was once made exclusively by this process, it is often called wood alcohol. Currently, methanol is prepared from synthesis gas, a mixture of CO and H_2 . When CO and H_2 are passed over a catalyst at the right temperature and pressure, methanol is formed.



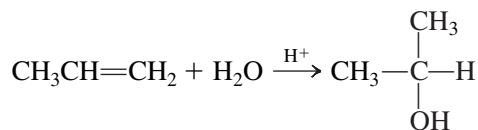
Ethanol (often known simply as alcohol) is formed in the fermentation of various grains. (Therefore, it is also known as grain alcohol.) In fermentation, the sugars and other carbohydrates in grains are converted to ethanol and carbon dioxide by the enzymes in yeast.



Industrially, ethanol is prepared by reacting ethylene with water in the presence of an acid catalyst.



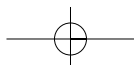
2-Propanol (isopropyl alcohol) can be prepared from propene (propylene) in the same way.



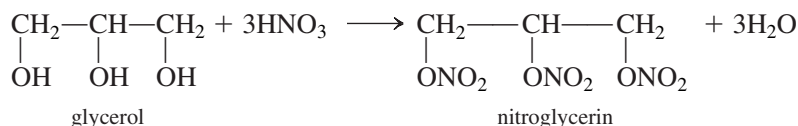
Methanol has been used as a solvent for shellac, as a denaturant for ethanol (it makes ethanol undrinkable), and as an antifreeze for automobile radiators. It is very toxic when ingested. In small doses it causes blindness, and in large doses it can cause death.

Ethanol is present in alcoholic beverages such as beer, wine, and liquor. The “proof” of an alcoholic beverage is two times the percent by volume of alcohol. If a certain brand of bourbon is 100 proof, it contains 50% ethanol. Ethanol can also be mixed with gasoline to form a mixture called “gasohol,” which is used as a fuel. Ethanol is an excellent solvent and has been used as such in perfumes, medicines, and flavorings. Ethanol, as well as 2-propanol (also known as rubbing alcohol), are used as antiseptics and as rubbing compounds to cleanse the skin and lower a feverish person’s temperature. While ethanol is not as toxic as methanol, it can cause coma or death when ingested in large quantities. 2-Propanol is also quite toxic.

Ethylene glycol is the major component of antifreeze and coolant used in automobiles. It is also used to make polymers, the most common of which is Dacron, a polyester.



Glycerol, which can be obtained from fats, is used in many applications where a lubricant and/or softener is needed. It has been used in pharmaceuticals, cosmetics, foodstuffs, and some liqueurs. When glycerol reacts with nitric acid, it produces nitroglycerin. Nitroglycerin is a powerful explosive.



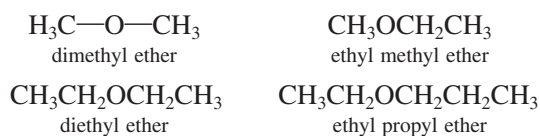
Nitroglycerin is also a strong smooth-muscle relaxant and vasodilator and has been used to lower blood pressure and to treat angina pectoris.

16-8 Ethers (R—O—R)

Looking Ahead! The next class of compounds also has an oxygen bonded to two other atoms. In ethers, however, the order of bonds is different from that in alcohols.

An **ether** contains an oxygen bonded to two hydrocarbon groups (rather than one hydrocarbon group and one hydrogen as in alcohols). The simplest ether, dimethyl ether, is an isomer of ethanol but has very different properties.

The common names of ethers are obtained by giving the alkyl groups on either side of the oxygen and adding *ether*.



Diethyl ether is made industrially by reacting ethanol with sulfuric acid. In this reaction, two ethanol molecules are joined together, with the loss of an H₂O molecule.



The most commonly known ether, diethyl ether (or ethyl ether, or just ether), was, in the past, used extensively as an anesthetic. It has the advantage of being an excellent muscle relaxant that doesn't affect blood pressure, pulse rate, or rate of respiration greatly. On the other hand, ether has an irritating effect on the respiratory passages and often causes nausea. Its flammability is also a drawback because of the danger of fire and explosions. Diethyl ether is rarely used now as an anesthetic. Other anesthetics that do not have its disadvantages have taken its place.

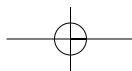
16-9 Aldehydes (R—C(=O)—H) and Ketones (R—C(=O)—R')

Looking Ahead! The next two classes of compounds also have oxygen as the lone hetero atom. In these two classes, however, the oxygen is bonded to only one carbon by a double bond.

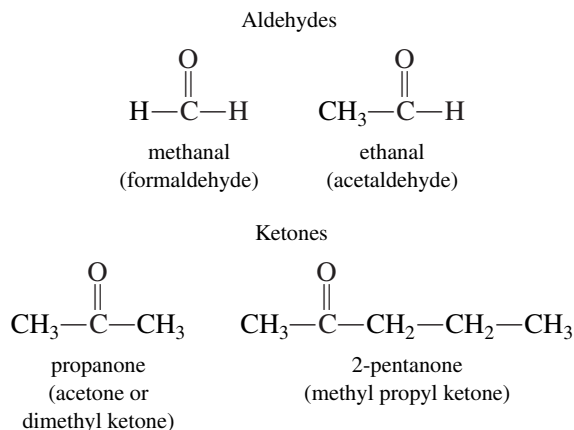
The functional group of aldehydes and ketones is a carbonyl group. A **carbonyl group** is a carbon with a double bond to an oxygen.



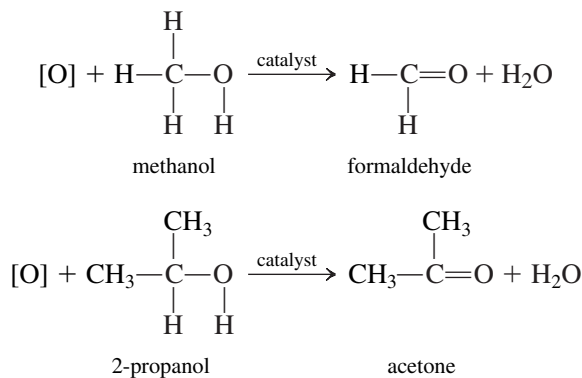
In **aldehydes** the carbonyl group is bound to at least one hydrogen, whereas in **ketones** the carbonyl group is bound to two hydrocarbon groups.



Aldehydes are named by dropping the *-e* of the corresponding alkane name and substituting *-al*. Therefore, the two-carbon aldehyde is ethanal. Ketones are named by taking the alkane name, dropping the *-e*, and substituting *-one*. The common names of ketones are obtained by naming the alkyl groups on either side of the C=O and adding *ketone*.

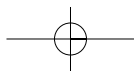


Many aldehydes and ketones are prepared by the oxidation of alcohols. Industrially, the alcohol is oxidized by heating it in the presence of oxygen and a catalyst. About half of the methanol produced industrially is used to make formaldehyde by oxidation. Acetone can be prepared in the same fashion by oxidation of 2-propanol. In the following reactions, the [O] represents an oxidizing agent that removes hydrogen (to form H₂O) from the alcohol.

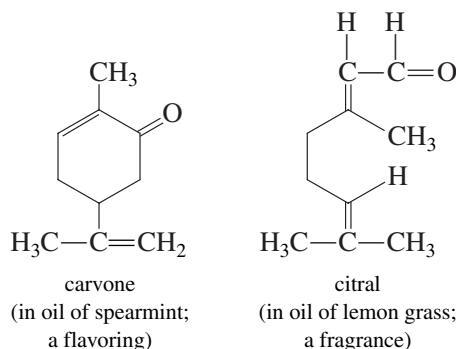


Aldehydes and ketones have uses as solvents, in the preparation of polymers, as flavorings, and in perfumes. The simplest aldehyde, formaldehyde, has been used as a disinfectant, antiseptic, germicide, fungicide, and embalming fluid (as a 37% by mass water solution). It has also been used in the preparation of polymers such as Bakelite (the first commercial plastic) and Melmac (used to make dishes). Formaldehyde polymers have also been used as coatings on fabrics to give “permanent press” characteristics.

The simplest ketone, acetone, has been used mainly as a solvent. It is soluble in water and dissolves relatively polar and nonpolar molecules. It is an excellent solvent for paints and coatings.



More complex aldehydes and ketones, such as the following two examples, are used in flavorings and perfumes.

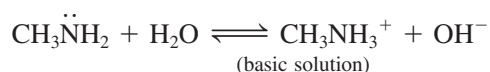
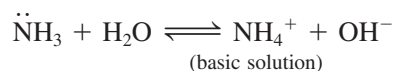


The specimen is preserved in a formaldehyde solution.

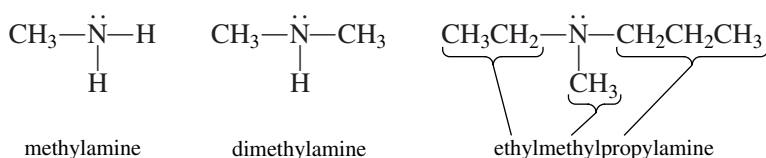
16-10 Amines (R—NH₂)

Looking Ahead! In this section, we will introduce a class of compounds that has nitrogen as the hetero atom. This class of organic compounds is known as amines and includes many familiar medications.

An **amine** contains a nitrogen with single bonds to a hydrocarbon group and two other hydrocarbon groups or hydrogens. The nitrogen in amines has one pair of unshared electrons similar to ammonia, NH₃. As we learned in Chapter 12, NH₃ utilizes the unshared pair of electrons to form weakly basic solutions in water. In a similar manner, amines are characterized by their ability to act as bases.



The common names of amines are obtained by listing the alkyl groups (in alphabetical order) attached to the nitrogen and adding *-amine*.



Simple amines are prepared by the reaction of ammonia with alkyl halides (e.g., CH₃Cl). In the reaction shown below, the electron pair on the nitrogen forms a bond to the CH₃ group forming a methyl ammonium cation. The amine can then be prepared by the reaction with a strong base such as NaOH.

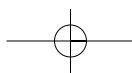
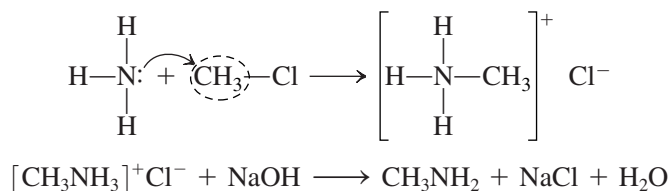
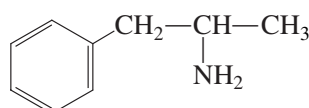




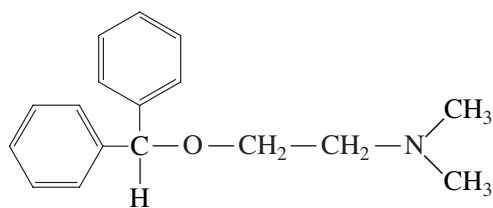
Figure 16-6 Amines
The active ingredient in an antihistamine is an organic amine.

Amines are used in the manufacture of dyes, drugs, disinfectants, and insecticides. They also occur naturally in biological systems and are important in many biological processes.

Amine groups are present in many synthetic and naturally occurring drugs. (See Figure 16-6.) They may be useful as antidepressants, antihistamines, antibiotics, antiobesity preparations, anti-nauseants, analgesics, antitussives, diuretics, and tranquilizers, among others. Frequently, a drug may have more than one use. Codeine, for example, is both an analgesic (pain reliever) and an antitussive agent (cough suppressant). Often, a drug may be obtained from plants or animals. One such class of compounds is the alkaloids, which are amines found in plants. Two common drugs are



amphetamine
(Benzedrine;
synthetic
appetite depressant,
stimulant)



diphenhydramine
(synthetic antihistamine)

16-11 Carboxylic Acids (R—C(=O)—O—H), Esters (R—C(=O)—O—R'), and Amides (R—C(=O)—NH_2)

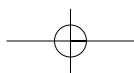
Looking Ahead! Another class of compounds that we will discuss in this chapter is known as the carboxylic acids. The acids and two classes that are derivatives of the acids (esters and amides) are our final topics in this introduction to organic chemistry.

Carboxylic Acids

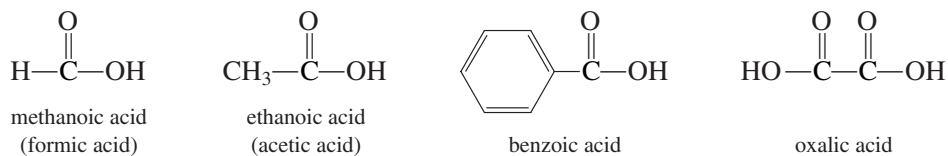
Acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$), the sour component of vinegar, is an example of a carboxylic acid. **Carboxylic acids** contain the functional group



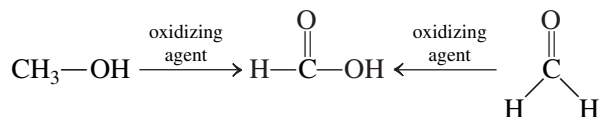
known as a **carboxyl group**. For example, the condensed structure of acetic acid is CH_3COOH . Carboxylic acids are named by dropping the *-e* from the



alkane name and substituting *-oic acid*. Examples of some common carboxylic acids are



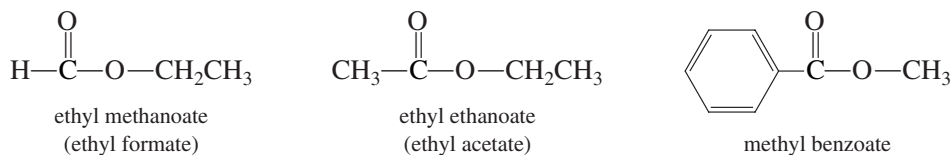
Carboxylic acids are made by the oxidation of either alcohols or aldehydes. Formic acid, which was first isolated by distilling red ants, can be made by oxidizing either methanol or formaldehyde.



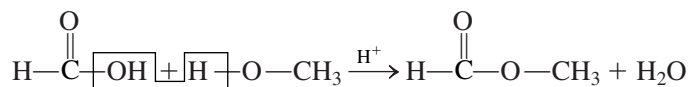
Acetic acid can be made from the oxidation of ethanol. In fact, this is what happens when wine becomes “sour.” Wine vinegar is produced by air oxidation of alcohol in ordinary wine.

Esters

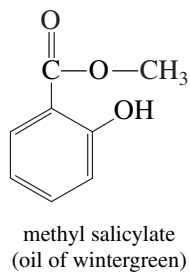
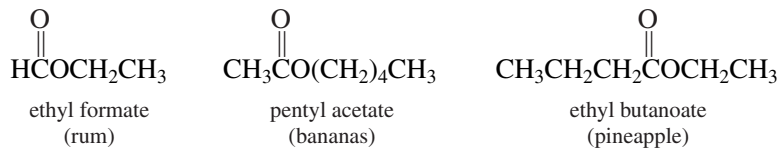
An **ester** is a derivative of a carboxylic acid, where a hydrocarbon group is substituted for the hydrogen in the carboxyl group. Esters are named by giving the name of the alkyl group attached to the oxygen, followed by the acid name with the *-ic* ending replaced by *-ate*. Some examples of esters are



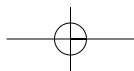
Esters are made by the reaction of alcohols with carboxylic acids. In the reaction, H_2O is split off from the molecules (OH from the acid and H from the alcohol) as the remnants of the two molecules are joined.



We all distinguish the various fruits by their unique odors. These pleasant odors are all caused by esters. Four of these esters are shown with their familiar odors.

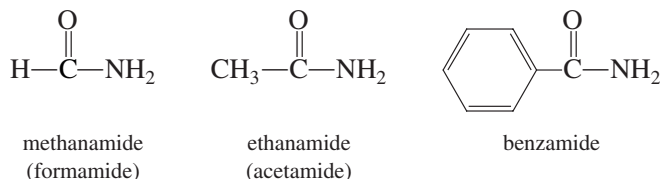


The sour taste of vinegar is due to acetic acid.

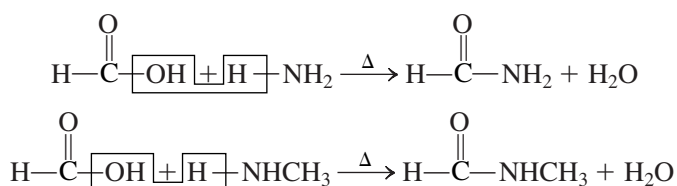


Amides

An **amide** is also a derivative of a carboxylic acid, where an amino group is substituted for the hydroxyl group of the acid. Amides are named by dropping the *-oic acid* portion of the carboxylic acid name and substituting *-amide*. Examples of amides are



Amides are made by a reaction similar to that in the preparation of esters. In this case, however, the carboxylic acid reacts with ammonia or an amine instead of alcohol. Again, water is split off from the two reacting molecules, and the two remnants unite.

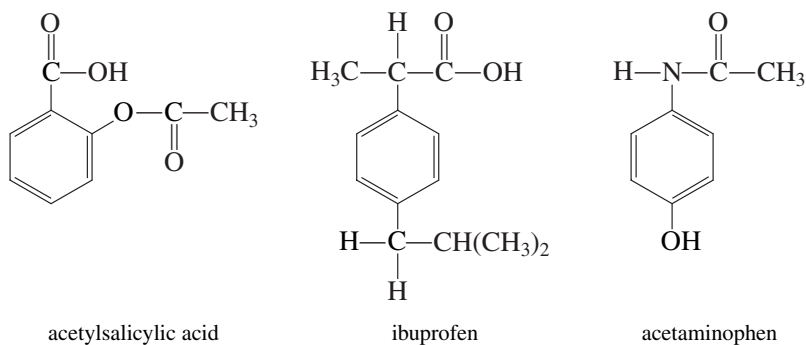


Uses in Painkillers and Plastics

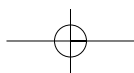
Carboxylic acids, esters, and amides are frequently present in compounds that have medicinal uses. Salicylic acid has both antipyretic (fever-reducing) and analgesic (pain-relieving) properties. It has the disadvantage, however, of causing severe irritation of the stomach lining. Acetylsalicylic acid (aspirin), which is both an acid and an ester, doesn't irritate the stomach as much. Aspirin is broken up in the small intestine to form salicylic acid, which is then absorbed. Some people are allergic to aspirin and must take aspirin substitutes. The common aspirin substitutes are acetaminophen and ibuprofen. Acetaminophen is the active ingredient in Tylenol and Datril. Ibuprofen is the active ingredient in Advil and Nuprin.



Many painkillers contain carboxylic acid, ester, or amide groups.



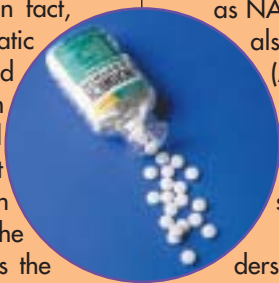
One of the biggest uses for carboxylic acids, esters, and amides is in the formation of condensation polymers. In **condensation polymers**, a small molecule (usually H_2O) is given off during formation of the polymers. These are different from the polymers discussed earlier that resulted from the joining of alkenes (called *addition* polymers). Two of the most widely known condensation polymers are Nylon 6,6 (see Figure 16-7)



Aspirin—An Old Drug with a New Life

Hippocrates was a physician who lived in the fifth century B.C. He is considered the father of medicine. In fact, brand-new physicians still recite the “Hippocratic Oath.” Hippocrates was said to have administered to his patients a powder that was extracted from the willow tree. The powder apparently relieved the ravages of fever and moderated pain. If that actually happened, Hippocrates would have been an early user of a compound much like aspirin. The bark of willow trees contains salicylic acid. It is the precursor to acetylsalicylic acid, which we know as aspirin.

In the 1800s, salicylic acid and its salt, sodium salicylate, were used as an antipyretic (a substance that reduces fever). It did have some bad side effects, though. It was very hard on the stomach and in many cases caused ulcers. In 1897, a scientist named Felix Hoffman worked for a company known as Bayer & Co. in Germany that manufactured dyes. Hoffman was searching for a drug that would relieve his father’s severe arthritis. He wanted a compound that was like salicylic acid but that was less harsh on the stomach. By combining salicylic acid with acetic anhydride, he produced acetylsalicylic acid, a derivative of salicylic acid. He had produced aspirin, which did indeed help his father. In 1899 Bayer began to manufacture aspirin, which, at first, was used mainly as an antipyretic. In 1903 it began to be used more as an analgesic (pain reliever) and to reduce inflammation.



Aspirin is now one of a large class of drugs known as NASIDs (nonsteroid antiinflammatory drugs) which also includes ibuprofen (Advil) and naproxen (Aleve). Although aspirin was a big improvement over salicylic acid, it still can cause stomach trouble, so other newer (and more expensive) drugs are now being used which have fewer side effects.

In the 1970s, scientists began to finally understand how aspirin works. It was found that it inhibits the release of hormone-like substances in the body called *prostaglandins*. These substances affect the elasticity of blood vessels and the function of blood platelets. Platelets are responsible for clotting, and aspirin inhibits this function. It has been found that small, daily doses of aspirin can prevent heart attacks. It is now taken regularly by millions just for this purpose. Even more recently, studies have shown that patients who have taken aspirin for at least two years have developed Alzheimer’s disease (a form of dementia) at half the rate of a control group. Small doses of aspirin have also been found to relieve high blood pressure in pregnant women.

Billions of dollars have been spent searching for new drugs to combat heart disease and Alzheimer’s disease. It is ironic that one of the most effective drugs to prevent these conditions has been in medicine cabinets for over a century.

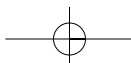
It’s more than a headache remedy.



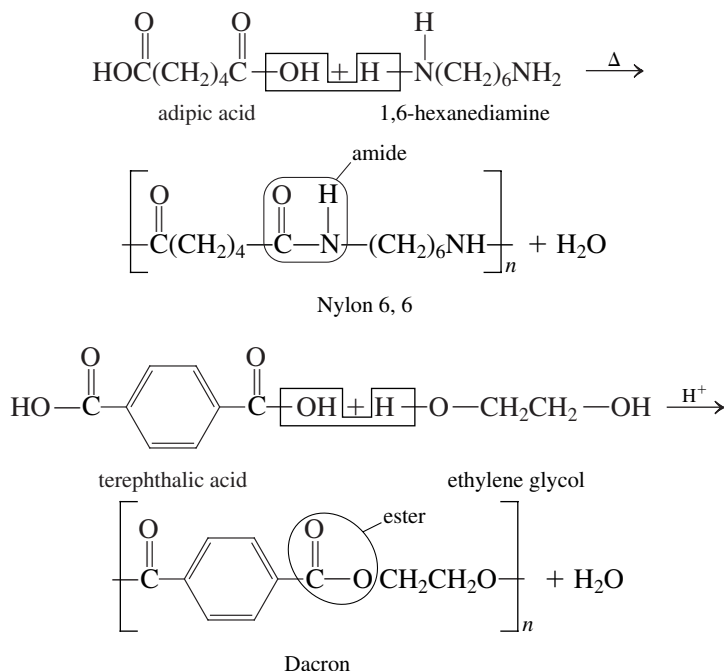
Dacron is used in these sails. It is strong, light, and does not “wet.”



Figure 16-7 Nylon
Nylon was first synthesized by DuPont chemists. It was one of the first synthetic fibers.



and Dacron. The first is a polyamide, made from a diacid and a diamine; the second is a polyester, made from a diacid and a dialcohol (diol). Both of these polymers are used to make fibers.



Looking Back! The presence of a double or triple bond or a hetero atom has a substantial effect on the nature of a hydrocarbon. These are called functional groups and determine the types of chemical reactions that the compound undergoes. For example, the presence of a carboxyl group makes the compound acidic in water, but the presence of an amine group makes the compound basic in water. Oxygen is the most common hetero atom. Its presence in a compound may produce an alcohol, ether, aldehyde, ketone, carboxylic acid, or ester depending on the environment of the oxygen atom or atoms in the molecule.

Learning Check B checking it out

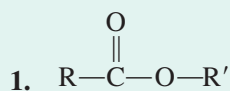
B-1. Fill in the blanks.

The functional group in an alcohol is known as a _____ group. In ethers, the oxygen is attached to two _____ groups. The functional group in aldehydes and ketones is a _____ group. In aldehydes, the functional group is attached to at least one _____ atom. The hetero atom in an amine is a _____ atom. The functional group of a carboxylic acid is a _____ group. In esters, a hydrocarbon group replaces a _____ in the acid, whereas in amides an amine group replaces the _____ group of the acid.

B-2. Identify the class of compound from the following functional groups.

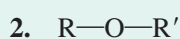
R and R' = CH₃

R = CH₃, R' = H



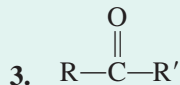
a. _____

b. _____



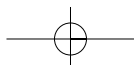
c. _____

d. _____



e. _____

f. _____



4. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ g. _____
5. $\text{R}-\text{NH}-\text{R}'$ h. _____

B-3. Give the common names of each compound in problem B-2.

Additional Examples: Exercises 16-38, 16-40, 16-42, and 16-44.

chapter **R** review

putting it together

Chemical compounds have traditionally been divided into two general groups—**organic** and **inorganic**. To introduce the more than 10 million registered organic compounds, we need to find common properties or molecular structures so as to classify them into more specific groups. The first classification is the **hydrocarbons**, which can be further subdivided according to the type of bonds in the molecules of the various compounds. Each of these groups forms a **homologous series** designated by a general formula. The four hydrocarbon groups are summarized in the following table.

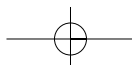
Name of Series	General Formula	Example	Name	Comments
alkane	$\text{C}_n\text{H}_{2n+2}$	C_3H_8	propane	Alkanes contain only single bonds and are saturated .
alkene	C_nH_{2n}	C_3H_6	propene propylene	Alkenes contain double bonds and are unsaturated .
alkyne	$\text{C}_n\text{H}_{2n-2}$	C_3H_4	propyne	Alkynes contain triple bonds and are unsaturated.
aromatic	—	C_6H_6	benzene	Aromatic compounds are cyclic, unsaturated hydrocarbons, but are less reactive than alkenes.

Isomers, which are more conveniently illustrated with **condensed formulas**, exist for all but the simplest members of these groups. The major sources of alkanes are natural gas and petroleum. Because of the difference in **volatility** of the alkane components of petroleum, they can be separated by distillation in a refinery. By processes of **cracking**, **re-forming**, and **alkylation**, these **petrochemicals** that are found in natural sources can be used to make many other useful hydrocarbons.

The nomenclature of hydrocarbons is somewhat complicated because of the use of both formal IUPAC names and popular common names. In the IUPAC method, **alkyl groups** are named as **substituents** on the longest hydrocarbon chain.

Hydrocarbons all have important uses: alkanes for fuel, alkenes to make **polymers**, and alkynes to make alkenes for various polymers. Aromatics and **derivatives** of aromatics find application as solvents, drugs, and flavors.

The focal point of chemical reactivity in an organic compound is the **functional group**. This may be a double or triple bond in a hydrocarbon or a **heteroatom** that is incorporated into the molecule. Functional groups include the **hydroxyl**, **carbonyl**, and **carboxyl groups**. Derivatives of the carboxyl group include esters and amides. If an ester or amide linkage is made on both sides of a molecule,



condensation polymers, which are known as polyesters and polyamides, respectively, are formed.

The bonding environment of the hetero atom in a functional group imposes certain common properties on compounds containing that group. Thus the functional group defines a class of compounds. Eight classes of organic compounds and their functional group, formula, example, and name are summarized in the following table.

Name of Class	Functional Group	General Formula ^a	Example	IUPAC Name (Common Name)
alcohols	$\begin{array}{c} \\ -\text{C}-\ddot{\text{O}}-\text{H} \\ \end{array}$	R—OH	CH ₃ CH ₂ OH	ethanol (ethyl alcohol)
ethers	$\begin{array}{c} \qquad \\ -\text{C}-\ddot{\text{O}}-\text{C}- \\ \qquad \end{array}$	R—O—R'	CH ₃ OCH ₂ CH ₃	(ethyl methyl ether)
aldehydes	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\text{H} \end{array}$	R—C(=O)—H	CH ₃ CH ₂ CHO	propanal (propionaldehyde)
ketones	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\text{C}-\text{C}- \\ \qquad \end{array}$	R—C(=O)—R'	CH ₃ COCH ₂ CH ₃	butanone (ethyl methyl ketone)
amines	$\begin{array}{c} \\ -\text{C}-\ddot{\text{N}}- \\ \end{array}$	R—NH ₂	CH ₃ CH ₂ NH ₂	(ethylamine)
carboxylic acids	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\ddot{\text{O}}-\text{H} \end{array}$	R—C(=O)—OH	CH ₃ CH ₂ CH ₂ COOH	butanoic acid (butyric acid)
esters	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\ddot{\text{O}}-\text{C}- \\ \qquad \end{array}$	R—C(=O)—OR'	CH ₃ COOCH ₃	methyl ethanoate (methyl acetate)
amides	$\begin{array}{c} \text{:O:} \\ \\ -\text{C}-\ddot{\text{N}}- \\ \end{array}$	R—C(=O)—NR ₂	CH ₃ CONH ₂	ethanamide (acetamide)

^aR and R' stand for hydrocarbon groups (e.g., alkyl). They may be different groups or the same group. R may also represent a hydrogen atom in aldehydes, carboxylic acids, esters, and amides.

Exercises

Lewis Structures and Isomers

16-1. Draw Lewis structures for each of the following compounds. (More than one structure may be possible.)

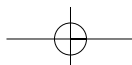
- (a) CH₃Br (c) C₄H₈ (e) C₂H₇N
(b) C₃H₄ (d) CH₅N (f) C₃H₈O

16-2. Draw Lewis structures for each of the following compounds. (More than one structure may be possible.)

- (a) C₅H₁₀ (b) C₂H₄O (c) C₄H₉Cl (d) C₃H₉N

16-3. Write all of the isomers for C₆H₁₄.

16-4. Write all of the isomers for C₆H₁₂.



16-5. Which of the following pairs of compounds are isomers of each other? Why or why not?

- (a) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{NH}_2$ and CH_3NHCH_3
 (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_3$
 (e) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ | \\ \text{OH} \end{array}$ and $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \\ | \\ \text{OH} \end{array}$

16-6. Which of the following pairs of compounds are isomers of each other? Why or why not?

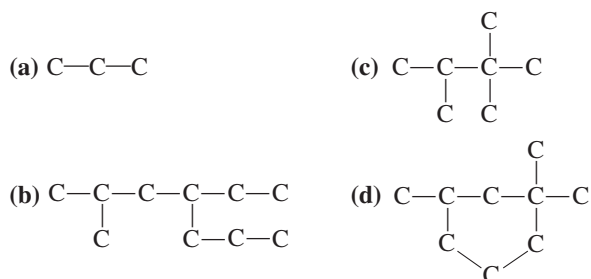
- (a) $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2$
 (b) $\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ | \\ \text{Cl} \end{array}$ and $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_3 \\ | \\ \text{Cl} \end{array}$
 (c) $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_3 \\ | \\ \text{NH}_2 \end{array}$ and $\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\ | \\ \text{NH}_2 \end{array}$
 (d) $(\text{CH}_3)_3\text{N}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

Alkanes

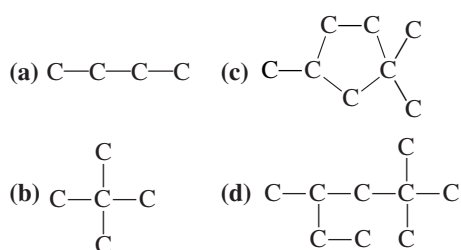
16-7. Which of the following are formulas of open-chain alkanes?

- (a) C_4H_{10} (c) C_8H_{14} (e) C_7H_{15} (g) $\text{C}_{18}\text{H}_{38}$
 (b) C_3H_7 (d) $\text{C}_{10}\text{H}_{22}$ (f) C_7H_{14} (h) C_9H_{15}

16-8. The following skeletal structures represent alkanes. Fill in the proper number of hydrogens on each carbon atom.



16-9. The following skeletal structures represent alkanes. Fill in the proper number of hydrogens on each carbon atom.



16-10. Which of the following are formulas of alkyl groups?

- (a) C_4H_8 (c) C_6H_{10} (e) C_6H_{13}
 (b) C_4H_9 (d) C_6H_6 (f) C_6H_{11}

16-11. Write the formulas of any compounds listed in exercise 16-7 that could be a cyclic alkane.

16-12. Write the formulas of any alkyl groups listed in exercise 16-7.

16-13. Which of the following could be the formula of a cyclic alkane?

- (a) C_8H_{18} (b) C_5H_8 (c) C_6H_6 (d) C_5H_{10}

16-14. Write the condensed structure for each of the following compounds.

- (a) 3-methylpentane (d) 4-ethyl-2-methylheptane
 (b) *n*-hexane (e) 3-isopropylhexane
 (c) 2,4,5-trimethyloctane (f) 2,2-dimethyl-4-*t*-butylnonane

16-15. Write the condensed structure for each of the following compounds.

- (a) cyclopentane (d) 3-ethyl-3-methylhexane
 (b) *n*-pentane (e) 3,5-dimethyl-4-isopropyloctane
 (c) 3,3-dimethylpentane

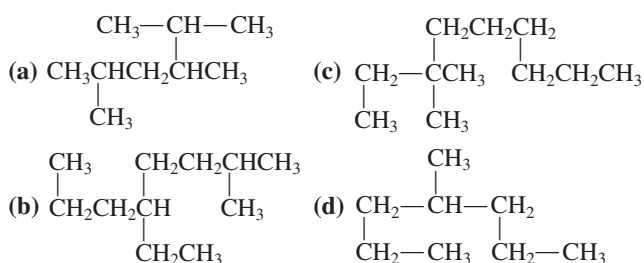
16-16. Write the structure and the correct IUPAC name for

- (a) 2-ethyl-3-methylpentane
 (b) 5-*n*-propyl-5-isopropylhexane

16-17. Write the structure and the correct IUPAC name for

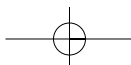
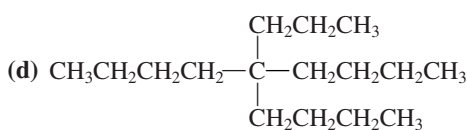
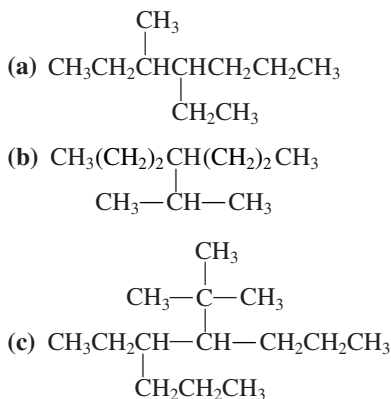
- (a) 2,3-diethylpentane
 (b) 4-methyl-5-isopropylhexane

16-18. How many carbons are in the longest chain of each of the following compounds? Write the name of the longest alkane chain for each.

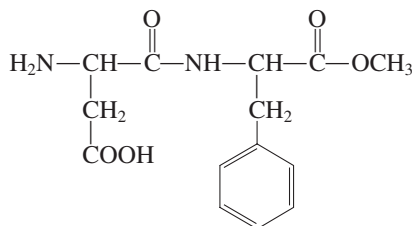


16-19. Name the substituents attached to the longest chains in the previous exercise and give the IUPAC names for the compounds.

16-20. Give the longest chain, the substituents, and the proper IUPAC name for the following compounds.



16-43. Aspartame is an effective sweetener that is used as a low-calorie substitute for sugar. Identify the functional groups present in an aspartame molecule.



16-44. Write condensed structures for the following compounds.

- (a) *n*-butyl alcohol (e) 3-pentanone
 (b) di-*n*-propyl ether (f) propanoic acid
 (c) trimethylamine (g) methyl acetate
 (d) propanal (h) propanamide

***16-45.** Name the following compounds.

- (a) $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_2\text{CH}_3$ (d) $(\text{CH}_3)_3\text{C}-\text{OH}$
 (b) $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{OH}$ (e) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{H}$
 (c) $\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{NH}_2$

***16-46.** Name the following compounds.

- (a) $\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{OC}_2\text{H}_5$ (e) $\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{H}$
 (b) $(\text{C}_2\text{H}_5)_2\text{NH}$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 (d) $\text{CH}_3\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2\text{CH}_2\text{CH}_3$

General Problems

16-47. Identify the following as an alkane, alkene, or alkyne. Assume that the compounds are not cyclic.

- (a) C_8H_{16} (c) C_4H_8 (e) CH_4 (g) $\text{C}_{18}\text{H}_{38}$
 (b) C_5H_{12} (d) $\text{C}_{20}\text{H}_{38}$ (f) $\text{C}_{10}\text{H}_{20}$

16-48. The following are possible names for one specific alkane. Write the structure and choose the correct name.

- (a) 2-ethylpentane
 (b) 1-ethyl-1-methylbutane
 (c) 2-*n*-propylbutane
 (d) 4-methylhexane
 (e) 3-methylhexane

16-49. There are three isomers for dichlorobenzene. In these molecules, two chlorines are substituted for two hydrogens on the benzene rings. Write the Lewis structures for the three isomers.

16-50. Write the condensed structures of a compound with seven carbon atoms in each of the four hydrocarbon classes.

16-51. Write the condensed structure of a compound with five carbon atoms containing each of the eight hetero atom functional groups discussed.

16-52. Complete the following equations.

- (a) $\text{C}_3\text{H}_8 + \text{excess O}_2 \longrightarrow$
 (b) $\text{CH}_2=\text{CHCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+}$
 (c) $\text{C}_2\text{H}_5\text{Cl} + 2\text{NH}_3 \longrightarrow$
 (d) $\text{NH}(\text{CH}_3)_2(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow$
 (e) $\text{CH}_3\text{CH}_2\text{COOH} + \text{NH}(\text{CH}_3)_2 \longrightarrow$
 (f) $\text{HC}\equiv\text{CH} + \text{HBr} \longrightarrow$
 (g) $\text{CH}_3\text{CH}_2\text{COOH} + \text{H}_2\text{O} \longrightarrow$

16-53. Complete the following equations.

- (a) $\text{C}_3\text{H}_7\text{OH} + \text{excess O}_2 \longrightarrow$
 (b) $\text{CH}_2=\text{CHCH}_3 + \text{Br}_2 \longrightarrow$
 (c) $\text{NH}(\text{CH}_3)_2 + \text{H}_2\text{O} \xrightarrow{\text{catalyst}}$
 (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + [\text{O}] \xrightarrow{\text{catalyst}}$
 (e) $\text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{OH} \longrightarrow$
 (f) $\text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) + \text{NaOH} \longrightarrow$

16-54. Give a general method for making each of the following classes of compounds.

- (a) alcohols (e) amides
 (b) ketones (f) aldehydes
 (c) carboxylic acids (g) amines
 (d) esters

16-55. Tell how the following can be obtained from natural sources.

- (a) ethanol (d) methane
 (b) acetic acid (e) gasoline
 (c) methanol

16-56. Give one possible use for each of the following compounds or class of compounds.

- (a) formaldehyde (e) amines
 (b) acetic acid (f) esters
 (c) ethylene glycol (g) alkenes
 (d) acetylsalicylic acid (h) alkanes

***16-57.** There are three isomers with the formula $\text{C}_3\text{H}_8\text{O}$ and three isomers with the formula $\text{C}_3\text{H}_6\text{O}_2$. Show the Lewis structures of these six compounds and the common names of each. All contain one of the functional groups discussed.

***16-58.** There are two isomers with the formula $\text{C}_3\text{H}_6\text{O}$ and four isomers with the formula $\text{C}_3\text{H}_9\text{N}$. Show the Lewis structures of these six compounds and the common names of each. All contain one of the functional groups discussed except hydroxyl.

***16-59.** Glycine has the formula $\text{C}_2\text{H}_5\text{NO}_2$. It is a member of a class of compounds called amino acids that combine in long chains to form proteins. Glycine contains both an amine and a carboxylic acid group. Write the structure for glycine. Write an equation illustrating the reaction of glycine as an acid in water and an equation illustrating its reaction as a base in water. Illustrate how two glycine molecules can combine to form an amide linkage (also called a peptide linkage).

