Organic Chemistry

22

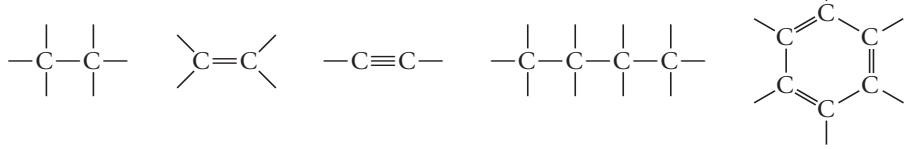
The Philadelphia Museum of Art / Art Resource, NY

The wine in the goblet can be produced by the fermentation of glucose (present in all the fruits shown in the painting) to ethyl alcohol.

What is life? It is the flash of a firefly in the night.
It is the breath of a buffalo in the wintertime.
It is the little shadow which runs across grass
And loses itself in the sunset.

—DYING WORDS OF CROWFOOT (1890)

Organic chemistry deals with the compounds of carbon, of which there are literally millions. More than 90% of all known compounds contain carbon atoms. There is a simple explanation for this remarkable fact. Carbon atoms bond to one another to a far greater extent than do atoms of any other element. Carbon atoms may link together to form chains or rings.



The bonds may be single (one electron pair), double (two electron pairs), or triple (three electron pairs).

There are a wide variety of different organic compounds that have quite different structures and properties. However, all these substances have certain features in common:

1. ***Organic compounds are ordinarily molecular rather than ionic.*** Most of the compounds we discuss consist of small, discrete molecules. Many of them are gases or liquids at room temperature.
2. ***Each carbon atom forms a total of four covalent bonds.*** This is illustrated by the structures above. A particular carbon atom may form four single bonds, two single bonds and a double bond, two double bonds, or one single bond and a triple bond. One way or another, though, the bonds add up to four.
3. ***Carbon atoms may be bonded to each other or to other nonmetal atoms, most often hydrogen, a halogen, oxygen, or nitrogen.*** In most organic compounds:
   - a hydrogen or halogen atom (F, Cl, Br, I) forms one covalent bond, —H, —X
   - an oxygen atom forms two covalent bonds, —O— or =O
   - a nitrogen atom forms three covalent bonds, —N—, =N—, or ≡N

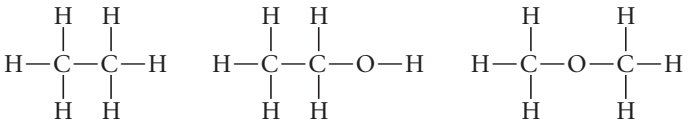
Carbon always follows the octet rule in stable compounds.

Chapter Outline

In this chapter, we consider

- the simplest type of organic compound, called a **hydrocarbon,** which contains only two kinds of atoms, hydrogen and carbon. Hydrocarbons can be classified as alkanes (Section 22-1), alkenes and alkynes (Section 22-2), and aromatics (Section 22-3).
- organic compounds containing oxygen or nitrogen atoms in addition to carbon and hydrogen (Section 22-4).
- the phenomenon of isomerism, which is very common among organic compounds. This topic is introduced in Section 22-1 but discussed more generally in Section 22-5.
- different types of organic reactions (Section 22-6).

Throughout this chapter, we will represent molecules by *structural formulas*, which show all the bonds present. Thus we have



To save space we often write condensed structural formulas such as

CH_3CH_3 or C_2H_6 $\quad$ CH_3CH_2OH or C_2H_5OH $\quad$ $CH_3—O—CH_3$ or $(CH_3)_2O$

22-1 Saturated Hydrocarbons: Alkanes

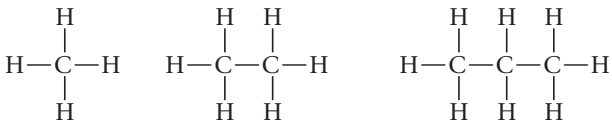
One large and structurally simple class of hydrocarbons includes those substances in which all the carbon-carbon bonds are single bonds. These are called **saturated hydrocarbons**, or **alkanes.** In the alkanes the carbon atoms are bonded to each other in chains, which may be long or short, straight or branched.

The ratio of hydrogen to carbon atoms is a maximum in alkanes, hence the term "saturated" hydrocarbon. The general formula of an alkane containing n carbon atoms is

The outer surfaces of these molecules contain mainly H atoms.

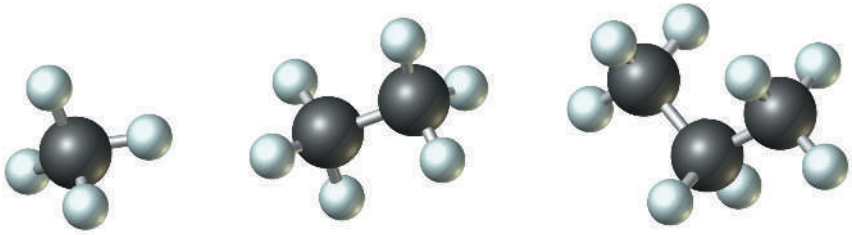
$$C_nH_{2n+2}$$

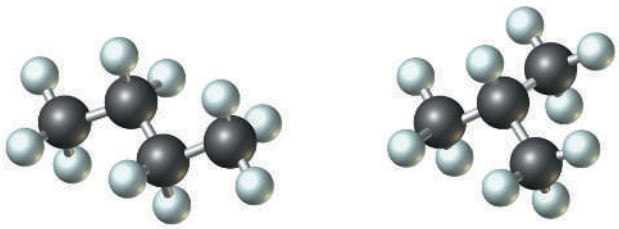
The simplest alkanes are those for which $n = 1$ (CH_4), $n = 2$ (C_2H_6), or $n = 3$ (C_3H_8):



Around the carbon atoms in these molecules, and indeed in any saturated hydrocarbon, there are four single bonds involving sp^3 hybrid orbitals. As would be expected from the VSEPR model, these bonds are directed toward the corners of a regular tetrahedron. The bond angles are approximately 109.5°, the tetrahedral angle. This means that in propane (C_3H_8) and in the higher alkanes, the carbon atoms are arranged in a "zigzag" pattern (Figure 22.1).

Figure 22.1 The three simplest alkanes. The bond angles in methane, ethane, and propane are all close to 109.5°, the tetrahedral angle.



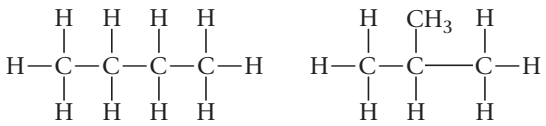


$CH_3CH_2CH_2CH_3$
butane

CH_3CHCH_3
|
CH_3
2-methylpropane

Figure 22.2 Butane and 2-methylpropane, the isomers of C_4H_{10}.

Two different alkanes are known with the molecular formula C_4H_{10}. In one of these, called butane, the four carbon atoms are linked in a "straight (unbranched) chain." In the other, called 2-methylpropane, there is a "branched chain." The longest chain in the molecule contains three carbon atoms; there is a CH_3 branch from the central carbon atom. The geometries of these molecules are shown in Figure 22.2. The structures are



butane

2-methylpropane

Compounds having the same molecular formula but different molecular structures are called **structural isomers.** Butane and 2-methylpropane are referred to as structural isomers of C_4H_{10}. They are two distinct compounds with their own characteristic physical and chemical properties.

In structural isomers, the atoms are bonded in different patterns; the skeletons are different.

EXAMPLE 22.1

Draw structures for the isomers of C_5H_{12}.

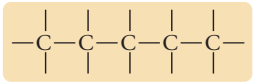
STRATEGY

1. Start by writing all five-carbon atoms in a straight chain. Call this structure isomer (I).
2. Write a four-carbon chain structure bonding the fifth carbon atom to one of the C atoms in the straight chain.

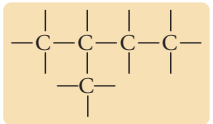
   Note that bonding the fifth C atom to either end of the straight chain gives you isomer (I). You have to attach the C atom next to the terminal atom (on either end).
3. Write a three-carbon chain. Do not attach the remaining two carbon atoms as a chain to either end of the three-carbon chain. You will get Isomer (I). Attaching one carbon atom to each end of the three-carbon chain also gives you isomer (I).

SOLUTION

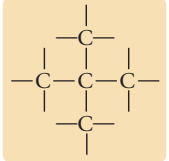
Isomer (I) — isomer (I) — five-C chain:



Isomer (II) — isomer (II) — four-C chain:



Isomer (III) — isomer (III) — three-C chain:



Remember, these molecules are three-dimensional.

If you want a really tedious job, try drawing the 366,319 structural isomers of $C_{20}H_{42}$.

Structural isomers have different properties. For example, the three isomers of C_5H_{12} in Example 22.1 boil at different temperatures.

Structure	Normal Boiling Point
I	36°C
II	28°C
III	10°C

In general, long "skinny" isomers like I tend to have higher boiling points than highly branched isomers like III. Dispersion forces become weaker as chain branching increases. This principle is used in the seasonal blending of gasoline. A greater percentage of more volatile, highly branched alkanes is included in winter, making combustion occur more readily at lower temperatures.

Nomenclature

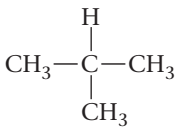
As organic chemistry developed, it became apparent that some systematic way of naming compounds was needed. About 80 years ago, the International Union of Pure and Applied Chemistry (IUPAC) devised a system that is usable for all organic compounds. To illustrate this system, we will show how it works with alkanes.

For straight-chain alkanes such as

$CH_3—CH_2—CH_3$ (propane) $\qquad$ $CH_3—CH_2—CH_2—CH_3$ (butane)

the IUPAC name consists of a single word. These names, for up to eight carbon atoms, are listed in Table 22.1.

With alkanes containing a branched chain, such as

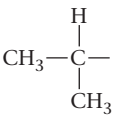


2-methylpropane

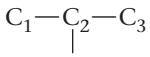
the name is more complex. A branched-chain alkane such as 2-methylpropane can be considered to be derived from a straight-chain alkane by replacing one or more hydrogen atoms by alkyl groups. The name consists of two parts:

- a *suffix* that identifies the parent straight-chain alkane. To find the suffix, count the number of carbon atoms in the longest continuous chain. For a three-carbon chain, the suffix is *propane;* for a four-carbon chain it is *butane,* and so on.
- a *prefix* that identifies the branching alkyl group (Table 22.1) and indicates by a number the carbon atom where branching occurs. In 2-methylpropane,

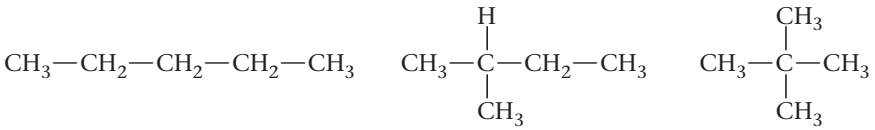
Table 22.1 Nomenclature of Alkanes

Straight-Chain Alkanes		Alkyl Groups	
Methane	CH_4	Methyl	$CH_3—$
Ethane	CH_3CH_3	Ethyl	$CH_3—CH_2—$
Propane	$CH_3CH_2CH_3$	Propyl	$CH_3—CH_2—CH_2—$
Butane	$CH_3(CH_2)_2CH_3$	Isopropyl	
Pentane	$CH_3(CH_2)_3CH_3$		
Hexane	$CH_3(CH_2)_4CH_3$		
Heptane	$CH_3(CH_2)_5CH_3$		
Octane	$CH_3(CH_2)_6CH_3$	Butyl	$CH_3—CH_2—CH_2—CH_2—$

referred to above, the methyl group is located at the second carbon from the end of the chain:



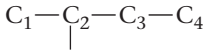
Following this system, the IUPAC names of the isomers of pentane are



pentane | 2-methylbutane | 2,2-dimethylpropane

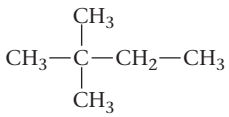
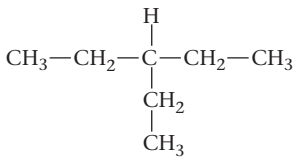
Notice that

- if the same alkyl group is at two branches, the prefix *di-* is used (2,2-dimethylpropane). If there were three methyl branches, we would write trimethyl, and so on.
- the number in the name is made as small as possible. Thus, we write 2-methylbutane, numbering the chain from the left



rather than from the right.

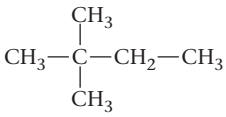
EXAMPLE 22.2

Assign IUPAC names to  and 

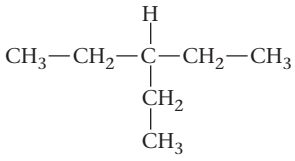
STRATEGY

1. Find the longest carbon chain. That is the parent chain, which is written at the end (see Table 22.1).
2. Count the alkyl groups attached to the straight chain and identify them by referring to the right column of Table 22.1. Write the names of these alkyl groups before the name of the straight chain.
3. Number the carbon atoms from left to right to indicate the carbon atoms to which the alkyl groups are bonded.

SOLUTION



1. Longest chain	four carbon atoms = butane
2. Alkyl groups	two one-carbon groups = methyl = dimethyl
3. Number of C atom bonded	both groups at the C_2 position
4. Name	2,2-dimethylbutane



1. Longest chain	five carbon atoms = pentane

continued

2. Alkyl groups	one two-carbon group = ethyl
3. Number of C atom bonded	C_3
4. Name	3-ethylpentane

Sources and Uses of Alkanes

Photo by John W. Bova

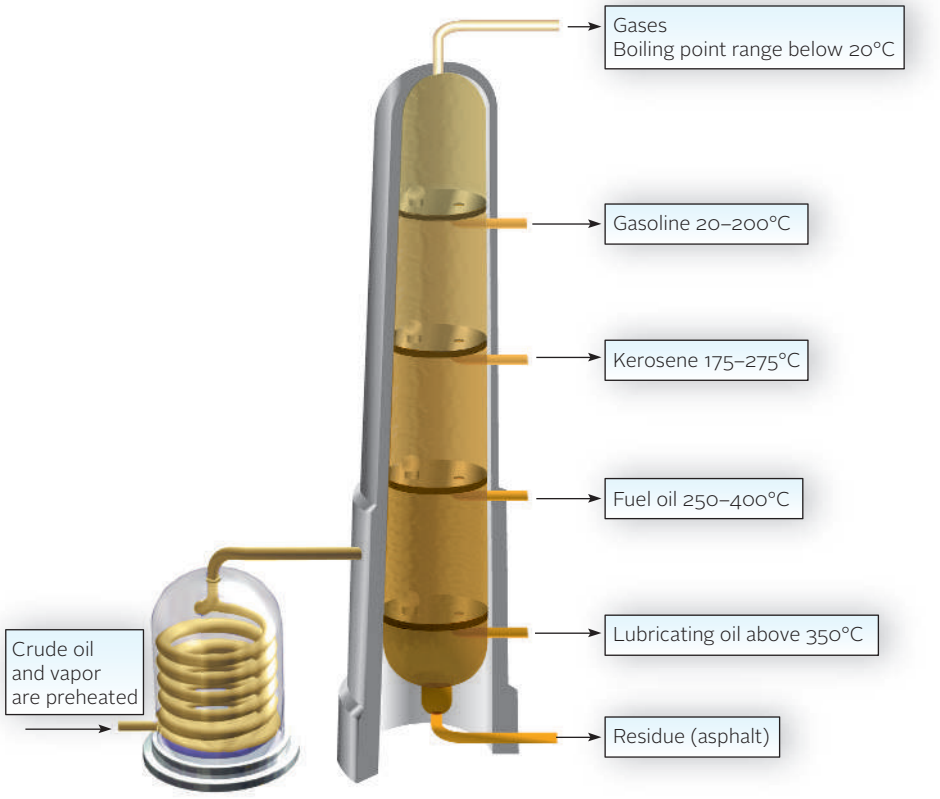
Figure 22.3 This cylinder contains propane gas and is used for home heating.

Natural gas, transmitted around the United States and Canada by pipeline, consists largely of methane (80%–90%), with smaller amounts of C_2H_6, C_3H_8, and C_4H_{10}. Cylinders of "bottled gas," used with campstoves, barbecue grills, and the like, contain liquid propane (C_3H_8) and butane (C_4H_{10}). Homes that do not have access to a gas line sometimes use large propane tanks for heating (Figure 22.3). The pressure remains constant as long as any liquid is present, then drops abruptly to zero, indicating that it's time for a refill.

The higher alkanes are most often obtained from petroleum, a dark brown, viscous liquid dispersed through porous rock deposits. Distillation of petroleum gives a series of fractions of different boiling points (Figure 22.4). The most important of these is gasoline; distillation of a liter of petroleum gives about 250 mL of "straight-run" (with no chemical additives) gasoline. It is possible to double the yield of gasoline by converting higher- or lower-boiling fractions to hydrocarbons in the gasoline range (C_5 to C_{12}).

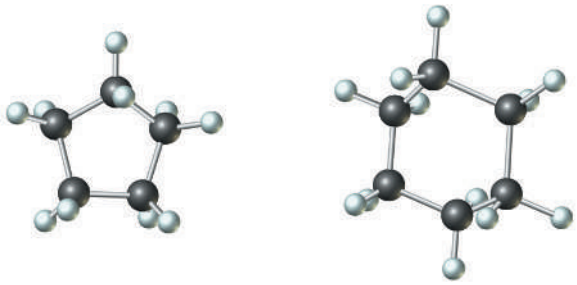
Gasoline-air mixtures tend to ignite prematurely, or "knock," rather than burn smoothly. The *octane number* of a gasoline is a measure of its resistance to knock. It is determined by comparing the knocking characteristics of a gasoline

Courtesy of Ashland Oil Company



a b

Figure 22.4 Petroleum distillation. (a) A distillation tower at a petroleum refinery. (b) A diagram showing the boiling points of the petroleum fractions separated by distillation.

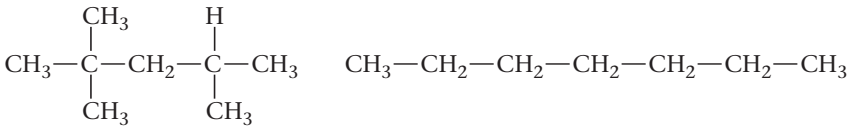


C_5H_{10}
cyclopentane

C_6H_{12}
cyclohexane

Figure 22.5 Cycloalkanes. Cyclopentane and cyclohexane, the two most common cycloalkanes.

sample with those of isooctane (the common name of one of the isomers of octane) and heptane:



isooctane

heptane

Isooctane, which is highly branched, burns smoothly with little knocking and is assigned an octane number of 100. Heptane, being unbranched, knocks badly. It is given an octane number of zero. Gasoline with the same knocking properties as a mixture of 90% isooctane and 10% heptane is rated as "90 octane."

To obtain premium gasoline of octane number above 80, it is necessary to use additives of one type or another. Until the mid-1970s, the principal antiknock agent was tetraethyllead, $(C_2H_5)_4Pb$. Its use was phased out because it poisons catalytic converters and contaminates the environment with lead compounds. To replace tetraethyllead, oxygen-containing organic compounds such as ethanol, C_2H_5OH, are added to gasoline to promote smooth, complete combustion.

Petroleum contains hydrocarbons other than the open-chain alkanes considered to this point. These include **cycloalkanes** in which 3 to 30 CH_2 groups are bonded into closed rings. The structures of the two most common hydrocarbons of this type are shown in Figure 22.5. Cyclopentane and cyclohexane, where the bond angles are close to the ideal tetrahedral angle of 109.5°, are stable liquids with boiling points of 49°C and 81°C, respectively.

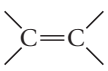
Cycloalkanes, like alkanes, are saturated hydrocarbons containing only single bonds. Notice, though, that as a result of ring formation, each cycloalkane molecule contains two fewer hydrogen atoms than the corresponding alkane.

Number of C Atoms	3	4	5	6	*n*
Formula of alkane	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_nH_{2n+2}
Formula of cycloalkane	C_3H_6	C_4H_8	C_5H_{10}	C_6H_{12}	C_nH_{2n}

22-2 Unsaturated Hydrocarbons: Alkenes and Alkynes

In an *unsaturated hydrocarbon,* at least one of the carbon-carbon bonds in the molecule is a multiple bond. As a result, there are fewer hydrogen atoms in an unsaturated hydrocarbon than in a saturated one with the same number of carbons. We will consider two types of unsaturated hydrocarbons:

- **alkenes,** in which there is one carbon-carbon double bond in the molecule:



Replacing a single bond with a double bond eliminates two hydrogen atoms. Hence the general formula of an alkene is

$$C_nH_{2n}$$

as compared with C_nH_{2n+2} for an alkane.

- **alkynes,** in which there is one carbon-carbon triple bond in the molecule:

$$—C\equiv C—$$

Again, two hydrogen atoms are "lost" when a double bond is converted to a triple bond. Hence the general formula of an alkyne is

$$C_nH_{2n-2}$$

EXAMPLE 22.3

What is the molecular formula of the alkane, alkene, and alkyne containing six carbon atoms, and of the alkane containing ten hydrogen atoms?

STRATEGY

Apply the formulas:

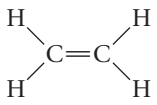
C_nH_{2n+2} for alkanes
C_nH_{2n} for alkenes
C_nH_{2n-2} for alkynes

SOLUTION

Six C atoms	alkane: $n = 6$; H atoms $= 2n + 2 = 2(6) + 2 = 14 \longrightarrow C_6H_{14}$ alkene: $n = 6$; H atoms $= 2n = 2(6) = 12 \longrightarrow C_6H_{12}$ alkyne: $n = 6$; H atoms $= 2n - 2 = 2(6) - 2 = 10 \longrightarrow C_6H_{10}$
Alkane with ten H atoms	alkane with 10 H atoms: $2n + 2 = 10$; $n = 4 \longrightarrow C_4H_{10}$

Alkenes

The simplest alkene is ethene, C_2H_4 (common name, ethylene). Its structural formula is



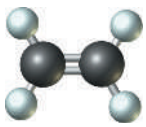
ethene

You may recall that we discussed the bonding in ethene in Chapter 7. The double bond in ethene and other alkenes consists of a sigma bond and a pi bond. The ethene molecule is planar. There is no rotation about the double bond, since that would require "breaking" the pi bond. The bond angle in ethene is 120°, corresponding to sp^2 hybridization about each carbon atom. The geometries of ethene and the next member of the alkene series, C_3H_6, are shown in Figure 22.6.

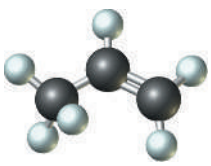
Ethene is produced in larger amounts than any other organic chemical, about 1.7×10^7 metric tons annually in the United States. It is made by heating ethane to about 700°C in the presence of a catalyst.

$$C_2H_6(g) \longrightarrow C_2H_4(g) + H_2(g)$$

Ethene is used to make a host of organic compounds; it is also the starting material for the preparation of polyethylene (Chapter 23). Since it is a plant hormone, ethene finds application in agriculture. It is used to ripen fruit that has been picked green to avoid spoilage in shipping. Exposure to ethene at very low concentrations produces the colors we associate with ripe bananas and oranges.



$H_2C=CH_2$
ethene

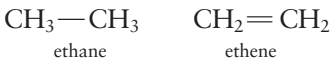


$CH_3CH=CH_2$
propene

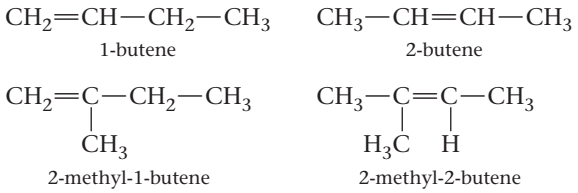
Figure 22.6 The two simplest alkenes. Ethylene is planar, as is the $—CH=CH_2$ region of propene.

The names of alkenes are derived from those of the corresponding alkanes with the same number of carbon atoms per molecule. There are two modifications:

- the ending *-ane* is replaced by *-ene*.



- where necessary, a number is used to designate the double-bonded carbon; the number is made as small as possible.

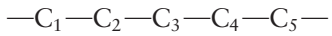


EXAMPLE 22.4

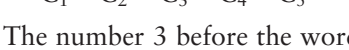
Give the structural formula for the alkene with the IUPAC name 3-ethyl-2-pentene.

STRATEGY AND SOLUTION

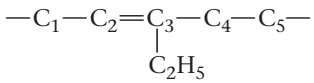
1. Start with the parent hydrocarbon. Pent means 5, so draw a five-carbon chain.



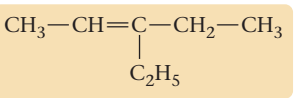
2. The suffix *-ene* means that there is a double bond, and the number 2 before the hydrocarbon means that the double bond is inserted at C_2 position.



3. The number 3 before the word *ethyl* means that an ethyl group is bonded to C_3.



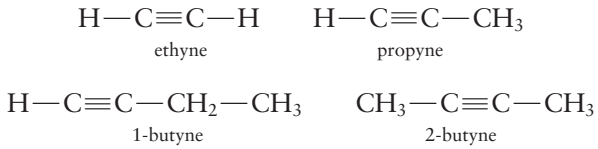
4. Add the missing hydrogen atoms to get the final answer.



(C_7H_{14})

Alkynes

The IUPAC names of alkynes are derived from those of the corresponding alkenes by replacing the suffix *-ene* with *-yne*. Thus we have



The most important alkyne by far is the first member of the series, commonly called acetylene. Recall from Chapter 7 that the C_2H_2 molecule is linear, with 180° bond angles. The triple bond consists of a sigma bond and two pi bonds; each carbon atom is sp-hybridized. The geometries of acetylene and the next member of the series, C_3H_4, are shown in Figure 22.7.

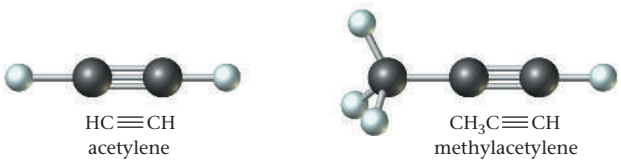


Figure 22.7 The two simplest alkynes. Both molecules contain four atoms in a straight line.

Figure 22.8 Welding with an oxyacetylene torch.

Thermodynamically, acetylene is unstable with respect to decomposition to the elements:

$$C_2H_2(g) \longrightarrow 2C(s) + H_2(g) \qquad \Delta G^\circ = -209.2 \text{ kJ at } 25^\circ C$$

At high pressures, this reaction can occur explosively. For that reason, cylinders of acetylene do not contain the pure gas. Instead the cylinder is packed with an inert, porous material that holds a solution of acetylene gas in acetone.

You are probably most familiar with acetylene as a gaseous fuel used in welding and cutting metals (Figure 22.8). When mixed with pure oxygen in a torch, acetylene burns at temperatures above 2000°C. The heat comes from the reaction

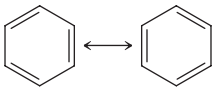
$$C_2H_2(g) + \tfrac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l) \qquad \Delta H = -1300 \text{ kJ}$$

The reaction gives off a brilliant white light, which served as a source of illumination in the headlights of early automobiles.

22-3 Aromatic Hydrocarbons and Their Derivatives

Aromatic hydrocarbons, sometimes referred to as *arenes,* can be considered as derivatives of benzene, C_6H_6. Benzene is a transparent, volatile liquid (bp = 80°C) that was discovered by Michael Faraday in 1825. Its formula, C_6H_6, suggests a high degree of unsaturation, yet its properties are quite different from those of alkenes or alkynes.

As pointed out in Chapter 7, the atomic orbital (valence bond) model regards benzene as a resonance hybrid of the two structures



In these "line-angle" formulas it is understood that there is a carbon atom at each vertex of the hexagon; hydrogen atoms are not shown. This model is consistent with many of the properties of benzene. The molecule is a planar hexagon with bond angles of 120°. The hybridization of each carbon is sp^2. However, this structure is misleading in one respect. Chemically, benzene does not behave as if double bonds were present.

A more satisfactory model of the electron distribution in benzene, based on molecular orbital theory (Appendix 4), assumes that

- each carbon atom forms three sigma bonds, one to a hydrogen atom and two to adjacent carbon atoms.
- the three electron pairs remaining are spread symmetrically over the entire molecule to form "delocalized" pi bonds.

There are three pi bonds in the benzene molecule.

This model is often represented by the structure

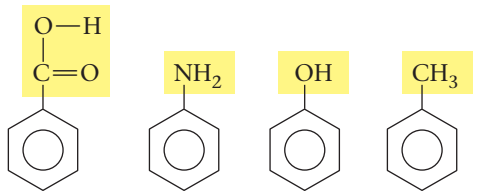
where it is understood that

- a carbon atom is at each corner of the hexagon.
- an H atom is bonded to each carbon atom.
- the circle in the center of the molecule represents the six delocalized electrons.

At one time, benzene was widely used as a solvent, both commercially and in research and teaching laboratories. That use has largely disappeared because of its toxicity. Chronic exposure to benzene vapor leads to various blood disorders and, in extreme cases, aplastic anemia and leukemia. It appears that the culprits are oxidation products of the aromatic ring, formed in an attempt to solubilize benzene and thus eliminate it from the body.

Derivatives of Benzene

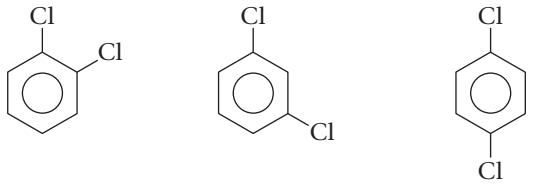
Among the more common monosubstituted benzenes are the following:



benzoic acid | aniline | phenol | toluene

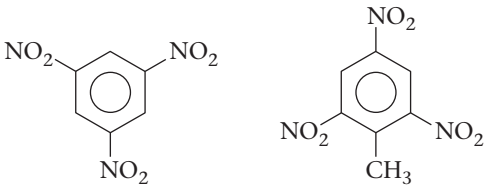
Phenol was the first commercial antiseptic; its introduction into hospitals in the 1870s led to a dramatic decrease in deaths from postoperative infections. Its use for this purpose has long since been abandoned because phenol burns exposed tissue, but many modern antiseptics are phenol derivatives. Toluene has largely replaced benzene as a solvent because it is much less toxic. Oxidation of toluene in the body gives benzoic acid, which is readily eliminated and has none of the toxic properties of the oxidation products of benzene. Indeed, benzoic acid or its sodium salt (Na^+, $C_6H_5COO^-$ ions) is widely used as a preservative in foods and beverages, including fruit juices and soft drinks.

When there are two groups attached to the benzene ring, three isomers are possible. These are designated by the prefixes *ortho-*, *meta-*, and *para-*, often abbreviated as *o-*, *m-*, and *p-*.



o-dichlorobenzene | *m*-dichlorobenzene | *p*-dichlorobenzene

Numbers can also be used; these three compounds may be referred to as 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene, respectively. When three or more substituents are present, numbers become mandatory.

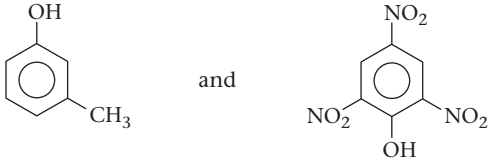


1,3,5-trinitrobenzene | 2,4,6-trinitrotoluene (TNT)

In the structure at the right, it is understood that the CH_3 group of toluene is at position 1. Notice that the numbers used are as small as possible.

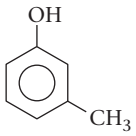
EXAMPLE 22.5

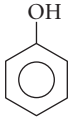
Name the following compounds as derivatives of phenol.



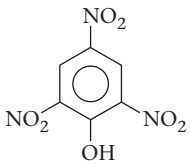
continued

SOLUTION



Parent compound  is called phenol.

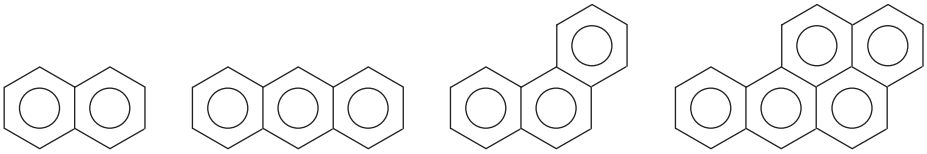
CH_3 (methyl) is in the *meta* position.
name: *meta*-methylphenol; common name: *meta*-cresol



The parent compound is phenol.
Number the carbon atom to which the OH group is bonded C_1.
The NO_2 (nitro) groups are in the C_2, C_4, and C_6 positions whether you count in a clockwise or counterclockwise manner.
name: 2,4,6-trinitrophenol; common name: picric acid

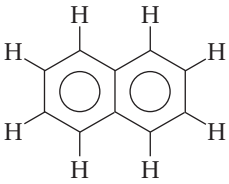
Condensed Ring Structures

In another type of aromatic hydrocarbon, two or more benzene rings are fused together. Naphthalene is the simplest compound of this type. Fusion of three benzene rings gives two different isomers, anthracene and phenanthrene.



naphthalene $C_{10}H_8$ | anthracene $C_{14}H_{10}$ | phenanthrene $C_{14}H_{10}$ | benzo[a]pyrene $C_{20}H_{12}$

It is important to realize that in these structures no hydrogen atoms are bonded to the carbons at the juncture of two rings. The eight hydrogen atoms in naphthalene are located as shown below.



Certain compounds of this type are potent carcinogens. One of the most dangerous is benzo[a]pyrene, which has been detected in cigarette smoke. It is believed to be a cause of lung cancer, to which smokers are susceptible.

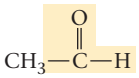
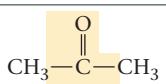
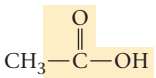
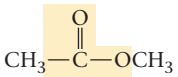
22-4 Functional Groups

Many organic molecules can be derived from hydrocarbons by substituting a **functional group** for a hydrogen atom. The functional group can be a nonmetal atom or a small group of atoms that is bonded to carbon. Table 22.2 lists the types of functional groups commonly found in organic compounds.

Alcohols and Ethers

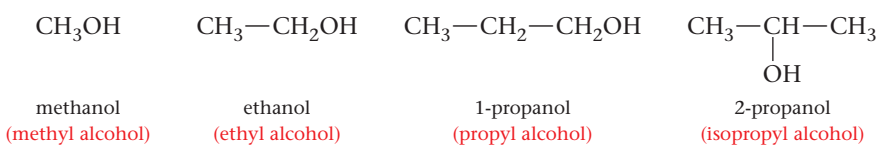
Alcohols have the general structural formula

Table 22.2 Common Functional Groups

Group	Class	Example	Name*
—OH	Alcohols	C_2H_5OH	Ethanol (ethyl alcohol)
—O—	Ethers	$CH_3—O—CH_3$	Dimethyl ether
	Aldehydes		Ethanal (acetaldehyde)
	Ketones		Propanone (acetone)
	Carboxylic acids		Ethanoic acid (acetic acid)
	Esters		Methyl acetate
	Amines	CH_3NH_2	Aminomethane (methylamine)

*Common names are shown in red.

where R is an **alkyl group.** Alcohols are named by substituting the suffix *-ol* for the *-ane* suffix of the corresponding alkane. For the first four alcohols we have (common names in red):



Ethers have the general structure

$$R—O—R'$$

where the two alkyl groups can be the same (e.g., $R = R' = CH_3$) or different ($R = CH_3$; $R' = C_2H_5$). Ethers are ordinarily named by citing the two alkyl groups:

$$\underset{\text{dimethyl ether}}{CH_3—O—CH_3} \qquad \underset{\text{ethyl methyl ether}}{CH_3—O—C_2H_5}$$

Table 22.3 compares two physical properties, boiling point and water solubility, of alcohols, ethers, and alkanes of similar molar masses. Notice that

- alcohols have boiling points much higher than those of alkanes of comparable molar mass. This reflects the fact that alcohol molecules, like H_2O, are strongly hydrogen-bonded to one another. Ethers cannot do this, since they do not contain OH groups, so they have boiling points much lower than those of comparable alcohols.
- alcohols and ethers of low molar mass are generally soluble in water. Ethers, like alcohols, can form hydrogen bonds with water, making use of the OH groups in the water molecule.

About 3×10^9 kg of methanol are produced annually in the United States from *synthesis gas,* a mixture of carbon monoxide and hydrogen:

$$CO(g) + 2H_2(g) \xrightarrow[250\text{ atm, }350°C]{ZnO,Cr_2O_3} CH_3OH(g)$$

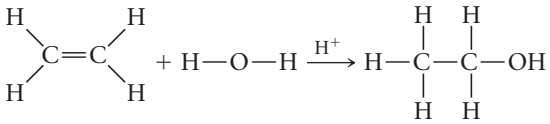
Methanol is also formed as a byproduct when charcoal is made by heating wood in the absence of air. For this reason, it is sometimes called wood alcohol. Methanol is used in jet fuels and as a solvent, gasoline additive, and starting material for several industrial syntheses. It is a deadly poison; ingestion of as little as 25 mL can be fatal. The antidote in this case is a solution of sodium hydrogen carbonate, $NaHCO_3$.

Table 22.3 Physical Properties of Simple Alkanes, Alcohols, and Ethers

Name	Structure	Molar Mass	Boiling Point	Water Solubility
Propane	$CH_3CH_2CH_3$	44 g/mol	−42°C	Insoluble
Ethanol	CH_3CH_2OH	46 g/mol	78°C	Soluble
Dimethyl ether	CH_3OCH_3	46 g/mol	−23°C	Soluble
Butane	$CH_3CH_2CH_2CH_3$	58 g/mol	0°C	Insoluble
1-Propanol	$CH_3CH_2CH_2OH$	60 g/mol	97°C	Soluble
Ethyl methyl ether	$CH_3CH_2OCH_3$	60 g/mol	11°C	Soluble

Ethanol, the most common alcohol, can be made by the fermentation of sugar (Figure 22.9) or grain—hence its common name "grain alcohol." It is the active ingredient of alcoholic beverages, in which it is present at various concentrations (4%–8% in beer, 12%–15% in wine, and 40% or more in distilled spirits). The "proof" of an alcoholic beverage is twice the volume percentage of ethanol; an 86-proof bourbon whiskey contains 43% (by volume) ethanol. The flavor of alcoholic beverages is due to impurities; ethanol itself is tasteless and colorless.

Industrial ethanol is made by the reaction of ethylene with water, using sulfuric acid as a catalyst.



Frequently, ethanol that is not destined for human consumption is "denatured" by adding small quantities of methanol or benzene. This avoids the high federal tax on beverage alcohol; denatured alcohol is poisonous.

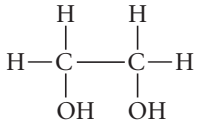
Courtesy of Professor James M. Bobbit, Twenty Mile Vineyard

Figure 22.9 Making wine. Wine (*far right*) is produced from the glucose in grape juice (left) by fermentation. The reaction is

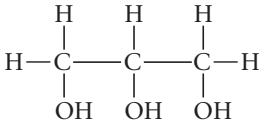
$$C_6H_{12}O_6(aq) \longrightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

The purpose of the bubble chamber in the fermentation jug *(center)* is to allow the carbon dioxide to escape but prevent oxygen from entering and oxidizing ethyl alcohol to acetic acid.

Certain alcohols contain two or more —OH groups per molecule. Perhaps the most familiar compounds of this type are ethylene glycol and glycerol:



ethylene glycol

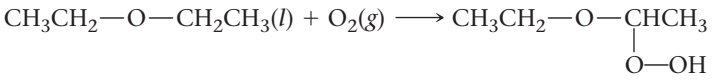


glycerol

Ethylene glycol is widely used as an antifreeze. Glycerol is formed as a byproduct in making soaps. It is a viscous, sweet-tasting liquid used in making drugs, antibiotics, plastics, and explosives (nitroglycerin).

The only ether that you are likely to encounter in the laboratory is diethyl ether, often referred to simply as "ether." It was first used as an anesthetic in the 1840s. Today we use other compounds for that purpose, for at least a couple of reasons. For one thing, ether vapor is highly flammable. For another, liquid ether, on standing in contact with air, tends to form compounds called hydroperoxides, which are potent explosives.

"Laughing gas," N_2O, is sometimes used by dentists.

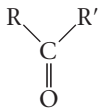


diethyl ether — a hydroperoxide

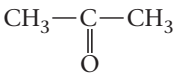
Aldehydes and Ketones

All these compounds contain the **carbonyl group**

In a **ketones**, two hydrocarbon groups (alkyl or aromatic) are bonded to the central carbon atom, giving the general structure



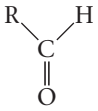
where (as with ethers) R and R′ can be the same or different. In the simplest ketone, commonly called *acetone,* R = R′ = CH_3. The structural formula of acetone is ordinarily written as



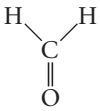
acetone (IUPAC name = propanone)

with the understanding that the bond angle around the central carbon atom is approximately 120°.

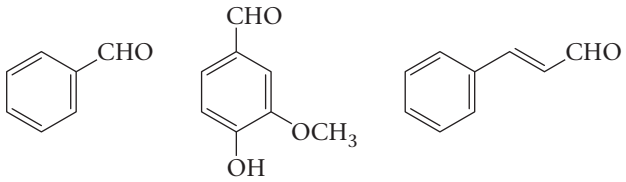
In **aldehydes,** at least one of the two "groups" bonded to carbon must be a hydrogen atom:



R can be any hydrocarbon group or, in the simplest case, *formaldehyde,* a second hydrogen atom:



formaldehyde (IUPAC name = methanal)



benzaldehyde (oil of almonds) | vanillin (vanilla bean) | cinnamaldehyde (oil of cinnamon)

Figure 22.10 "Aromatic" aldehydes. Benzaldehyde, vanillin, and cinnamaldehyde are aldehydes with pleasant aromas that are found in almonds, vanilla beans, and cinnamon, respectively.

Acetone (bp = 56°C) is completely water-soluble and dissolves a wide variety of organic compounds as well. Accordingly, it is one of the most important industrial solvents. You may be most familiar with it as the solvent in nail polish remover.

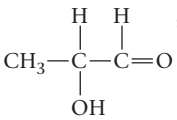
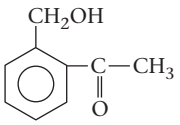
Normally, only small amounts of acetone are produced in the human body. Diabetics produce larger amounts, sometimes enough to give their breath a sweet odor.

Formaldehyde (bp = −21°C) is ordinarily found in the laboratory in the form of a concentrated water solution (37% HCHO) known as formalin. At one time it was widely used as a preservative for biological specimens. That application has declined now that formaldehyde has been shown to be carcinogenic. Industrially, it is still used as a component of adhesives used in making plywood and fiberboard.

Formaldehyde, as a gas or in water solution, has a distinctly unpleasant odor. Higher "aromatic" aldehydes such as those shown in Figure 22.10 are a lot more pleasant to deal with; they are used in flavorings and even perfumes.

EXAMPLE 22.6

Classify each of the following as an alcohol, ether, aldehyde, or ketone.

$CH_3—O—CH_2CH_2CH_3$,  , and 

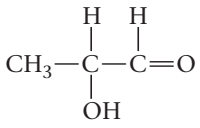
STRATEGY

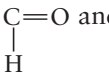
Identify the functional group and use Table 22.2. Note that more than one functional group may be involved.

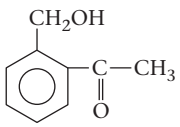
SOLUTION

$CH_3—O—CH_2—CH_2—CH_3$

Functional group: —O—
The molecule is an ether.



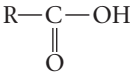
Functional groups:  and —OH
The molecule is an aldehyde and an alcohol.



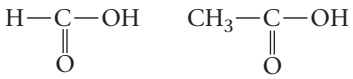
Functional groups: C=O and —OH
The molecule is a ketone and an alcohol.

Carboxylic Acids and Esters

Carboxylic acids have the following general structure:



As usual, R is a hydrocarbon group or, in the simplest case, a hydrogen atom. The acidic hydrogen atom is the one bonded to oxygen. The IUPAC name of a carboxylic acid is obtained by substituting the suffix "-oic acid" for the final "e" in the name of the corresponding alkane. In practice, such names are seldom used. For example, the first two members of the series are commonly referred to as formic acid and acetic acid.



methanoic acid (formic acid) ethanoic acid (acetic acid)

According to legend, formic acid used to be made by distilling ants (Latin, *formica*). Acetic acid is the active ingredient of vinegar, responsible for its sour taste. "White" vinegar is made by adding pure acetic acid to water, forming a 5% solution. "Brown" or "apple cider" vinegar is made from apple juice; the ethyl alcohol formed by fermentation is oxidized to acetic acid.

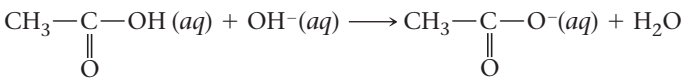
Homemade wine often contains some vinegar.

The most important property of carboxylic acids is implied by their name: they act as weak acids in water solution.

$$RCOOH(aq) \rightleftharpoons H^+(aq) + RCOO^-(aq)$$

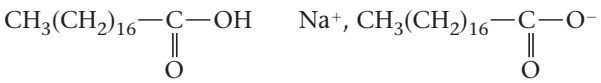
Carboxylic acids vary considerably in strength. Among the strongest is trichloroacetic acid ($K_a = 0.20$); a 0.10 *M* solution of $Cl_3C—COOH$ is about 73% ionized. Trichloroacetic acid is an ingredient of over-the-counter preparations used to treat canker sores and remove warts.

Treatment of a carboxylic acid with the strong base NaOH forms the sodium salt of the acid. With acetic acid, the acid-base reaction is



Evaporation gives the salt sodium acetate, which contains Na^+ and CH_3COO^- ions. Many of the salts of carboxylic acids have important uses. Sodium and calcium propionate (Na^+ or Ca^{2+} ions, $CH_3CH_2COO^-$ ions) are added to bread, cake, and cheese to inhibit the growth of mold.

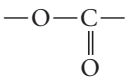
Soaps are sodium salts of long-chain carboxylic acids such as stearic acid:



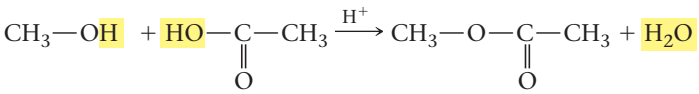
stearic acid sodium stearate, a soap

The cleaning action of soap reflects the nature of the long-chain carboxylate anion. The long hydrocarbon group is a good solvent for greases and oils, and the ionic COO^- group gives water solubility.

Reactions between an alcohol and a carboxylic acid form **esters**, containing the functional group



often abbreviated —COO—. The reaction between methyl alcohol and acetic acid is typical



methyl alcohol acetic acid methyl acetate

The common name of an ester consists of two words. The first word (methyl, ethyl, . . .) is derived from that of the alcohol; the second word (formate, acetate, . . .)

Table 22.4 Properties of Esters

Ester	Structure	Odor, Flavor
Ethyl formate	$CH_3CH_2—O—\underset{\underset{O}{\|}}{C}—H$	Rum
Isobutyl formate	$(CH_3)_2CHCH_2—O—\underset{\underset{O}{\|}}{C}—H$	Raspberry
Methyl butyrate	$CH_3—O—\underset{\underset{O}{\|}}{C}—(CH_2)_2CH_3$	Apple
Ethyl butyrate	$CH_3CH_2—O—\underset{\underset{O}{\|}}{C}—(CH_2)_2CH_3$	Pineapple
Isopentyl acetate	$(CH_3)_2CH(CH_2)_2—O—\underset{\underset{O}{\|}}{C}—CH_3$	Banana
Octyl acetate	$CH_3(CH_2)_7—O—\underset{\underset{O}{\|}}{C}—CH_3$	Orange
Pentyl propionate	$CH_3(CH_2)_4—O—\underset{\underset{O}{\|}}{C}—CH_2CH_3$	Apricot

is the name of the acid with the *-ic* suffix replaced by *-ate*. Thus ethyl formate (Table 22.4) is made from ethyl alcohol and formic acid:

$$\underset{\text{ethyl alcohol}}{CH_3CH_2OH} \qquad \underset{\text{formic acid}}{HCOOH}$$

Many esters have pleasant odors; they are commonly found in natural and synthetic fragrances.

EXAMPLE 22.7

Show the structure of the following:

a the three-carbon alcohol with an —OH group at the end of the chain and the three-carbon carboxylic acid.

STRATEGY

1. Write the parent compound chain.
2. Put the functional group in the specified position.
3. Fill in the structural formula with H atoms.

SOLUTION

Alcohol

1. Parent compound chain — C—C—C
2. Functional group — C—C—C—OH
3. Hydrogen atoms — $CH_3—CH_2—CH_2—OH$

Carboxylic acid

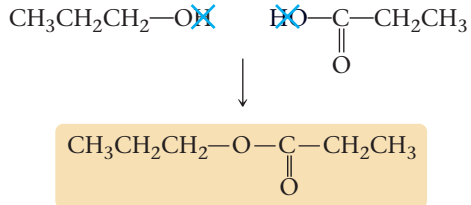
1. Parent compound chain — C—C—C
2. Functional group — $C—C—\underset{\underset{O}{\|}}{C}—OH$
3. Hydrogen atoms — $CH_3CH_2—\underset{\underset{O}{\|}}{C}—OH$

continued

b the ester formed when the alcohol and the carboxylic acid react.

STRATEGY AND SOLUTION

Join the acid and the alcohol and remove OH from the functional group (COOH) of the acid and the H from the functional group (OH) of the alcohol.

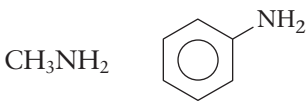


Amines

Amines were discussed earlier (Chapter 13). Here we will concentrate on *primary* amines, in which two hydrogens are bonded to a nitrogen atom, giving as a general formula

$$R—NH_2$$

where R may be an alkyl or aromatic group:



methylamine aniline

In Chapter 23, we'll look at the chemistry of amino acids, which contain both NH_2 and COOH groups.

Methylamine, the first member of the series,

- is a flammable gas at 25°C and 1 atm; its boiling point and critical temperature are −6°C and 157°C, respectively.
- has a somewhat unpleasant fishy smell. Other primary amines with more obnoxious odors include

putrescine cadaverine

- is a weak base with a K_b (4×10^{-4}) about 20 times that of ammonia (1.8×10^{-5}) and a million times the value for aniline (4×10^{-10}).
- reacts essentially completely with strong acid:

$$CH_3NH_2(aq) + H^+(aq) \longrightarrow CH_3NH_3^+(aq)$$

but gives an equilibrium mixture with acetic acid:

$$CH_3NH_2(aq) + CH_3COOH(aq) \rightleftharpoons CH_3NH_3^+(aq) + CH_3COO^-(aq)$$

EXAMPLE 22.8 GRADED

Consider methylamine, CH_3NH_2.

a Calculate the equilibrium constant K when it reacts with H^+ in the following reaction:

$$CH_3NH_2(aq) + H^+(aq) \longrightarrow CH_3NH_3^+(aq)$$

ANALYSIS

Information given:	reaction ($CH_3NH_2(aq) + H^+(aq) \longrightarrow CH_3NH_3^+(aq)$)
Information implied:	K_a for $CH_3NH_3^+$
Asked for:	K

continued

STRATEGY

1. Note that the given equation is the reverse of the equation for the dissociation of a weak acid.
2. Find K_a for $CH_3NH_3^+$ in Appendix 1 and use the reciprocal rule (Chapter 12).

SOLUTION

1. K_a expression	$CH_3NH_3^+(aq) \rightleftharpoons CH_3NH_2(aq) + H^+(aq)$ $\quad K_a = 2.4 \times 10^{-11}$
2. K	$CH_3NH_2(aq) + H^+(aq) \rightleftharpoons CH_3NH_3^+(aq)$ $\quad K = 1/K_a = 1/2.4 \times 10^{-11}$ $= 4.2 \times 10^{10}$

b Calculate the equilibrium constant K for its reaction with acetic acid:

$$CH_3NH_2(aq) + CH_3COOH(aq) \rightleftharpoons CH_3NH_3^+(aq) + CH_3COO^-(aq)$$

ANALYSIS

Information given:	reaction ($CH_3NH_2(aq) + CH_3COOH(aq) \longrightarrow CH_3NH_3^+(aq) + CH_3COO^-(aq)$) From (a): K (4.2×10^{10}) for the reaction $CH_3NH_2(aq) + H^+(aq) \rightleftharpoons CH_3NH_3^+(aq)$
Information implied:	K_a for CH_3COOH
Asked for:	K

STRATEGY

1. Break up the given equation into two reactions

   $CH_3NH_2 \rightleftharpoons CH_3NH_3^+$ (1)

   $CH_3COOH \rightleftharpoons CH_3COO^-$ (2)
2. Find K for each reaction.
3. Combine the two equations and their Ks. Apply the Rule of Multiple Equilibria (Chapter 12).

SOLUTION

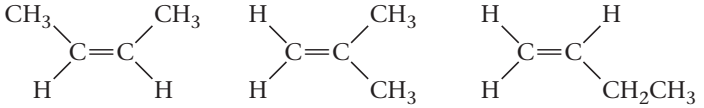
K for equation (1)	From (a): $K_1 = 4.2 \times 10^{10}$
K for equation (2)	From Appendix 1: $K_2 = K_a = 1.8 \times 10^{-5}$
Combine both equations	$CH_3NH_2(aq) + H^+(aq) \rightleftharpoons CH_3NH_3^+(aq)$ $\quad K_1 = 4.2 \times 10^{10}$ $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$ $\quad K_2 = 1.8 \times 10^{-5}$ $CH_3NH_2(aq) + CH_3COOH(aq) \rightleftharpoons CH_3NH_3^+(aq) + CH_3COO^-(aq)$
K	$K = K_1 \times K_2 = (4.2 \times 10^{10})(1.8 \times 10^{-5}) = 7.5 \times 10^5$

22-5 Isomerism in Organic Compounds

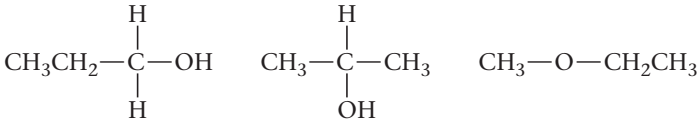
Isomers are distinctly different compounds, with different properties, that have the same molecular formula. In Section 22-1, we considered structural isomers of alkanes. You will recall that butane and 2-methylpropane have the same molecular formula, C_4H_{10}, but different structural formulas. In these, as in all structural isomers, the order in which the atoms are bonded to each other differs.

Structural isomerism is common among all types of organic compounds. For example, there are:

1. Three structural isomers of the alkene C_4H_8:



2. Three structural isomers with the molecular formula C_3H_8O. Two of these are alcohols; the third is an ether.

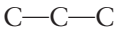


EXAMPLE 22.9

Consider the molecule $C_3H_6Cl_2$, which is derived from propane, C_3H_8, by substituting two Cl atoms for H atoms. Draw the structural isomers of $C_3H_6Cl_2$.

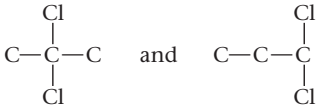
STRATEGY AND SOLUTION

1. All these compounds have three carbon atoms, hence the same skeleton.

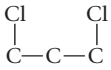


Note that the terminal C atoms are equivalent. The middle C atom is not.

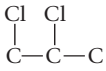
2. Bond 2 Cl atoms to the second C atom for the first isomer, and 2 Cl atoms to the terminal C atom for the second isomer.



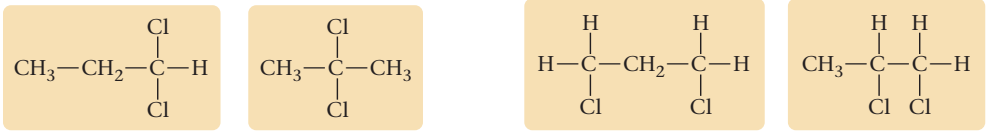
3. Bond a Cl atom to each terminal C atom for the third isomer.



4. Bond a Cl atom to a terminal C atom and the other Cl atom to the middle C atom for the fourth isomer.

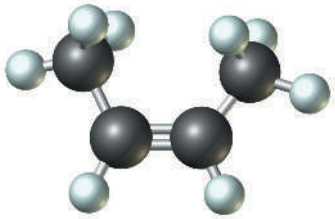


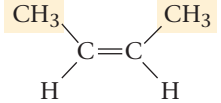
5. Add the appropriate number of H atoms to the C atoms so that there are four bonds around each C atom.



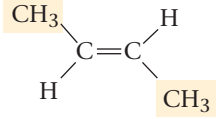
Geometric *(cis-trans)* Isomers

As we saw earlier, there are three structural isomers of the alkene C_4H_8. You may be surprised to learn that there are actually *four* different alkenes with this molecular formula. The "extra" compound arises because of a phenomenon called **geometric isomerism.** There are two different geometric isomers of the structure shown on the left, on the previous page, under (1).

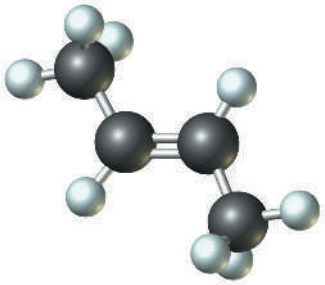




cis isomer
bp = 4°C



trans isomer
bp = 1°C



In the ***cis* isomer**, the two CH_3 groups (or the two H atoms) are as close to one another as possible. In the ***trans* isomer**, the two identical groups are farther apart. The two forms exist because there is no free rotation about the carbon-to-carbon double bond. The situation is analogous to that with *cis-trans* isomers of square planar complexes (Chapter 19). In both cases, the difference in geometry is responsible for isomerism; the atoms are bonded to each other in the same way.

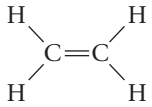
Geometric, or *cis-trans,* isomerism is common among alkenes. It occurs when both of the double-bonded carbon atoms are joined to two different atoms or groups. The other two structural isomers of C_4H_8 shown under (1) on page 566 do not show *cis-trans* isomerism. In both cases the carbon atom at the left is joined to two identical hydrogen atoms.

EXAMPLE 22.10

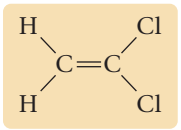
Draw all the isomers of the molecule $C_2H_2Cl_2$ in which two of the H atoms of ethylene are replaced by Cl atoms.

STRATEGY AND SOLUTION

1. Write the structure for ethylene.

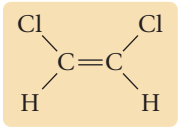


2. Substitute two Cl atoms for the two H atoms on the right.



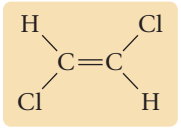
Substituting two Cl atoms for the two H atoms on the left gives the identical structure just written.

3. Substitute Cl atoms for the two H atoms at the top (1 H atom per C atom).



Substituting two Cl atoms for the two H atoms on the bottom gives the identical structure.

4. Substitute a Cl atom for the H atom on the top right and the other Cl atom for the H atom on the bottom left.

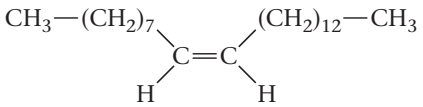


These are all the isomers that can be drawn.

END POINT

1. The first structure does not show any *cis-trans* isomerism because the two Cl atoms are bonded to the same C atom.
2. The second structure is the *cis*-isomer.
3. The third structure is the *trans*-isomer.

Cis and *trans* isomers differ from one another in their physical and, to a lesser extent, their chemical properties. They may also differ in their physiological behavior. For example, the compound *cis*-9-tricosene



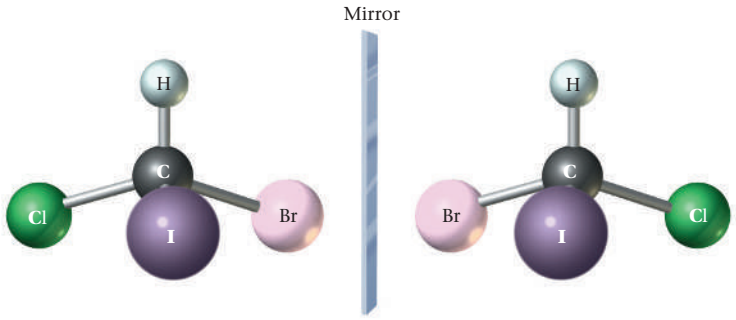


Figure 22.11 Optical isomers. These isomers of CHClBrI are mirror images of each other.

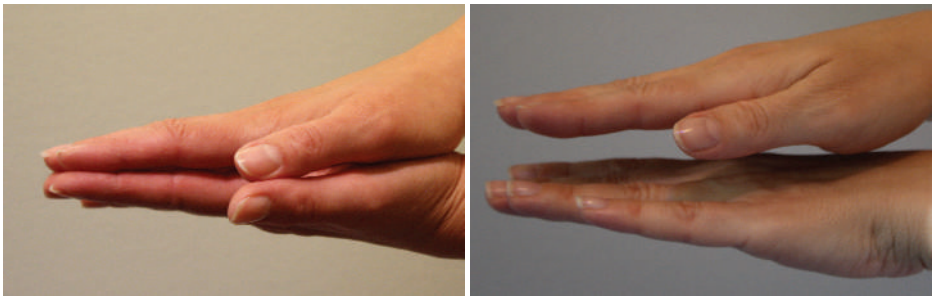


Figure 22.12 Mirror images. The right hand cannot be superimposed on the left hand. They are mirror images of each other.

is a sex attractant secreted by the female housefly. The *trans* isomer is totally ineffective in this capacity.

Optical Isomers

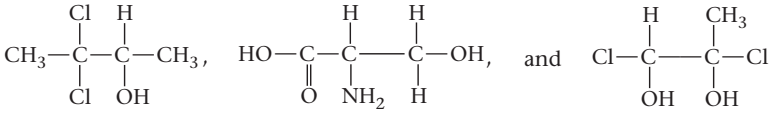
Optical isomers arise when at least one carbon atom in a molecule is bonded to four different atoms or groups. Consider, for example, the methane derivative CHClBrI. As you can see from Figure 22.11, there are two different forms of this molecule, which are mirror images of one another. The mirror images are not superimposable; that is, you cannot place one molecule over the other so that identical groups are touching. In this sense, the two isomers resemble right and left hands (Figure 22.12).

There is another way to convince yourself that the two structures shown in Figure 22.11 are different isomers. Imagine yourself directly above the hydrogen atom, looking down at the rest of the molecule. In the structure at the left, the atoms Cl, Br, I, in that order, are arranged in a clockwise pattern. With the structure at the right, in order to move from Cl to Br to I, you have to move counterclockwise.

A molecule such as CHClBrI, which exists in two different forms that are not superimposable mirror images, is said to be *chiral*. The two different forms are referred to as **enantiomers,** or optical isomers. Any molecule in which four different groups are bonded to carbon will be chiral; the carbon atom serves as a **chiral center.** Molecules may contain more than one chiral center, in which case there can be more than two enantiomers.

EXAMPLE 22.11

In the following structural formulas, locate each chiral carbon atom.

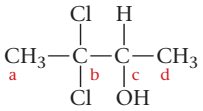


continued

STRATEGY

Look for carbon atoms that have four different atoms or groups bonded to them. As soon as you see two (or more) identical atoms or groups, you can stop counting. The C atom is not chiral.

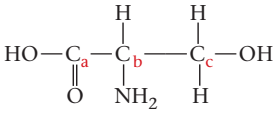
SOLUTION



C_a has three hydrogen atoms bonded to it. It is not chiral.
C_b has two chlorine atoms bonded to it. It is not chiral.
C_c has four different groups/atoms bonded to it:

1 H, 1 OH, 1 CH_3, 1 CH_3—CCl_2

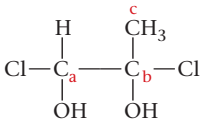
It is chiral.
C_d has three hydrogen atoms bonded to it. It is not chiral.



C_a has only three groups/atoms bonded to it. It is not chiral.
C_b has four different groups/atoms bonded to it:

1 H, 1 NH_2, 1 COOH, 1 CH_2OH

It is chiral.
C_c has two hydrogen atoms bonded to it. It is not chiral.



C_a has four different groups/atoms bonded to it:

1 H, 1 OH, 1 Cl, 1 C—Cl

It is chiral.
C_b has four different groups/atoms bonded to it:

1 CH_3, 1 OH, 1 Cl, 1 C—Cl

It is chiral.
C_c has three hydrogen atoms bonded to it. It is not chiral.

The term "optical isomerism" comes from the effect that enantiomers have on plane-polarized light, such as that produced by a Polaroid lens (Figure 22.13). When this light is passed through a solution containing a single enantiomer, the plane is rotated from its original position. One isomer rotates it to the right (clockwise) and the other to the left (counterclockwise). If both isomers are present in equal amounts, we obtain what is known as a **racemic mixture.** In this case, the two rotations offset each other and there is no effect on plane-polarized light.

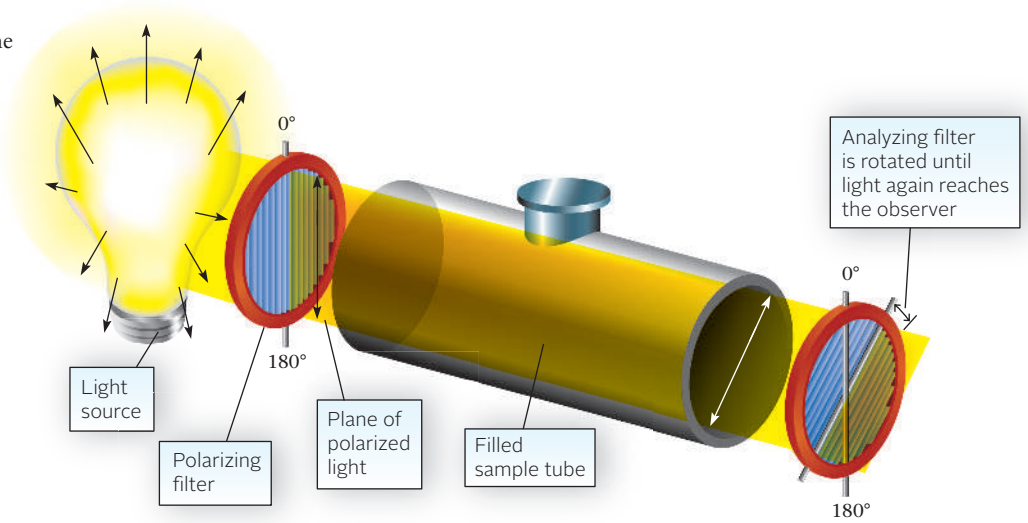
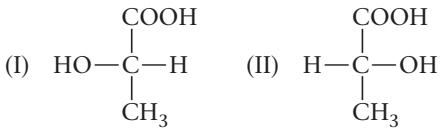


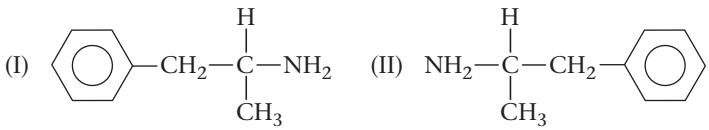
Figure 22.13 A polarimeter. The sample tube contains an optically active compound. The analyzing filter has been turned clockwise to restore the light field and measure the rotation caused by the sample.

Except for their effect on plane-polarized light, two enantiomers of a chiral compound have identical physical properties. For example, the two isomers of lactic acid shown below have the same melting point, 52°C, and density, 1.25 g/mL.



enantiomers of lactic acid

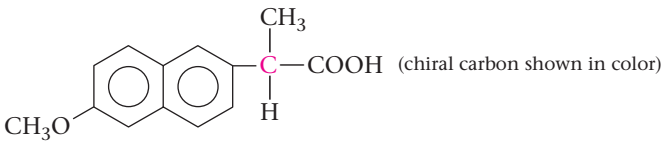
On the other hand, because enantiomers differ in their three-dimensional structure, they often interact with biochemical molecules in different ways. As a result, they may show quite different physiological properties. Consider, for example, amphetamine, often used illicitly as an "upper" or "pep pill." Amphetamine consists of two enantiomers:



enantiomers of amphetamine

Enantiomer I, called Dexedrine, is by far the stronger stimulant. It is from two to four times as active as Benzedrine, the racemic mixture of the two isomers.

In the 1990s, a large number of so-called chiral drugs containing a single enantiomer came on the market. One of the first of these was naproxen (trade name Aleve®).



(chiral carbon shown in color)

The naproxen that you buy over the counter at your local pharmacy consists of a single enantiomer, which is an effective analgesic (pain killer). The other enantiomer is not a pain killer; even worse, it can cause liver damage.

Of the 100 best-selling drugs on the market today, about half consist of a single enantiomer. Chiral drugs are used to treat all kinds of illnesses, from arthritis to asthma, from heartburn to heart disease. In general, these drugs are prepared by either of two different methods. One possibility is to resolve a racemic mixture into its components. This was first done in the mid-nineteenth century by Louis Pasteur (1822–1895). He used a magnifying glass and a pair of tweezers to separate crystals of enantiomers. Today resolution can be accomplished much more quickly by using modern separation techniques such as liquid chromatography (Chapter 1).

A different approach to making chiral drugs is *asymmetric synthesis*. An optically inactive precursor is converted to the drug by a reaction that uses a special catalyst, usually an enzyme (Chapter 11). If all goes well, the product is a single enantiomer with the desired physiological effect. In 2001, William S. Knowles (1917–2012), Ryoji Noyori (1938–), and K. Barry Sharpless (1941–) won the Nobel Prize in Chemistry for work in this area.

22-6 Organic Reactions

The reactions that take place in organic chemistry differ in important ways from those discussed earlier in this text. In particular, the species taking part in organic reactions are most often molecules rather than ions. Again, most organic reactions take place between pure substances or in nonpolar solvents as opposed to water.

Ions tend to react fast.

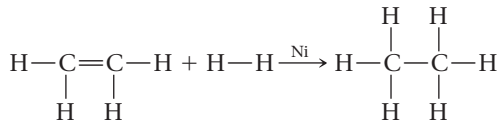
Generally speaking, organic reactions occur more slowly than inorganic ones. In this section we will look at four general types of organic reactions known as addition, elimination, condensation, and substitution.

Addition Reactions

In **addition reactions**, a small molecule (e.g., H_2, Cl_2, HCl, H_2O) adds across a double or triple bond. A simple example is the addition of hydrogen gas to ethene in the presence of a nickel catalyst.

Double and triple bonds are much more reactive than single bonds.

Figure 22.14 Test for an alkene. At the left is a solution of bromine in carbon tetrachloride. Addition of a few drops of an alkene causes the red color to disappear as the alkene reacts with the bromine.



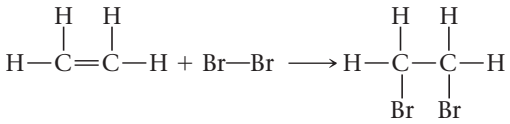
With ethyne (acetylene), one or two moles of H_2 may add, depending upon the catalyst and the conditions used.

Hydrogenation has found commercial application in the conversion of liquid to solid fats. Vegetable oils contain a relatively high proportion of double bonds. Treatment with hydrogen under pressure in the presence of a catalyst converts double bonds to single bonds and produces solids such as margarine.

As we saw earlier (Section 22-4), ethanol can be made from ethene by "adding" water in the presence of an acid catalyst. This process is referred to as **hydration:**

$$C_2H_4(g) + H_2O(l) \xrightarrow{H^+} C_2H_5OH(l)$$

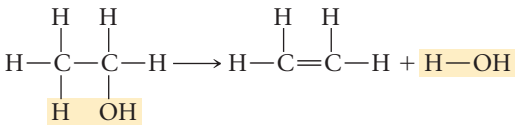
Still another species that adds readily to ethene is elementary bromine (Figure 22.14):



Elimination and Condensation Reactions

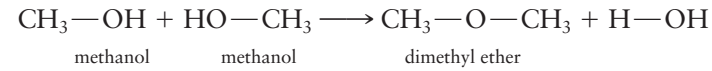
Elimination reactions are, in a sense, the reverse of addition reactions. They involve the elimination of two groups from adjacent carbon atoms, converting a saturated molecule into one that is unsaturated. An example is the dehydration of ethanol, which occurs when it is heated with sulfuric acid:

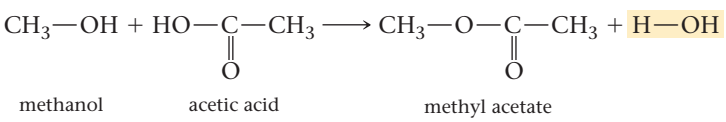
The H_2SO_4 absorbs the H_2O and drives the reaction to the right.



This is, of course, the reverse of the addition reaction by which ethanol is formed.

Somewhat similar reactions, referred to as **condensation reactions**, occur when two molecules combine by splitting out a small molecule such as H_2O. The molecules that combine may be the same or different:





The first reaction offers a general way of preparing ethers from alcohol. The second reaction is that of esterification, referred to earlier.

Substitution Reactions

Substitution reactions are those in which an atom or group of atoms in a molecule is replaced by a different atom or group. Substitution reactions are very common in organic chemistry. Examples include the following:

- chlorination of alkanes. When a mixture of methane and chlorine gases is exposed to light, the following reaction occurs:

$$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$$

- a very similar reaction with benzene:

$$C_6H_6(l) + Cl_2(g) \xrightarrow{FeCl_3} C_6H_5Cl(l) + HCl(g)$$

- the nitration of benzene:

$$C_6H_6(l) + HNO_3(l) \xrightarrow{H_2SO_4} C_6H_5NO_2(l) + H_2O(l)$$

  In this case the nitro group, NO_2, substitutes for a hydrogen atom in the benzene ring.

- formation of an alcohol from an alkyl halide:

$$C_2H_5Br(l) + OH^-(aq) \longrightarrow C_2H_5OH(aq) + Br^-(aq)$$

  Here a bromine atom is replaced by an —OH group.

EXAMPLE 22.12

Classify each of the following as an addition, elimination, condensation, or substitution reaction.

(a) $C_2H_5OH(aq) + H^+(aq) + Br^-(aq) \longrightarrow C_2H_5Br(l) + H_2O$

(b) $C_6H_{12}(l) + Cl_2(g) \longrightarrow C_6H_{12}Cl_2(l)$

(c) $C_7H_8(l) + 2Cl_2(g) \longrightarrow C_7H_6Cl_2(l) + 2HCl(g)$

(d) $C_5H_{11}Cl(l) \longrightarrow C_5H_{10}(l) + HCl(g)$

SOLUTION

(a) substitution (Br for OH) (b) addition (C_6H_{12} is an alkene)

(c) substitution (Cl for H) (d) elimination (HCl lost)

CHEMISTRY **BEYOND** THE CLASSROOM

Cholesterol

An organic compound that we hear a great deal about nowadays is cholesterol, whose structure is shown in Figure A. Your body contains about 140 g of cholesterol; it is synthesized in the liver at the rate of 2 to 3 g/day. Cholesterol is essential to life for two reasons. It is a major component of all cell membranes, and it serves as the starting material for the synthesis of sex hormones, adrenal hormones, bile acids, and vitamin D.

Cholesterol, which is water-insoluble, is transported through the blood in the form of soluble protein complexes known as lipoproteins. There are two types of complexes: low-density (LDL), which contain mostly cholesterol, and high-density (HDL), which contain relatively little cholesterol. Commonly, these complexes are referred to as "LDL cholesterol" and "HDL cholesterol," respectively.

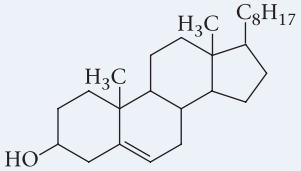
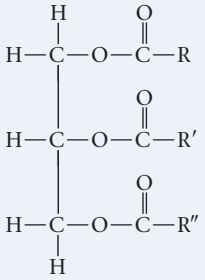


Figure A Cholesterol.

LDL, or "bad," cholesterol builds up as a plaque-like deposit on the interior walls of arteries. This process used to be called hardening of the arteries; today it is referred to as *atherosclerosis*. It can lead to cardiovascular diseases, including strokes and heart attacks. In contrast, HDL or "good" cholesterol retards or even reduces arterial deposits.

The relative amounts of LDL and HDL cholesterol in your bloodstream depend, at least in part, on your diet. In particular, they depend on the total amount and the type of fat that you eat. Fats (triglycerides) are esters of glycerol with long-chain carboxylic acids. The general structure of a fat can be represented as



where R, R′, and R″ are hydrocarbon residues typically containing 13 to 21 carbon atoms. Depending on the nature of these residues, we can distinguish among:

- *saturated fats,* in which R, R′, and R″ contain no multiple bonds. These are "bad" in the sense that they lead to high levels of LDL relative to HDL cholesterol.
- *monounsaturated fats,* in which each residue contains one double bond. These are much better nutritionally unless, God forbid, the hydrogen atoms on opposite sides of the double bonds are trans to one another. So-called *trans* fats are bad news.
- *polyunsaturated fats,* in which the hydrocarbon residues contain more than one double bond, are good guys, particularly if a double bond is located on the third or sixth carbon atom from the $-CH_3$ end of the residue. These so-called omega fats are the best of all.

Figure B shows the composition of various fats (solids) and oils (liquids). Now you know why sunflower seeds are better for you than coconuts.

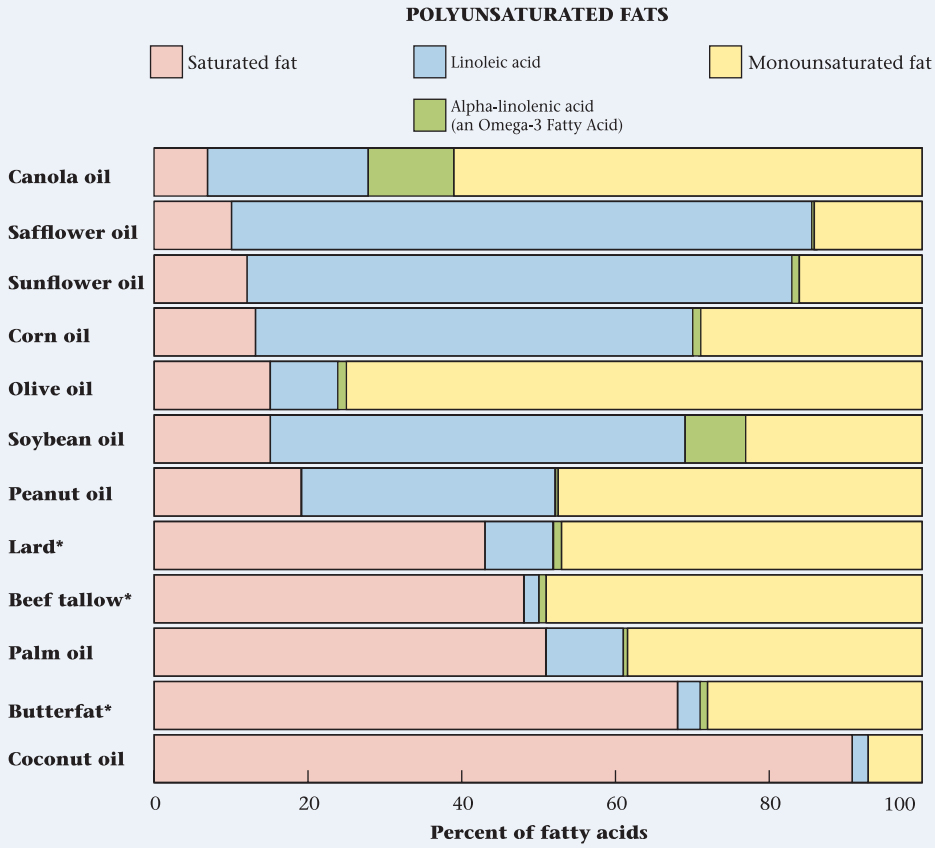


Figure B The composition of some common fats and oils. Fatty acids provide the R, R′, and R″ hydrocarbon residues in the general structure of a fat or oil shown in the text. Fats and oils all contain a mixture of saturated, monounsaturated, and polyunsaturated fatty acids.

*Cholesterol content (mg/Tbsp): Lard 12; Beef Tallow 14; Butterfat 33. No cholesterol in any vegetable-based oil.

Key Concepts

1. Draw
   - structural isomers
   (Examples 22.1 and 22.9; Problems 29–38)
   - geometric isomers
   (Example 22.10; Problems 39–42)
   - optical isomers, containing chiral carbon atoms
   (Example 22.11; Problems 43–46)
2. Name
   - alkanes
   (Example 22.2; Problems 5–10)

- unsaturated hydrocarbons
  (Example 22.4; Problems 11, 12)
- aromatic compounds
  (Example 22.5; Problems 13, 14)

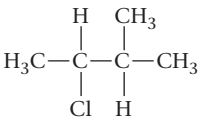
3. Distinguish between alkanes, cycloalkanes, alkenes, and alkynes.
   (Example 22.3; Problems 1–4)
4. Distinguish between alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, and amines.
   (Example 22.6; Problems 15–18)
5. Draw structural formulas for compounds containing the functional groups listed in Table 22.2.
   (Example 22.7; Problems 19–22)
6. Determine equilibrium constants for the reaction of amines with strong or weak acids.
   (Example 22.8; Problems 27, 28)
7. Classify an organic reaction as addition, elimination, condensation, or substitution.
   (Example 22.12; Problems 47–50)

Key Terms

addition reactions
alcohols
aldehydes
alkanes
alkenes
alkyl group
alkynes
amines
aromatic hydrocarbons
carboxylic acids
chiral center
cis isomer
condensation reactions
cycloalkanes
elimination reactions
enantiomers
esters
ethers
functional group
geometric isomerism
hydrocarbon
ketones
optical isomers
racemic mixture
structural isomers
substitution reactions
trans isomer

Summary Problem

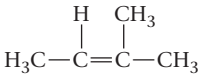
Consider the alkyl halide that has the structure



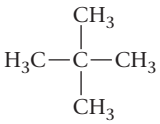
(a) Write the name of the alkyl halide and that of the alkane from which it is derived.
(b) Draw the structure of the compound formed when HCl is eliminated from the alkyl halide. Write its name and classify it as an alkane, alkene, or alkyne.
(c) Draw the structures and write the names of all the alkanes that are structurally isomeric to the alkane equivalent to (a).
(d) Write the names of all the alkenes that are structurally isomeric to (b).
(e) Does the alkyl halide exhibit optical isomerism? If so, how many chiral carbon atoms does it have?
(f) Take an isomer from (c) and add a functional group to make it
1. an aldehyde
2. a ketone
3. an amine
4. an ether
5. a carboxylic acid
Write the structural formula of each species obtained.
(g) Draw the structure of the species formed when this alkyl halide undergoes substitution with an OH^- ion.
(h) Draw the condensed structural formula and write the name of the ester formed when 1-pentanol reacts with formic acid, HCOOH.

Answers

(a) 2-chloro-3-methylbutane; 2-methylbutane

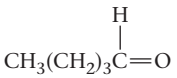
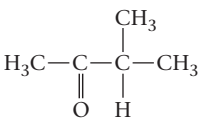
(b)  2-methyl-2-butene; alkene

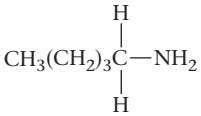
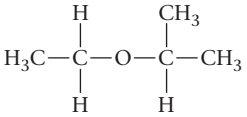
(c) $CH_3CH_2CH_2CH_2CH_3$ pentane

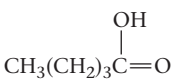
 2,2-dimethylpropane

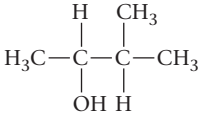
(d) 1-pentene; 2-methyl-1-butene; 3-methyl-1-butene; *cis*-2-pentene; *trans*-2-pentene

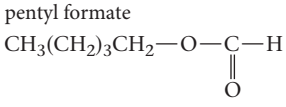
(e) yes; 1

(f) **(1)**  **(2)** 

(3)  **(4)** 

(5) 

(g) 

(h) pentyl formate 

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

22-1 Saturated Hydrocarbons: Alkanes

22-2 Unsaturated Hydrocarbons: Alkenes and Alkynes

22-3 Aromatic Hydrocarbons and Their Derivatives

1. Classify each of the following hydrocarbons as alkanes, alkenes, or alkynes.
(**a**) C_6H_{14} (**b**) C_3H_4 (**c**) C_9H_{18}

2. Classify each of the following hydrocarbons as alkanes, alkenes, or alkynes.
(**a**) $C_{12}H_{24}$ (**b**) C_7H_{12} (**c**) $C_{13}H_{28}$

3. Write the formula for
(**a**) an alkene with two carbon atoms.
(**b**) an alkane with 22 hydrogen atoms.
(**c**) an alkyne with three carbon atoms.

4. Write the formula for
(**a**) an alkyne with 16 hydrogen atoms.
(**b**) an alkene with 44 hydrogen atoms.
(**c**) an alkane with ten carbon atoms.

5. Name the following alkanes.

(**a**) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(**b**) $CH_3-CH_2-\underset{\displaystyle CH_2}{\underset{|}{CH}}-CH_3$ with CH_3 on the CH_2

(**c**) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_2}{\underset{|}{CH}}-CH_3$ with CH_3 on the CH_2

(**d**) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle H-\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3}{\underset{|}{CH}}-CH_3$

6. Name the following alkanes.

(**a**) $CH_3-(CH_2)_5-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(**b**) $(CH_3)_4C$

(**c**) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-C(CH_3)_3$

(**d**) $CH_3-\underset{\displaystyle CH_2-CH_3}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-(CH_2)_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

7. Write structural formulas for the following alkanes.
(**a**) 3-ethylpentane (**b**) 2,2-dimethylbutane
(**c**) 2-methyl-3-ethylheptane (**d**) 2,3-dimethylpentane

8. Write structural formulas for the following alkanes.
(**a**) 2,2,4-trimethylpentane (**b**) 2,2-dimethylpropane
(**c**) 4-isopropyloctane (**d**) 2,3,4-trimethylheptane

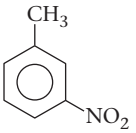
9. The following names are incorrect; draw a reasonable structure for the alkane and give the proper IUPAC name.
(**a**) 5-isopropyloctane (**b**) 2-ethylpropane
(**c**) 1,2-dimethylpropane

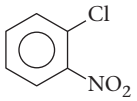
10. Follow the directions of Problem 9 for the following names.
(**a**) 2,2-dimethylbutane (**b**) 4-methylpentane
(**c**) 2-ethylpropane

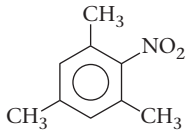
11. Name the following alkenes.
(**a**) $CH_2=C-(CH_3)_2$
(**b**) $(CH_3)_2-C=C-(CH_3)_2$
(**c**) $CH_3-CH=CH-CH_2CH_3$
(**d**) $CH_3-\underset{\displaystyle CH_2-CH_3}{\underset{|}{C}}=CH_2$

12. Write structural formulas for the following alkynes.
(**a**) 2-pentyne (**b**) 4-methyl-2-pentyne
(**c**) 2-methyl-3-hexyne (**d**) 3,3-dimethyl-1-butyne

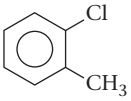
13. Name the following compounds as derivatives of nitrobenzene.

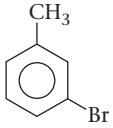
(**a**) 

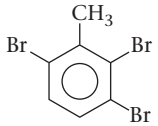
(**b**) 

(**c**) 

14. Name the following compounds as derivatives of toluene.

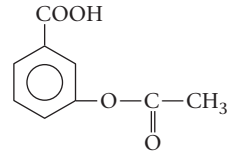
(**a**) 

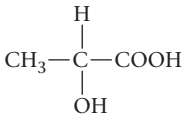
(**b**) 

(**c**) 

22-4 Functional Groups

15. Classify each of the following as a carboxylic acid, ester, and/or alcohol.
(**a**) $HO-CH_2-CH_2-CH_2-OH$

(b) 

(c) 

16. Classify each of the following as a carboxylic acid, ester, and/or alcohol.

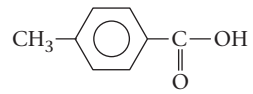
(a) $CH_3—(CH_2)_3—OH$

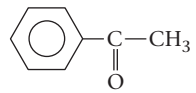
(b) $CH_3—CH_2—C(=O)—O—CH_2—CH_3$

(c) $CH_3—CH_2—O—C(=O)—(CH_2)_6—COOH$

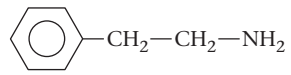
17. In each of the following, name the functional group (i.e., ester, aldehyde, etc.).

(a) $CH_3—CH=CH—CH_2—OH$

(b) 

(c) 

(d) $CH_3—CH_2—C(=O)—H$

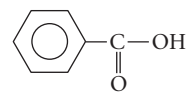
(e) 

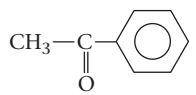
18. In each of the following, name the functional group (i.e., ester, aldehyde, etc.).

(a) $CH_2=CH—O—CH_3$

(b) $CH_3—CH_2—C(=O)—O—CH_3$

(c) $CH_3—CH_2—CH_2—NH_2$

(d) 

(e) 

19. Give the structure of

(a) a four-carbon straight-chain alcohol with an —OH group not at the end of the chain.

(b) a five-carbon straight-chain carboxylic acid.

(c) the ester formed when these two compounds react.

20. Give the structure of

(a) a three-carbon alcohol with the —OH group on the center carbon.

(b) a four-carbon branched-chain carboxylic acid.

(c) the ester formed when these two compounds react.

21. Write the structural formula of the ester formed by methyl alcohol with

(a) formic acid. (b) acetic acid.

(c) $CH_3—(CH_2)_6—COOH$.

22. Write the structural formulas of all the esters that can be formed by ethylene glycol with formic and acetic acids. (One or both of the —OH groups of ethylene glycol can react.)

23. Arrange these compounds in order of increasing boiling point. Values in °C are 0, 11, and 97.

(a) $CH_3CH_2CH_2OH$

(b) $CH_3CH_2—O—CH_3$

(c) $CH_3CH_2CH_2CH_3$

24. Arrange these compounds in order of increasing boiling point.

(a) 1-butanol, butane, diethylether

(b) hexane, 1-hexanol, dipropylether

25. The K_b for ethylamine ($CH_3CH_2NH_2$) is 4.3×10^{-4}. What is the pH of a 0.250 *M* solution of ethylamine? Compare with the pH of a 0.250 *M* solution of ammonia ($K_b = 1.86 \times 10^{-5}$).

26. When aniline, $C_6H_5NH_2$ ($K_b = 7.4 \times 10^{-10}$), reacts with a strong acid, its conjugate acid, $C_6H_5NH_3^+$, is formed. Calculate the pH of a 0.100 *M* solution of $C_6H_5NH_3^+$ and compare it with the pH of acetic acid ($K_a = 1.86 \times 10^{-5}$).

27. When ethylamine, a weak base ($K_b = 4.3 \times 10^{-4}$), reacts with formic acid, a weak acid ($K_a = 1.8 \times 10^{-4}$), the following reaction takes place:

$$CH_3CH_2NH_2(aq) + HCOOH(aq) \rightleftharpoons CH_3CH_2NH_3^+(aq) + HCOO^-(aq)$$

Calculate *K* for this reaction.

28. When the conjugate acid of aniline, $C_6H_5NH_3^+$, reacts with the acetate ion, the following reaction takes place:

$$C_6H_5NH_3^+(aq) + CH_3COO^-(aq) \rightleftharpoons C_6H_5NH_2(aq) + CH_3COOH(aq)$$

If K_a for $C_6H_5NH_3^+$ is 1.35×10^{-5} and K_a for CH_3COOH is 1.86×10^{-5}, what is *K* for the reaction?

22-5 Isomerism in Organic Compounds

29. Draw the structural isomers of the alkane C_6H_{14}.

30. Draw the structural isomers of the alkene C_4H_8.

31. Draw the structural isomers of C_4H_9Cl in which one hydrogen atom of a C_4H_{10} molecule has been replaced by chlorine.

32. Draw the structural isomers of $C_3H_6Cl_2$ in which two of the hydrogen atoms of C_3H_8 have been replaced by chlorine atoms.

33. There are three compounds with the formula C_6H_4ClBr in which two of the hydrogen atoms of the benzene molecule have been replaced by halogen atoms. Draw structures for these compounds.

34. There are three compounds with the formula $C_6H_3Cl_3$ in which three of the hydrogen atoms of the benzene molecule have been replaced by chlorine atoms. Draw structures for these compounds.

35. Write structures for all the structural isomers of double-bonded compounds with the molecular formula C_5H_{10}.

36. Write structures for all the structural isomers of compounds with the molecular formula C_4H_6ClBr in which Cl and Br are bonded to a double-bonded carbon.

37. Draw structures for all the alcohols with molecular formula $C_5H_{12}O$.

38. Draw structures for all the saturated carboxylic acids with four carbon atoms per molecule.

39. Of the compounds in Problem 35, which ones show geometric isomerism? Draw the *cis*- and *trans*- isomers.

40. Of the compounds in Problem 36, which ones show geometric isomerism? Draw the *cis*- and *trans*- isomers.

41. Maleic acid and fumaric acid are the *cis*- and *trans*- isomers, respectively, of $C_2H_2(COOH)_2$, a dicarboxylic acid. Draw and label their structures.

42. For which of the following is geometric isomerism possible?

(a) $(CH_3)_2C{=}CCl_2$ **(b)** $CH_3ClC{=}CCH_3Cl$

(c) $CH_3BrC{=}CCH_3Cl$

43. Which of the following can show optical isomerism?

(a) 2-bromo-2-chlorobutane

(b) 2-methylpropane

(c) 2,2-dimethyl-1-butanol

(d) 2,2,4-trimethylpentane

44. Which of the following compounds can show optical isomerism?

(a) dichloromethane

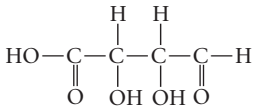
(b) 1,2-dichloroethane

(c) bromochlorofluoromethane

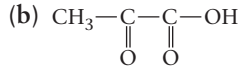
(d) 1-bromoethanol

45. Locate the chiral carbon(s), if any, in the following molecules.

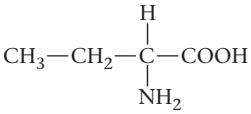
(a)



(b)

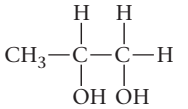


(c)

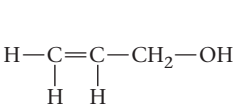


46. Locate the chiral carbon(s), if any, in the following molecules.

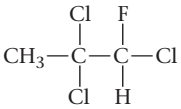
(a)



(b)



(c)



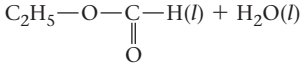
22-6 Organic Reactions

47. Classify the following reactions as addition, substitution, elimination, or condensation.

(a) $C_2H_2(g) + HBr(g) \longrightarrow C_2H_3Br(l)$

(b) $C_6H_5OH(s) + HNO_3(l) \longrightarrow C_6H_4(OH)(NO_2)(s) + H_2O(l)$

(c) $C_2H_5OH(aq) + HCOOH(aq) \longrightarrow$



48. Classify the following reactions according to the categories listed in Question 47.

(a) $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)$

(b) $C_3H_7OH(l) \longrightarrow C_3H_6(g) + H_2O(l)$

(c) $CH_3OH(l) + C_2H_5OH(l) \longrightarrow CH_3{-}O{-}C_2H_5(l) + H_2O(l)$

49. Name the products formed when the following reagents add to 1-butene.

(a) H_2 **(b)** Br_2

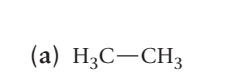
50. Name the products obtained when the following reagents add to 2-methyl-2-butene.

(a) Cl_2 **(b)** I_2

Unclassified

51. Which of the following are expected to show bond angles of 109.5°? 120°? 180°?

(a) $H_3C{-}CH_3$ **(b)**



(c) $H_3C{-}C{\equiv}C{-}CH_3$

52. What does the "circle" represent in the structural formula of benzene?

53. Calculate $[H^+]$ and the pH of a 0.10 *M* solution of chloroacetic acid ($K_a = 1.5 \times 10^{-3}$).

54. Explain what is meant by the following.

(a) a saturated fat

(b) a soap

(c) the "proof" of an alcoholic beverage

(d) denatured alcohol

55. The general formula of an alkane is C_nH_{2n+2}. What is the general formula of an

(a) alkene? **(b)** alkyne?

(c) alcohol derived from an alkane?

56. Write a balanced net ionic equation for the reaction of

(a) $(CH_3)_2NH$ with hydrochloric acid.

(b) acetic acid with a solution of barium hydroxide.

(c) 2-chloropropane with a solution of sodium hydroxide.

Challenge Problems

57. The structure of cholesterol is given in the text (see Figure A, page 573). What is its molecular formula?

58. Draw structures for all the alcohols with molecular formula $C_6H_{14}O$.

59. What mass of propane must be burned to bring one quart of water in a saucepan at 25°C to the boiling point? Use data in Appendix 1 and elsewhere and make any reasonable assumptions.

60. Write an equation for the reaction of chloroacetic acid ($K_a = 1.5 \times 10^{-3}$) with trimethylamine ($K_b = 5.9 \times 10^{-5}$). Calculate the equilibrium constant for the reaction. If 0.10 *M* solutions of these two species are mixed, what will be their concentrations at equilibrium?