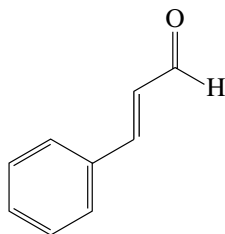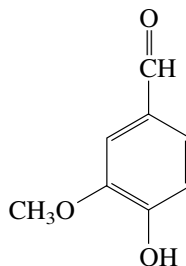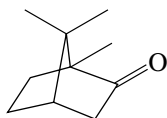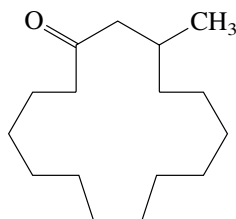Citral

Cinnamaldehyde

Vanillin

Camphor

Muscone
(3-methylcyclopentadecanone)

12.4 CARBOXYLIC ACIDS

Carboxylic acids are compounds containing a carboxy group, that is, a carbonyl group with an attached hydroxy group. The systematic name for a carboxylic acid uses as the root the longest chain with the carboxy group at one end with the suffix -oic acid added. As with aldehydes, the chain is always numbered beginning with the carbon of the carboxy group.
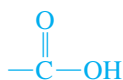
Carboxy group
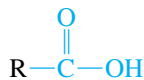
Carboxylic acid
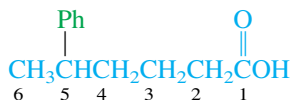
5-Phenylhexanoic acid
(Numbering always begins with the carboxy carbon.)

3-Butynoic acid

2-Chlorocyclopentanecarboxylic acid
(In similar fashion to the use of the -carbaldehyde suffix in naming aldehydes, cyclic compounds with the carboxy group attached to the ring use the name of the ring with the suffix -carboxylic acid.)

Because of their acidic character, carboxylic acids are relatively easy to isolate from natural sources. Thus, the number of carboxylic acids isolated early in the history of organic chemistry and given common names is quite large. Many of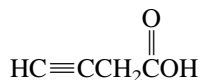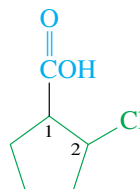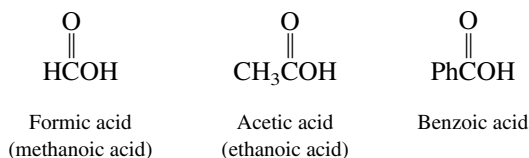 these common names have persisted in the organic literature. A few with which you should be familiar are formic acid, originally isolated from ants (Latin for ant is *formica*) and acetic acid, originally isolated from vinegar (Latin for vinegar is *acetum*). As mentioned earlier, the root for a four-carbon chain, but-, was derived from the common name for the four-carbon acid, butyric acid, which was isolated from rancid butter (Latin for butter is *butyrum*). Similarly, the root for a three-carbon chain, prop-, was derived from the common name for the three-carbon acid, propionic acid. This acid was considered to be the smallest one derived from fats and its name is derived from the Greek words *pro-* (first) and *pion* (fat). Aromatic carboxylic acids are named as derivatives of benzoic acid.

$$\underset{\substack{\text{Formic acid}\\ \text{(methanoic acid)}}}{\overset{\overset{\displaystyle O}{\|}}{HCOH}} \qquad \underset{\substack{\text{Acetic acid}\\ \text{(ethanoic acid)}}}{\overset{\overset{\displaystyle O}{\|}}{CH_3COH}} \qquad \underset{\substack{\text{Benzoic acid}}}{\overset{\overset{\displaystyle O}{\|}}{PhCOH}}$$

PROBLEM 12.11

Provide names for these compounds:
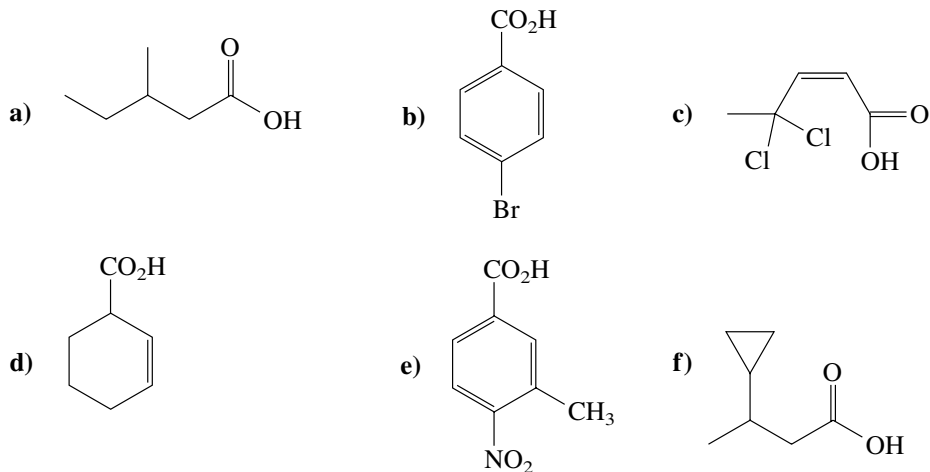
PROBLEM 12.12

Draw structures for these compounds:
a) 6-Bromo-3,5-dichlorohexanoic acid
b) Cyclobutanecarboxylic acid
c) *m*-Chlorobenzoic acid
d) (*E*)-3-Phenyl-2-propenoic acid

The carboxy group is more polar than a carbonyl group or a hydroxy group, and it can form hydrogen bonds to other carboxy groups. Therefore, carboxylic acids melt and boil at somewhat higher temperatures than alcohols of similar molecular weight. As was

the case with alcohols, the smaller carboxylic acids are miscible with water. As expected, their solubility decreases as the size of the hydrocarbon group increases.

PROBLEM 12.13

Hydrogen bonding is quite strong in the case of acetic acid and persists even in the gas phase where two molecules form a dimer held together by two hydrogen bonds. Suggest a structure for the hydrogen-bonded dimer of acetic acid.

Carboxylic acids are weak acids ($pK_a \approx 5$) and react by donating the proton attached to the oxygen of the carboxy group as illustrated in the following equation:
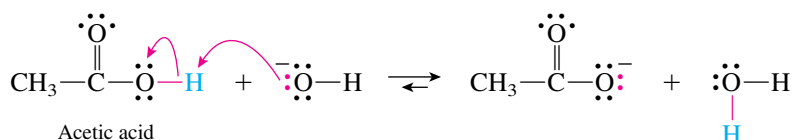
Acetic acid

Although carboxylic acids do occur naturally, they most often are found as their ester or amide derivatives. Acetic acid is a major industrial chemical, produced in excess of 3 billion pounds annually. Some acids, such as acetylsalicylic acid (aspirin) and ibuprofen, have found considerable use in the medical field.
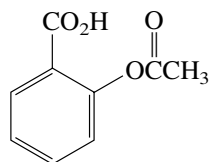
Acetylsalicylic acid
(aspirin)
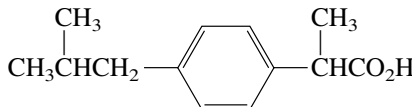
Ibuprofen

12.5   DERIVATIVES OF CARBOXYLIC ACIDS

Removal of the hydroxy group of a carboxylic acid leaves a carbonyl group with an attached alkyl group, which is called an **acyl group.** If the acyl group is bonded to a hydrogen, an aldehyde results. If it is bonded to a carbon, a ketone results. And if it is bonded to a hydroxy group, a carboxylic acid is produced. However, if the acyl group is bonded to another **heteroatom** (not C or H) group, such as Cl or NH_2, a series of compounds called carboxylic acid derivatives is produced. The most important of these, along with their names and the suffixes used in their nomenclature, are listed in Table 12.1.

Acyl group

Table 12.1   Carboxylic Acid Derivatives

Structure	Name of Functional Group	Suffix
$R-\overset{\overset{\displaystyle O}{\parallel}}{C}-Cl$	Acid chloride or acyl chloride	-yl chloride
$R-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-\overset{\overset{\displaystyle O}{\parallel}}{C}-R'$	Acid anhydride	-ic anhydride
$R-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-R'$	Ester	-ate
$R-\overset{\overset{\displaystyle O}{\parallel}}{C}-NH_2$	Amide	-amide
$R-C\equiv N$	Nitrile	-nitrile
$R-\overset{\overset{\displaystyle O}{\parallel}}{C}-O^-$	Carboxylate salt	-ate

Carboxylic acid derivatives are all named by using the same root as the carboxylic acid from which they are derived. Note that the root always begins with the carbon of the carbonyl group and this carbon is always given the number 1.

Acid chlorides (or **acyl chlorides**) result from substituting a chlorine for the hydroxy group of a carboxylic acid. Although other acid halides also exist, they are seldom encountered. Acid chlorides are named by replacing the -ic acid of the carboxylic acid name (either common or systematic) with -yl chloride.

$$CH_3\overset{\overset{\displaystyle O}{\parallel}}{C}-Cl \qquad\qquad CH_3CH\underset{4\quad\,\,\,3}{=}CH\underset{2}{C}\overset{\overset{\displaystyle O}{\parallel}}{}-\underset{1}{Cl}$$

Acetyl chloride
(ethanoyl chloride)

(The common and most used name for
the related carboxylic acid is acetic acid.
The -ic acid is replaced by -yl chloride.)

2-Butenoyl chloride

(The corresponding carboxylic acid is
2-butenoic acid.)

Acid anhydrides result from substituting the acyl group of one acid for the hydroxy hydrogen of another. They are called anhydrides because they can be viewed as resulting from the loss of water from two carboxylic acid molecules (removing H from one and OH from the other). Symmetrical anhydrides derived from two molecules of the

same carboxylic acid are most often encountered. These are simply named by replacing *acid* in the name of the carboxylic acid with *anhydride*.
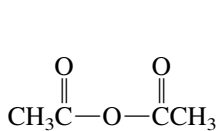

Acetic anhydride
(ethanoic anhydride)
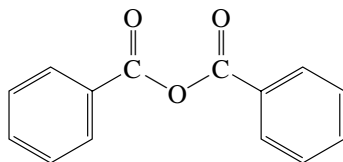
Benzoic anhydride

Esters can be viewed as resulting from the combination of a carboxylic acid with an alcohol, using the alkoxy (OR) group of the alcohol to replace the hydroxy (OH) group of the acid. The name must therefore designate both the alcohol part and the acid part of the ester. The name uses two separate words. First the R group of the alcohol is named just like other *groups* we have encountered, using a -yl suffix. This is the first word in the name. Then the acid part is named as usual, and the -ic acid suffix is re-placed with -ate. This is the second word in the name.
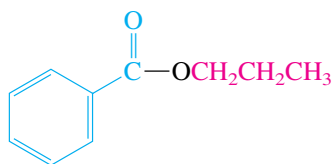
Propyl benzoate
(The red part of this ester is derived from the alcohol [propanol], and the blue part from the carboxylic acid [benzoic acid]. Be careful to correctly identify which part of each ester comes from the acid and which from the alcohol. Note that *propyl* and *benzoate* are separate words.)
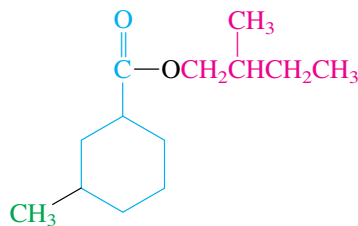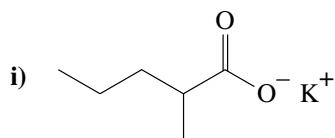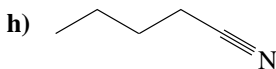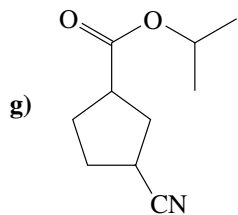
(2-Methylbutyl) 3-methylcyclohexanecarboxylate
(The complex group from the alcohol portion of the ester is named in the same manner as the complex groups of alkanes.)

Amides can be viewed as resulting from the replacement of the OH of a carboxylic acid with an NH_2 (primary amide), NHR (secondary amide), or NR_2 (tertiary amide) group. To name an amide, the longest carbon chain having the carbonyl group at one terminus is chosen as the root, as usual. Systematic names are formed by replacing the final -e of the *hydrocarbon name* for this root with -amide. Amide names can also be derived from common names of acids by replacing -ic acid or -oic acid with -amide. Other groups attached to the nitrogen are designated with the prefix *N*-, as was done in the case of amines.

$$CH_3CH_2CH_2CH_2C-NH_2$$
(with O double bonded to C)

Pentanamide
a primary amide
(This name is derived from the five carbon hydrocarbon, pentane.)

$$CH_2=CHCHCH=CHCNHCH_2CH_3$$
6   5   4   3   2   1
(with CH$_3$ above carbon 4, and O above carbonyl C)

N-Ethyl-4-methyl-2,5-hexadienamide
or N-ethyl-4-methylhexa-2,5-dienamide
a secondary amide
(Note the N- that is used to show that the ethyl group is bonded to the nitrogen.)

$$H-C-N-CH_3$$
(with O double bonded to C, and CH$_3$ on N)

N,N-Dimethylformamide
(DMF), a tertiary amide
(The common name for the one-carbon carboxylic acid is formic acid.)

On first consideration, **nitriles** do not appear to be related to the other carboxylic acid derivatives because they have no acyl group. However, they can be viewed as resulting from the removal of H_2O from a primary amide (loss of both H's from the N and the O from the carbonyl group), and their chemical reactions are related to other carboxylic acid derivatives. Therefore, it is convenient to include them with the other carboxylic acid derivatives. They are named in a similar manner to amides; that is, -nitrile is appended to the hydrocarbon name. (Do not forget to count the carbon of the —CN group and to give this carbon the number 1.) Common names are obtained from the common name of the carboxylic acid by replacing the -ic acid or -oic acid with -onitrile. In complex compounds the —CN group can be named as a cyano group.

$$CH_3C \equiv CCH_2C \equiv N$$
5   4   3 2   1

3-Pentynenitrile
(This is a systematic name. Because the C of the CN must be given the number 1, the related hydrocarbon is 3-pentyne.)

Benzonitrile
(The related carboxylic acid is benzoic acid.)

Methyl 4-cyanobenzoate
(In a complex compound like this, with more than one functional group, the —CN is named as a substituent group, a cyano group, attached to the root in the same manner as a halogen.)

Carboxylate salts consist of a carboxylate anion (the anion formed by removal of the proton from the OH of a carboxylic acid) and a cation. They are named in a manner similar to esters, using two words. The first word designates the cation. The second word designates the carboxylate anion, using the -ate suffix, just as is done for esters.

$$CH_3C-O^- \ Na^+$$
(with O double bonded to C)

Sodium acetate

$$C-O^- \ NH_4^+$$
(benzene ring with CH$_3$ substituent, and O double bonded to C)

Ammonium 3-methylbenzoate

PROBLEM 12.14

Provide names for these compounds:

a)

b) $CH_3CH_2COCCH_2CH_3$ (with two C=O groups)

c) $CH_3CH_2COCH_3$ (with C=O)

d)

e)

f)

g)

h)

i)

PROBLEM 12.15

Draw structures for these compounds:

a) Propanoyl chloride
b) *N,N*-Dimethylacetamide
c) Pentanoic anhydride
d) Sodium *p*-nitrobenzoate
e) Hexanamide
f) Isopropyl acetate
g) Benzyl benzoate
h) Ethyl cyclopentanecarboxylate
i) 3-Chlorobenzonitrile
j) 3-Methylheptanenitrile

Acid chlorides, acid anhydrides, and esters all contain the carbonyl group but the presence of this polar group has only a small effect on their melting and boiling points. Amides, however, are considerably more polar because of the significant contribution of a charged resonance structure to the resonance hybrid. In addition, primary and secondary amides, with hydrogens bonded to the nitrogen, can also form hydrogen bonds

among themselves. For these reasons, amides melt and boil at even higher temperatures than do carboxylic acids of similar molecular mass.

$$R-\overset{\overset{\displaystyle \cdot\cdot\\ \cdot O \cdot}{\|}}{C}-NH_2 \longleftrightarrow R-\overset{\overset{\displaystyle :\overset{\cdot\cdot}{O}:^-}{|}}{C}=\overset{+}{N}H_2$$
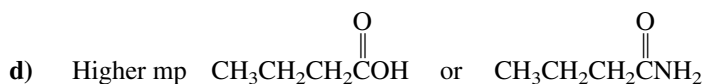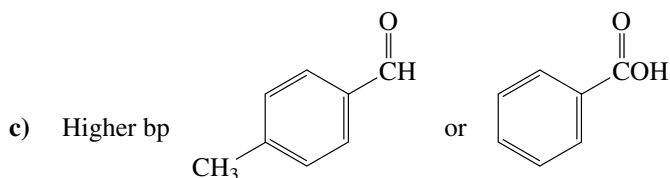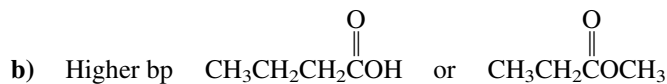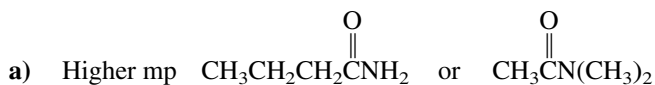
An amide

Table 12.2 lists the melting points and boiling points of a series of compounds of nearly identical molecular mass but containing a variety of different functional groups. Note the increase in the melting point and boiling point that occurs when the polar carbonyl group is introduced. The effect is small (or may be absent) for the ester but is more significant for the aldehyde and ketone, especially on their boiling points. There is an additional increase in the boiling point for the alcohol due to hydrogen bonding and a further increase in the melting and boiling points of the carboxylic acid due to its polar, hydrogen-bonding carboxy group. Finally, the amide has the highest melting and boiling points because of its highly polar nature in combination with its ability to form hydrogen bonds.

Table 12.2   Comparison of the Effect of Functional Groups on Melting and Boiling Points of Compounds of Comparable Molecular Mass

Structure	Functional Group	mp (°C)	bp (°C)
$CH_3CH_2CH_2CH_2CH_3$	Alkane	−130	36
$CH_3CH_2OCH_2CH_3$	Ether	−116	35
$CH_3\overset{\overset{\displaystyle O}{\|}}{C}OCH_3$	Ester	−98	57
$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}H$	Aldehyde	−99	76
$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3$	Ketone	−86	80
$CH_3CH_2CH_2CH_2OH$	Alcohol	−90	117
$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH$	Carboxylic acid	−21	141
$CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}NH_2$	Amide	81	213

PROBLEM 12.16

Explain which compound has the higher melting point or boiling point:

a)   Higher mp $CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}NH_2$ or $CH_3\overset{\overset{\displaystyle O}{\|}}{C}N(CH_3)_2$

b)   Higher bp $CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH$ or $CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}OCH_3$

c)   Higher bp

[structure: 4-methylbenzaldehyde with CH group and O]   or   [structure: benzoic acid, COH with O]

d)   Higher mp $CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH$ or $CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}NH_2$

In general, acid chlorides and acid anhydrides are too reactive to occur naturally, and nitriles are rare in nature. Esters and amides, on the other hand, are very common. Many esters have pleasant odors, often sweet or fruity, and are responsible for the fragrant odors of fruits and flowers. They are components of many flavorings, both natural and artificial. For example, isopentyl acetate has a strong banana odor, and methyl butanoate is used as an artificial rum flavoring. Typical fats are triesters formed from long-chain "fatty" acids and the triol glycerol.
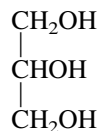
$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3 \qquad CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3$$

Isopentyl acetate   Methyl butanoate

[structure: A fat — glycerol triester with three $C(CH_2)_{16}CH_3$ chains]
CH_2—O—$\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_{16}CH_3$
CH—O—$\overset{\overset{\displaystyle O}{\|}}{C}(CH_2)_{16}CH_3$
CH_2—O—$\overset{\underset{\displaystyle O}{\|}}{C}(CH_2)_{16}CH_3$

CH_2OH
$CHOH$
CH_2OH
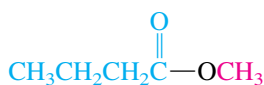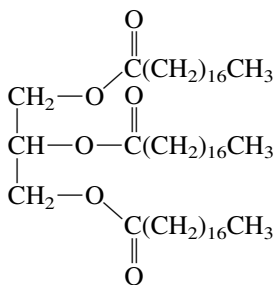
A fat   Glycerol

Amides often have pronounced physiological activity; acetaminophen, a common pain reliever, and the diethyl amide of lysergic acid (LSD), a hallucinogen, are two ex-

amples. The important peptide bond of proteins is actually an amide bond. Dimethyl-formamide (DMF) and dimethylacetamide (DMA) are important solvents in the organic laboratory. They are highly polar and are capable of dissolving many ionic reagents in addition to less polar organic compounds. They are fairly unreactive because the bond between the carbonyl group and the nitrogen of an amide is reasonably strong, and they do not have hydrogens on the nitrogens that might react as acids. They are especially good solvents for S_N2 reactions because they are aprotic.
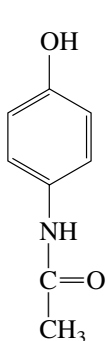
Acetaminophen
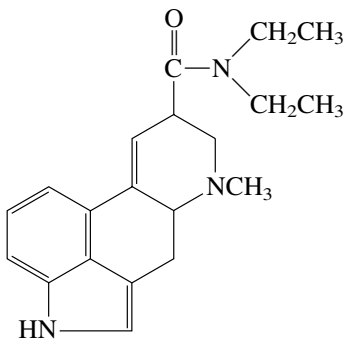
Lysergic acid diethylamide
(LSD)
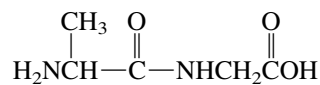
A dipeptide

Dimethylformamide
(DMF)
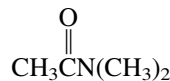
Dimethylacetamide
(DMA)

Focus On

Fragrant Organic Compounds

Many organic compounds have very powerful odors. Some of these odors are dis-agreeable; others are pleasant. This is especially true of esters, which often have fruity odors, and aldehydes and ketones, many of which have floral odors. In fact, aldehydes, ketones, and esters, with relatively simple structures, are major components of numer-ous natural scents and flavors. These natural materials are usually extremely complex mixtures, sometimes containing hundreds of compounds. Artificial scents and flavors usually contain fewer components, but many still have complex recipes consisting of dozens of ingredients. Isopentyl acetate (banana) and methyl butanoate (rum) are ex-amples of fragrant esters that were mentioned earlier. Other examples include isopen-tenyl acetate, the flavoring used in Juicy Fruit gum; ethyl phenylacetate, which has a honey odor; methyl salicylate, a major component of oil of wintergreen; and benzyl ac-etate, which composes more than 60% of jasmine oil. Coumarin has an odor that is of-

ten described as "new-mown hay" or "woody" and is used in men's toiletries. Along with vanillin (see page 477), it is a component of natural vanilla. A combination of these two compounds, prepared synthetically in the laboratory, is used in artificial vanilla, and the flavoring in cream soda consists of coumarin and vanillin.

Isopentenyl acetate
(Juicy Fruit gum)

Ethyl phenylacetate
(honey)

Methyl salicylate
(wintergreen)

Benzyl acetate
(jasmine)

Coumarin
(new-mown hay)
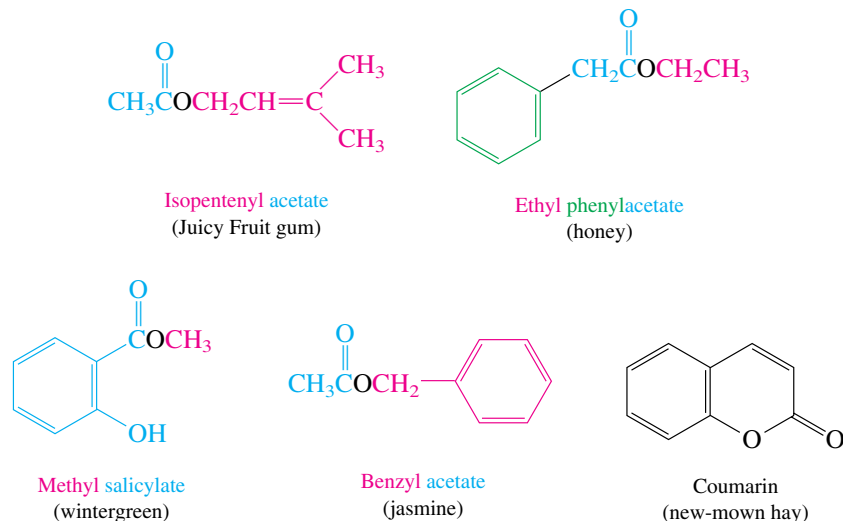
Although many esters are used in artificial flavorings, they are less often employed as ingredients of perfumes because they are slowly hydrolyzed to a carboxylic acid and an alcohol on the skin, as shown in the following equation:
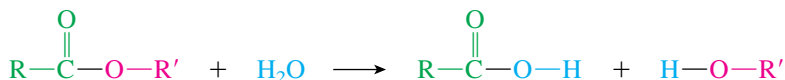
This is quite undesirable in a perfume because many carboxylic acids have objectionable odors. For example, the sharp, penetrating odor of vinegar is due to acetic acid, butanoic acid (butyric acid) smells like rancid butter, and 2-methylpropanoic acid (isobutyric acid) is a component of sweat. A common name for hexanoic acid is caproic acid, derived from the Latin word *caper,* which means goat. If you have ever been around goats, perhaps you can imagine the odor of hexanoic acid.

Butanoic acid
(butyric acid)
(rancid butter)

2-Methylpropanoic acid
(isobutyric acid)
(sweat)

Hexanoic acid
(caproic acid)
(goat)
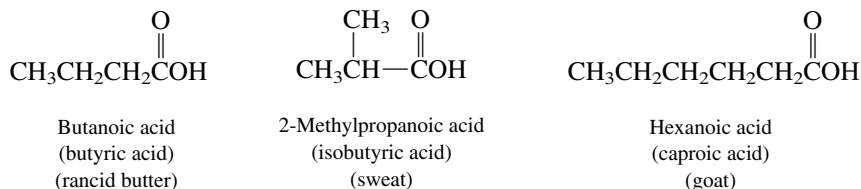
Aldehydes and ketones are also important components of many fragrances and flavors. For example, butanal (butyraldehyde) is used to impart a buttery flavor to margarine and other foods. Because aldehydes are slowly oxidized to carboxylic acids by the oxygen of air, it is readily apparent how the odor of rancid butter arises. Although α-pentylcinnamaldehyde does not occur naturally, it has been found to have a powerful jasmine odor and is used in many perfumes and soaps. α-Ionone is a naturally oc-

Continued

curring ketone with an odor resembling violets. Many large-ring ketones have a musky odor and are prized ingredients in perfumes. Muscone (see page 477), which was first isolated from the musk deer, has a 15-membered ring, and civetone, from the civet cat, has a 17-membered ring. These compounds were extremely expensive when they could only be obtained from natural sources. Once their structures were determined, they were prepared in the laboratory. Although the preparation of such large rings is difficult, these synthetic materials are still considerably less expensive than their natural counterparts. Other fragrant aldehydes and ketones are mentioned on pages 476–477.
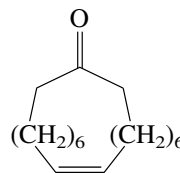

Butanal
butyraldehyde
(buttery)
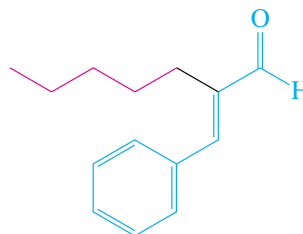
α-Pentylcinnamaldehyde
(jasmine)
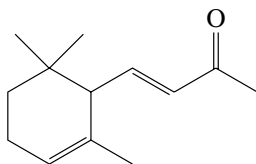
α-Ionone
(violets)

Civetone
(musky)

12.6 SULFUR AND PHOSPHORUS COMPOUNDS

Sulfur occurs directly beneath oxygen in the periodic table, and, like oxygen, it often exhibits a valence of two. Therefore, sulfur analogs of alcohols and ethers are often encountered. However, because sulfur is in the third period of the periodic table, it can also have a higher valence. Structures with four or six bonds to a sulfur are common. In organic chemistry the most important of these "expanded valence" compounds have the sulfur bonded to one or two extra oxygens.

Similarly, phosphorus occurs directly beneath nitrogen in the periodic table and therefore often exhibits a valence of three. Again, structures with an expanded valence, having five bonds to the phosphorus, are common, especially when the extra bonds are to oxygen. This book is not concerned with all the possible sulfur and phosphorus compounds, nor does it spend much time on their nomenclature. Instead, it concentrates on those of most importance in organic chemistry and biochemistry. Let's begin with a discussion of some common sulfur compounds.