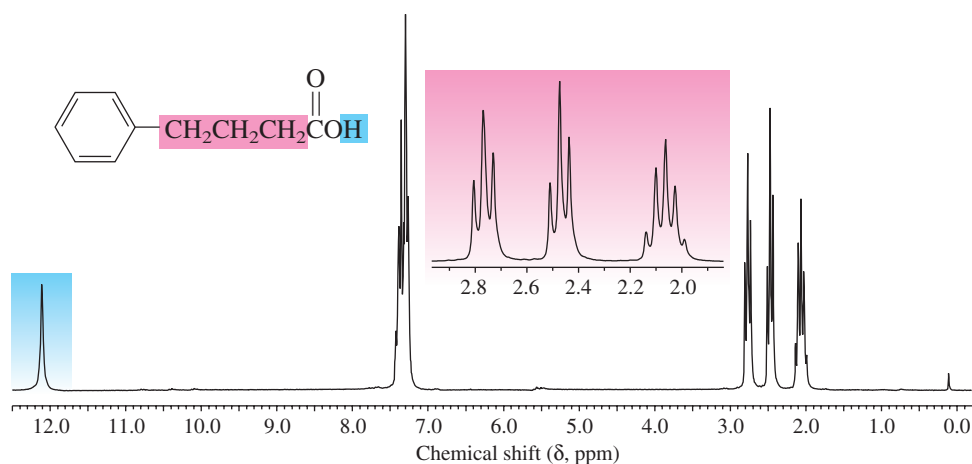
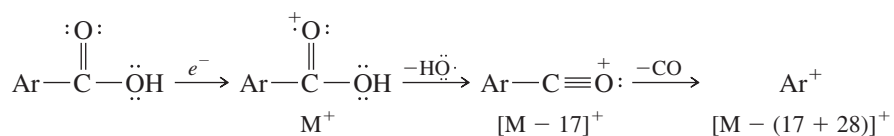


**FIGURE 19.9**

The 200-MHz  $^1\text{H}$  NMR spectrum of 4-phenylbutanoic acid. The peak for the proton of the  $\text{CO}_2\text{H}$  group is at  $\delta$  12.

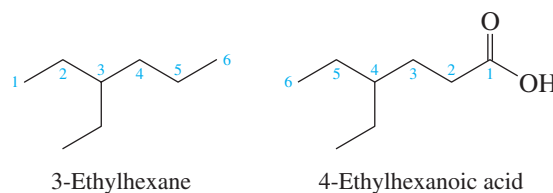


**Mass Spectrometry:** Aside from a peak for the molecular ion, which is normally easy to pick out, aliphatic carboxylic acids undergo a variety of fragmentation processes. The dominant fragmentation in aromatic acids corresponds to loss of OH, then loss of CO.

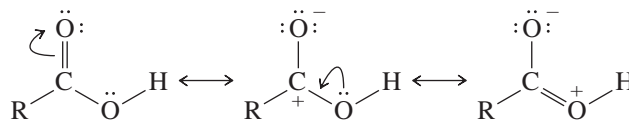


## 19.19 SUMMARY

**Section 19.1** Carboxylic acids take their names from the alkane that contains the same number of carbons as the longest continuous chain that contains the  $-\text{CO}_2\text{H}$  group. The *-e* ending is replaced by *-oic acid*. Numbering begins at the carbon of the  $-\text{CO}_2\text{H}$  group.

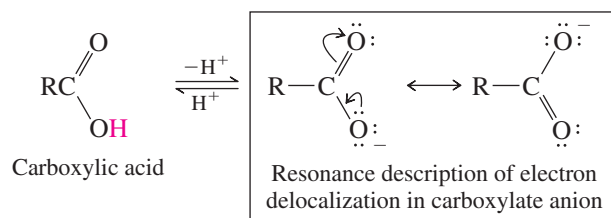


**Section 19.2** Like the carbonyl group of aldehydes and ketones, the carbon of a  $\text{C}=\text{O}$  unit in a carboxylic acid is  $sp^2$ -hybridized. Compared with the carbonyl group of an aldehyde or ketone, the  $\text{C}=\text{O}$  unit of a carboxylic acid receives an extra degree of stabilization from its attached OH group.

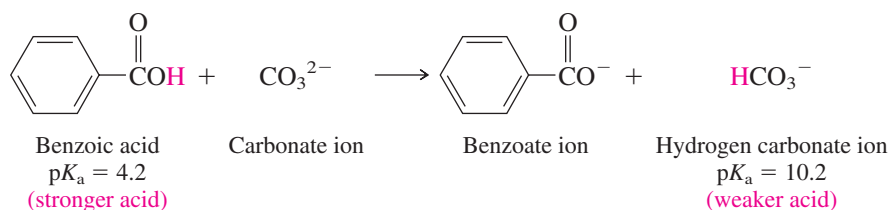


**Section 19.3** Hydrogen bonding in carboxylic acids raises their melting points and boiling points above those of comparably constituted alkanes, alcohols, aldehydes, and ketones.

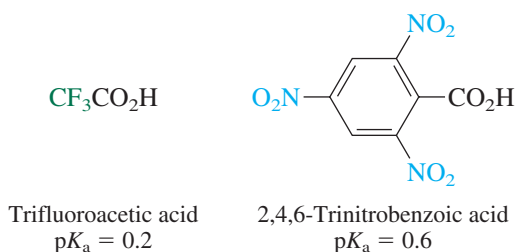
**Section 19.4** Carboxylic acids are weak acids and, in the absence of electron-attracting substituents, have  $\text{p}K_a$ 's of approximately 5. Carboxylic acids are much stronger acids than alcohols because of the electron-withdrawing power of the carbonyl group (inductive effect) and its ability to delocalize negative charge in the carboxylate anion (resonance effect).



Section 19.5 Although carboxylic acids dissociate to only a small extent in water, they are deprotonated almost completely in basic solution.

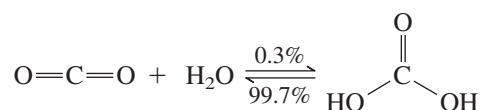


Sections 19.6–19.7 Electronegative substituents, especially those within a few bonds of the carboxyl group, increase the acidity of carboxylic acids.



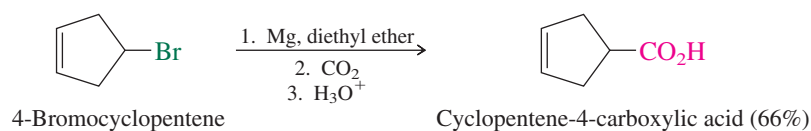
Section 19.8 Dicarboxylic acids have separate  $pK_a$  values for their first and second ionizations.

Section 19.9 Carbon dioxide and carbonic acid are in equilibrium in water. Carbon dioxide is the major component.

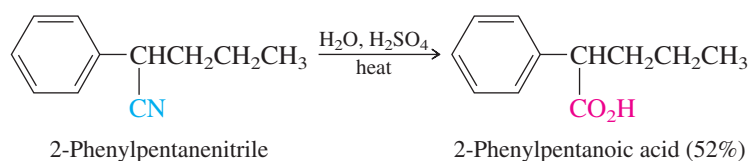


Section 19.10 Several of the reactions introduced in earlier chapters can be used to prepare carboxylic acids (Table 19.4).

Section 19.11 Carboxylic acids can be prepared by the reaction of Grignard reagents with carbon dioxide.



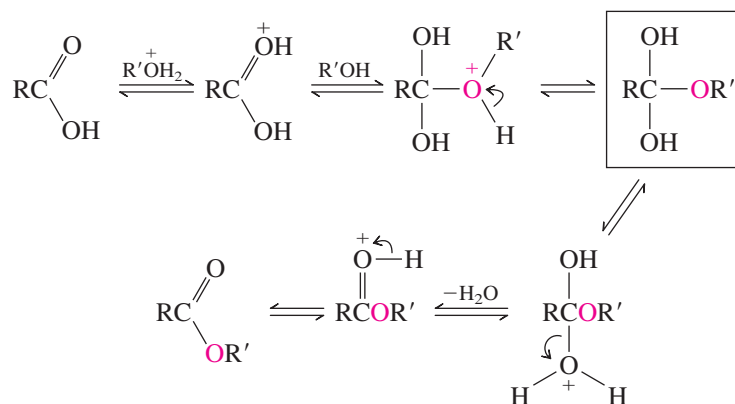
Section 19.12 Nitriles are prepared from primary and secondary alkyl halides by nucleophilic substitution with cyanide ion and can be converted to carboxylic acids by hydrolysis.



Likewise, the cyano group of a cyanohydrin can be hydrolyzed to  $-CO_2H$ .

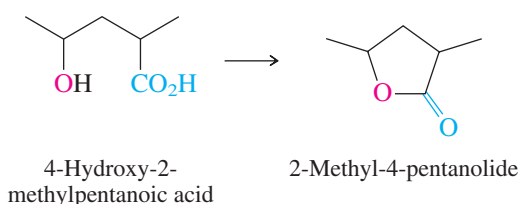
Section 19.13 Among the reactions of carboxylic acids, their conversions to acyl chlorides, primary alcohols, and esters were introduced in earlier chapters and were reviewed in Table 19.5.

Section 19.14 The mechanism of acid-catalyzed esterification involves some key features that are fundamental to the chemistry of carboxylic acids and their derivatives.

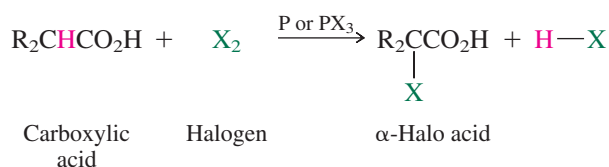


Protonation of the carbonyl oxygen activates the carbonyl group toward nucleophilic addition. Addition of an alcohol gives a tetrahedral intermediate (shown in the box in the preceding equation), which has the capacity to revert to starting materials or to undergo dehydration to yield an ester.

Section 19.15 An intramolecular esterification can occur when a molecule contains both a hydroxyl and a carboxyl group. Cyclic esters are called *lactones* and are most stable when the ring is five- or six-membered.

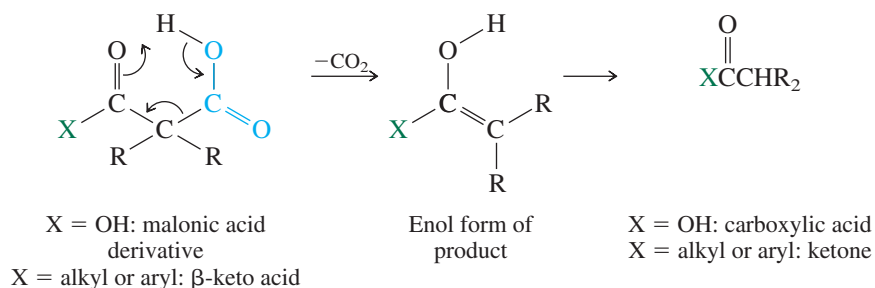


Section 19.16 Halogenation at the  $\alpha$ -carbon atom of carboxylic acids can be accomplished by the *Hell-Volhard-Zelinsky reaction*. An acid is treated with chlorine or bromine in the presence of a catalytic amount of phosphorus or a phosphorus trihalide:



This reaction is of synthetic value in that  $\alpha$ -halo acids are reactive substrates in nucleophilic substitution reactions.

Section 19.17 1,1-Dicarboxylic acids (malonic acids) and  $\beta$ -keto acids undergo thermal decarboxylation by a mechanism in which a  $\beta$ -carbonyl group assists the departure of carbon dioxide.



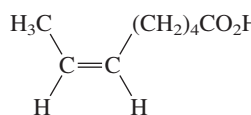
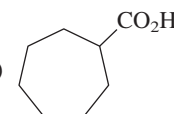
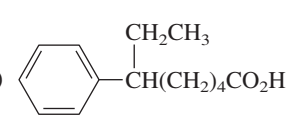
Section 19.18 Carboxylic acids are readily identified by the presence of strong IR absorptions near  $1700\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ) and between  $2500$  and  $3500\text{ cm}^{-1}$  ( $\text{OH}$ ), a  $^1\text{H}$  NMR signal for the hydroxyl proton at  $\delta$  10–12, and a  $^{13}\text{C}$  signal for the carbonyl carbon near  $\delta$  180.

## PROBLEMS

**19.13** Many carboxylic acids are much better known by their common names than by their systematic names. Some of these follow. Provide a structural formula for each one on the basis of its systematic name.

- 2-Hydroxypropanoic acid (better known as *lactic acid*, it is found in sour milk and is formed in the muscles during exercise)
- 2-Hydroxy-2-phenylethanoic acid (also known as *mandelic acid*, it is obtained from plums, peaches, and other fruits)
- Tetradecanoic acid (also known as *myristic acid*, it can be obtained from a variety of fats)
- 10-Undecenoic acid (also called *undecylenic acid*, it is used, in combination with its zinc salt, to treat fungal infections such as athlete's foot)
- 3,5-Dihydroxy-3-methylpentanoic acid (also called *mevalonic acid*, it is an important intermediate in the biosynthesis of terpenes and steroids)
- (*E*)-2-Methyl-2-butenoic acid (also known as *tiglic acid*, it is a constituent of various natural oils)
- 2-Hydroxybutanedioic acid (also known as *malic acid*, it is found in apples and other fruits)
- 2-Hydroxy-1,2,3-propanetricarboxylic acid (better known as *citric acid*, it contributes to the tart taste of citrus fruits)
- 2-(*p*-Isobutylphenyl)propanoic acid (an antiinflammatory drug better known as *ibuprofen*)
- o*-Hydroxybenzenecarboxylic acid (better known as *salicylic acid*, it is obtained from willow bark)

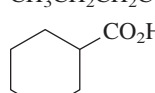
**19.14** Give an acceptable IUPAC name for each of the following:

- $\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{H}$
- $\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{K}$
- $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CO}_2\text{H}$
- 
- $\text{HO}_2\text{C}(\text{CH}_2)_6\text{CO}_2\text{H}$
- $\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{CO}_2\text{H})_2$
- 
- 

**19.15** Rank the compounds in each of the following groups in order of decreasing acidity:

- Acetic acid, ethane, ethanol
- Benzene, benzoic acid, benzyl alcohol
- Propanedial, 1,3-propanediol, propanedioic acid, propanoic acid
- Acetic acid, ethanol, trifluoroacetic acid, 2,2,2-trifluoroethanol, trifluoromethanesulfonic acid ( $\text{CF}_3\text{SO}_2\text{OH}$ )
- Cyclopentanecarboxylic acid, 2,4-pentanedione, cyclopentanone, cyclopentene

**19.16** Identify the more acidic compound in each of the following pairs:

- $\text{CF}_3\text{CH}_2\text{CO}_2\text{H}$  or  $\text{CF}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$  or  $\text{CH}_3\text{C}\equiv\text{CCO}_2\text{H}$
- 
 or
 