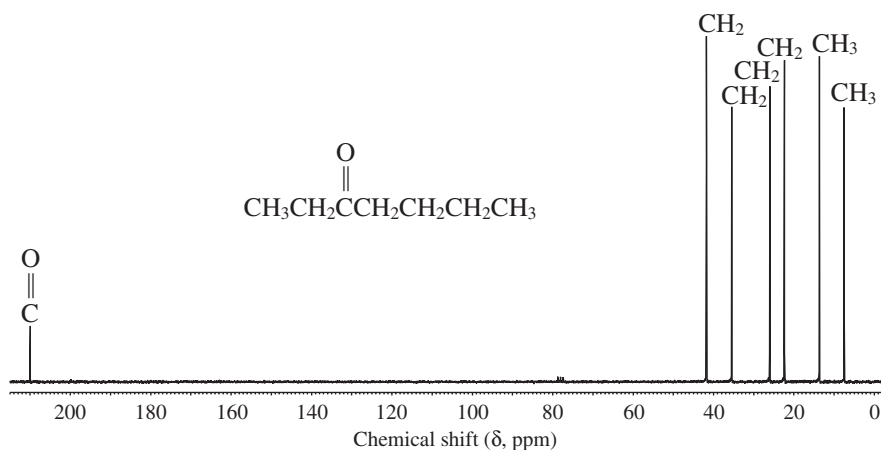
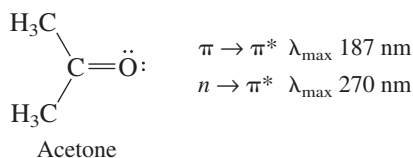


FIGURE 17.14

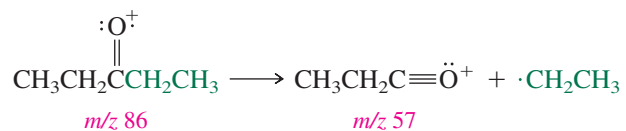
The ^{13}C NMR spectrum of 3-heptanone. Each signal corresponds to a single carbon. The carbonyl carbon is the least shielded and appears at δ 210.



more strongly held than the lone-pair electrons, the $\pi \rightarrow \pi^*$ transition is of higher energy and shorter wavelength than the $n \rightarrow \pi^*$ transition. For simple aldehydes and ketones, the $\pi \rightarrow \pi^*$ transition is below 200 nm and of little use in structure determination. The $n \rightarrow \pi^*$ transition, although weak, is of more diagnostic value.



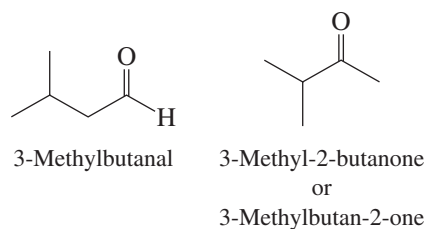
Mass Spectrometry: Aldehydes and ketones typically give a prominent molecular ion peak in their mass spectra. Aldehydes also exhibit an M-1 peak. A major fragmentation pathway for both aldehydes and ketones leads to formation of acyl cations (acylium ions) by cleavage of an alkyl group from the carbonyl. The most intense peak in the mass spectrum of diethyl ketone, for example, is m/z 57, corresponding to loss of ethyl radical from the molecular ion.



17.18 SUMMARY

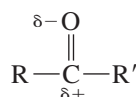
The chemistry of the carbonyl group is probably the single most important aspect of organic chemical reactivity. Classes of compounds that contain the carbonyl group include many derived from carboxylic acids (acyl chlorides, acid anhydrides, esters, and amides) as well as the two related classes discussed in this chapter: *aldehydes* and *ketones*.

Section 17.1 The substitutive IUPAC names of aldehydes and ketones are developed by identifying the longest continuous chain that contains the carbonyl group and replacing the final *-e* of the corresponding alkane by *-al* for aldehydes and *-one* for ketones. The chain is numbered in the direction that gives the lowest locant to the carbon of the carbonyl group.



Ketones may also be named using functional class IUPAC nomenclature by citing the two groups attached to the carbonyl in alphabetical order followed by the word *ketone*. Thus, 3-methyl-2-butanone (substitutive) becomes isopropyl methyl ketone (functional class).

Section 17.2 The carbonyl carbon is sp^2 -hybridized, and it and the atoms attached to it are coplanar. Aldehydes and ketones are polar molecules. Nucleophiles attack $C=O$ at carbon (positively polarized) and electrophiles, especially protons, attack oxygen (negatively polarized).



Section 17.3 Aldehydes and ketones have higher boiling points than hydrocarbons, but have lower boiling points than alcohols.

Section 17.4 The numerous reactions that yield aldehydes and ketones discussed in earlier chapters and reviewed in Table 17.1 are sufficient for most syntheses.

Sections 17.5–17.13 The characteristic reactions of aldehydes and ketones involve *nucleophilic addition* to the carbonyl group and are summarized in Table 17.5. Reagents of the type HY react according to the general equation

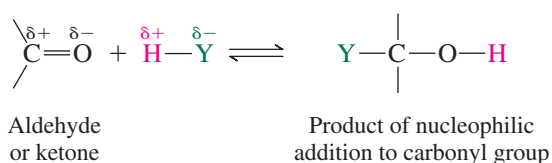


TABLE 17.5 Nucleophilic Addition to Aldehydes and Ketones

Reaction (section) and comments	General equation and typical example
Hydration (Section 17.6) Can be either acid- or base-catalyzed. Equilibrium constant is normally unfavorable for hydration of ketones unless R, R', or both are strongly electron-withdrawing.	$\begin{array}{c} \text{O} \\ \\ \text{RCR}' \end{array} + \text{H}_2\text{O} \rightleftharpoons \begin{array}{c} \text{OH} \\ \\ \text{RCR}' \\ \\ \text{OH} \end{array}$ <p style="text-align: center;">Aldehyde or ketone Water Geminal diol</p> $\begin{array}{c} \text{O} \\ \\ \text{ClCH}_2\text{CCH}_3 \end{array} \xrightleftharpoons{\text{H}_2\text{O}} \begin{array}{c} \text{OH} \\ \\ \text{ClCH}_2\text{CCH}_3 \\ \\ \text{OH} \end{array}$ <p style="text-align: center;">Chloroacetone (90% at equilibrium) Chloroacetone hydrate (10% at equilibrium)</p>
Cyanohydrin formation (Section 17.7) Reaction is catalyzed by cyanide ion. Cyanohydrins are useful synthetic intermediates; cyano group can be hydrolyzed to $-\text{CO}_2\text{H}$ or reduced to $-\text{CH}_2\text{NH}_2$.	$\begin{array}{c} \text{O} \\ \\ \text{RCR}' \end{array} + \text{HCN} \rightleftharpoons \begin{array}{c} \text{OH} \\ \\ \text{RCR}' \\ \\ \text{CN} \end{array}$ <p style="text-align: center;">Aldehyde or ketone Hydrogen cyanide Cyanohydrin</p> $\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_2\text{CH}_3 \xrightarrow[\text{H}^+]{\text{KCN}} \begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_3 \\ \\ \text{CN} \end{array}$ <p style="text-align: center;">3-Pentanone 3-Pentanone cyanohydrin (75%)</p>

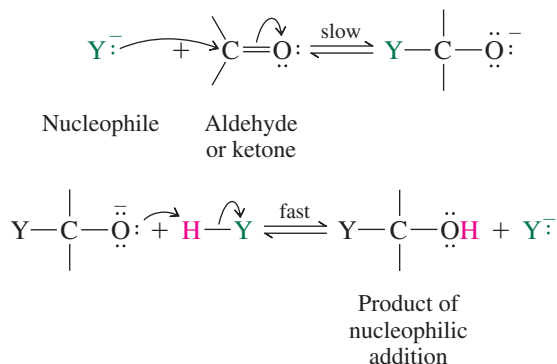
—Continued

TABLE 17.5 Nucleophilic Addition to Aldehydes and Ketones (Continued)

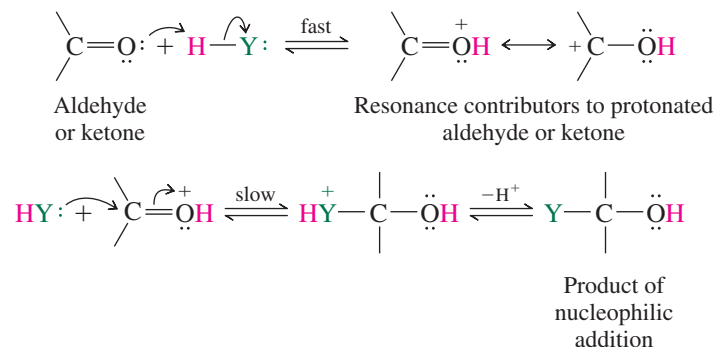
Reaction (section) and comments	General equation and typical example
<p>Acetal formation (Sections 17.8–17.9) Reaction is acid-catalyzed. Equilibrium constant normally favorable for aldehydes, unfavorable for ketones. Cyclic acetals from vicinal diols form readily.</p>	$\text{RCR}' + 2\text{R}''\text{OH} \xrightleftharpoons{\text{H}^+} \begin{array}{c} \text{OR}'' \\ \\ \text{RCR}' \\ \\ \text{OR}'' \end{array} + \text{H}_2\text{O}$ <p>Aldehyde or ketone Alcohol Acetal Water</p> <p><i>m</i>-Nitrobenzaldehyde Methanol <i>m</i>-Nitrobenzaldehyde dimethyl acetal (76–85%)</p>
<p>Reaction with primary amines (Section 17.10) Isolated product is an imine (Schiff's base). A carbinolamine intermediate is formed, which undergoes dehydration to an imine.</p>	$\text{RCR}' + \text{R}''\text{NH}_2 \rightleftharpoons \begin{array}{c} \text{NR}'' \\ \\ \text{RCR}' \end{array} + \text{H}_2\text{O}$ <p>Aldehyde or ketone Primary amine Imine Water</p> <p>2-Methylpropanal <i>tert</i>-Butylamine <i>N</i>-(2-Methyl-1-propylidene)-<i>tert</i>-butylamine (50%)</p>
<p>Reaction with secondary amines (Section 17.11) Isolated product is an enamine. Carbinolamine intermediate cannot dehydrate to a stable imine.</p>	$\text{RCCH}_2\text{R}' + \text{R}''_2\text{NH} \rightleftharpoons \begin{array}{c} \text{R}''\text{NR}'' \\ \\ \text{RC}=\text{CHR}' \end{array} + \text{H}_2\text{O}$ <p>Aldehyde or ketone Secondary amine Enamine Water</p> <p>Cyclohexanone Morpholine 1-Morpholinocyclohexene (85%)</p>
<p>The Wittig reaction (Sections 17.12–17.13) Reaction of a phosphorus ylide with aldehydes and ketones leads to the formation of an alkene. A versatile method for the regiospecific preparation of alkenes.</p>	$\text{RCR}' + (\text{C}_6\text{H}_5)_3\text{P}^+-\text{C}^-(\text{A})(\text{B}) \longrightarrow \begin{array}{c} \text{R} \quad \text{A} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{R}' \quad \text{B} \end{array} + (\text{C}_6\text{H}_5)_3\text{P}^+-\text{O}^-$ <p>Aldehyde or ketone Wittig reagent (an ylide) Alkene Triphenylphosphine oxide</p> <p>Acetone 1-Pentylidetriphenylphosphorane 2-Methyl-2-heptene (56%) Triphenylphosphine oxide</p>

Aldehydes undergo nucleophilic addition more readily and have more favorable equilibrium constants for addition than do ketones.

The step in which the nucleophile attacks the carbonyl carbon is rate-determining in both base-catalyzed and acid-catalyzed nucleophilic addition. In the base-catalyzed mechanism this is the first step.

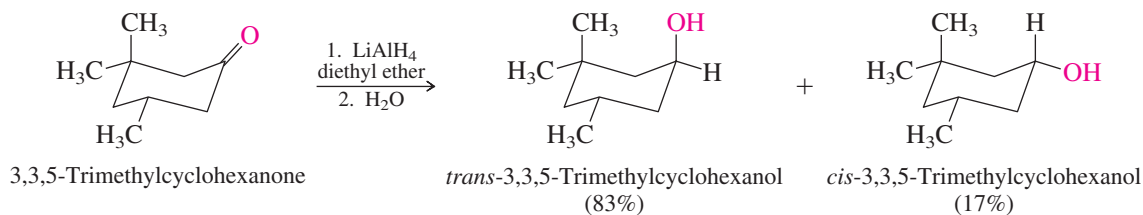


Under conditions of acid catalysis, the nucleophilic addition step follows protonation of the carbonyl oxygen. Protonation increases the carbocation character of a carbonyl group and makes it more electrophilic.

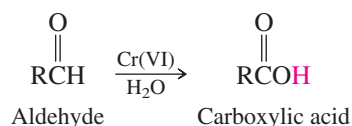


Often the product of nucleophilic addition is not isolated but is an intermediate leading to the ultimate product. Most of the reactions in Table 17.5 are of this type.

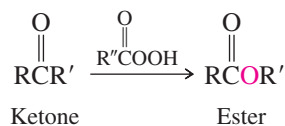
Section 17.14 Nucleophilic addition to the carbonyl group is *stereoselective*. When one direction of approach to the carbonyl group is less hindered than the other, the nucleophile normally attacks at the less hindered face.



Section 17.15 Aldehydes are easily oxidized to carboxylic acids.



Section 17.16 The oxidation of ketones with peroxy acids is called the *Baeyer-Villiger oxidation* and is a useful method for preparing esters.

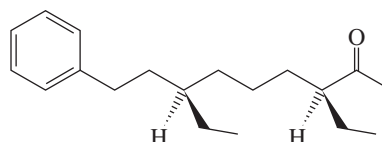


Section 17.17 A strong peak near 1700 cm^{-1} in the IR spectrum is characteristic of compounds that contain a $\text{C}=\text{O}$ group. The ^1H and ^{13}C NMR spectra of aldehydes and ketones are affected by the deshielding of a $\text{C}=\text{O}$ group. The proton of an $\text{H}-\text{C}=\text{O}$ group appears in the δ 8–10 range. The carbon of a $\text{C}=\text{O}$ group is at δ 190–210.

PROBLEMS

- 17.22** (a) Write structural formulas and provide IUPAC names for all the isomeric aldehydes and ketones that have the molecular formula $\text{C}_5\text{H}_{10}\text{O}$. Include stereoisomers.
 (b) Which of the isomers in part (a) yield chiral alcohols on reaction with sodium borohydride?
 (c) Which of the isomers in part (a) yield chiral alcohols on reaction with methylmagnesium iodide?
- 17.23** Each of the following aldehydes or ketones is known by a common name. Its substitutive IUPAC name is provided in parentheses. Write a structural formula for each one.
- Chloral (2,2,2-trichloroethanal)
 - Pivaldehyde (2,2-dimethylpropanal)
 - Acrolein (2-propenal)
 - Crotonaldehyde [(*E*)-2-butenal]
 - Citral [(*E*)-3,7-dimethyl-2,6-octadienal]
 - Diacetone alcohol (4-hydroxy-4-methyl-2-pentanone)
 - Carvone (5-isopropenyl-2-methyl-2-cyclohexenone)
 - Biacetyl (2,3-butanedione)

17.24 The African dwarf crocodile secretes a volatile substance believed to be a sex pheromone. It is a mixture of two stereoisomers, one of which is shown:



- Give the IUPAC name for this compound, including *R* and *S* descriptors for its chirality centers.
 - One component of the scent substance has the *S* configuration at both chirality centers. How is this compound related to the one shown? Are the compounds enantiomers, or diastereomers?
- 17.25** Predict the product of the reaction of propanal with each of the following:
- Lithium aluminum hydride, followed by water
 - Sodium borohydride, methanol
 - Hydrogen (nickel catalyst)
 - Methylmagnesium iodide, followed by dilute acid
 - Sodium acetylide, followed by dilute acid
 - Phenyllithium, followed by dilute acid
 - Methanol containing dissolved hydrogen chloride
 - Ethylene glycol, *p*-toluenesulfonic acid, benzene
 - Aniline ($\text{C}_6\text{H}_5\text{NH}_2$)
 - Dimethylamine, *p*-toluenesulfonic acid, benzene
 - Hydroxylamine
 - Hydrazine
 - Product of part (l) heated in triethylene glycol with sodium hydroxide
 - p*-Nitrophenylhydrazine
 - Semicarbazide