**Exercise 16-1** Draw valence-bond structures and an atomic-orbital model for carbon monoxide. Why can the bond energy of this molecule be expected to be higher than for other carbonyl compounds (see Table 16-1)? Explain why the dipole moment of \(\ce{CO}\) is very small (0.13 debye).

**Exercise 16-2** Which of the following compounds would you expect to have zero or nearly zero dipole moments? Give your reasoning and don’t forget possible conformational equilibria. (Models will be helpful.)

![Diagrams showing various compounds]

**Exercise 16-3** The discussion in Section 16-1B explicitly refers to addition of polar reagents to carbonyl groups. Therefore an ionic mechanism is implied. Consider whether the same reactivity differences would be expected for ethene and methanal in the radical-chain addition of hydrogen bromide to methanal and ethene initiated by peroxides. What about the relative equilibrium constants? Show your reasoning. (Review Section 10-7.)

**Exercise 16-4** Which compound in each of the following pairs would you expect to be more reactive toward addition of a common nucleophilic agent such as hydroxide ion to the carbonyl bond? Indicate your reasoning.

- a. 2-propanone and 1,1,1-trichloro-2-propanone
- b. 2,2-dimethylpropanal and 2-propanone
- c. methyl 2-oxopropanoate and methyl 3-oxobutanoate
- d. 2-propanone and 2,3-butanedione
- e. 2-oxopropanenitrile and 2-propanone
- f. ketene \(\ce{CH_2=C=O}\) and cyclobutanone
- g. bicyclo[2.1.1]-5-hexanone and cyclobutanone

**Exercise 16-5** Use the infrared spectra given in Figure 16-2 and the data of Tables 9-2 and 16-3 to deduce the type of carbonyl compound giving rise to each spectrum.
Exercise 16-6 A hydrocarbon isolated from a plant extract was treated with ozone, and the ozonide decomposed with zinc to give two ketones, A and B, which were readily separated by gas chromatography. Ketone A gave a mass spectrum identical with that of Figure 9-52c while ketone B gave mass spectral peaks at \(m/e = 100, 85, 58, 43\). With this information, suggest possible structures for these ions and the parent hydrocarbon. Give your reasoning.

Exercise 16-7 Show how structures can be deduced for the four substances with the infrared and NMR spectra shown in Figure 16-3.
Figure 16-3: Infrared and proton NMR spectra of four organic compounds. See Exercise 16-7.

Exercise 16-8 Assuming that you had ready access to ultraviolet, infrared, NMR, and mass spectrometers, which spectral technique would you select to differentiate as unambiguously as possible between the following pairs of compounds? Give your reasoning in enough detail to show that you understand how well each technique is capable of distinguishing between the members of each pair (\(\ce{D} =\) hydrogen of mass 2)

a. 2-butanone and 2-butanone-\(\ce{D_3}\)
b. 3-cyclohexenone and 2-cyclohexenone
c. 4-penten-2-one and 4,4-dichloro-1-pentene
d. propanal and 2-butanone
e. 3-hexanone-6-\(\ce{D_3}\) and 3-hexanone-1-\(\ce{D_3}\)

Exercise 16-9 Write equations to show the steps involved in the following carbonyl-addition reactions: (a) base-catalyzed addition of ethanol to ethanal to form the corresponding hemiacetal, 1-ethoxyethanol; (b) formation of 1-ethoxyethanol from ethanol and ethanal, but under conditions of acid catalysis; (c) formation of 1,1-diethoxyethane from 1-ethoxyethane and ethanol with an acid catalyst; and (d) formation of diethyl carbonate \(\ce{(CH_3CH_2O)_2C=O}\) from ethanol and carbonyl dichloride.

Exercise 16-10 One possible way of carrying out the cyanohydrin reaction would be to dispense with hydrogen cyanide and just use the carbonyl compound and sodium cyanide. Would the equilibrium constant for cyanohydrin formation be more favorable, or less favorable, with 2-propanone and sodium cyanide in water compared to 2-propanone and hydrogen cyanide in water? Give your reasoning.
Exercise 16-11 What should be the equation for the rate of formation of 2-propanone cyanohydrin by the mechanism given in Section 16-4A, (a) if the first step is slow and the second fast? (b) If the second step is slow and the first fast? (Review Sections 4-4C and 8-4A.)

Exercise 16-12 Explain what factors would operate to make the equilibrium constant for cyanohydrin formation 1000 times greater for cyclohexanone than for cyclopentanone. Why? What would you expect for cyclobutanone relative to cyclopentanone? Why?

Exercise 16-13

a. Phosphorus ylides can be prepared by heating triphenylphosphine, \(\text{C}_6\text{H}_5\text{P}\), with a primary alkyl halide, \(\text{RCH}_2\text{X}\), in a solvent such as benzene. The initial product then is mixed with an equivalent quantity of a very strong base, such as phenyllithium in ether. Write equations for the reactions and probable mechanisms involved, using ethyl bromide as the alkyl halide.

b. Using the phosphorus ylide prepared according to Part a, draw structures for the products you would expect it to form with 2-pentanone.

Exercise 16-14 Show the structures of the reaction products to be expected in each of the steps listed.

a.

\[
\begin{align*}
\text{CICH}_2\text{OCH}_3 & \quad 1. \ (\text{C}_6\text{H}_5\text{P}) & \quad 2. \ \text{C}_6\text{H}_5\text{Li} & \quad 3. \ \text{cyclohexanone} \\
\text{benzene, 60 hr, 50°} & \quad \text{ether} & \quad \text{ether, -30°, 15 hr} & \\
& & & \\
& & & \\
\end{align*}
\]

b.

\[
\begin{align*}
\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \quad 1. \ (\text{C}_6\text{H}_5\text{P})\text{ (excess)} & \quad 2. \ \text{C}_6\text{H}_5\text{Li} & \quad 3. \ \text{cyclopentane} \\
30 \text{ min, 250°} & \quad \text{ether} & \quad \text{ether} & \quad (2 \text{ moles}) \\
& & & \\
& & & \\
\end{align*}
\]

Exercise 16-15*

a. Write valence-bond structures for diazomethane, \(\text{CH}_2\text{N}_2\), that accord with the fact that the actual molecule is a gas at room temperature and has a much smaller dipole moment (see Section 16-1B) than is suggested by the dipolar structure, \(\overset{\ominus}{\text{C}} \text{H}_2 - \overset{\oplus}{\text{N}} \overset{\equiv}{\text{N}}\).

b. 1,2-Diazacyclopropene, \(\text{CH}_2\text{N}_2\), is a stable isomer of diazomethane. Would you expect this substance to act as an ylide? Give your reasoning.

c. Phosphorus and sulfur ylides of the type \(-\overset{\ominus}{\text{C}} \overset{\oplus}{\text{X}}\), but not the corresponding nitrogen ylides, \(\overset{\ominus}{\text{C}} \overset{\equiv}{\text{N}} \overset{\equiv}{\text{C}}\), are not to be regarded as being strictly dipolar, but rather to possess \(\overset{\ominus}{\text{C}} \overset{\equiv}{\text{X}}\) bonds with considerable double-bond character, as expressed by the valence-bond structures

\[
\overset{\ominus}{\text{C}} \overset{\oplus}{\text{P}} \leftrightarrow \overset{\ominus}{\text{C}} \equiv \text{P} \quad \overset{\ominus}{\text{C}} \overset{\equiv}{\text{S}} \leftrightarrow \overset{\ominus}{\text{C}} \overset{\equiv}{\text{S}}
\]
Use Figure 6-4 to explain why phosphorus and sulfur ylides are more stable than corresponding nitrogen ylides.

Exercise 16-16*  

a. Show the intermediate substances and indicate the probable mechanisms involved in the synthesis of the sulfur ylide \(\text{3}\) by the following sequence:

\[
\text{ICl}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{1. } (\text{C}_6\text{H}_5)_3\text{S}} \text{Ag}^+\text{Br}^- \text{in} \text{CH}_2\text{Cl}_2 \xrightarrow{\text{2. } \text{NaH}} \xrightarrow{\text{3. } \text{KOH}} \text{S(C}_6\text{H}_5)_3
\]

b. Draw structures for the products expected from the reaction of \(\text{3}\) with cyclopentanone.

Exercise 16-17 The equilibrium constants for hydration are especially large for methanal, trichloroethanal, cyclopropanone, and compounds with the grouping \(\text{(COCOCOC)}\). Explain.

Exercise 16-18 Sodium hydrogen sulfite addition products are decomposed to the parent carbonyl compounds when treated with mild acid or mild alkali. Write equations for the reactions involved and explain why the substances are unstable both in acid and base.

Exercise 16-19 Explain how sodium hydrogen sulfite might be used to separate cyclohexanone (bp \(156^\circ\text{C}\)) from cyclohexanol (bp \(161^\circ\text{C}\)).

Exercise 16-20 Write a reasonable mechanism for the polymerization of methanal in water solution under the influence of a basic catalyst. Would you expect base catalysis to produce any 1,3,5-trioxacyclohexane? Why?

Exercise 16-21 How many different configurational isomers are there for paraldehyde? Draw the conformation expected to be most stable for each. Review Section 12-3D.

Exercise 16-22* What kind of reagents might be used to convert paraformaldehyde into a more thermally stable material? Give your reasoning.

Exercise 16-23* Why should the equilibrium for formation of \(\text{(CH}_3\text{)}_2\text{C}=\text{NR}\) from \(\text{(CH}_3\text{)}_2\text{C}=\text{O}\) and \(\text{RNH}_2\) be less favorable in strong acid than in neutral water solution? Be sure you consider the equilibria for the interaction of the acid with \textit{all} of the participants. Give your reasoning.

Exercise 16-24  

a. How many different positional and stereoisomers are possible of a monomethyl-substituted hexamethylenetetramine?  

b. How many stereoisomers are possible for structure \(\text{4}\)?  

c. Name compound \(\text{4}\) as an azacycloalkane in accord with the systematic rules for cyclic compounds (Sections 12-8 and 15-11A).

Exercise 16-25 Suggest a method of synthesis of each of the following compounds, starting with an appropriate aldehyde or ketone. Indicate which of the products you expect to be mixtures of configurational isomers.
Exercise 16-26 Write an equation to show the rearrangement of ethylideneamethanamine to \(\ce{N-methylethenamine}\). Use bond energies to calculate the \(\Delta H^0\) of the rearrangement. Assuming \(\Delta S^0 = 0\), which would be the more stable isomer? Would you expect that corrections for electron delocalization may be necessary for either of these compounds? Give your reasoning.

Exercise 16-27 How could you prepare the enamine \(6\) from suitable ketone and amine starting materials? Specify the catalyst required and draw the structure of any by-products that you may expect to form in the reaction.

Exercise 16-28 Write equations to show how you would convert 2-butanone to 2-methoxy-2-methylthiobutane by way of the corresponding \(\alpha\)-chloro ether.

Exercise 16-29 Write a reasonable mechanism for the reaction of hydrogen chloride and methanol with methanal to give methoxychloromethane (methyl chloromethyl ether), Equation 16-7, that is consistent with the fact that the reaction occurs under conditions where neither dichloromethane nor chloromethane is formed.
**Exercise 16-30** Cyclopentanone-1-\(^{14}C\) treated successively with phosphorus pentachloride and alkali gives 1-chlorocyclopentane-1-\(^{14}C\). This substance on treatment with phenyllithium at \(120^\circ\text{o}\) affords \(^{14}C\)-labeled 1-phenylcyclopentene, which on vigorous oxidation gives benzoic acid \(\text{C}_6\text{H}_5\text{CO}_2\) containing in its carboxyl carbon just half of the total \(^{14}C\) of the 1-phenylcyclopentene. Write equations for all the reactions involved and write a mechanism for the phenyllithium substitution that accounts for the \(^{14}C\) distribution.

**Exercise 16-31** Work out reasonable mechanisms for the reactions of phosphorus pentachloride and sulfur tetrafluoride with carbonyl groups. Both phosphorus and sulfur can accommodate five (or more) bonded atoms, and the structure of phosphorus pentachloride in the solid state is \(\left\{\text{PCl}_4^+\right\}\left\{\text{PCl}_6^-\right\}\).

**Exercise 16-32** Show how you could prepare the following substances from the indicated starting materials:

- a. 4-methylcyclohexanone from 4-methylenecyclohexanone
- b. 4-(hydroxymethyl)cyclohexanone from 4-oxocyclohexanecarboxylic acid
- c. 4-hydroxybutanoic acid from 4-oxobutanoic acid
- d. 2,2,2-trichloroethanol from 2,2,2-trichloroethanal

**Exercise 16-33** Assume that an equimolar mixture of methanal and 2,2-dimethylpropanal (each undergoes the Cannizzaro reaction by itself) is heated with sodium hydroxide solution. Write equations for the various possible combinations of Cannizzaro reactions which may occur. Would you expect methanal used in excess to reduce, or oxidize, 2,2-dimethylpropanal? Give your reasoning.

**Exercise 16-34** Benzenecarbaldehyde (benzaldehyde, \(\text{C}_6\text{H}_5\text{CHO}\)) is oxidized to benzenecarboxylic acid (benzoic acid, \(\text{C}_6\text{H}_5\text{CO}_2\)) by acid permanganate. The rate of the oxidation is proportional to the concentrations of \(\text{H}^+\), aldehyde, and \(\text{MnO}_4^-\). The reaction is much slower with \(\text{C}_6\text{H}_5\text{CDO}\) than with \(\text{C}_6\text{H}_5\text{CHO}\). When the reaction is carried wout in \(\text{H}_2\text{O}\) with \(\text{MnO}_4^-\), the product is \(\text{C}_6\text{H}_5\text{CO}_2\text{H}\). With \(\text{C}_6\text{H}_5\text{CHO}\), \(\text{H}_2\text{O}\), and \(\text{MnO}_4^-\), the \(\text{C}_6\text{H}_5\text{CO}_2\text{H}\) contains \(18\text{O}\). Write a mechanism for the reaction that is consistent with all the above facts. (Notice that the \(\text{C}_6\text{H}_5\) group is not involved.) Give your reasoning.

**Exercise 16-35** A radical-chain reaction similar to that described for the air oxidation of benzaldehyde occurs in the peroxide-initiated addition of aldehydes to alkenes (see Table 10-3). Write a mechanism for the peroxide-induced addition of ethanal to propene to give 2-pentanone.

**Exercise 16-36** Certain aldehydes decompose to hydrocarbons and carbon monoxide when heated in the presence of peroxides:

\[
\text{CH}_3\text{CHO} \xrightarrow{\text{ROOR}} \text{CH}_3\text{CH}_2\text{CHO} \xrightarrow{\text{ROOR}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{CO}
\]

Write a reasonable chain mechanism for such reactions that is supported by calculations of the \(\Delta H^0\) values for the propagation steps. Use needed data from Table 4-3 and Table 4-6. Your answer should reflect the fact that this reaction does not proceed well with most aldehydes unless the reactants are heated (about above \(120^\circ\text{o}\)).
Exercise 16-37 An elegant modification of the two-step procedure to prepare ketones from alkenes by hydroxylation and oxidative cleavage of the diol formed uses a small amount of potassium permanganate (or osmium tetroxide, \(\text{OsO}_4\)) as the catalyst and sodium periodate as the oxidizing agent:

\[
\text{HO}_2\text{C}--\text{CH}_2 \xrightarrow{\text{NaIO}_4 \ (\text{OsO}_4 \text{ or } \text{KMnO}_4)} \text{HO}_2\text{C}--\text{O} \\
70\%
\]

Explain how the reaction sequence could operate to enable \(\text{KMnO}_4\) (or \(\text{OsO}_4\)) to function overall as a catalyst rather than as a reagent.

Exercise 16-38 Write mechanism for the oxidative cleavage of 1,2-diols by lead tetraethanoate and sodium periodate based on consideration of the mechanism of chromic acid oxidation (Section 15-6B).

Exercise 16-39 Explain how resonance can be used to account for the fact that the \(\Delta H^0\) for reduction of \(\text{CH}_3\text{CO}_2\text{H}\) to \(\text{CH}_3\text{CHO}\) is about 18 \(\text{kcal mol}^{-1}\) more positive than calculated from bond energies, whereas \(\Delta H^0\) for the corresponding reduction of \(\text{CH}_3\text{COCl}\) to \(\text{CH}_3\text{CHO}\) is about as expected from bond energies. Would you expect \(\Delta H^0\) for reduction of \(\text{CH}_3\text{CONH}_2\) to be as expected from the pertinent bond energies? Why?

Exercise 16-40 Write a sequence of reactions whereby 2-methylpropene may be converted to 2-methylpropanal by way of a pinacol-type rearrangement. Would you expect any concomitant formation of 2-butanone? Explain.

Exercise 16-41 Predict the products to be expected from acid-catalyzed rearrangement of 1,2-propanediol and 2-methyl-2,3-butanediol.

Exercise 16-42 Treatment of tetramethyloxacyclopropane,

\[
\text{(CH}_3\text{)}_2\text{C}--\text{C(CH}_3\text{)}_2
\]

, with acid products pinacolone. Explain.

Exercise 16-43 How could one dehydrate 2,3-dimethyl-2,3-butanediol to 2,3-dimethyl-1,3-butadiene without forming excessive amounts of 3,3-dimethyl-2-butanone in the process?

Exercise 16-44 Strong acid converts 1,1-diphenyl-1,2-ethanediol first to diphenylethananal and then more slowly to 1,2-diphenylethanone (benzyl phenyl ketone). Explain how and why kinetic and equilibrium control may be expected in this case to give different products.

Exercise 16-45 Write equations for the acid-catalyzed rearrangement of 1,3,3-trimethylbutyl hydroperoxide and predict the favored product therefrom.

Exercise 16-46 Propose a possible synthesis of each of the following compounds from the indicated reagents and conditions where specified. Assume that any additional needed reagents are available. Reactions from other parts of Section 16-9 may be used.
a. cyclohexanecarbaldehyde from cyclohexane by way of a hydroformylation reaction

b. cyclopentylmethanol from cyclopentene

c.  
\[
\begin{array}{c}
\text{O} \\
\text{C} \text{CH}_2 \\
\end{array}
\]

from  
\[
\begin{array}{c}
\text{O} \\
\text{C} \text{CH}_2 \\
\end{array}
\]

d. heptanal from 1-heptene and \(\ce{(CH_3)_2S=O}\)

e.  
\[
\begin{array}{c}
\text{CHO} \\
\text{CHO} \\
\text{CH}_2 \\
\end{array}
\]

from  
\[
\begin{array}{c}
\text{pentene} \\
\end{array}
\]
(two ways)

f.  
\[
\begin{array}{c}
\text{O} \\
\text{C} \text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5 \\
\end{array}
\]

from \(\ce{(C_6H_5)_2C=O}\) and cyclopentane by way of a Wittig reaction (Section 16-4A)

Exercise 16-47*

a. Show the steps and reaction conditions by which 2-methyl-1,3-butadiene can be converted to 3-methylcyclopentanone by an alkylborane, \(\ce{RBH_2}\), when \(\ce{R}\) is a large alkyl group.

b. Suggest a route to each of the following compounds from the indicated starting materials: (1) 2-methyl-4-heptanone from propene and 2-methylpropene, and (2) octanedial from 1,5-hexadiene.

Exercise 16-48 Write equations for the synthesis of the following substances based on the indicated starting materials. Give the reaction conditions as accurately as possible.
a. 2-methylpropanal from 3-methylbutanol
b. 1-cyclobutylmethanol from cyclobutanecarboxylic acid
c. pentanediaol from cyclopentanone
d. cyclobutane from methylenecyclobutane
e. 2,2,2-trichloroethyl trichloroethanoate from 2,2,2-trichloroethanal
f. cyclopentene-1-carboxylic acid from cyclopentanone

**Exercise 16-49** Write reasonable mechanisms for each of the following reactions. Support your formulations with detailed analogies insofar as possible.

a. 
\[
\text{H-C-C-H + NaOH} \xrightleftharpoons[\text{H_2O}]{\text{Na}_2\text{CO}_3} \text{HOCH}_2\text{CO}_2\text{Na}
\]

b. \[
\ce{CH_3COC_3} + \ce{NH_2OH} \xrightleftharpoons[\text{H_2O}]{\text{Na}_2\text{CO}_3} \ce{CH_3C(NOH)CH_3} + \ce{H_2O}\] (Notice that this is a base-catalyzed reaction.)

c. 
\[
\text{CH}_3\text{C}-\text{C}-\text{CH}_3 \xrightarrow{\text{Ag}^+} \text{CH}_3\text{CH}_2\text{C} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{C}-\text{C}-\text{CH}_3
\]

d. Hexamethylenetetramine from methanal and ammonia. (Consider the possibility of \(\ce{CH_2=NH}\) as an intermediate for the stepwise formation of \(\ce{N\text{-N\text{'-N\text{''}}}}\)tris(hydroxymethyl)-1,3,5-triazacyclohexane as an intermediate followed by acid-induced condensation of the latter with ammonia.)

**Exercise 16-50** It is important to be able to decide whether a plausible-looking reaction actually will proceed as written. The following equations represent "possible" synthetic reactions. Consider each carefully and decide whether it will proceed as written. Show your reasoning. If you think another reaction would occur, write an equation for it.

a. \[
\ce{CH_3CH(OC_2H_5)_2} + 2 \ce{NaOCH_3} \xrightleftharpoons[\text{excess : CH_3OH}]{50^\circ} \ce{CH_3CH(OCH_3)_2} + 2 \ce{NaOC_2H_5}\]

b. \[
\ce{(CH_3)_3CCOCH_2CH_3} + \ce{KMnO_4} \xrightleftharpoons[\text{KOH}]{\text{H}_2\text{O}} \ce{(CH_3)_3COH} + \ce{CH_3CH_2CO_2K}\]

c. \[
\ce{CH_3CCL(CH_3)CH_2Cl} + 2 \ce{NaOCH_3} \xrightleftharpoons[50^\circ]{\text{excess}} \ce{CH_3C(CH_3)(OCH_3)CH_2OCH_3} + 2 \ce{NaCl}\]

d. \[
\ce{CH_3CH_2CH=O} + \ce{C_6H_5CO_3H} \rightarrow \ce{CH_3CH_2O-COH} + \ce{C_6H_5CO_2H}\]
e. $\text{\ce{O=CH-CO_2H}} + \text{\ce{NaBH_4}} \overset{\text{\ce{CH_3OH}}}{\longrightarrow} \text{\ce{O=CH-CH_2OH}}$

f. $\text{\ce{CH_2=O}} + \text{\ce{(CH_3)_2C=O}} + \text{\ce{NaOH}} \rightarrow \text{\ce{HCO_2Na}} + \text{\ce{(CH_3)_2CHOH}}$

Exercise 16-51 Write a mechanism for the oxidation of sodium methanoate (formate) to carbon dioxide by potassium permanganate which is consistent with the following facts:

(a) \( v = k \left[ \text{\ce{HCO_2^-}} \right] \left[ \text{\ce{MnO_4^-}} \right] \)

(b) the $\text{\ce{CO_2}}$ has no $\text{\ce{^{18}O}}$ in it if oxidized with $\text{\ce{Mn^{18}O_4^-}}$

(c) $\text{\ce{DCO_2^-}}$ is oxidized at one seventh the rate of $\text{\ce{HCO_2^-}}$

Compare your mechanism with that generally accepted for the Cannizzaro reaction.

Exercise 16-52 2-Propanone reacts with trichloromethane in the presence of potassium hydroxide to give 1,1,1-trichloro-2-methyl-2-propanol. What is likely to be the mechanism of this reaction? What further evidence could be gained to establish the mechanism? (If you do not see a possible answer, refer to Section 14-7B for helpful information.)

Exercise 16-53 The structure of the sex attractant of the silkworm, "bombykol", is given in Section 5-6 as structure (30). The compound has been synthesized by the route given below. Write the structures of each of the synthetic intermediates A-F.

Contributors