Exercise 24-1 Amides with structures like the following are difficult to prepare and are relatively unstable. Explain.

Exercise 24-2

a. Name each of the following compounds by the system described in Section 24-1B:

(i) \( \text{CH}_2=\text{CH-CONH}_2 \)  
(ii) 

\[
\text{N} \quad \text{NCH}_3 \\
\text{CH} \quad \text{CH} \\
\text{C} \quad \text{N} \\
\text{C} \quad \text{CH}_3 \\
\text{O} \\
\]

(iii) 

\[
\text{CH} \quad \text{N} \\
\text{C} \quad \text{C} \\
\text{CH} \quad \text{CH}_3 \\
\text{O} \\
\]

(The common name is acetanilide)

b. Write a structure to represent each compound shown:

(i) \( \text{N} \)-ethylbenzenecarboxamide
(ii) \( \text{N} \)-cyclohexyl-2-methylpropanamide

Exercise 24-3 Show how structures can be deduced for the two substances with the molecular formulas \( \text{C}_5\text{H}_9\text{NO}_3 \) and \( \text{C}_{10}\text{H}_{13}\text{NO} \) from their infrared and NMR spectra as given in Figure 24-3.
Figure 24-3: The infrared and proton NMR spectra of a substance \(\text{C}_{10}\text{H}_{13}\text{NO}\) and a substance \(\text{C}_5\text{H}_9\text{NO}_3\) (see Exercise 24-3). The proton spectra were taken at \(60 \text{ MHz}\) with TMS as 0.0 ppm.

Exercise 24-4 Primary amides give a strong peak at \(m/e\) 44 in their mass spectra. Indicate the nature of this peak and suggest how it might be formed.

Exercise 24-5*

a. The \(\text{\^{15}N}\) NMR spectrum with proton decoupling (Section 9-10I) of \(\text{\^{15}N}\)-methylmethanamide (Figure 24-4) shows two closely spaced signals of unequal height. Explain how these peaks arise and what you would expect the spectrum to look like if it were taken at \(150^\circ\text{o}\).

Figure 24-4: Natural-abundance \(\text{\^{15}N}\) spectrum of \(\text{\^{15}N}\)-methylmethanamide, \(\text{HCONHCH}_3\).
taken at \(18.2 \: \text{MHz}\) with proton decoupling. The large and small peaks are separated by \(2 \: \text{ppm}\). See Exercise 24-5.

b. The proton-decoupled \(\ce{^{15}N}\) spectra of lactams dissolved in \(\ce{CHCl_3}\) show only one peak when the ring size is 5, 6, 7, 8, 10, and 11, but two unequal peaks when the ring size is 9. Account for this behavior. (Review Section 12-7.)

Exercise 24-6 Explain how the temperature variation of the proton NMR spectrum of \(\ce{N},\ce{N}-\text{dimethylmethanamide}\) in strongly acidic solution might be used to decide whether amides accept a proton on nitrogen or oxygen. Review Section 24-1D.

Exercise 24-7

a. Draw the two important valence-bond structures for a nitrilium ion \(\ce{[RCNR]^+}\) and write the steps involved in hydration of a nitrilium ion to an amide, \(\ce{RCONHR}\).

b. Would you expect \(\ce{^{15}N}\)-methylethanamide to be formed from methanol and ethanenitrile in \(\ce{H_2SO_4}\)? Explain.

Exercise 24-8 Nitriles are converted readily to amides with hydrogen peroxide in dilute sodium hydroxide solution. The reaction is

\[
\ce{RC \equiv N + 2 H_2O_2 \overset{OH^-}{\longrightarrow} RCONH_2 + O_2 + H_2O}
\]

The rate equation is

\[
v = k \left[ \ce{H_2O_2} \right] \left[ \overset{\ominus}{\ce{OH}} \right] \left[ \ce{RC \equiv N} \right]
\]

When hydrogen peroxide labeled with \(\ce{^{18}O}\) is used in ordinary water \(\ce{H_2^{16}O}\), the resulting amide is labeled with \(\ce{^{18}O}\). Write a mechanism for this reaction that is consistent with all the experimental facts. Notice that hydrogen peroxide is a weak acid \(K_a \sim 10^{-12}\), and in the absence of hydrogen peroxide, dilute sodium hydroxide attacks nitriles very slowly.

Exercise 24-9 Show how the following transformations could be achieved: \(\ce{C_6H_5CH_2CO_2CH_3 \rightarrow C_6H_5CH_2C(CH_3)_2OH \rightarrow C_6H_5CH_2C(CH_3)_2NHCHO}\). Name the product by the system used in Section 24-1B.

Exercise 24-10 Complete the following reactions to show the structures of the products formed:

a. 
Exercise 24-11 Nitriles of the type \(\text{RCH}_2\text{CN}\) undergo a self-addition reaction analogous to the aldol addition in the presence of strong bases such as lithium amide. Hydrolysis of the initial reaction product with dilute acid yields a cyanoketone, \(\text{RCH}_2\text{COCH(CN)R}\). Show the steps that are involved in the mechanism of the overall reaction and outline a scheme for its use to synthesize large-ring ketones of the type \(\text{C}(\text{H}_2)\_n \text{C}=\text{O}\) from dinitriles of the type \(\text{NC}(\text{CH}_2)\_n \text{CN}\).

Exercise 24-12 Show how the following substances can be synthesized from the indicated starting materials:

a. \(\text{CH}(\text{CH}_3)_3\text{CN}\) from \(\text{CH}(\text{CH}_3)_3\text{Cl}\) (two ways)
b. \(\text{CH}_3\text{CH}=\text{CHCN}\) from \(\text{CH}_2=\text{CHCH}_2\text{Br}\)
c. \(\text{CH}_2=\text{CHCO}_2\text{H}\) from \(\text{CH}_3\text{CHO}\)

Exercise 24-13 Propanedinitrile [malononitrile, \(\text{HC}(\text{CH}_2)\text{CN}\)] reacts with tetracyanoethene in the presence of base to yield a compound of formula \(\text{HC}(\text{CN})_5\), which is a monobasic acid of strength similar to sulfuric acid. What is the structure of this compound and why is it such a strong acid? Write a mechanism for the formation of the compound that is based in part on the Michael addition (Section 17-5B).

Exercise 24-14 Show how the following compounds may be synthesized from the indicated starting materials. (It may be necessary to review parts of Chapters 22 and 23 to work this exercise.)

a. 1-methyl-3,5-dinitrobenzene from methylbenzene
b. 1-methyl-2,6-dinitrobenzene from 4-methylbenzenesulfonyl acid (notice that \(\text{SO}_3\text{H}\) can be removed by hydrolysis; Section 22-4G)
c. 2,4-dinitrobenzenamine from chlorobenzene
d. 1-chloro-3,5-dinitrobenzene from chlorobenzene
e. 1,2,3-trinitrobenzene from 4-chlorobenzenesulfonyl acid
Exercise 24-15 Tetracyanoethene in benzene forms an orange solution, but when this solution is mixed with a solution of anthracene in benzene, a brilliant blue-green color is produced, which fades rapidly; colorless crystals of a compound of composition \(\ce{C_{14}H_{10} \cdot C_2(CN)_4}\) then are deposited. Explain the color changes that occur and write a structure for the crystalline product.

Exercise 24-16 Would you expect the dipole moment measured for 1,3,5-trinitrobenzene in 1,3,5-trimethylbenzene solution to be the same as in tetrachloromethane solution? Explain.

Exercise 24-17 Anthracene (mp \(\sigma^{217^\circ}\)) forms a red crystalline complex (mp \(\sigma^{164^\circ}\)) with 1,3,5-trinitrobenzene (mp \(\sigma^{121^\circ}\)). If you were to purify anthracene as this complex, how could you regenerate the anthracene free of trinitrobenzene?

Exercise 24-18* Write the mechanistic steps to show how 1,2-diphenyldiazene oxide and 1,2-diphenyldiazene may be formed by base-induced condensation reactions of nitrosobenzene with \(\ce{N(4ClCH_2)}\)-phenylazanol and benzenamine, respectively. What product would you expect to be formed from nitrosobenzene and \(\ce{N(CH_3)_2}\)-(4-chlorophenyl)azanol? Give your reasoning.

Exercise 24-19 What kind of properties and reactions would you expect the double bond of nitroethene to have? Consider the ease of electrophilic and nucleophilic addition reactions as well as cycloadditions.

Exercise 24-20 Show how the following compounds can be prepared from the commercially available nitroalkanes obtained from the nitration of propane. (It may be desirable to review the material on aldol and Michael additions in Chapters 17 and 18.)

a. \(\ce{HOCH_2CH_2NO_2}\)
b. \(\ce{CH_2=CHNO_2}\)
c. \(\ce{O_2NOCH_2}_3\)
d. \(\ce{(O_2NOCH_2)_3CNO_2}\)
e. \(\ce{(N \equiv \equiv CCH_2CH_2)_3CNO_2}\)
f. \(\ce{H_2NCH_2CH_2C(CH_3)_2NH_2}\)

Exercise 24-21 Show how 2-methyl-2-nitropropane may be synthesized from (a) \(\ce{\text{tert-}}\)butyl alcohol and (b) 2,2-dimethylpropanoic acid. (Review Sections 23-12E and 24-3B if necessary.)

Exercise 24-22 Arguing on the basis of mechanistic principles and knowledge of related reactions, work out products that may be expected for the following reactions:

a. \(\ce{(CH_3)_2NNH}_2 + \ce{HONO}\)
b. \(\ce{(CH_3)_2NNHCH_3 + \ce{HONO}\})
c. \(\ce{(CH_3)_2NN(CH_3)_2 + \ce{HONO}\})
d. \(\ce{CH_3CONHNH_2 + \ce{Br_2 + \ce{NaOH}\})}\)

Exercise 24-23 Arrange the following azo substances in order of their expected rates of thermal decomposition to
produce nitrogen. Give your reasoning.

a. 
\[
\begin{array}{c}
\text{H}_2\text{N=NN=H}_2
\end{array}
\]

b. \(\ce{(CH_3)_3C-N=N-C(CH_3)_3}\)

c. 
\[
\begin{array}{c}
\text{H}_2\text{N=N=H}_2
\end{array}
\]

d. \(\ce{CH_3-N=N-CH_3}\)

e. 
\[
\begin{array}{c}
\text{H}_2\text{C=N=N}
\end{array}
\]

**Exercise 24-24** Devise a synthesis (more than one step may be required) of \(\ce{(2)}\) from 2-propanone, hydrazine, and hydrogen cyanide. What would you expect this substance to yield when heated in (a) a perfluorohydrocarbon solvent and (b) a solution of bromine in carbon tetrachloride?

**Exercise 24-25** Write the important resonance structures that contribute to the resonance hybrid of diazomethane and show how these can be used to rationalize the formation of methyl ethanoate from diazomethane and ethanoic acid.

**Exercise 24-26** Write reasonable mechanisms based on analogy for the following reaction:

a. \(\ce{\text{CH}_3\text{COCl} + 2 \text{CH}_2\text{N}_2 \rightarrow \text{CH}_3\text{COCHN}_2 + \text{CH}_3\text{Cl}}\)

b. \(\ce{\text{CH}_3\text{COCl} + \text{CH}_2\text{N}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{Cl} + \text{N}_2}\)

c. \(\ce{\text{CH}_3\text{COCHN}_2 \underset{\text{heat}}{\overset{\text{powdered glass}}{\longrightarrow}} \text{CH}_3\text{-CH=C=O} + \text{N}_2}\)

d. 
\[
\begin{array}{c}
\text{H}_2\text{O}
\end{array}
\xrightarrow{\text{CH}_3\text{N}_2 \text{CH}_3\text{OH}} \begin{array}{c}
\text{H}_2\text{O}
\end{array}
\]

e.
Exercise 24-27 Show how the following substances might be made by synthesis based on diazomethane reactions.

a. hexanedioic acid (from butanedioic acid)

b. 2,2-dimethylcyclopropanone (see Section 17-11)

c. 

Exercise 24-28* Knowing that ketones and hydrazine react to give hydrazones, show how the combination of ketone, \(\text{NH}_3\), and \(\text{NH}_2\text{Cl}\) can react to give diazacyclopropanes. In working out a mechanism, start with the fact that the following reaction occurs in good yield:

\[
\text{R} = \text{C} = \text{N} - \text{R}' + \text{NH}_2\text{Cl} \rightarrow \text{R} = \text{C} = \text{N} - \text{R}'
\]

Exercise 24-29* Explain why 1,2-diazacyclopropene reacts with acids much more slowly than does diazomethane.

Exercise 24-30 Show how the following transformations may be achieved with the aid of azide derivatives:

a. \(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{NH}_2\)

b. 

c. 

Exercise 24-31 Suggest a route for the synthesis of each of the following compounds from the indicated starting material:

a. 2-methylpropanenitrile from 2-methylpropanal

b. \((\text{CH}_3\text{CO}_2\text{CH}_2)_3\text{C-NO}_2\) from nitromethane

c. \(\text{N}-\text{tert}-\text{butylbenzenecarboxamide}\) from benzenecarbonitrile (benzeonitrile)

Exercise 24-32

a. Make a chart of the mp, bp, and solubilities in water, ether, dilute acid, and dilute base of each of the following compounds: octanamine, \(\text{N}-\text{butylbutanamine}\), 1-nitrobutane, \(\text{N},\text{N}-\text{dimethylethanamide}\), \(\text{N},\text{N}-\text{dipropylpropanamide}\), and 2-nitro-2-methylbutane.
b. Outline a practical procedure for separation of an equimolal mixture of each of the compounds in Part a into the pure components. Notice that selective reactions are not suitable unless the reaction product can be reconverted to the starting material. Fractional distillation will not be accepted here as a practical means of separation of compounds that have boiling points less than \(25^\circ\text{C}\) apart.

**Exercise 24-33** For each of the following pairs of compounds give a chemical test, preferably a test-tube reaction, that will distinguish between the two compounds:

a. \(\text{\((CH_3)_3CNH_2\)}\) and \(\text{\((CH_3)_2NC_2H_5\)}\)

b. \(\text{\((CH_3)_3CH\_2NO\_2\)}\) and \(\text{\((CH_3)_3CONH\_2\)}\)

c. \(\text{\((CH_3)_3CH\_2\equiv NC\_2H\_5\)}\) and \(\text{\((CH_3)\_2\equiv C\_CH\_2NH\_2\)}\)

d. \(\text{\((CH_3)_3CH\_2N\text{HCl}\)}\) and \(\text{\((CH_3)_3CON\text{HCOCH}\_3\)}\)

e. \(\text{\((CH_3)_3NH\text{HCOCH}\_3\)}\) and \(\text{\((CH_3)_3NH\text{COCH}\_2\)}\)

**Exercise 24-34** Explain how you would use spectroscopic means to distinguish between the compound pairs in Exercise 24-33. Be specific about what you would expect to observe.

**Exercise 24-35** Using spectroscopic methods, how could you distinguish one isomer from the other in the following pairs? Be specific about what you would expect to observe in each case.

a. 2-methylbenzenamine and \(\text{\((CH_3)\_2CN\)}\)-methylbenzenamine

b. propanamide and \(\text{\((CH_3)\_2CN\)}\)-dimethylmethanamide

c. nitroethane and ethyl nitrite

d. 3-oxobutanenitrile and 2-butynamide

**Exercise 24-36** Compound A of molecular formula \(\text{\((C_6H_{12}O_2}\)}\) (which can be obtained resolved into chiral forms) is insoluble in dilute acid and dilute base, but reacts with aqueous nitrous acid to give compound B of formula \(\text{\((C_6H_{10}O_4}\)}\), which readily loses water on heating to give C, \(\text{\((C_6H_8O_3}\)}\). Compound A reacts with a solution of bromine and sodium hydroxide in water to give D, \(\text{\((C_4H_{12}N_2}\)}\), which on treatment with nitrous acid in the presence of perchloric acid gives 2-butanone. Write structures showing configurations for compounds A, B, C, and D and equations for all the reactions involved.

**Exercise 24-37** How would you synthesize the following compounds from the indicated starting materials? Write equations for the reactions involved and indicate the reaction conditions.

a. phenylnitroethanoic acid from ethyl phenylethanoate

b. 3-phenylpropanoic acid from phenylethanoic acid

**Exercise 24-38** Show by equations how each of the following substances might be synthesized from the indicated materials. Specify reagents and approximate reaction conditions.

a. \(\text{\((CH_3)\_2CN\)}\)-phenylethanamide from benzene

b. 1,2-dinitrobenzene from \(\text{\((CH_3)\_2CN\)}\)-phenylethanamide
c. 4-nitro-1-nitrosobenzene from \(\text{N}\)-phenylethanamide  

d. 1,3,5-trideuteriobenzene from \(\text{N}\)-phenylethanamide  

e. 2,4-dinitrophenyldiazane (2,4-dinitrophenyldrazine) from benzene

**Exercise 24-39** For each of the following pairs of compounds give a chemical test, preferably a test-tube reaction, that will distinguish the two compounds. Write a structural formula for each compound and equations for the reactions involved.

a. 1-methyl-3-nitrobenzene and phenylnitromethane  
b. 1-methyl-4-nitrobenzene and benzenecarboxamide  
c. benzenamine and cyclohexanamine  
d. \(\text{N}\)-methylbenzenamine and 4-methylbenzenamine  
e. \(\text{N}\)-nitroso-\(\text{N}\)-methylbenzenamine and 4-nitroso-\(\text{N}\)-methylbenzenamine

**Exercise 24-40** Show how the following substances may be synthesized from benzene, nitrobenzene, and halogenated or alkylbenzenes, using the reactions discussed in this chapter and in Chapters 22 and 23.

a. 3-nitrobenzenamine  
b. 1-bromo-4-nitrosobenzene  
c. 2-methyl-5-nitrobenzenamine  
d. 1-(4-bromophenyl)-2-(4-chlorophenyl)diazane  
e. phenyl-(4-nitrophenyl)diazene  
f. 1-phenyl-2-(4-methylphenyl)diazene 1-oxide

**Contributors**