CHAPTER 70 Qualitative Organic Analysis

PRELAB EXERCISE: In the identification of an unknown organic compound, certain procedures are more valuable than others. For example, far more information is obtained from an IR spectrum than from a refractive index measurement. Outline, in order of priority, the steps you will employ in identifying your unknown.

Identification and characterization of the structures of unknown substances are an important part of organic chemistry. It is often, of necessity, a micro process, for example, in drug analyses. It is sometimes possible to establish the structure of a compound on the basis of spectra alone (IR, UV, and NMR), but these spectra must usually be supplemented with other information about the unknown: physical state, elementary analysis, solubility, and confirmatory tests for functional groups. Conversion of the unknown to a solid derivative of known melting point will often provide final confirmation of structure.

However, before spectra are run, other information about the sample must be obtained. Is it homogeneous (test by thin-layer, gas, or liquid chromatography)? What are its physical properties (melting point, boiling point, color, solubility in various solvents)? Is it soluble in a common NMR solvent? It might also be necessary to determine which elements are present in the sample and its percentage elemental composition (mass spectroscopy).

Nevertheless, an organic chemist can often identify a sample in a very short time by performing solubility tests and some simple tests for functional groups, coupled with spectra that have not been compared to a database. Conversion of the unknown to a solid derivative of known melting point will often provide final confirmation of structure. This chapter provides the information needed to carry out this type of qualitative analysis of an organic compound.

Procedures

All experiments in this chapter can, if necessary, be run on two to three times the indicated quantities of material.

Physical State

Check for Sample Purity

Distill or recrystallize as necessary. Constant boiling point and sharp melting point are indicators, but beware of azeotropes and eutectics. Check homogeneity by TLC, gas, HPLC, or paper chromatography.

Note the Color

Common colored compounds include nitro and nitroso compounds (yellow), α-diketones (yellow), quinones (yellow to red), azo compounds (yellow to red), and polyconjugated olefins and ketones (yellow to red). Phenols and amines are often brown to dark-purple because of traces of air oxidation products.

CAUTION: Do not taste an unknown compound. To note the odor, cautiously smell the cap of the container and do it only once.

Note the Odor

Some liquid and solid amines are recognizable by their fishy odors; esters are often pleasantly fragrant. Alcohols, ketones, aromatic hydrocarbons, and aliphatic olefins have characteristic odors. On the unpleasant side are thiols, isonitriles, and low-molecular weight carboxylic acids.

Make an Ignition Test

Heat a small sample on a spatula; first hold the sample near the side of a microburner to see if it melts normally and then burns. Heat it in the flame. If a large ashy residue is left after ignition, the unknown is probably a metal salt. Aromatic compounds often burn with a smoky flame.

Spectra

Obtain infrared and nuclear magnetic resonance spectra following the procedures of Chapters 12 and 13. If these spectra indicate the presence of conjugated double bonds, aromatic rings, or conjugated carbonyl compounds, obtain the UV spectrum following the procedures of Chapter 14. Interpret the spectra as fully as possible by reference to the sources cited at the end of the various spectroscopy chapters.

Explanation

Elementary Analysis, Sodium Fusion

This method for detection of nitrogen, sulfur, and halogen in organic compounds depends on the fact that fusion of substances containing these elements with sodium yields NaCN, Na_2S, and NaX (X = Cl, Br, I). These products can, in turn, be readily identified. The method has the advantage that the most usual elements other than C, H, and O present in organic compounds can all be detected following a single fusion, although the presence of sulfur sometimes

Rarely performed by professional chemists

interferes with the test for nitrogen. Unfortunately, even in the absence of sulfur, the test for nitrogen is sometimes unsatisfactory (nitro compounds in particular). Practicing organic chemists rarely perform this test. Either they know which elements their unknowns contain, or they have access to a mass spectrometer or atomic absorption instrument.

CAUTION: Manipulate sodium with a knife and forceps; never touch it with the fingers. Wipe it free of kerosene with a dry towel or filter paper; return scraps to the bottle or destroy scraps with methyl or ethyl alcohol, never with water. Safety glasses! Hood!

Do not use $CHCl_3$ or CCl_4 as samples in sodium fusion. They react extremely violently.

Place a 3-mm cube of sodium[1] (30 mg, no more)[2] in a 10 × 75-mm Pyrex test tube, and support the tube in a vertical position (Fig. 70.1). Have a microburner with small flame ready to move under the tube, place an estimated 20 mg of solid on a spatula or knife blade, put the burner in place, and heat until the sodium first melts and then vapor rises 1.5–2.0 cm in the tube. Remove the burner, and at once drop the sample onto the hot sodium. If the substance is a liquid add 2 drops of it. If there is a flash or small explosion the fusion is complete; if not, heat briefly to produce a flash or a charring. Then let the tube cool to room temperature, be sure it is cold, add a drop of methanol, and let it react. Repeat until 10 drops have been added. With a stirring rod break up the char to uncover sodium. When you are sure that all sodium has reacted, empty the tube into a 13 × 100-mm test tube, hold the small tube pointing away from you or a neighbor, and pipette into it 1 mL of water. Boil and stir the mixture, and pour the water into the larger tube; repeat with 1 mL more water. Then transfer the solution with a Pasteur pipette to a 2.5-cm funnel (fitted with a fluted filter paper) resting in a second 13 × 100-mm test tube. Portions of the alkaline filtrate are used for the tests that follow.

(a) Nitrogen

Run each test on a known and an unknown.

The test is done by boiling a portion of the alkaline solution from the solution fusion with iron(II) sulfate and then acidifying. Sodium cyanide reacts with iron(II) sulfate to produce ferrocyanide, which combines with iron(III) salts, inevitably formed by air oxidation in the alkaline solution, to give insoluble Prussian Blue, $NaFe[Fe(CN)_6]$. Iron(II) and iron(III) hydroxide precipitate along with the blue pigment but dissolve on acidification.

Place 50 mg of powdered iron(II) sulfate (this is a large excess) in a 10 × 75-mm test tube, add 0.5 mL of the alkaline solution from the fusion, heat the mixture gently with shaking to the boiling point, and then—without cooling—acidify with dilute sulfuric acid (hydrochloric acid is unsatisfactory). A deep-blue precipitate indicates the presence of nitrogen. If the coloration is dubious, filter through a 2.5-cm funnel and see if the paper shows blue pigment.

Cleaning Up Dilute the test solution with water and flush down the drain.

Notes for the instructor

1. Sodium spheres $\frac{1}{16}''$ to $\frac{1}{4}''$ are convenient.
2. A dummy 3-mm cube of rubber can be attached to the sodium bottle to indicate the correct amount.

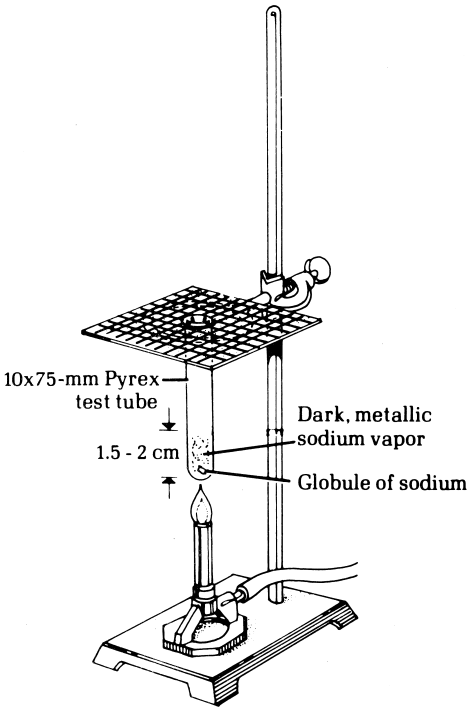


FIG. 70.1 Sodium fusion, just prior to addition of sample.

(b) Sulfur

1. Dilute 1 drop of the alkaline solution with 1 mL of water, and add a drop of sodium nitroprusside; a purple coloration indicates the presence of sulfur.
2. Prepare a fresh solution of sodium plumbite by adding 10% sodium hydroxide solution to 0.2 mL of 0.1 *M* lead acetate solution until the precipitate just dissolves, and add 0.5 mL of the alkaline test solution. A black precipitate or a colloidal brown suspension indicates the presence of sulfur.

$Na_2(NO)Fe(CN)_6 \cdot 2H_2O$

Sodium nitroprusside

Cleaning Up Dilute the test solution with water and flush down the drain.

(c) Halogen

Differentiation of the halogens

Acidify 0.5 mL of the alkaline solution from the fusion with dilute nitric acid (indicator paper) and, if nitrogen or sulfur has been found present, boil the solution (hood) to expel HCN or H_2S. On addition of a few drops of silver nitrate solution, halide ion is precipitated as silver halide. Filter with minimum exposure to light on a 2.5-cm funnel, wash with water, and then with 1 mL of concentrated ammonia solution. If the precipitate is white and readily soluble in ammonium hydroxide solution it is AgCl; if it is pale yellow and not readily soluble it is AgBr; if it is yellow and insoluble it is AgI. Fluorine is not detected in this test since silver fluoride is soluble in water.

Do not waste silver nitrate.

Cleaning Up Dilute the test solution with water and flush down the drain.

> Run tests on knowns in parallel with unknowns for all qualitative organic reactions. In this way, interpretations of positive reactions are clarified and defective test reagents can be identified and replaced.

Beilstein Test for Halogens

A fast, easy, reliable test

Heat the tip of a copper wire in a burner flame until no further coloration of the flame is noticed. Allow the wire to cool slightly, then dip it into the unknown (solid or liquid), and again heat it in the flame. A green flash is indicative of chlorine, blue-green of bromine, and blue of iodine; fluorine is not detected because copper fluoride is not volatile. The Beilstein test is very sensitive; halogen-containing impurities may give misleading results. Run the test on a compound known to contain halogen for comparison to your unknown.[3]

Solubility Tests

Weigh and measure carefully.

Like dissolves like; a substance is most soluble in that solvent to which it is most closely related in structure. This statement serves as a useful classification scheme for all organic molecules. The solubility measurements are done at room temperature with 1 drop of a liquid, or 5 mg of a solid (finely crushed), and 0.2 mL of solvent. The mixture should be rubbed with a rounded stirring rod and shaken vigorously. Lower members of a homologous series are easily classified; higher members become more like the hydrocarbons from which they are derived.

If a very small amount of the sample fails to dissolve when added to some of the solvent, it can be considered insoluble; and, conversely, if several portions dissolve readily in a small amount of the solvent, the substance is obviously soluble.

If an unknown seems to be more soluble in dilute acid or base than in water, the observation can be confirmed by neutralization of the solution; the original material will precipitate if it is less soluble in a neutral medium.

If both acidic and basic groups are present, the substance may be amphoteric and therefore soluble in both acid and base. Aromatic aminocarboxylic acids are amphoteric, like aliphatic ones, but they do not exist as zwitterions. They are soluble in both dilute hydrochloric acid and sodium hydroxide, but not in bicarbonate solution. Aminosulfonic acids exist as zwitterions; they are soluble in alkali but not in acid.

The solubility tests are not infallible and many borderline cases are known. Carry out the tests according to the scheme of Fig. 70.2 and the following "Notes to Solubility Tests," and tentatively assign the unknown to one of the groups I–X.

3. http://odin.chemistry.uakron.edu/organic_lab/beil/
With seven very good color photos from the University of Akron, the Beilstein test is clearly demonstrated on this Web site. The dramatic differences among chlorine (green), bromine (blue-green), and iodine (blue) are quite clearly seen.

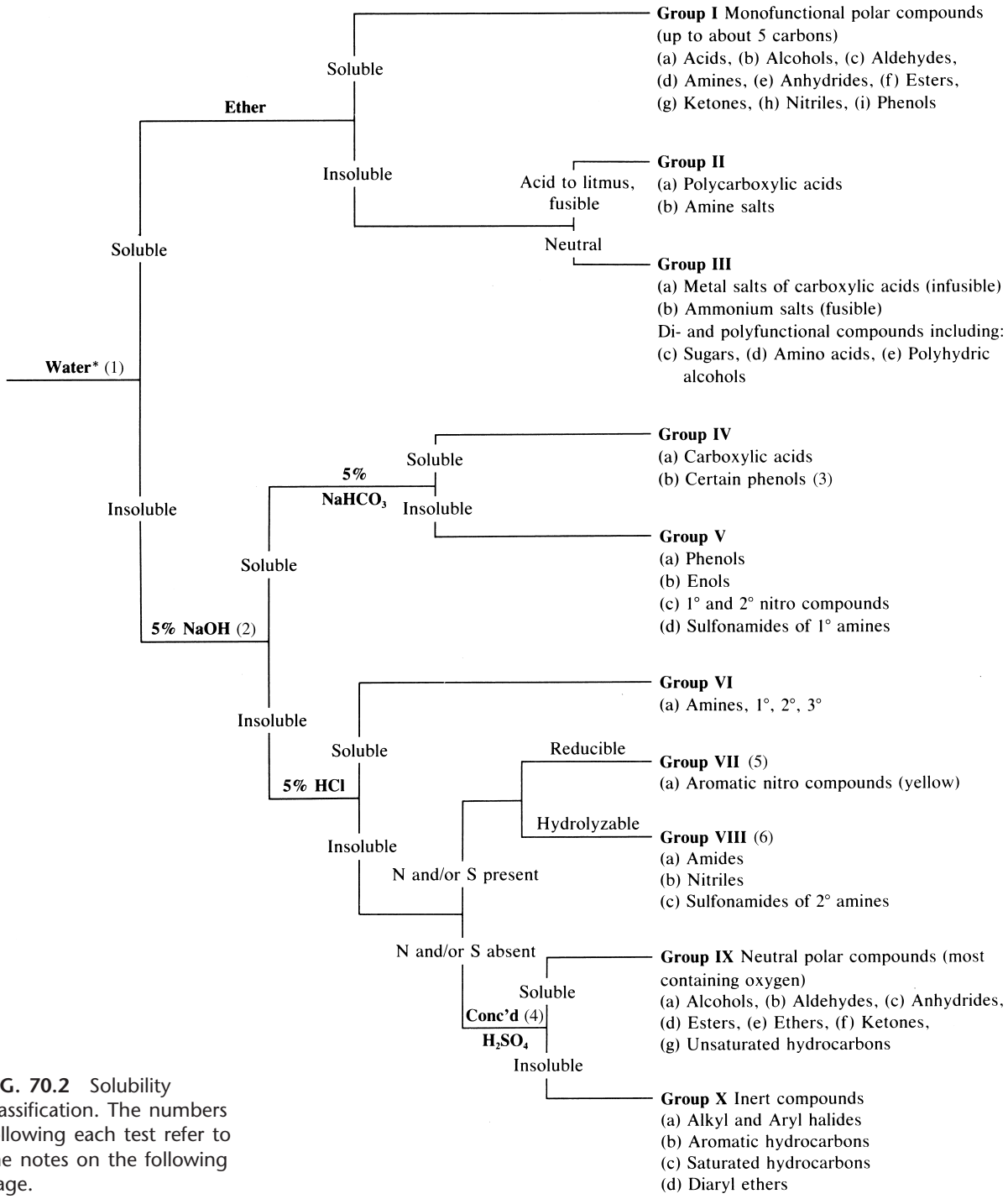


FIG. 70.2 Solubility classification. The numbers following each test refer to the notes on the following page.

Cleaning Up Because the quantities of material used in these tests are extremely small, and because no hazardous substances are handed out as unknowns, it is possible to dilute the material with a large quantity of water and flush it down the drain.

Notes to Solubility Tests

1. Groups I, II, III (soluble in water). Test the solution with pH paper. If the compound is not easily soluble in cold water, treat it as water insoluble but test with indicator paper.
2. If the substance is insoluble in water but dissolves partially in 5% sodium hydroxide, add more water; the sodium salts of some phenols are less soluble in alkali than in water. If the unknown is colored, be careful to distinguish between the *dissolving* and the *reacting* of the sample. Some quinones (colored) *react* with alkali and give highly colored solutions. Some phenols (colorless) *dissolve and then* become oxidized to give colored solutions. Some compounds (e.g., benzamide) are hydrolyzed with such ease that careful observation is required to distinguish them from acidic substances.

See Fig. 70.2.

3. Nitrophenols (yellow), aldehydophenols, and polyhalophenols are sufficiently strongly acidic to react with sodium bicarbonate.
4. Oxygen- and nitrogen-containing compounds form oxonium and ammonium ions in concentrated sulfuric acid and dissolve.
5. On reduction in the presence of hydrochloric acid, these compounds form water-soluble amine hydrochlorides. Dissolve 250 mg of tin(II) chloride in 0.5 mL of concentrated hydrochloric acid, add 50 mg of the unknown, and warm. The material should dissolve with the disappearance of the color and give a clear solution when diluted with water.
6. Most amides can be hydrolyzed by short boiling with 10% sodium hydroxide solution; the acid dissolves with evolution of ammonia. Reflux 100 mg of the sample and 10% sodium hydroxide solution for 15–20 min. Test for the evolution of ammonia, which confirms the elementary analysis for nitrogen and establishes the presence of a nitrile or amide.

Classification Tests

After the unknown is assigned to one of the solubility groups (Fig. 70.2) on the basis of solubility tests, the possible type should be further narrowed by application of classification tests; for example, for alcohols, or methyl ketones, or esters.

Complete Identification—Preparation of Derivatives

Once the unknown has been classified by functional group, the physical properties should be compared with those of representative members of the group (see tables at the end of this chapter). Usually, several possibilities present themselves, and the choice can be narrowed by preparation of derivatives. Select derivatives that distinguish most clearly among the possibilities.

Classification Tests

Group I. Monofunctional Polar Compounds (up to ca. 5 carbons)

(a) Acids

(Table 70.1, page 784; Derivatives, page 779)

No classification test is necessary. Carboxylic and sulfonic acids are detected by testing aqueous solutions with litmus. Acyl halides may hydrolyze during the solubility test.

(b) Alcohols

(Table 70.2, page 786; Derivatives, pages 779–780)

Jones' Oxidation. Dissolve 5 mg of the unknown in 0.5 mL of pure acetone in a test tube, and add to this solution 1 small drop of Jones' reagent (chromic acid in sulfuric acid). A positive test is formation of a green color within 5 sec upon addition of the orange-yellow reagent to a primary or secondary alcohol. Aldehydes also give positive tests, but tertiary alcohols do not.

CAUTION: Cr^{+6} dust is toxic.

Reagent: Dissolve/suspend 13.4 g of chromium trioxide in 11.5 mL of concentrated sulfuric acid, and add this carefully with stirring to enough water to bring the volume to 50 mL.

Cleaning Up Place the test solution in the hazardous waste container.

Handle dioxane with care. It is a suspected carcinogen.

Cerium(IV) Nitrate Test [Ammonium Hexanitratocerium(IV) Test]. Dissolve 15 mg of the unknown in a few drops of water or dioxane in a reaction tube. Add to this solution 0.25 mL of the reagent, and mix thoroughly. Alcohols cause the reagent to change from yellow to red.

Reagent: Dissolve 22.5 g of ammonium hexanitratocerium(IV), $Ce(NH_4)_2(NO_3)_6$, in 56 mL of 2 *N* nitric acid.

Cleaning Up Dilute the solution with water and flush down the drain.

(c) Aldehydes

(Table 70.3, page 787; Derivatives, pages 442 and 444; ch. 36)

2,4-Dinitrophenylhydrazones. All aldehydes and ketones readily form bright-yellow to dark-red 2,4-dinitrophenylhydrazones. Yellow derivatives are formed from isolated carbonyl groups and orange-red to red derivatives from aldehydes or ketones conjugated with double bonds or aromatic rings.

Dissolve 10 mg of the unknown in 0.5 mL of ethanol, and then add 0.75 mL of 2,4-dinitrophenylhydrazine reagent. Mix thoroughly and let sit for a few minutes. A yellow to red precipitate is a positive test.

Reagent: Dissolve 1.5 g of 2,4-dinitrophenylhydrazine in 7.5 mL of concentrated sulfuric acid. Add this solution, with stirring, to a mixture of 10 mL of water and 35 mL of ethanol.

Cleaning Up Place the test solution in the hazardous waste container.

Schiff Test. Add 1 drop (30 mg) of the unknown to 1 mL of Schiff's reagent. A magenta color will appear within 10 min with aldehydes. Compare the color of your unknown with that of a known aldehyde.

Reagent: Prepare 50 mL of a 0.1% aqueous solution of *p*-rosaniline hydrochloride (fuchsin). Add 2 mL of a saturated aqueous solution of sodium bisulfite. After 1 h add 1 mL of concentrated hydrochloric acid.

Bisulfite Test. Follow the procedure in Chapter 36. Nearly all aldehydes and most methyl ketones form solid, water-soluble bisulfite addition products.

Destroy used Tollens' reagent promptly with nitric acid. It can form explosive fulminates.

Tollens' Test. Follow the procedure in Chapter 36. A positive test, deposition of a silver mirror, is given by most aldehydes, but not by ketones.

(d) Amides and Amines

(Tables 70.4, 70.5, and 70.6, pages 788–791; Derivatives of amines, pages 780–781)

Hinsberg Test. Follow the procedure in Chapter 43, using benzenesulfonyl chloride to distinguish between primary, secondary, and tertiary amines.

(e) Anhydrides and Acid Halides

(Table 70.7, page 791; Derivatives, page 781–782) Anhydrides and acid halides will react with water to give acidic solutions, detectable with litmus paper. They easily form benzamides and acetamides.

Acidic Iron(III) Hydroxamate Test. With iron(III) chloride alone a number of substances give a color that can interfere with this test. Dissolve 2 drops (or about 30 mg) of the unknown in 1 mL of ethanol, and add 1 mL of 1 *N* hydrochloric acid followed by 1 drop of 10% aqueous iron(III) chloride solution. If any color except yellow appears you will find it difficult to interpret the results from the following test.

Add 2 drops (or about 30 mg) of the unknown to 0.5 mL of a 1 *N* solution of hydroxylamine hydrochloride in alcohol. Add 2 drops of 6 *M* hydrochloric acid to the mixture, warm it slightly for 2 min, and boil it for a few seconds. Cool the solution, and add 1 drop of 10% ferric chloride solution. A red-blue color is a positive test.

Cleaning Up Neutralize the reaction mixture with sodium carbonate, dilute with water, and flush down the drain.

(f) Esters

(Table 70.8, page 792. Derivatives are prepared from component acid and alcohol obtained on hydrolysis.)

Esters, unlike anhydrides and acid halides, do not react with water to give acidic solutions and do not react with acidic hydroxylamine hydrochloride. They do, however, react with alkaline hydroxylamine.

Alkaline Iron(III) Hydroxamate Test. First test the unknown with iron(III) chloride alone. [See under Group I(e), Acidic Iron(III) Hydroxamate Test.]

To a solution of 1 drop (30 mg) of the unknown in 0.5 mL of 0.5 *N* hydroxylamine hydrochloride in ethanol, add 2 drops of 20% sodium hydroxide solution. Heat the solution to boiling, cool slightly, and add 1 mL of 1 *N* hydrochloric acid. If cloudiness develops add up to 1 mL of ethanol. Add 10% iron(III) chloride solution dropwise with thorough mixing. A red-blue color is a positive test. Compare your unknown with a known ester.

Cleaning Up Neutralize the solutions with sodium carbonate, dilute with water, and flush down the drain.

(g) Ketones

(Table 70.14, page 796; Derivatives, pages 442 and 444)

2,4-Dinitrophenylhydrazone. See under Group I(c), Aldehydes. All ketones react with 2,4-dinitrophenylhydrazine reagent.

Iodoform Test for Methyl Ketones. Follow the procedure in Chapter 36.

A positive iodoform test is given by substances containing the $CH_3\overset{\overset{O}{\|}}{C}-$ group or by compounds easily oxidized to this group, e.g., CH_3COR, CH_3CHOHR, CH_3CH_2OH, CH_3CHO, $RCOCH_2COR$. The test is negative for compounds of the structure CH_3COOR, CH_3CONHR, and other compounds of similar structure that give acetic acid on hydrolysis. It is also negative for $CH_3COCH_2CO_2R$, CH_3COCH_2CN, $CH_3COCH_2NO_2$.

Bisulfite Test. Follow the procedure in Chapter 36. Aliphatic methyl ketones and unhindered cyclic ketones form bisulfite addition products. Methyl aryl ketones, such as acetophenone, $C_6H_5COCH_3$, fail to react.

(h) Nitriles

(Table 70.15, page 797. Derivatives prepared from the carboxylic acid obtained by hydrolysis.)

At high temperature nitriles (and amides) are converted to hydroxamic acids by hydroxylamine:

$$RCN + 2\ H_2NOH \longrightarrow RCONHOH + NH_3$$

The hydroxamic acid forms a red-blue complex with iron(III) ion. The unknown must first give a negative test with hydroxylamine at lower temperature [Group I(f), Alkaline Iron(III) Hydroxamate Test] before trying this test.

Hydroxamic Acid Test for Nitriles (and Amides). To 1 mL of a 1 *M* hydroxylamine hydrochloride solution in propylene glycol add 15 mg of the unknown dissolved in the minimum amount of propylene glycol. Then add 0.5 mL of 1 *N* potassium hydroxide in propylene glycol, and boil the mixture for 2 min. Cool the mixture, and add 0.1 to 0.25 mL of 10% iron(III) chloride solution. A red-blue color is a positive test for almost all nitrile and amide groups, although benzanilide fails to give a positive test.

Cleaning Up Because the quantity of material is extremely small, the test solution can be diluted with water and flushed down the drain.

(i) Phenols

(Table 70.17, page 798; Derivatives, page 783)

Iron(III) Chloride Test. Dissolve 15 mg of the unknown compound in 0.5 mL of water or water-alcohol mixture, and add 1–2 drops of 1% iron(III) chloride solution. A red, blue, green, or purple color is a positive test.

Cleaning Up Because the quantity of material is extremely small, the test solution can be diluted with water and flushed down the drain.

CAUTION: $CHCl_3$ is a carcinogen.

A more sensitive test for phenols consists of dissolving or suspending 15 mg of the unknown in 0.5 mL of chloroform and adding 1 drop of a solution made by dissolving 0.1 g of iron(III) chloride in 10 mL of chloroform. Addition of a drop of pyridine, with stirring, will produce a color if phenols or enols are present.

Group II. Water-Soluble Acidic Salts, Insoluble in Ether

Amine Salts

[Table 70.5 (1° and 2° amines), pages 789–790; Table 70.6 (3° amines), page 791]

The free amine can be liberated by addition of base and extraction into ether. Following evaporation of the ether, the Hinsberg test, Group I(d), can be applied to determine if the compound is a primary, secondary, or tertiary amine.

The acid iron(III) hydroxamate test, Group I(d), can be applied directly to the amine salt (see the Hinsburg test, page 770).

Group III. Water-Soluble Neutral Compounds, Insoluble in Ether

(a) Metal Salts of Carboxylic Acids

(Table 70.1, carboxylic acids, page 784; Derivatives, page 779)

The free acid can be liberated by addition of acid and extraction into an appropriate solvent, after which the carboxylic acid can be characterized by mp or bp before proceeding to prepare a derivative.

(b) Ammonium Salts

(Table 70.1, carboxylic acids, page 784; Derivatives, page 779)

Ammonium salts on treatment with alkali liberate ammonia, which can be detected by its odor and the fact that it will turn red litmus to blue. A more sensitive test utilizes the copper(II) ion, which is blue in the presence of ammonia [see Group VIII a(i)]. Ammonium salts will not give a positive hydroxamic acid test (Ih) as given by amides.

(c) Sugars

See Chapter 36 for Tollens' test and Chapter 63 for phenylosazone formation.

(d) Amino Acids

Add 2 mg of the suspected amino acid to 1 mL of ninhydrin reagent, boil for 20 sec, and note the color. A blue color is a positive test.

Reagent: Dissolve 0.2 g of ninhydrin in 50 mL of water.

Cleaning Up Because the quantity of material is extremely small, the test solution can be diluted with water and flushed down the drain.

(e) Polyhydric Alcohols

(Table 70.2, page 786; Derivatives, pages 779–780)

Periodic Acid Test for vic-Glycols.[4] Vicinal glycols (hydroxyl groups on adjacent carbon atoms) can be detected by reaction with periodic acid. In addition to 1,2-glycols, a positive test is given by α-hydroxy aldehydes, α-hydroxy ketones, α-hydroxy acids, and α-amino alcohols, as well as 1,2-diketones.

To 2 mL of periodic acid reagent add 1 drop (no more) of concentrated nitric acid and shake. Then add 1 drop or a small crystal of the unknown. Shake

4. R. L. Shriner, R. C. Fuson, D. Y. Curtin, and T. C. Morill. *The Systematic Identification of Organic Compounds,* 6th ed., JohnWiley & Sons, Inc., New York, 1980.

for 15 sec, and add 1–2 drops of 5% aqueous silver nitrate solution. Instantaneous formation of a white precipitate is a positive test.

Reagent: Dissolve 0.25 g of paraperiodic acid (H_5IO_6) in 50 mL of water.

Cleaning Up Because the quantity of material is extremely small, dilute the test solution with water and flush down the drain.

Group IV. Certain Carboxylic Acids, Certain Phenols, and Sulfonamides of 1° Amines

(a) Carboxylic Acids

Solubility in both 5% sodium hydroxide and sodium bicarbonate is usually sufficient to characterize this class of compounds. Addition of mineral acid should regenerate the carboxylic acid. The neutralization equivalent can be obtained by titrating a known quantity of the acid (ca. 50 mg) dissolved in water-ethanol with 0.1 *N* sodium hydroxide to a phenolphthalein end point.

(b) Phenols

Negatively substituted phenols such as nitrophenols, aldehydrophenols, and polyhalophenols are sufficiently acidic to dissolve in 5% sodium bicarbonate. See Group I(i) for the iron(III) chloride test for phenols; however, this test is not completely reliable for these acidic phenols.

Group V. Acidic Compounds, Insoluble in Bicarbonate

(a) Phenols

See Group I(i).

(b) Enols

See Group I(i).

(c) 1° and 2° Nitro Compounds

(Table 70.16, page 797; Derivatives, page 780)

Iron(II) Hydroxide Test. To a small vial (capacity (1–2 mL) add 5 mg of the unknown to 0.5 mL of freshly prepared ferrous sulfate solution. Add 0.4 mL of a 2 *N* solution of potassium hydroxide in methanol, cap the vial, and shake it. The appearance of a red-brown precipitate of iron(III) hydroxide within 1 min is a positive test. Almost all nitro compounds give a positive test within 30 sec.

Reagents: Dissolve 2.5 g of ferrous ammonium sulfate in 50 mL of deoxygenated (by boiling) water. Add 0.2 mL of concentrated sulfuric acid and a piece

of iron to prevent oxidation of the ferrous ion. Keep the bottle tightly stoppered. The potassium hydroxide solution is prepared by dissolving 5.6 g of potassium hydroxide in 50 mL of methanol.

Cleaning Up Because the quantity of material is extremely small, the test solution can be diluted with water and flushed down the drain after neutralization with dilute hydrochloric acid.

(d) Sulfonamides of 1° Amines

An extremely sensitive test for sulfonamides (Feigl, *Spot Tests in Organic Analysis*) consists of placing a drop of a suspension or solution of the unknown on sulfonamide test paper followed by a drop of 0.5% hydrochloric acid. A red color is a positive test for sulfonamides.

The test paper is prepared by dipping filter paper into a mixture of equal volumes of a 1% aqueous solution of sodium nitrite and a 1% methanolic solution of *N*,*N*-dimethyl-1-naphthylamine. Allow the filter paper to dry in the dark.

CAUTION: *Handle* N,N-*dimethyl-1-naphthylamine with care. As a class, aromatic amines are quite toxic and many are carcinogenic. Handle them all with care—in a hood if possible.*

Cleaning Up Place the test paper in the solid hazardous waste container.

Group VI. Basic Compounds, Insoluble in Water, Soluble in Acid

Amines

See Group I(d).

Group VII. Reducible, Neutral *N*- and *S*-Containing Compounds

Aromatic Nitro Compounds

See Group V(c).

Group VIII. Hydrolyzable, Neutral *N*- and *S*-Containing Compounds (identified through the acid and amine obtained on hydrolysis)

(a) Amides

Unsubstituted amides are detected by the hydroxamic acid test, Group I(h).

(1) Unsubstituted Amides. Upon hydrolysis, unsubstituted amides liberate ammonia, which can be detected by reaction with cupric ion [Group III(b)].

To 1 mL of 20% sodium hydroxide solution, add 25 mg of the unknown. Cover the mouth of the reaction tube with a piece of filter paper moistened with

a few drops of 10% copper(II) sulfate solution. Boil for 1 min. A blue color on the filter paper is a positive test for ammonia.

Cleaning Up Neutralize the test solution with 10% hydrochloric acid, dilute with water, and flush down the drain.

(2) Substituted Amides. The identification of substituted amides is not easy. There are no completely general tests for the substituted amide groups and hydrolysis is often difficult.

Hot sodium hydroxide solution is corrosive; use care.

Hydrolyze the amide by refluxing 250 mg with 2.5 mL of 20% sodium hydroxide for 20 min. Isolate the primary or secondary amine produced, by extraction into ether, and identify as described under Group I(d). Liberate the acid by acidification of the residue, isolate by filtration or extraction, and characterize by bp or mp and the mp of an appropriate derivative.

Use care in shaking concentrated sulfuric acid.

Cleaning Up Dilute the test solution with water and flush down the drain.

(3) Anilides. Add 50 mg of the unknown to 1.5 mL of concentrated sulfuric acid. Carefully stopper the reaction tube with a rubber stopper, and shake vigorously. (*Caution!*) Add 25 mg of finely powdered potassium dichromate. A blue-pink color is a positive test for an anilide that does not have substituents on the ring (e.g., acetanilide).

Dichromate dust is carcinogenic, when inhaled. Cr^{+6} is not a carcinogen when applied to the skin or ingested.

Cleaning Up Carefully add the solution to water, neutralize with sodium carbonate, and flush down the drain.

(b) Nitriles

See Group I(h).

(c) Sulfonamides

See Group V(d).

Group IX. Neutral Polar Compounds, Insoluble in Dilute Hydrochloric Acid, Soluble in Concentrated Sulfuric Acid (most compounds containing oxygen)

(a) Alcohols

See Group I(b).

(b) Aldehydes

See Group I(c).

(c) Anhydrides

See Group I(e).

(d) Esters

See Group I(f).

(e) Ethers

(Table 70.9, page 793)

Ethers are very unreactive. Care must be used to distinguish ethers from those hydrocarbons that are soluble in concentrated sulfuric acid.

$Fe[Fe(SCN)_6]$

Iron(III) hexathiocyanatoferrate(III)

Ferrox Test. In a dry test tube grind together, with a stirring rod, a crystal of iron(III) ammonium sulfate (or iron(III) chloride) and a crystal of potassium thiocyanate. Iron(III) hexathiocyanatoferrate(III) will adhere to the stirring rod. In a clean tube place 3 drops of a liquid unknown or a saturated toluene solution of a solid unknown, and stir with the rod. The salt will dissolve if the unknown contains oxygen to give a red-purple color, but it will not dissolve in hydrocarbons or halocarbons. Diphenyl ether does not give a positive test.

Alkyl ethers are generally soluble in concentrated sulfuric acid; alkyl aryl and diaryl ethers are not soluble.

Cleaning Up Place the mixture in the hazardous waste container.

(f) Ketones

(Table 70.14, page 796; Derivatives, pages 442 and 444).

(g) Unsaturated Hydrocarbons

(Table 70.12, page 794)

Use care in working with the bromine solution

Bromine in Carbon Tetrachloride. Dissolve 1 drop (20 mg) of the unknown in 0.5 mL of carbon tetrachloride. Add a 2% solution of bromine in carbon tetrachloride dropwise with shaking. If more than 2 drops of bromine solution are required to give a permanent red color, unsaturation is indicated. The bromine solution must be fresh.

Cleaning Up Place the mixture in the halogenated solvents container.

Potassium Permanganate Solution. Dissolve 1 drop (20 mg) of the unknown in reagent grade acetone and add a 1% aqueous solution of potassium permanganate dropwise with shaking. If more than one drop of reagent is required to give a purple color to the solution, unsaturation or an easily oxidized

functional group is present. Run parallel tests on pure acetone and, as usual, a compound known to be an alkene.

Cleaning Up Dilute the solution with water and flush down the drain.

Group X. Inert Compounds. Insoluble in Concentrated Sulfuric Acid

(a) Alkyl and Aryl Halides

Alkyl Halides (Table 70.10, page 793)
Aryl Halides (Table 70.11, page 794)

Do not waste silver nitrate.

Alcoholic Silver Nitrate. Add 1 drop of the unknown (or saturated solution of 10 mg of unknown in ethanol) to 0.2 mL of a saturated solution of silver nitrate. A precipitate that forms within 2 min is a positive test for an alkyl bromide, or iodide, or a tertiary alkyl chloride, as well as alkyl halides.

If no precipitate forms within 2 min, heat the solution to boiling. A precipitate of silver chloride will form from primary and secondary alkyl chlorides. Aryl halides and vinyl halides will not react.

Cleaning Up Because the quantity of material is extremely small, it can be diluted with water and flushed down the drain.

(b) Aromatic Hydrocarbons

(Table 70.13, page 795; Derivatives, pages 780 and 782)

Aromatic hydrocarbons are best identified and characterized by UV and NMR spectroscopy, but the Friedel–Crafts reaction produces a characteristic color with certain aromatic hydrocarbons.

Keep moisture away from aluminum chloride.
***CAUTION:** Chloroform is carcinogenic. Carry out this test in a hood.*

Friedel–Crafts Test. Heat a test tube containing about 50 mg of anhydrous aluminum chloride in a hot flame to sublime the salt up onto the sides of the tube. Add a solution of about 10 mg of the unknown dissolved in a drop of chloroform to the cool tube in such a way that it comes into contact with the sublimed aluminum chloride. Note the color that appears.

Nonaromatic compounds fail to give a color with aluminum chloride, benzene and its derivatives give orange or red colors, naphthalenes a blue or purple color, biphenyls a purple color, phenanthrene a purple color, and anthracene a green color.

Cleaning Up Place the test mixture in the halogenated organic solvents container.

(c) Saturated Hydrocarbons

Saturated hydrocarbons are best characterized by NMR and IR spectroscopy, but they can be distinguished from aromatic hydrocarbons by the Friedel–Crafts test [Group X(b)].

(d) Diaryl Ethers

Because they are so inert, diaryl ethers are difficult to detect and may be mistaken for aromatic hydrocarbons. They do not give a positive Ferrox test (see p. 777) for ethers and do not dissolve in concentrated sulfuric acid. Their infrared spectra, however, are characterized by an intense C—O single-bond, stretching vibration in the region 1270–1230 cm^{-1}.

Derivatives

1. Acids

(Table 70.1)

p-Toluidides and Anilides. Reflux a mixture of the acid (100 mg) and thionyl chloride (0.5 mL) in a reaction tube for 0.5 h. Cool the reaction mixture, and add 0.25 g of aniline or *p*-toluidine in 3 mL of toluene. Warm the mixture on the steam bath for 2 min, and then wash with 1-mL portions of water, 5% hydrochloric acid, 5% sodium hydroxide, and water. The toluene is dried briefly over anhydrous calcium chloride pellets and evaporated in the hood; the derivative is recrystallized from water or ethanol–water.

CAUTION: p-*Toluidine is a highly toxic irritant.*

Cleaning Up Dilute the aqueous layers with water and flush down the drain. Place the drying agent in the hazardous waste container.

Amides. Reflux a mixture of the acid (100 mg) and thionyl chloride (0.5 mL) for 0.5 h. Transfer the cool reaction mixture into 1.4 mL of ice-cold concentrated ammonia. Stir until reaction is complete, collect the product by filtration, and recrystallize it from water or water–ethanol.

Thionyl chloride is an irritant. Use it in a hood.

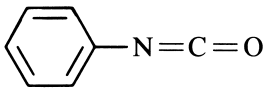
Cleaning Up Neutralize the aqueous filtrate with 10% hydrochloric acid, dilute with water, and flush down the drain.

2. Alcohols

(Table 70.2)

3,5-Dinitrobenzoates. Gently boil 100 mg of 3,5-dinitrobenzoyl chloride and 25 mg of the alcohol for 5 min. Cool the mixture, pulverize any solid that forms, and add 2 mL of 2% sodium carbonate solution. Continue to grind and stir the solid with the sodium carbonate solution (to remove 3,5-dinitrobenzoic acid) for about a minute, filter, and wash the crystals with water. Dissolve the product in about 2.5–3 mL of hot ethanol, add water to the cloud point, and allow crystallization to proceed. Wash the 3,5-dinitrobenzoate with water–alcohol and dry.

Note to instructor: Check to ascertain that the 3,5-dinitrobenzoyl chloride has not hydrolyzed. The mp should be >65°C. Reported mp is 68–69°C.



Phenyl isocyanate

CAUTION: *Lachrymator*

Cleaning Up Dilute the aqueous filtrate with water and flush down the drain.

Phenylurethanes. Mix 100 mg of anhydrous alcohol (or phenol) and 100 mg of phenyl isocyanate (or α-naphthylurethane), and heat on the steam bath for 5 min. (If the unknown is a phenol add a drop of pyridine to the reaction mixture.) Cool, add about 1 mL of ligroin, heat to dissolve the product, filter hot to remove a small amount of diphenylurea which usually forms, and cool the filtrate in ice, with scratching, to induce crystallization.

Cleaning Up Place the ligroin filtrate in the organic solvents container.

3. Aldehydes

(Table 70.3)

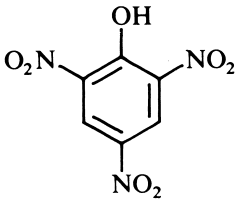
Semicarbazones. See Chapter 36. Use 0.5 mL of the stock solution and an estimated 1 mmol of the unknown aldehyde (or ketone).

2,4-Dinitrophenylhydrazones. See Chapter 36. Use 1 mL of the stock solution of 0.1 *M* 2,4-dinitrophenylhydrazine and an estimated 0.1 mmol of the unknown aldehyde (or ketone).

4. Primary and Secondary Amines

(Table 70.5)

Benzamides. Add about 0.25 g of benzoyl chloride in small portions with vigorous shaking and cooling to a suspension of 0.5 mmol of the unknown amine in 0.5 mL of 10% aqueous sodium hydroxide solution. After about 10 min of shaking the mixture is made pH 8 (pH paper) with dilute hydrochloric acid. The lumpy product is removed by filtration, washed thoroughly with water, and recrystallized from ethanol–water.



Picric acid
(2,4,6-Trinitrophenol)

Handle pure acid with care (explosive). It is sold as a moist solid. Do not allow to dry out.

Cleaning Up Dilute the filtrate with water and flush down the drain.

Picrates. Add a solution of 30 mg of the unknown in 1 mL of ethanol (or 1 mL of a saturated solution of the unknown) to 1 mL of a saturated solution of picric acid (2,4,6-trinitrophenol, a strong acid) in ethanol, and heat the solution to boiling. Cool slowly, remove the picrate by filtration, and wash with a small amount of ethanol. Recrystallization is not usually necessary; in the case of hydrocarbon picrates the product is often too unstable to be recrystallized.

Cleaning Up See page 523 for the treatment of solutions containing picric acid.

Acetamides. Reflux about 0.5 mmol of the unknown with 0.2 mL of acetic anhydride for 5 min, cool, and dilute the reaction mixture with 2.5 mL of water.

Acetic anhydride is corrosive. Work with this in a hood.

Initiate crystallization by scratching, if necessary. Remove the crystals by filtration, and wash thoroughly with dilute hydrochloric acid to remove unreacted amine. Recrystallize the derivative from alcohol–water. Amines of low basicity, e.g., *p*-nitroaniline, should be refluxed for 30–60 min with 1 mL of pyridine as a solvent. The pyridine is removed by shaking the reaction mixture with 5 mL of 2% sulfuric acid solution; the product is isolated by filtration and recrystallized.

Cleaning Up Neutralize the filtrate from the usual reaction with sodium carbonate. Then dilute it with water and flush down the drain. If pyridine is used as the solvent, neutralize the filtrate with sodium carbonate and extract it with ligroin. Place the ligroin/pyridine in the organic solvents container; dilute the aqueous layer with water and flush down the drain.

5. Tertiary Amines

(Table 70.6)

Picrates. See under Primary and Secondary Amines.

$$R_3N + CH_3I \rightarrow R_3\overset{+}{N}CH_3I^-$$

Methiodides. Reflux 100 mg of the amine and 100 mg of methyl iodide for 5 min on the steam bath. Cool, scratch to induce crystallization, and recrystallize the product from ethyl alcohol or ethyl acetate.

Methyl iodide is a suspected carcinogen.

Cleaning Up Because the filtrate may contain some methyl iodide, place it in the halogenated solvents container.

6. Anhydrides and Acid Chlorides

(Table 70.7)

Acids. Reflux 40 mg of the acid chloride or anhydride with 1 mL of 5% sodium carbonate solution for 20 min or less. Extract unreacted starting material with 1 mL of ether, if necessary, and acidify the reaction mixture with dilute sulfuric acid to liberate the carboxylic acid.

Cleaning Up Place the ether in the organic solvents container; dilute the aqueous layer with water and flush it down the drain.

Amides. Because the acid chloride (or anhydride) is already present, simply mix the unknown (50 mg) and 0.7 mL of ice-cold concentrated ammonia until reaction is complete, collect the product by filtration, and recrystallize it from water or ethanol–water.

Cleaning Up Neutralize the filtrate with dilute hydrochloric acid and flush it down the drain.

Anilides. Reflux 40 mg of the acid halide or anhydride with 100 mg of aniline in 2 mL of toluene for 10 min. Wash the toluene solution with 5-mL portions each of water, 5% hydrochloric acid, 5% sodium hydroxide, and again with water. The toluene solution is dried over anhydrous calcium chloride and evaporated; the anilide is recrystallized from water or ethanol–water.

Cleaning Up Dilute the combined aqueous layers with water and flush down the drain. Place the soldium sulfate in the aromatic amines hazardous waste container.

7. Aryl Halides

(Table 70.11)

Nitration. Add 0.4 mL of concentrated sulfuric acid to 100 mg of the aryl halide (or aromatic compound) and stir. Add 0.4 mL of concentrated nitric acid dropwise with stirring and shaking while cooling the reaction mixture in water. Then heat and shake the reaction mixture in a water bath at about 50°C for 15 min, pour into 2 mL of cold water, and collect the product by filtration. Recrystallize from methanol to constant melting point.

Use great care when working with fuming nitric acid.

To nitrate unreactive compounds, use fuming nitric acid in place of concentrated nitric acid.

Cleaning Up Dilute the filtrate with water, neutralize with sodium carbonate, and flush the solution down the drain.

Sidechain Oxidation Products. Dissolve 0.2 g of sodium dichromate in 0.6 mL of water, and add 0.4 mL of concentrated sulfuric acid. Add 50 mg of the unknown and boil for 30 min. Cool, add 0.4–0.6 mL of water, and then remove the carboxylic acid by filtration. Wash the crystals with water and recrystallize from methanol–water.

Cleaning Up Place the filtrate from the reaction, after neutralization with sodium carbonate, in the hazardous waste container.

8. Hydrocarbons: Aromatic

(Table 70.13)

Nitration. See preceding, under Aryl Halides.

Picrates. See preceding, under Primary and Secondary Amines.

9. Ketones

(Table 70.14)

Semicarbazones and 2,4-dinitrophenylhydrazones. See preceding directions under Aldehydes.

10. Nitro Compounds

(Table 70.16)

Reduction to Amines. Place 100 mg of the unknown in a reaction tube, add 0.2 g of tin, and then—in portions—2 mL of 10% hydrochloric acid. Reflux for 30 min, add 1 mL of water, then add slowly, with good cooling, sufficient 40% sodium hydroxide solution to dissolve the tin hydroxide. Extract the reaction mixture with three 1-mL portions of *t*-butyl methyl ether, dry the ether extract over anhydrous calcium chloride pellets, wash the drying agent with ether, and evaporate the ether to leave the amine. Determine the boiling point or melting point of the amine and then convert it into a benzamide or acetamide as described under the section on Primary and Secondary Amines.

Cleaning Up Neutralize the aqueous layer with 10% hydrochloric acid, remove the tin hydroxide by filtration, and discard it in the nonhazardous solid waste container. Dilute the filtrate with water and flush down the drain. After the ether evaporates from the calcium chloride, place it in the nonhazardous waste container.

11. Phenols

(Table 70.17)

α-Naphthylurethane. Follow the procedure for preparation of a phenylurethane under the Alcohols section.

Use great care when working with bromine. Should any touch the skin wash it off with copious quantities of water. Work in a hood and wear disposable gloves.

Bromo Derivative. In a reaction tube dissolve 160 mg of potassium bromide in 1 mL of water. *Carefully* add 100 mg of bromine. In a separate flask dissolve 20 mg of the phenol in 0.2 mL of methanol, and add 0.2 mL of water. Add about 0.3 mL of the bromine solution with swirling (hood); continue the addition of bromine until the yellow color of unreacted bromine persists. Add 0.6–0.8 mL of water to the reaction mixture, and shake vigorously. Remove the product by filtration, and wash well with water. Recrystallize from methanol-water.

Cleaning Up Destroy any unreacted bromine by adding sodium bisulfite solution dropwise until the color dissipates. Then dilute the solution with water and flush it down the drain.

TABLE 70.1 Acids

			Derivatives		
			p-*Toluidide*[a]	*Anilide*[b]	*Amide*[c]
bp	mp	Compound	mp	mp	mp
101		Formic acid	53	47	43
118		Acetic acid	126	106	79
139		Acrylic acid	141	104	85
141		Propionic acid	124	103	81
162		*n*-Butyric acid	72	95	115
163		Methacrylic acid		87	102
165		Pyruvic acid	109	104	124
185		Valeric acid	70	63	106
186		2-Methylvaleric acid	80	95	79
194		Dichloroacetic acid	153	118	98
202–203		Hexanoic acid	75	95	101
237		Octanoic acid	70	57	107
254		Nonanoic acid	84	57	99
	31–32	Decanoic acid	78	70	108
	43–45	Lauric acid	87	78	100
	47–49	Bromoacetic acid		131	91
	47–49	Hydrocinnamic acid	135	92	105
	54–55	Myristic acid	93	84	103
	54–58	Trichloroacetic acid	113	97	141
	61–62	Chloroacetic acid	162	137	121
	61–62.5	Palmitic acid	98	90	106
	67–69	Stearic acid	102	95	109
	68–69	3,3-Dimethylacrylic acid		126	107
	71–73	Crotonic acid	132	118	158
	77–78.5	Phenylacetic acid	136	118	156
	101–102	Oxalic acid dihydrate		257	400 (dec)
	98–102	Azelaic acid (nonanedioic)	164 (di)	107 (mono)	93 (mono)
				186 (di)	175 (di)
	103–105	*o*-Toluic acid	144	125	142
	108–110	*m*-Toluic acid	118	126	94
	119–121	DL-Mandelic acid	172	151	133
	122–123	Benzoic acid	158	163	130
	127–128	2-Benzoylbenzoic acid		195	165
	129–130	2-Furoic acid	107	123	143
	131–133	DL-Malic acid	178 (mono)	155 (mono)	
			207 (di)	198 (di)	163 (di)
	131–134	Sebacic acid	201	122 (mono)	170 (mono)
				200 (di)	210 (di)

(continued)

a. For preparation, see page 779.
b. For preparation, see page 779.
c. For preparation, see page 779.

TABLE 70.1 *continued*

			Derivatives		
			p-*Toluidide*[a]	*Anilide*[b]	*Amide*[c]
bp	mp	Compound	mp	mp	mp
	134–135	*E*-Cinnamic acid	168	153	147
	134–136	Maleic acid	142 (di)	198 (mono)	260 (di)
				187 (di)	
	135–137	Malonic acid	86 (mono)	132 (mono)	
			253 (di)	230 (di)	
	138–140	2-Chlorobenzoic acid	131	118	139
	140–142	3-Nitrobenzoic acid	162	155	143
	144–148	Anthranilic acid	151	131	109
	147–149	Diphenylacetic acid	172	180	167
	152–153	Adipic acid	239	151 (mono)	125 (mono)
				241 (di)	220 (di)
	153–154	Citric acid	189 (tri)	199 (tri)	210 (tri)
	157–159	4-Chlorophenoxyacetic acid		125	133
	158–160	Salicylic acid	156	136	142
	163–164	Trimethylacetic acid		127	178
	164–166	5-Bromosalicylic acid		222	232
	166–167	Itaconic acid		190	191 (di)
	171–174	D-Tartaric acid		180 (mono)	171 (mono)
				264 (di)	196 (di)
	179–182	3,4-Dimethoxybenzoic acid		154	164
	180–182	4-Toluic acid	160	145	160
	182–185	4-Anisic acid	186	169	167
	187–190	Succinic acid	180 (mono)	143 (mono)	157 (mono)
			255 (di)	230 (di)	260 (di)
	201–203	3-Hydroxybenzoic acid	163	157	170
	203–206	3,5-Dinitrobenzoic acid		234	183
	210–211	Phthalic acid	150 (mono)	169 (mono)	149 (mono)
			201 (di)	253 (di)	220 (di)
	214–215	4-Hydroxybenzoic acid	204	197	162
	225–227	2,4-Dihydroxybenzoic acid		126	228
	236–239	Nicotinic acid	150	132	128
	239–241	4-Nitrobenzoic acid	204	211	201
	299–300	Fumaric acid		233 (mono)	270 (mono)
				314 (di)	266 (di)
	>300	Terephthalic acid		334	

a. For preparation, see page 779.
b. For preparation, see page 779.
c. For preparation, see page 779.

TABLE 70.2 Alcohols

			Derivatives	
			3,5-Dinitrobenzoate[a]	*Phenylurethane*[b]
bp	mp	Compound	mp	mp
65		Methanol	108	47
78		Ethanol	93	52
82		2-Propanol	123	88
83		*t*-Butyl alcohol	142	136
96–98		Allyl alcohol	49	70
97		1-Propanol	74	57
98		2-Butanol	76	65
102		2-Methyl-2-butanol	116	42
104		2-Methyl-3-butyn-2-ol	112	
108		2-Methyl-1-propanol	87	86
114–115		Propargyl alcohol		63
114–115		3-Pentanol	101	48
118		1-Butanol	64	61
118–119		2-Pentanol	62	oil
123		3-Methyl-3-pentanol	96(62)	43
129		2-Chloroethanol	95	51
130		2-Methyl-1-butanol	70	31
132		4-Methyl-2-pentanol	65	143
136–138		1-Pentanol	46	46
139–140		Cyclopentanol	115	132
140		2,4-Dimethyl-3-pentanol	75	95
146		2-Ethyl-1-butanol	51	
151		2,2,2-Trichloroethanol	142	87
157		1-Hexanol	58	42
160–161		Cyclohexanol	113	82
170		Furfuryl alcohol	80	45
176		1-Heptanol	47	60(68)
178		2-Octanol	32	oil
178		Tetrahydrofurfuryl alcohol	83	61
183–184		2,3-Butanediol		201 (di)
183–186		2-Ethyl-1-hexanol		34
187		1,2-Propanediol		153 (di)
194–197		Linaloöl		66
195		1-Octanol	61	74
196–198		Ethylene glycol	169	157 (di)
204		1,3-Butanediol		122
203–205		Benzyl alcohol	113	77
204		1-Phenylethanol	95	92
219–221		2-Phenylethanol	108	78
230		1,4-Butanediol		183 (mono)
231		1-Decanol	57	59

(continued)

a. For preparation, see page 779.
b. For preparation, see page 780.

TABLE 70.2 *continued*

			Derivatives	
			3,5-Dinitrobenzoate[a]	*Phenylurethane*[b]
bp	mp	Compound	mp	mp
259		4-Methoxybenzyl alcohol		92
	33–35	Cinnamyl alcohol	121	90
	38–40	1-Tetradecanol	67	74
	48–50	1-Hexadecanol	66	73
	58–60	1-Octadecanol	77(66)	79
	66–67	Benzhydrol	141	139
	147	Cholesterol	195	168

a. For preparation, see page 779.
b. For preparation, see page 780.

TABLE 70.3 Aldehydes

			Derivatives	
			Semicarbazone[a]	*2,4-Dinitrophenylhydrazone*[b]
bp	mp	Compound	mp	mp
21		Acetaldehyde	162	168
46–50		Propionaldehyde	89(154)	148
63		Isobutyraldehyde	125(119)	187(183)
75		Butyraldehyde	95(106)	123
90–92		3-Methylbutanal	107	123
98		Chloral	90	131
104		Crotonaldehyde	199	190
117		2-Ethylbutanal	99	95(130)
153		Heptaldehyde	109	108
162		2-Furaldehyde	202	212(230)
163		2-Ethylhexanal	254	114(120)
179		Benzaldehyde	222	237
195		Phenylacetaldehyde	153	121(110)
197		Salicylaldehyde	231	248
204–205		4-Tolualdehyde	234(215)	232
209–215		2-Chlorobenzaldehyde	146(229)	213
247		2-Ethoxybenzaldehyde	219	
248		4-Anisaldehyde	210	253

(continued)

a. For preparation, see page 444.
b. For preparation, see page 442.

TABLE 70.3 *continued*

			Derivatives	
			Semicarbazone[a]	*2,4-Dinitrophenylhydrazone*[b]
bp	mp	Compound	mp	mp
250–252		*E*-Cinnamaldehyde	215	255
	33–34	1-Naphthaldehyde	221	254
	37–39	2-Anisaldehyde	215	254
	42–45	3,4-Dimethoxybenzaldehyde	177	261
	44–47	4-Chlorobenzaldehyde	230	254
	57–59	3-Nitrobenzaldehyde	246	293
	81–83	Vanillin	230	271

a. For preparation, see page 444.
b. For preparation, see page 442.

TABLE 70.4 Amides

bp	mp	Name of Compound	mp	Name of Compound
153		*N*,*N*-Dimethylformamide	127–129	Isobutyramide
164–166		*N*,*N*-Dimethylacetamide	128–129	Benzamide
210		Formamide	130–133	Nicotinamide
243–244		*N*-Methylformanilide	177–179	4-Chloroacetanilide
	26–28	*N*-Methylacetamide		
	79–81	Acetamide		
	109–111	Methacrylamide		
	113–115	Acetanilide		
	116–118	2-Chloroacetamide		

TABLE 70.5 Primary and Secondary Amines

			Derivatives		
			Benzamide[a]	*Picrate*[b]	*Acetamide*[c]
bp	mp	Compound	mp	mp	mp
33–34		Isopropylamine	71	165	
46		*t*-Butylamine	134	198	
48		*n*-Propylamine	84	135	
53		Allylamine		140	
55		Diethylamine	42	155	
63		*s*-Butylamine	76	139	
64–71		Isobutylamine	57	150	
78		*n*-Butylamine	42	151	
84		Diisopropylamine		140	
87–88		Pyrrolidine	oil	112	
106		Piperidine	48	152	
111		Di-*n*-propylamine	oil	75	
118		Ethylenediamine	244 (di)	233	172 (di)
129		Morpholine	75	146	
137–139		Diisobutylamine		121	86
145–146		Furfurylamine		150	
149		*N*-Methylcyclohexylamine	85	170	
159		Di-*n*-butylamine	oil	59	
182–185		Benzylamine	105	199	60
184		Aniline	163	198	114
196		*N*-Methylaniline	63	145	102
199–200		2-Toluidine	144	213	110
203–204		3-Toluidine	125	200	65
205		*N*-Ethylaniline	60	138(132)	54
208–210		2-Chloroaniline	99	134	87
210		2-Ethylaniline	147	194	111
216		2,6-Dimethylaniline	168	180	177
218		2,4-Dimethylaniline	192	209	133
218		2,5-Dimethylaniline	140	171	139
221		*N*-Ethyl-*m*-toluidine	72		
225		2-Anisidine	60(84)	200	85
230		3-Chloroaniline	120	177	72(78)
231–233		2-Phenetidine	104		79
241		4-Chloro-2-methylaniline	142		140
242		3-Chloro-4-methylaniline	122		105
250		4-Phenetidine	173	69	137
256		Dicyclohexylamine	153(57)	173	103

(continued)

a. For preparation, see page 780.
b. For preparation, see page 780.
c. For preparation, see page 780.

TABLE 70.5 *continued*

			Derivatives		
			Benzamide[a]	*Picrate*[b]	*Acetamide*[c]
bp	mp	Compound	mp	mp	mp
	35–38	*N*-Phenylbenzylamine	107	48	58
	41–44	4-Toluidine	158	182	147
	49–51	2,5-Dichloroaniline	120	86	132
	52–54	Diphenylamine	180	182	101
	57–60	4-Anisidine	154	170	130
	57–60	2-Aminopyridine	165 (di)	216(223)	
	60–62	*N*-Phenyl-1-naphthylamine	152		115
	62–65	2,4,5-Trimethylaniline	167		162
	64–66	1,3-Phenylenediamine	125 (mono)	184	87 (mono)
			240 (di)		191 (di)
	66	4-Bromoaniline	204	180	168
	68–71	4-Chloroaniline	192	178	179(172)
	71–73	2-Nitroaniline	110(98)	73	92
	97–99	2,4-Diaminotoluene	224 (di)		224 (di)
	100–102	1,2-Phenylenediamine	301	208	185
	104–107	2-Methyl-5-nitroaniline	186		151
	107–109	2-Chloro-4-nitroaniline	161		139
	112–114	3-Nitroaniline	157(150)	143	155(76)
	115–116	4-Methyl-2-nitroaniline	148		99
	117–119	4-Chloro-2-nitroaniline			104
	120–122	2,4,6-Tribromoaniline	198(204)		232
	131–133	2-Methyl-4-nitroaniline			202
	138–140	2-Methoxy-4-nitroaniline	149		
	138–142	1,4-Phenylenediamine	128 (mono)		162 (mono)
			300 (di)		304 (di)
	148–149	4-Nitroaniline	199	100	215
	162–164	4-Aminoacetanilide			304
	176–178	2,4-Dinitroaniline	202(220)		120

a. For preparation, see page 780.
b. For preparation, see page 780.
c. For preparation, see page 780.

TABLE 70.6 Tertiary Amines

		Derivatives	
		Picrate[a]	*Methiodide*[b]
bp	Compound	mp	mp
85–91	Triethylamine	173	280
115	Pyridine	167	117
128–129	2-Picoline	169	230
143–145	2,6-Lutidine	168(161)	233
144	3-Picoline	150	92(36)
145	4-Picoline	167	149
155–158	Tri-*n*-propylamine	116	207
159	2,4-Lutidine	180	113
183–184	*N*,*N*-Dimethylbenzylamine	93	179
216	Tri-*n*-butylamine	105	186
217	*N*,*N*-Diethylaniline	142	102
237	Quinoline	203	133(72)

a. For preparation, see page 780.
b. For preparation, see page 781.

TABLE 70.7 Anhydrides and Acid Halides

			Derivatives			
			Acid[a]		*Amide*[b]	*Anilide*[c]
bp	mp	Compound	bp	mp	mp	mp
52		Acetyl chloride	118		82	114
77–79		Propionyl chloride	141		81	106
102		Butyryl chloride	162		115	96
138–140		Acetic anhydride	118		82	114
167		Propionic anhydride	141		81	106
198–199		Butyric anhydride	162		115	96
198		Benzoyl chloride		122	130	163
225		3-Chlorobenzoyl chloride		158	134	122
238		2-Chlorobenzoyl chloride		142	142	118
	32–34	*cis*-1,2-Cyclohexanedicarboxylic anhydride		192		
	35–37	Cinnamoyl chloride		133	147	151
	39–40	Benzoic anhydride		122	130	163
	54–56	Maleic anhydride		130	181 (mono) 266 (di)	173 (mono) 187

(continued)

a. For preparation, see page 781.
b. For preparation, see page 781.
c. For preparation, see page 782.

TABLE 70.7 *continued*

			Derivatives			
			Acid[a]		*Amide*[b]	*Anilide*[c]
bp	mp	Compound	bp	mp	mp	mp
	72–74	4-Nitrobenzoyl chloride		241	201	211
	119–120	Succinic anhydride		186	157 (mono) 260 (di)	148 (mono) 230 (di)
	131–133	Phthalic anhydride		206	149 (mono) 220 (di)	170 (mono) 253 (di)
	254–258	Tetrachlorophthalic anhydride		250		
	267–269	1,8-Naphthalic anhydride		274		250–282 (di)

a. For preparation, see page 781.
b. For preparation, see page 781.
c. For preparation, see page 782.

TABLE 70.8 Esters

bp	mp	Compound	bp	mp	Compound
34		Methyl formate	169–170		Methyl acetoacetate
52–54		Ethyl formate	180–181		Dimethyl malonate
72–73		Vinyl acetate	181		Ethyl acetoacetate
77		Ethyl acetate	185		Diethyl oxalate
79		Methyl propionate	198–199		Methyl benzoate
80		Methyl acrylate	206–208		Ethyl caprylate
85		Isopropyl acetate	208–210		Ethyl cyanoacetate
93		Ethyl chloroformate	212		Ethyl benzoate
94		Isopropenyl acetate	217		Diethyl succinate
98		Isobutyl formate	218		Methyl phenylacetate
98		*t*-Butyl acetate	218–219		Diethyl fumarate
99		Ethyl propionate	222		Methyl salicylate
99		Ethyl acrylate	225		Dimethyl maleate
100		Methyl methacrylate	229		Ethyl phenylacetate
101		Methyl trimethylacetate	234		Ethyl salicylate
102		*n*-Propyl acetate	268		Diethyl suberate
106–113		*s*-Butyl acetate	271		Ethyl cinnamate
120		Ethyl butyrate	282		Dimethyl phthalate
127		*n*-Butyl acetate	298–299		Diethyl phthalate
128		Methyl valerate	298–299		Phenyl benzoate
130		Methyl chloroacetate	340		Dibutyl phthalate
131–133		Ethyl isovalerate		56–58	Ethyl *p*-nitrobenzoate
142		*n*-Amyl acetate		88–90	Ethyl *p*-aminobenzoate
142		Isoamyl acetate		94–96	Methyl *p*-nitrobenzoate
143		Ethyl chloroacetate		95–98	*n*-Propyl *p*-hydroxybenzoate
154		Ethyl lactate		116–118	Ethyl *p*-hydroxybenzoate
168		Ethyl caproate (ethyl hexanoate)		126–128	Methyl *p*-hydroxybenzoate

TABLE 70.9 Ethers

bp	mp	Compound	bp	mp	Compound
32		Furan	215		4-Bromoanisole
33		Ethyl vinyl ether	234–237		Anethole
65–67		Tetrahydrofuran	259		Diphenyl ether
94		*n*-Butyl vinyl ether	273		2-Nitroanisole
154		Anisole	298		Dibenzyl ether
174		4-Methylanisole		50–52	4-Nitroanisole
175–176		3-Methylanisole		56–60	1,4-Dimethoxybenzene
198–203		4-Chloroanisole		73–75	2-Methoxynaphthalene
206–207		1,2-Dimethoxybenzene			

TABLE 70.10 Halides

bp	Compound	bp	Compound
34–36	2-Chloropropane	100–105	1-Bromobutane
40–41	Dichloromethane	105	Bromotrichloromethane
44–46	Allyl chloride	110–115	1,1,2-Trichloroethane
57	1,1-Dichloroethane	120–121	1-Bromo-3-methylbutane
59	2-Bromopropane	121	Tetrachloroethylene
68	Bromochloromethane	123	3,4-Dichloro-1-butene
68–70	2-Chlorobutane	125	1,3-Dichloro-2-butene
69–73	Iodoethane	131–132	1,2-Dibromoethane
70–71	Allyl bromide	140–142	1,2-Dibromopropane
71	1-Bromopropane	142–145	1-Bromo-3-chloropropane
72–74	2-Bromo-2-methylpropane	146–150	Bromoform
74–76	1,1,1-Trichloroethane	147	1,1,2,2-Tetrachloroethane
81–85	1,2-Dichloroethane	156	1,2,3-Trichloropropane
87	Trichloroethylene	161–163	1,4-Dichlorobutane
88–90	2-Iodopropane	167	1,3-Dibromopropane
90–92	1-Bromo-2-methylpropane	177–181	Benzyl chloride
91	2-Bromobutane	197	(2-Chloroethyl)benzene
94	2,3-Dichloro-1-propene	219–223	Benzotrichloride
95–96	1,2-Dichloropropane	238	1-Bromodecane
96–98	Dibromomethane		

TABLE 70.11 Aryl Halides

			Derivatives			
			Nitration Product[a]		*Oxidation Product*[b]	
bp	mp	Compound	Position	mp	Name	mp
132		Chlorobenzene	2, 4	52		
156		Bromobenzene	2, 4	70		
157–159		2-Chlorotoluene	3, 5	63	2-Chlorobenzoic acid	141
162		4-Chlorotoluene	2	38	4-Chlorobenzoic acid	240
172–173		1,3-Dichlorobenzene	4, 6	103		
178		1,2-Dichlorobenzene	4, 5	110		
196–203		2,4-Dichlorotoluene	3, 5	104	2,4-Dichlorobenzoic acid	164
201		3,4-Dichlorotoluene	6	63	3,4-Dichlorobenzoic acid	206
214		1,2,4-Trichlorobenzene	5	56		
279–281		1-Bromonaphthalene	4	85		
	51–53	1,2,3-Trichlorobenzene	4	56		
	54–56	1,4-Dichlorobenzene	2	54		
	66–68	1,4-Bromochlorobenzene	2	72		
	87–89	1,4-Dibromobenzene	2, 5	84		
	138–140	1,2,4,5-Tetrachlorobenzene	3	99		
			3, 6	227		

a. For preparation, see page 782.
b. For preparation, see page 782.

TABLE 70.12 Hydrocarbons: Alkenes

bp	Compound	bp	Compound
34	Isoprene	149–150	1,5-Cyclooctadiene
83	Cyclohexene	152	DL-α-Pinene
116	5-Methyl-2-norbornene	160	Bicyclo[4.3.0]nona-3,7-diene
122–123	1-Octene	165–167	(−)-β-Pinene
126–127	4-Vinyl-1-cyclohexene	165–169	α-Methylstyrene
132–134	2,5-Dimethyl-2,4-hexadiene	181	1-Decene
141	5-Vinyl-2-norbornene	181	Indene
143	1,3-Cyclooctadiene	251	1-Tetradecene
145	4-Butylstyrene	274	1-Hexadecene
145–146	Cyclooctene	349	1-Octadecene
145–146	Styrene		

TABLE 70.13 Hydrocarbons: Aromatic

			Melting Point of Derivatives		
			Nitro[a]		*Picrate*[b]
bp	mp	Compound	Position	mp	mp
80		Benzene	1, 3	89	84
111		Toluene	2, 4	70	88
136		Ethylbenzene	2, 4, 6	37	96
138		*p*-Xylene	2, 3, 5	139	90
138–139		*m*-Xylene	2, 4, 6	183	91
143–145		*o*-Xylene	4, 5	118	88
145		4-*t*-Butylstyrene	2, 4	62	
145–146		Styrene			
152–154		Cumene	2, 4, 6	109	
163–166		Mesitylene	2, 4	86	97
			2, 4, 6	235	
165–169		α-Methylstyrene			
168		1,2,4-Trimethylbenzene	3, 5, 6	185	97
176–178		*p*-Cymene	2, 6	54	
189–192		4-*t*-Butyltoluene			
197–199		1,2,3,5-Tetramethylbenzene	4, 6	181(157)	
203		*p*-Diisopropylbenzene			
204–205		1,2,3,4-Tetramethylbenzene	5, 6	176	92
207		1,2,3,4-Tetrahydronaphthalene	5, 7	95	
240–243		1-Methylnaphthalene	4	71	142
	34–36	2-Methylnaphthalene	1	81	116
	50–51	Pentamethylbenzene	6	154	131
	69–72	Biphenyl	4, 4′	237(229)	
	80–82	1,2,4,5-Tetramethylbenzene	3, 6	205	
	80–82	Naphthalene	1	61(57)	149
	90–95	Acenaphthene	5	101	161
	99–101	Phenanthrene			144(133)
	112–115	Fluorene	2	156	87(77)
			2, 7	199	
	214–217	Anthracene			138

a. For preparation, see page 782.
b. For preparation, see page 780.

TABLE 70.14 Ketones

			Derivatives	
			Semicarbazone[a]	*2,4-Dinitrophenylhydrazone*[b]
bp	mp	Compound	mp	mp
56		Acetone	187	126
80		2-Butanone	136, 186	117
88		2,3-Butanedione	278	315
100–101		2-Pentanone	112	143
102		3-Pentanone	138	156
106		Pinacolone	157	125
114–116		4-Methyl-2-pentanone	132	95
124		2,4-Dimethyl-3-pentanone	160	88, 95
128–129		5-Hexen-2-one	102	108
129		4-Methyl-3-penten-2-one	164	205
130–131		Cyclopentanone	210	146
133–135		2,3-Pentanedione	122 (mono) 209 (di)	209
145		4-Heptanone	132	75
145		5-Methyl-2-hexanone	147	95
145–147		2-Heptanone	123	89
146–149		3-Heptanone	101	81
156		Cyclohexanone	166	162
162–163		2-Methylcyclohexanone	195	137
169		2,6-Dimethyl-4-heptanone	122	66, 92
169–170		3-Methylcyclohexanone	180	155
173		2-Octanone	122	58
191		Acetonylacetone	185 (mono) 224 (di)	257 (di)
202		Acetophenone	198	238
216		Phenylacetone	198	156
217		Isobutyrophenone	181	163
218		Propiophenone	182	191
226		4-Methylacetophenone	205	258
231–232		2-Undecanone	122	63
232		*n*-Butyrophenone	188	191
232		4-Chloroacetophenone	204	236
235		Benzylacetone	142	127
	35–37	4-Chloropropiophenone	176	223
	35–39	4-Phenyl-3-buten-2-one	187	227
	36–38	4-Methoxyacetophenone	198	228
	48–49	Benzophenone	167	238
	53–55	2-Acetonaphthone	235	262
	60	Desoxybenzoin	148	204
	76–78	3-Nitroacetophenone	257	228
	78–80	4-Nitroacetophenone		257
	82–85	9-Fluorenone	234	283
	134–136	Benzoin	206	245
	147–148	4-Hydroxypropiophenone		240

a. For preparation, see page 444.
b. For preparation, see page 442.

TABLE 70.15 Nitriles

bp	mp	Compound	bp	mp	Compound
77		Acrylonitrile	212		3-Tolunitrile
83–84		Trichloroacetonitrile	217		4-Tolunitrile
97		Propionitrile	233–234		Benzyl cyanide
107–108		Isobutyronitrile	295		Adiponitrile
115–117		*n*-Butyronitrile		30.5	4-Chlorobenzyl cyanide
174–176		3-Chloropropionitrile		32–34	Malononitrile
191		Benzonitrile		38–40	Stearonitrile
205		2-Tolunitrile		46–48	Succinonitrile
				71–73	Diphenylacetonitrile

TABLE 70.16 Nitro Compounds

			Amine Obtained by Reduction of Nitro Groups			
					Acetamide[a]	*Benzamide*[b]
bp	mp	Compound	bp	mp	mp	mp
210–211		Nitrobenzene	184		114	160
225		2-Nitrotoluene	200		110	146
225		2-Nitro-*m*-xylene	215		177	168
230–231		3-Nitrotoluene	203		65	125
245		3-Nitro-*o*-xylene	221		135	189
245–246		4-Ethylnitrobenzene	216		94	151
	34–36	2-Chloro-6-nitrotoluene	245		157(136)	173
	36–38	4-Chloro-2-nitrotoluene		21	139(131)	
	40–42	3,4-Dichloronitrobenzene		72	121	
	43–50	1-Chloro-2,4-dinitrobenzene		91	242 (di)	178 (di)
	52–54	4-Nitrotoluene		45	147	158
	55–56	1-Nitronaphthalene		50	159	160
	83–84	1-Chloro-4-nitrobenzene		72	179	192
	88–90	*m*-Dinitrobenzene		63	87 (mono)	125 (mono)
					191 (di)	240 (di)

a. For preparation, see page 780.
b. For preparation, see page 780.

TABLE 70.17 Phenols

			Derivatives	
			α-Naphthylurethane[a]	*Bromo*[b]
bp	mp	Compound	mp	mp
175–176		2-Chlorophenol	120	48 (mono)
				76 (di)
181	42	Phenol	133	95 (tri)
202	32–34	*p*-Cresol	146	49 (di)
				108 (tetra)
203		*m*-Cresol	128	84 (tri)
228–229		3,4-Dimethylphenol	141	171 (tri)
	32–33	*o*-Cresol	142	56 (di)
	42–43	2,4-Dichlorophenol		68
	42–45	4-Ethylphenol	128	
	43–45	4-Chlorophenol	166	90 (di)
	44–46	2,6-Dimethylphenol	176	79
	44–46	2-Nitrophenol	113	117 (di)
	49–51	Thymol	160	55
	62–64	3,5-Dimethylphenol		166 (tri)
	64–68	4-Bromophenol	169	95 (tri)
	74	2,5-Dimethylphenol	173	178 (tri)
	92–95	2,3,5-Trimethylphenol	174	
	95–96	1-Naphthol	152	105 (di)
	98–101	4-*t*-Butylphenol	110	50 (mono)
				67 (di)
	104–105	Catechol	175	192 (tetra)
	109–110	Resorcinol	275	112 (tri)
	112–114	4-Nitrophenol	150	142 (di)
	121–124	2-Naphthol	157	84
	133–134	Pyrogallol	173	158 (di)

a. For preparation, see page 783.
b. For preparation, see page 783.