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# PART

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# 4

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# Organic Qualitative Analysis

Organic chemists must regularly identify the compounds that are formed in chemical reactions or isolated from natural sources. Discovering the identity of an unknown organic compound requires finding which functional groups it contains and then determining its molecular and three-dimensional structure. Both chemical and spectroscopic methods are used by practicing organic chemists. As you progress through organic chemistry, you will have opportunities to learn and use the techniques of organic qualitative analysis while determining the identity of sample compounds whose identities are unknown to you (the test sample is designated the “unknown”).

Because well over 15 million different carbon compounds have been discovered, synthesized, and characterized, the experimental techniques in Part 4 deal with a number of chemical substances. The tables in the Appendix contain over 500 compounds; thus, a bit of sleuthing is generally necessary to identify an unknown compound. Part of the challenge of organic qualitative analysis lies in borderline cases and possible exceptions to the general rules for many of the tests. If you work with an open, unprejudiced mind, ready to make, test, and reject hypotheses, you will have more fun and be much more successful in finding the identities of unknowns. Your task is to reject every compound but the correct one, not to prove that an unknown is this or that.

Part 4, Organic Qualitative Analysis, is an extension of *Techniques in Organic Chemistry*, by Jerry R. Mohrig, Christina Noring Hammond, Paul F. Schatz, and Terence C. Morrill, ©2003 by W. H. Freeman and Company. Techniques 1–20 (Parts 1–3) appear in the printed book; Techniques 21–29 appear in Part 4 on this Web site. Techniques 21–29 contain cross-references to Techniques 1–20.

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The procedures in Part 4 are restricted to include only the following functional-group classes:

Alcohols  
Aldehydes  
Alkenes  
Amines  
Carboxylic acids  
Esters  
Ketones  
Phenols

The techniques in Part 4 introduce you to the fundamentals and the challenge of organic analysis. You will have better success if you remember two fundamental concepts:

1. You learn nothing definitive from any test carried out on an impure compound.
2. You must be systematic—don't jump to conclusions.

The process of identifying unknowns is analogous to solving a puzzle. You may be doing a lot of qualitative analysis if you become a professional chemist. Even if you become a physician, qualitative analysis and the thought processes of it are much like those of clinical diagnosis.

# 21

## IDENTIFICATION OF UNKNOWNNS

Five basic areas of experimental inquiry are useful for identifying an unknown compound. You need to develop an understanding for what information can be obtained from each of them. The five areas of inquiry are (1) physical properties [see Technique 22], (2) classification by solubility [see Technique 23], (3) spectroscopic analysis [see Technique 24], (4) classification tests for functional groups [see Technique 25], and (5) synthesis of solid derivatives [see Technique 26]. A sixth area of inquiry, elemental analysis by sodium fusion, is sometimes useful, but it is beyond the scope of this book (see Ref. 1). All the areas of experimental inquiry just listed depend on what can be called the structural theory of organic chemistry. By discovering how compounds act under certain conditions, a chemist can deduce what their structures are.

When undertaking each area of inquiry with an unknown substance, the importance of obtaining good experimental data cannot be overemphasized. Given the diversity of organic compounds, it is often impossible to avoid ambiguous results, but careful, well-planned experimental work and attention to details can greatly minimize them. Because you cannot work with any accuracy on a mixture of substances, the first step in any analysis must be the isolation and purification of individual components.

### 21.1

#### Safety Precautions with Unknowns

##### SAFETY PRECAUTIONS

You should treat any unknown as if it were toxic. Wear gloves while handling it; be careful not to spill it on your skin; do not breathe its vapor or dust.

Some common but toxic compounds have been omitted from the Appendix tables because we feel that especially dangerous compounds should not be given as unknowns. In the early days of organic chemistry, it was common not only to smell each new compound but also to taste a bit of it. We are much more alert to the dangers of toxic chemicals today, and therefore we never smell or taste any unknown compound. Only when an unknown compound has a penetrating, pronounced odor can the smell be useful to you in its identification.

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**21.2****Where to Begin?**

When you are asked to identify an unknown but pure compound, the first experiments you do should require you to observe and determine the physical properties of the unknown, to determine its solubility characteristics, and to examine its infrared (IR) and nuclear magnetic resonance (NMR) spectra. We recommend a sequence of investigative steps, but the order in which the tests are undertaken is not crucial. The determination and characterization of structure is usually more efficient when all the steps are carried out; however, your instructor may ask you to identify your unknown by using only a few of these strategies.

Familiarity with the spectral and solubility characteristics of your unknown compound, coupled with a knowledge of its physical properties, will help you decide which chemical classification tests to undertake. The chemical reactions that a compound undergoes are determined by the functional group(s) it contains. One of the major tools of organic qualitative analysis is the use of classification tests for specific functional groups. Depending on the results of your classification tests and evaluation of your spectroscopic and physical data, you may want to analyze your compound for the presence of halogen atoms.

Spectroscopic analysis and chemical classification tests are much the same for liquids and solids, although solids may have to be dissolved in a solvent before the tests can be done.

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**21.3****Purity of an Unknown**

The compounds listed in the tables in the Appendix are either liquids or solids at room temperature. There are special handling techniques for each physical state. The purification of volatile liquids can often be achieved through short-path distillation [see Technique 11.3a] or microscale distillation [see Technique 11.3b]. The boiling point of a pure liquid compound is an important physical constant and can be accurately determined from distillation data or by a microscale boiling-point determination [see Technique 11.1].

Handling small quantities of crystalline solids is normally simple. For example, less than 100 mg of a solid can be recrystallized if a microscale reaction tube or a Craig apparatus is used [see Technique 9.7]. Apparatus for microscale vacuum filtration is shown in Technique 9, Figure 9.7. Familiarity with microscale procedures serves as an excellent background for organic qualitative analysis.

When you are given an unknown compound, you may be told that it is pure. If not, you can assay its purity by the techniques of thin-layer chromatography [see Technique 15] or gas chromatography [see Technique 16], depending on the physical properties of the unknown. It is crucial that purification precede identification.

Chemical and spectrometric tests should be done only on pure compounds. If purification proves to be necessary, use distillation for a liquid compound or recrystallization for a solid compound. Melting points and boiling points are rarely meaningful when obtained with impure compounds.

Ethyl acetate is a developing solvent of medium polarity and would be a good first choice for TLC analysis if you are using silica gel plates. If you wish to select a TLC developing solvent according to a less arbitrary method, see Technique 15.5.

It is best to distill a liquid before undertaking a GC analysis, because GC conditions depend in large part on a compound's volatility. As a general rule of thumb, you would wish to begin the search for proper column conditions with a column temperature 30°–40°C below the compound's boiling point. See Technique 16.2 for the details of choosing a proper liquid stationary phase for your sample. Improperly using a gas chromatograph to analyze samples of low volatility (particularly salts of organic acids or bases) can plug the chromatograph and may give you misleading data caused by the appearance of decomposition products.

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## 21.4

### Completion of the Analysis

Once you have a large number of characteristics in hand, you can deduce the structure of a compound in much the same manner that you put together a jigsaw puzzle. Often a major clue is provided by very few results: For example, carboxylic acids of reasonably high molecular weight are insoluble in water but soluble in basic solutions; phenols, which are less acidic than carboxylic acids, show somewhat different solubility behavior in basic solution. Infrared analysis and chemical tests can be used to determine the functional groups present; each of these two techniques should corroborate the results of the other.

The last step of a compound's identification is often the synthesis of a solid derivative whose melting point can be compared to the melting points of known derivatives. Reported melting points for derivatives can be found in the tables in the Appendix.

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## TECHNIQUE

# 22

## PHYSICAL PROPERTIES

The physical properties of a compound that are of interest in qualitative analysis are its appearance and its melting point or boiling point.

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**22.1****Physical Appearance**

The physical appearance of an unknown will be your first datum in the search to discover its identity. Simply knowing that the compound is a solid rather than a liquid at room temperature narrows the search considerably. A few solids have characteristic bright colors that may be of great significance in reaching a final answer. The color of a liquid sample must be interpreted more cautiously. Many liquid compounds oxidize when they are stored for a long time. Often the oxidation products are intensely colored—yellow, green, red, brown, or black. In these cases the color of the liquid tells you little if anything useful. When oxidation has occurred, distillation of the liquid often leads to a pure, colorless distillate.

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**22.2****Melting Point or Boiling Point**

The melting point or boiling point of an unknown compound is of critical importance, not only because these physical constants definitely tell you whether your unknown is pure but also because most of the tables of possible unknowns list compounds by functional group in order of increasing melting and boiling points. The tables of compounds in the Appendix follow this pattern. Melting points tend to be more reliable than boiling points in this context.

**Accurate physical constants are a must!** For example, if you can trust a boiling point of a liquid alcohol that boils at  $132^{\circ} \pm 2^{\circ}\text{C}$ , you have narrowed the choice to only three or four possibilities from more than 40 liquid alcohols in Table 2 in the Appendix. You should remember that the melting points listed in standard tables may be  $2^{\circ}$ – $3^{\circ}\text{C}$  higher than your values; the highest melting point of the purified compounds is normally listed. If you have doubts about how to obtain an accurate melting range, review Technique 10.3. Also, keep in mind the importance of proper thermometer placement in obtaining accurate boiling points during a distillation [see Technique 11, Figure 11.6].

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**22.3****Compounds That Melt Near Room Temperature**

One source of confusion when determining physical properties commonly occurs with compounds that melt just above room temperature when they are pure. Sometimes their melting points can be depressed by as much as  $30^{\circ}\text{C}$  because of impurities. In other words, a compound could be listed as a low-melting-point solid in the tables in the Appendix, yet it could be in the liquid state when you receive it. You can determine if an unknown liquid freezes near room temperature by putting about 2 mL of it in a small test tube.

Place a thermometer in the test tube and immerse the test tube in a mixture of cracked ice and sodium chloride. If the liquid solidifies, remove the test tube from the ice bath and stir the mushy solid carefully and steadily. Note the temperature when the last crystals melt; this temperature is the melting point.

**TECHNIQUE****23****CLASSIFICATION  
BY SOLUBILITY**

Solubility tests should be performed on every general unknown because they are quick and reliable and use only a small amount of sample. One can gather valuable information about possible functional groups through the use of the solubility classifications. If you already know what functional groups a compound has, a complete series of solubility tests is not necessary.

Five common reagents are used for solubility tests: (1) water, (2) 2.5 M (9%) NaOH, (3) 0.6 M (5%) NaHCO<sub>3</sub>, (4) 1.5 M (5%) HCl, and (5) concentrated (96%) H<sub>2</sub>SO<sub>4</sub>. Except in the case of water, solubility experiments probe the acid-base properties of organic compounds. If a compound is an acid, you can obtain a relative measure of its acid strength by testing it against the weak base sodium bicarbonate and the stronger base sodium hydroxide.

Naturally, **any organic compound that is soluble in water is also likely to be soluble in 0.6 M NaHCO<sub>3</sub>, 1.5 M HCl, and 2.5 M NaOH solutions** because these solutions are composed largely of water. Continuing to test a water-soluble unknown with the other reagents will reveal virtually nothing further about the acid-base properties of the compound.

Table 23.1 summarizes the solubility of each functional-group class considered in this book. Figure 23.1 uses a flow diagram to present the same solubility data as that shown in Table 23.1. Use whichever is more convenient for you.

**23.1****Procedure for Solubility Tests****SAFETY INFORMATION**

Wear gloves while conducting the solubility tests. **Concentrated (96%) sulfuric acid** is corrosive and causes severe burns.

TABLE 23.1 Solubility summary<sup>a</sup>

	Water	2.5 M NaOH	0.6 M NaHCO <sub>3</sub>	1.5 M HCl	Conc. H <sub>2</sub> SO <sub>4</sub>
Alcohols	–(except under C <sub>6</sub> )	–	–	–	+
Aldehydes	–(except under C <sub>5</sub> )	–	–	–	+
Alkanes	–	–	–	–	–
Alkenes	–	–	–	–	+
Alkyl halides	–	–	–	–	–
Amines	–(except under C <sub>6</sub> )	–	–	+	b
Aryl halides	–	–	–	–	–
Carboxylic acids	–(except under C <sub>6</sub> )	+	+	–	+
Esters	–(except under C <sub>4</sub> )	– <sup>c</sup>	–	–	+
Ketones	–(except under C <sub>5</sub> )	–	–	–	+
Phenols	–(except for a few)	+	– <sup>d</sup>	–	+

- a. Compounds that are soluble in water may also be soluble in 0.5 M NaOH, 0.6 M NaHCO<sub>3</sub>, and 1.5 M HCl solutions because these solutions are largely composed of water.  
 b. If HCl solubility and the presence of nitrogen indicate that the compound is an amine, do not test solubility in concentrated H<sub>2</sub>SO<sub>4</sub> because a violent reaction can occur.  
 c. If cold.  
 d. Except for a few.

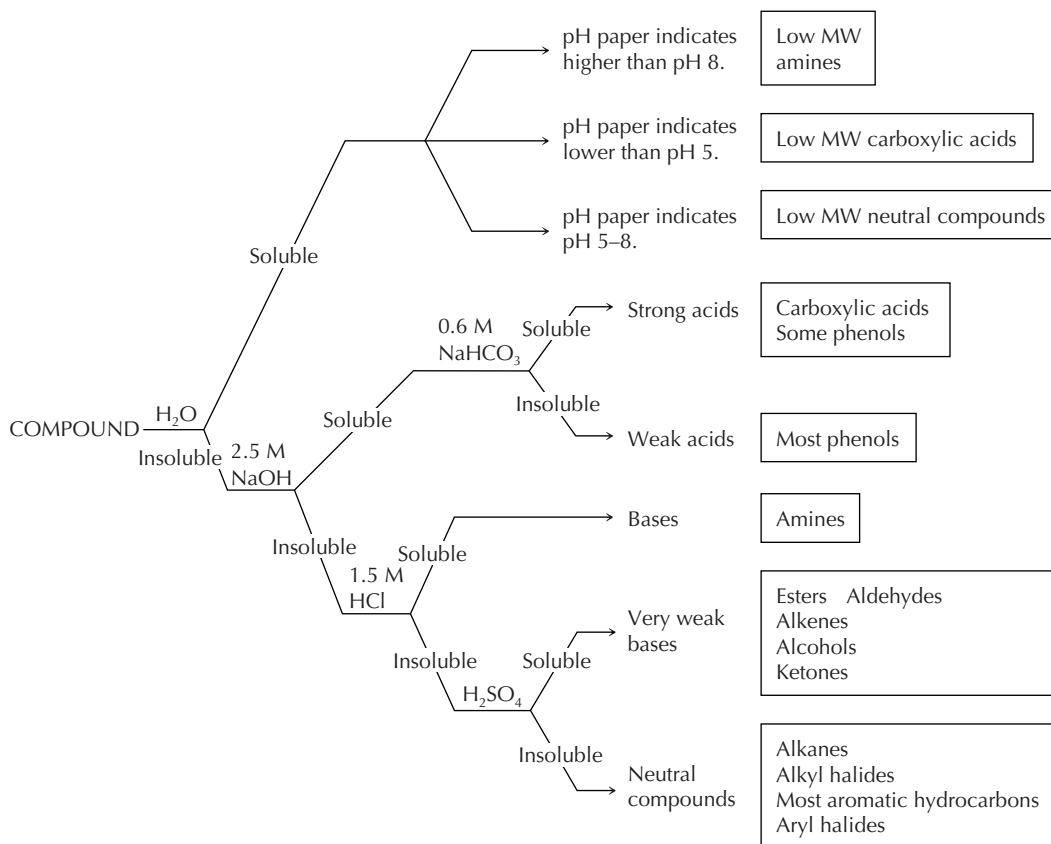


FIGURE 23.1 Solubility flowchart.

All solids must be *finely* powdered before weighing 15 mg on glassine weighing paper; use 1 drop (~0.05 mL) for a liquid unknown. Place the unknown sample in a small test tube and add 0.5 mL of solvent. Calibrated disposable plastic pipets provide reasonably accurate volume measurements for the solvent.

After you add the solvent, vigorously tap the test tube with your finger to ensure thorough mixing or use a vortex mixer if one is available. Because of changes in the refractive index, mixing lines may appear when a liquid dissolves. If a liquid unknown does not dissolve, you will see the tiny droplets that were dispersed by your tapping coalesce into a larger drop at the top or the bottom of the solvent solution, depending on the relative densities of the solvent and unknown. Sulfuric acid mixtures may require stirring with a small glass rod to thoroughly mix the solvent and sample, because the acid is very dense and viscous.

**CLEANUP:** Combine all aqueous test solutions from an unknown (except sulfuric acid—see the next paragraph) in a screw-capped centrifuge tube and adjust the pH with a few drops of dilute HCl to a pH of 7 as determined by pH test paper. Add 1 mL of ether to the centrifuge tube, cap the tube, and shake it to mix the layers. Allow the layers to separate, and remove the lower aqueous phase with a Pasteur pipet. Wash the aqueous phase down the sink or place it in the container for aqueous inorganic waste. Place the ether solution in the flammable (organic) waste container if you have determined that no halogen is present or in the halogenated-waste container if you have found that your unknown contains a halogen.

Cautiously pour the concentrated sulfuric acid test mixture into a beaker containing 30 mL of water and neutralize the solution with solid sodium carbonate. (**Caution: Foaming.**) Cool the solution to room temperature by adding a few ice chips, transfer it to a separatory funnel, and extract it with 4–5 mL of ether. Separate the layers. The lower aqueous phase may be washed down the sink or placed in the container for aqueous inorganic waste. Pour the ether solution into the flammable (organic) or halogenated-waste container as directed in the previous paragraph.

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## 23.2

### Interpretation of Data

Sometimes it is difficult to decide whether two layers are present at the very top of a liquid level or whether you are seeing an optical illusion. You should try solubility tests with several known reference compounds until you learn to distinguish the appearance of two layers from that of a normal meniscus. Solids may take several minutes to dissolve. When a colored compound dissolves, normally the solution also is colored.

We use the following standard but arbitrary definition of solubility throughout this set of organic qualitative analysis experiments: *If a compound is soluble in a solvent to the extent of approximately 3–5%*

(wt/v or v/v), the compound is declared to be “soluble” in that solvent. Therefore, if 15 mg of an unknown dissolves in 0.5 mL of a solvent, the unknown is considered to be soluble in that solvent. (One could imagine many other definitions of solubility, but this is a convenient one. Of course, all compounds are soluble in all solvents to a small extent. If a drop of hexane were put into the Atlantic Ocean, it would surely dissolve, yet by our definition of solubility; hexane is insoluble in water.)

### Solubility in Water

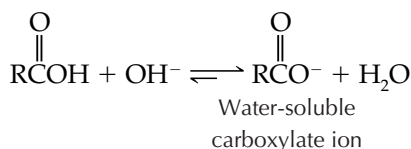
Most organic compounds are not soluble in distilled water, so if an unknown is insoluble in water, you have not learned much about it. However, if an unknown is water-soluble, you have learned a great deal. Solubility in water narrows the possibilities considerably, as shown in Table 23.1 and Figure 23.1.

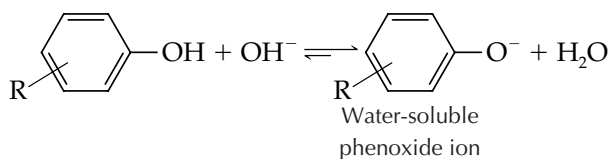
If a compound dissolves in water, you should estimate the pH of the resulting solution by using pH paper or litmus paper. It is best to wet a small stirring rod with the water solution and then touch the tip of it to the pH paper. In this way, the indicator dye of the pH paper does not dissolve, and a more accurate pH reading is possible. (See Figure 23.1 for the significance of a water solution whose pH is less than 5 or greater than 8.) *Note:* Distilled water itself often has a pH of 5–6 because of dissolved carbon dioxide, which forms a dilute solution of carbonic acid.

There is an indefinite borderline with respect to the solubility of carbon compounds in distilled water. For example, a few six-carbon alcohols, such as cyclohexanol, are soluble in water even though, according to Table 23.1, alcohols are water-soluble only if they have fewer than six carbons. The same kind of borderline solubility is to be found among all functional-group classes whose low-molecular-weight members are soluble in water. Multifunctional compounds, for example, polyhydroxy compounds such as carbohydrates, are often very soluble in water. Solubility depends on the exact structure of a compound, not only on the number of carbon atoms that it contains, and it is necessary to interpret solubility characteristics cautiously.

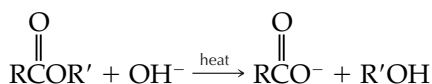
### Solubility in 2.5 M (9%) NaOH Solution

Organic acids, which are insoluble in water, normally dissolve in a 2.5 M (9%) NaOH solution. The pH of this solution is greater than 14, so any acid whose dissociation constant is greater than ( $pK_a < 12$ ) is converted almost entirely to its conjugate base. The conjugate base of a carboxylic acid ( $pK_a \sim 5$ ) is a carboxylate anion. The conjugate base of a phenol ( $pK_a \sim 10$ ) is a phenoxide ion. Ionic carboxylate salts and phenoxide salts are quite soluble in water. Thus, water-insoluble carboxylic acids and phenols will both dissolve in a 2.5 M sodium hydroxide solution.





The hydrolysis of esters is strongly promoted by sodium hydroxide, but the process is too slow to allow an ester to dissolve in 2.5 M NaOH within a few minutes. However, heating the mixture could produce a soluble carboxylate salt by hydrolysis of the ester. Thus, it is best not to use warm sodium hydroxide solution for this solubility classification.

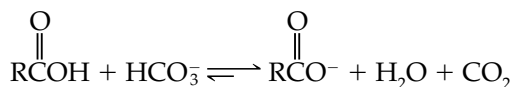


### Solubility in 0.6 M (5%) NaHCO<sub>3</sub>

#### Solution

*The test with 0.6 M NaHCO<sub>3</sub> solution is necessary only if the unknown is soluble in 2.5 M NaOH solution.*

When a compound is insoluble in water but soluble in 2.5 M NaOH, a third solubility test using 0.6 M (5%) sodium bicarbonate is called for. Sodium bicarbonate is a weaker base than sodium hydroxide; a 0.6 M NaHCO<sub>3</sub> solution has a pH of approximately 9. It dissolves a water-insoluble organic acid whose pK<sub>a</sub> is less than 7.5 by converting it to a water-soluble salt. Whereas carboxylic acids (pK<sub>a</sub> < 5) dissolve in a sodium bicarbonate solution (see equation), most phenols do not.



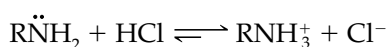
So the use of a 2.5 M NaOH solution followed by the addition of 0.6 M NaHCO<sub>3</sub> to another sample of the compound can distinguish organic acids from other organic compounds and can differentiate carboxylic acids from phenols.

Only a few phenols are acidic enough to completely dissolve in a 0.6 M NaHCO<sub>3</sub> solution. Phenol derivatives with strongly electron-withdrawing substituents are much stronger acids than phenol itself. For example, 4-nitrophenol has a pK<sub>a</sub> of 7.15; 4-nitrophenol dissolves in a 0.6 M NaHCO<sub>3</sub> solution.

When an acidic compound dissolves in a sodium bicarbonate solution, carbon dioxide gas is released. Observation of effervescence in a liquid confirms that an acid-base reaction did indeed occur.

### Solubility in 1.5 M (5%) HCl Solution

The only organic compounds that are insoluble in distilled water but soluble in dilute hydrochloric acid solution are amines, the major class of basic organic compound. Nearly all amines undergo reaction with HCl to produce ionic ammonium salts that are almost always soluble in water. This behavior is the same for tertiary (R<sub>3</sub>N), secondary (R<sub>2</sub>NH), and primary (RNH<sub>2</sub>) amines. The reaction of a primary amine can be represented as



**Solubility in  
Concentrated H<sub>2</sub>SO<sub>4</sub>  
(96%) Solution**

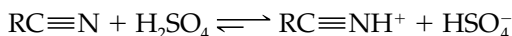
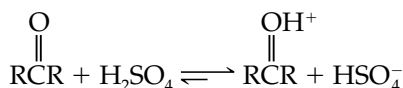
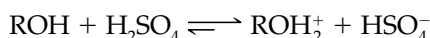
**SAFETY INFORMATION**

Concentrated (96%) sulfuric acid is corrosive and causes severe burns. Wear gloves and avoid contact with skin, eyes, and clothing. Immediately wash any spill off the skin with copious amounts of water.

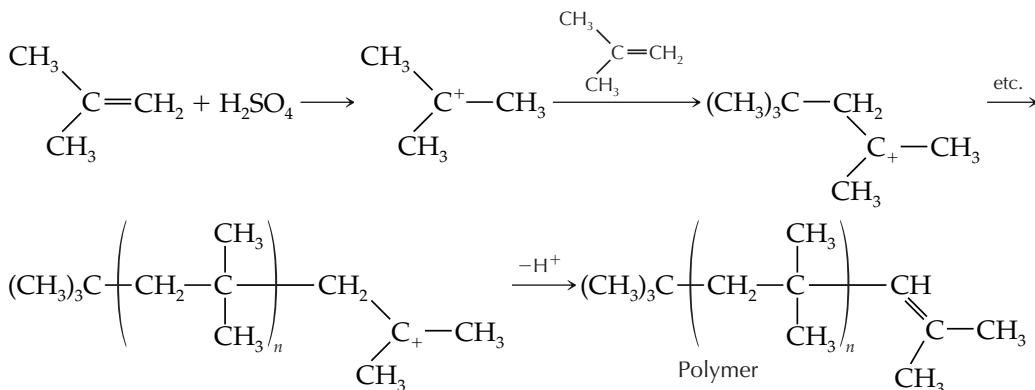
Water-insoluble compounds suspected to be amines should not be treated with concentrated H<sub>2</sub>SO<sub>4</sub> because the heat produced may lead to a violent reaction.

Concentrated sulfuric acid protonates all organic compounds that contain oxygen and/or nitrogen, as well as alkenes and a few aromatic hydrocarbons. These protonated organic compounds exist as ionic salts in sulfuric acid. Because sulfuric acid is a highly polar liquid, it dissolves the protonated compounds. The dissolution of compounds in H<sub>2</sub>SO<sub>4</sub> may also produce large amounts of heat and/or a change in the color of the solution.

All organic compounds that contain nitrogen or oxygen are weak bases. In aqueous mineral acid solutions of moderate concentration, the conjugate acids of these compounds are present in modest amounts. In concentrated sulfuric acid, however, these conjugate acids are often stable enough to be present in significant concentrations:



The solubility of alkenes in sulfuric acid results from protonation of the carbon-carbon double bond to form carbocations. (The carbocations in turn may react further, giving alkyl hydrogen sulfates—both of which are soluble in the sulfuric acid.) The carbocations may also react with unprotonated alkene to give insoluble brown polymers. A pronounced color change is thus a positive indication of a compound's solubility in sulfuric acid.



## INFRARED, NUCLEAR MAGNETIC RESONANCE, AND MASS SPECTROSCOPIC ANALYSIS

In a modern structure analysis, the powerful spectroscopic methods of IR, NMR, and MS play a major role, often the only role. Techniques 18–20 present these methods in detail, so they need not be repeated here. Rather, we discuss how to tackle the problem of determining the structure of an unknown compound by combining a variety of spectroscopic data. This approach may also be combined with tests relating to the compound's physical properties, solubility, and functional-group classification.

### *NMR Spectrum*

Nuclear magnetic resonance (NMR) spectroscopy is a particularly powerful technique. It is usually the best, most direct route to the determination of organic structure. One of the most important pieces of information in a  $^1\text{H}$  NMR spectrum is the chemical shift of the various kinds of protons in the sample. Usually, it is difficult or even impossible to decipher structural information from a  $^1\text{H}$  NMR spectrum without paying close attention to the chemical shifts of the NMR peaks. Table 19.2 lists some of the proton chemical shift information that is commonly needed. Carbon-13 ( $^{13}\text{C}$ ) NMR also provides structural information from chemical shifts, as shown in Table 19.12. Even with NMR analysis, however, it can be useful to see if your conclusions fit with other observations, such as those from infrared and mass spectroscopy and chemical reactivity. For example, if your NMR spectrum suggests that the unknown may be a carboxylic acid, the exceptionally broad O—H and the sharp, intense C=O stretching vibrations in its infrared (IR) spectrum (Table 18.2 and Figure 18.9) can provide important confirming evidence. The solubility characteristics of the compound in water and aqueous NaOH can also help.

### *Mass Spectrum*

The most obvious information from a compound's mass spectrum is its molecular mass. The molecular ion peak is often the peak at the greatest mass in the spectrum. In practice, however, it can be tricky to rely on this generalization, because impurities in the spectrometer may produce small peaks of higher molecular mass. Then it becomes difficult to know exactly what the molecular mass of your compound really is. In some compounds, the molecular ion peak can be negligibly small because of its extensive fragmentation in the electron beam. Mass spectrometry is discussed in more detail in Chapter 20.

### *IR Spectrum*

Because IR spectra often exhibit many absorption bands, it is difficult to extract all the rich structural information from an infrared spectrum. Nevertheless, infrared spectrometry is especially useful in identifying the functional groups in unknown compounds. Figure 18.6

and Table 18.2 contain useful information for the analysis of an unknown compound. A large amount of effort has been focused on the infrared spectra of carbonyl compounds. The carbon-oxygen double bond appears in many interesting compounds, and this bond acts like a well-behaved localized vibration. Therefore, accurate conclusions can be drawn from the exact position of a carbonyl band. Seven of the 15 functional group classes in Table 18.2 contain a C=O group. The usual frequency ranges for these carbonyl-stretching vibrations are

	cm <sup>-1</sup>
Aldehydes	1730–1660
Amides	1700–1640
Carboxylic acids	1740–1680
Esters	1760–1700
Ketones	1740–1660

Unsaturated, conjugated carbonyl compounds have their C=O stretching absorptions at the lower end of these frequency ranges. For example, whereas 2-butanone absorbs at 1715 cm<sup>-1</sup>, the conjugated ketone, acetophenone, absorbs at 1686 cm<sup>-1</sup>. The diaryl ketone, benzophenone, absorbs at about 1665 cm<sup>-1</sup>.

Another infrared region of great importance is between 4000 and 3000 cm<sup>-1</sup>, where the O—H and N—H stretching vibrations occur.

	cm <sup>-1</sup>	
Alcohols and phenols	3700–3100	(strong intensity)
Amides	3500–3100	(weak intensity)
Amines	3500–3100	(medium intensity)
Carboxylic acids	3300–2500	(medium intensity)

The O—H bond absorptions are usually intense [see Figure 18.7] and often quite broad, stretching over the entire 3300–2500 cm<sup>-1</sup> range for a carboxylic acid when the sample is a pure liquid or a mineral oil mull. This effect is largely due to intermolecular hydrogen bonding.

Although N—H stretching vibrations of amines are much weaker than O—H stretching bands, they are useful in the identification of primary amines. These compounds show twin peaks at 3550–3420 cm<sup>-1</sup> and 3450–3320 cm<sup>-1</sup>, absorptions corresponding to the asymmetric and symmetric N—H stretching vibrations [see Figure 18.8].

The fingerprint region (1500–900 cm<sup>-1</sup>) often contains so many bands that it is impractical to assign vibrations to them. This region does contain the C—O stretching frequency for alcohols that are normally intense.

The C—O stretching vibration of esters is also intense, appearing in the 1300–1100 cm<sup>-1</sup> region. The region below 1000 cm<sup>-1</sup>

Primary alcohols	1075–1000
Secondary alcohols	1125–1000
Tertiary alcohols	1210–1100

often reveals strong bands that are useful for characterizing aromatic compounds.

## 24.1

### Using Spectroscopic Data to Determine the Structure of an Unknown Compound

Determining the structure of an unknown organic compound by using only spectroscopy can be a fascinating puzzle. Even though NMR, infrared, and mass spectrometry are discussed in detail in Part 3, it may be instructive to include here two examples of overall spectroscopic analyses in the context of organic qualitative analysis.

#### Example 1

In Figure 24.1 you see the NMR, IR, and mass spectra of an unknown solid. Where to begin? The mass spectrum shows a prominent peak at 150 mass units, which is likely to be the molecular mass of the compound. The  $^1\text{H}$  NMR spectrum has a large set of peaks near 7.2 ppm, which is a strong indication of a benzene ring. This 300-MHz  $^1\text{H}$  spectrum, measured on a sample dissolved in  $\text{CDCl}_3$ , shows a relative integration of 5:2:2 for the three sets of peaks at 7.2, 2.9, and 2.5 ppm. Because there are five protons attached to the benzene ring, it seems to be a phenyl group,  $\text{C}_6\text{H}_5$ —. Now let's move to the infrared spectrum. The very broad, strong absorption in the region of  $3000\text{ cm}^{-1}$  is characteristic of the strongly hydrogen-bonded O—H stretching vibration of a carboxylic acid. Notice how it spans the whole  $3300$ – $2400\text{ cm}^{-1}$  region of the IR spectrum. If the compound is a carboxylic acid, there must also be an intense stretch in the carbonyl region of the infrared spectrum. There it is at  $1710\text{ cm}^{-1}$ !

We have used the simplest and most obvious aspects of all three spectra. They could have been used in any order up to this point. We have learned that it is likely that the compound is an aromatic carboxylic acid. Now let us return to the NMR spectrum. Two other groups of peaks are apparent. Where should peaks be for protons  $\alpha$  to the benzene ring and the carbonyl group of a carboxylic acid? Table 19.2 tells us that the carbonyl group deshields the  $\alpha$ -protons, so they should appear in the 1.9–3.0 ppm region—exactly where both sets of protons appear. Table 19.3 shows that protons  $\alpha$  to the benzene ring appear between 2.4 and 2.9 ppm.

It is time to make a proposal for the structure of the unknown compound. Let's say it is  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COOH}$ . Now let's look at the coupling pattern in the NMR spectrum (Figure 24.1). Notice that each set of peaks between 2 and 3 ppm is a triplet, showing two protons adjacent to each set of protons. This observation fits our

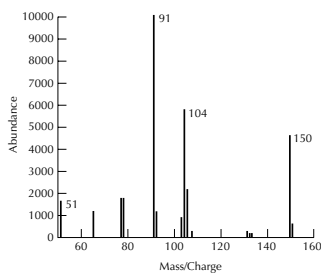
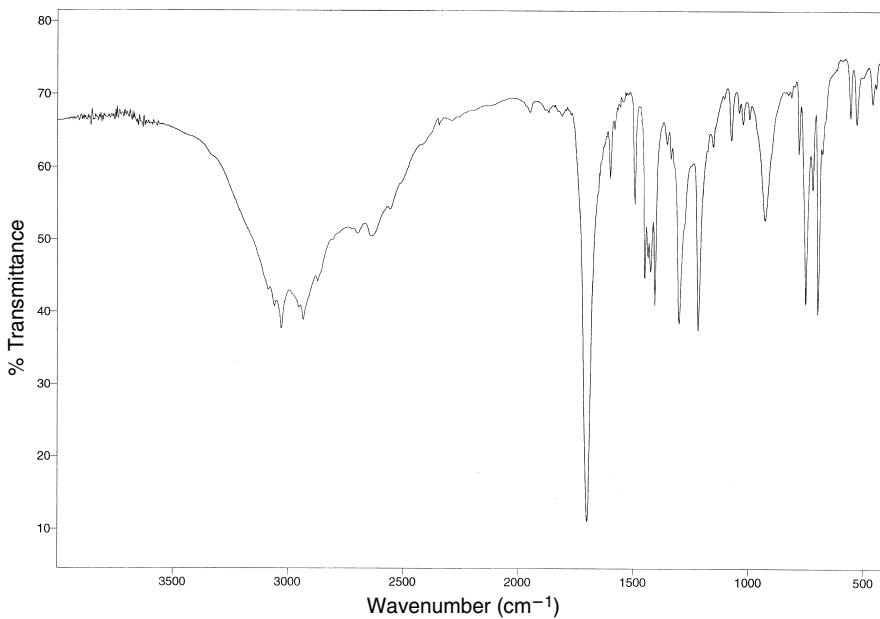
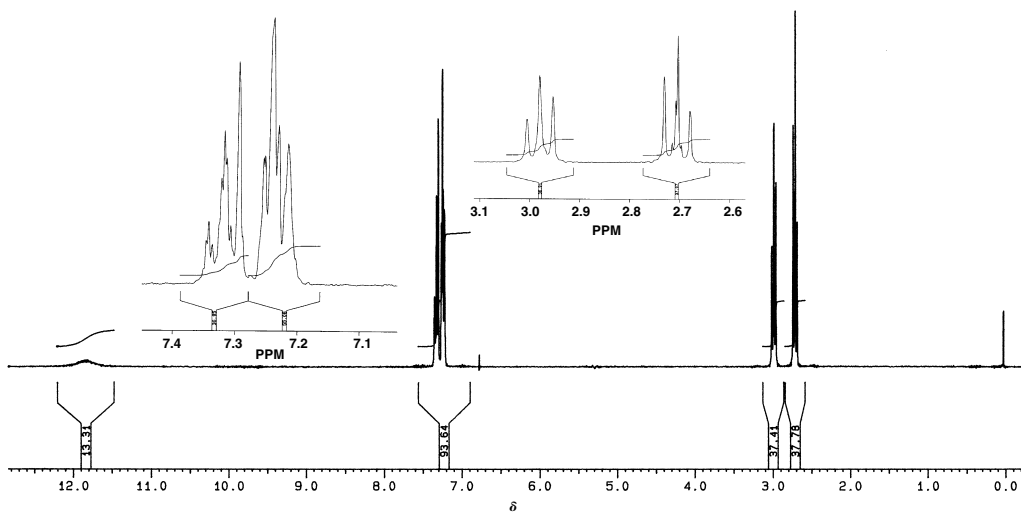


FIGURE 24.1 NMR, IR, and mass spectra for Example 1.

proposal. What about the relative integrations? This fits as well. The molecular ion at 150 is also consistent with a molecular mass of  $C_9H_{10}O_2$ . One could pay closer attention to the additional peaks in the infrared and mass spectra, such as the aromatic ring  $C=C$  stretch at  $1610\text{ cm}^{-1}$  and the  $C-O$  stretch at  $1290\text{ cm}^{-1}$ ; however, the major pieces already fit. But wait a minute! Where in the NMR spectrum is the carboxylic acid proton attached to oxygen? It is the small hump at about 11.8 ppm in the NMR spectrum, which fits with Table 19.2. It would be wise to do a chemical test at this point to confirm that the unknown is indeed a carboxylic acid. Solubility in 2.5 M NaOH solution and 0.6 M  $NaHCO_3$  (and insolubility in  $H_2O$ ) and a melting range of  $46^\circ-47^\circ C$  clinches the answer.

### Example 2

For Figure 24.2, we follow the same procedure we did for the first, that is, we look for the most useful information from all the spectra before analyzing any of them in detail. The NMR spectrum of this unknown liquid indicates five different kinds of protons. The two kinds farthest downfield, in the vicinity of 7 ppm, are likely to be due to aromatic protons. Their symmetry strongly suggests a disubstituted ring with the substituents in a *para*- or 1,4-relationship. The infrared spectrum shows a strong, broad absorption at about  $3400\text{ cm}^{-1}$ . It is not nearly as broad nor at such a low frequency as the  $O-H$  stretching vibration of a carboxylic acid; it is instead the  $O-H$  stretch of an alcohol. Note also that there is no carbonyl absorption in the vicinity of  $1700\text{ cm}^{-1}$ . If one were not confident at this point that the unknown is an alcohol, the chromic acid test for alcohols could be used to test the hypothesis. The mass spectrum shows a probable molecular ion with a mass of 138.

As in Example 1, let's return to a more thorough analysis of the NMR spectrum. The relative integrations of the five sets of peaks are in a ratio of 2:2:2:3:1. As well as the two sets of two aromatic protons each at 6.8 and 7.2 ppm, there are three additional kinds of protons in each molecule of the compound. The peak with relative integration of 1 is likely to be due to the  $O-H$  proton, and the peak with relative integration of 3 is likely to be a methyl group. Now we must use chemical shifts to determine the molecular environments of the methyl group and the remaining set of protons. The methyl singlet appears at about 3.8 ppm, which, according to Table 19.2, indicates a proton on a carbon atom  $\alpha$  to an oxygen atom of an alcohol or an ether. The methyl group must be attached as a methyl ether; there must be a methoxy ( $-OCH_3$ ) group attached to the benzene ring. Across the ring, there is a substituent that must contain the  $O-H$  group of the alcohol indicated by the IR spectrum. If the hydroxyl group were attached to a carbon that was also attached to the benzene ring, the methylene group would be farther downfield than 4 ppm because it would be attached both to an oxygen atom and a benzene ring. Using the data in Table 19.5, one can calculate a chemical shift of 4.6 ppm, which is very close to the measured value of 4.65 ppm.

A reasonable hypothesis for the structure of the unknown compound is  $CH_3OC_6H_4CH_2OH$ , 4-methoxybenzyl alcohol. The

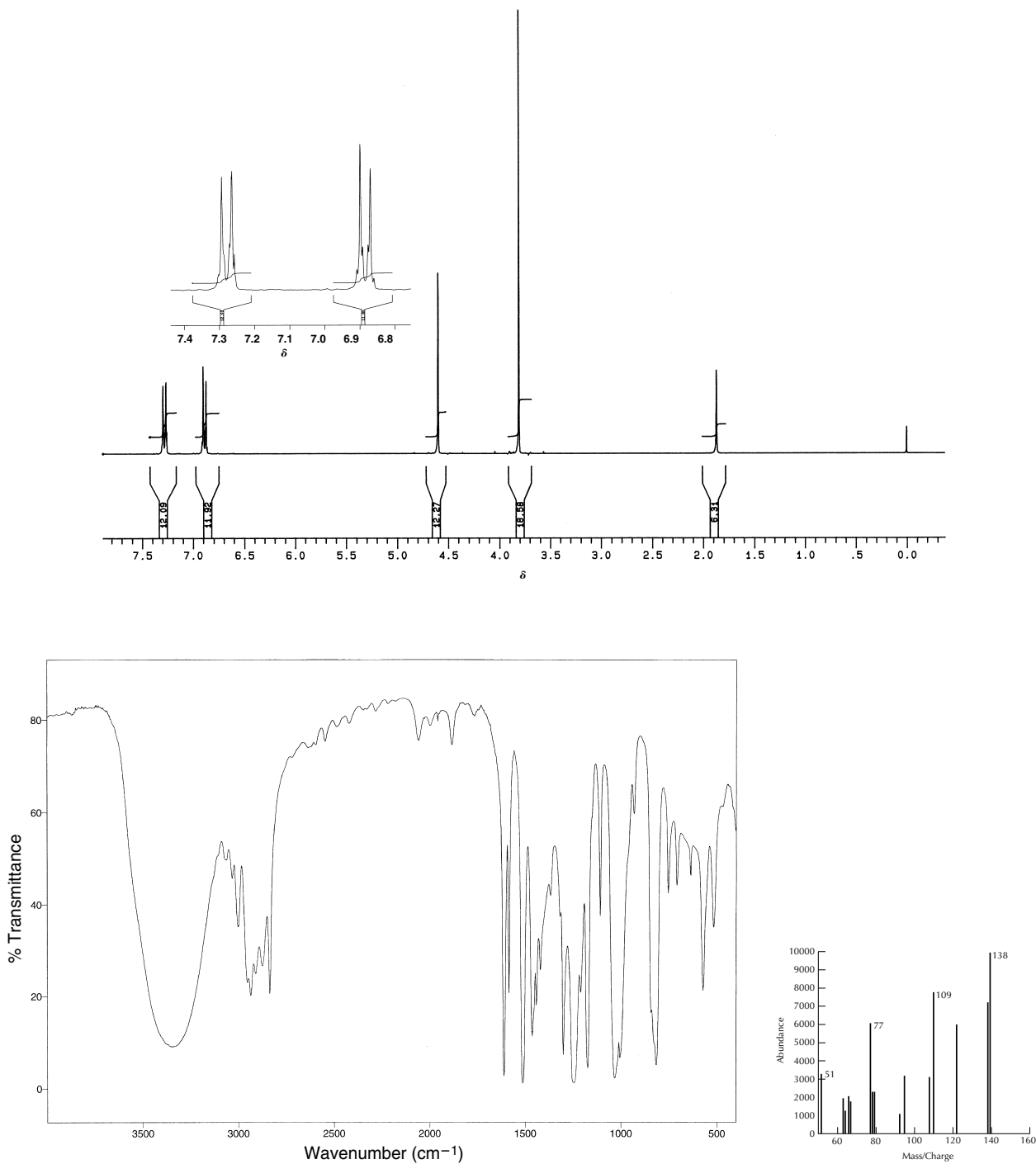


FIGURE 24.2 NMR, IR, and mass spectra for Example 2.

NMR spectrum fits! In the IR spectrum, there are peaks at about  $1620\text{ cm}^{-1}$ , due to the aromatic ring  $\text{C}=\text{C}$  stretch, and at about  $1250\text{ cm}^{-1}$ , due to  $\text{C}-\text{O}$  stretching vibrations. The molecular mass of 138 also fits for  $\text{C}_8\text{H}_{10}\text{O}_2$ . To complete the determination, one could confirm that the primary alcohol is oxidized in the chromic acid test and that its boiling point is  $259^\circ\text{C}$ .

**TECHNIQUE****25****CLASSIFICATION TESTS FOR  
FUNCTIONAL GROUPS**

If you have done everything recommended up to this point, you have examined the physical properties of the unknown compound, analyzed its solubility properties, and scrutinized its IR and NMR spectra. Even if you were asked to do only part of this list, you should have a number of pieces of valuable information. Now it is time to use a few classification tests for the specific functional group(s) that you suspect may be in the compound. The tests are listed under the functional groups to which they apply. We have included only the most dependable of the many classification tests that have been developed over the years.

You should plan carefully what chemical tests to use, based on the results you have obtained so far. You need not—indeed, should not—run all these classification tests. If your data suggest that your unknown may be a ketone with no other functional group present, you can confirm it by using the aldehyde and ketone classification tests. You would not want to waste time doing a Lucas test unless you suspect that the compound might also contain an alcohol group. In other words, be selective with the tests you run. Evaluate your hypotheses with crucial tests. If your early ideas need modification, then carefully reevaluate your data, make a new hypothesis, and proceed to test it.

***Use of Reference  
Compounds***

Always try out an unfamiliar classification test on one or two reference compounds of known structure before using the test on an unknown compound. For example, if you suspect that your compound may be an alkene, test whether it can decolorize bromine. You should first try this test on known compounds such as cyclohexene and cyclohexane so that you can observe directly both positive and negative results for the test. The frustration of ambiguous results can be minimized by doing control tests on reference compounds.

**Functional-Group Tests**

The following functional-group tests are presented in this chapter:

- Alcohols
  - Chromic acid oxidation
  - Iodoform test
  - Lucas test
- Aldehydes and ketones
  - Reaction with 2,4-dinitrophenylhydrazine
  - Oxidation of aldehydes with chromic acid
  - Iodoform test
  - Tollens test
- Alkenes
  - Reaction with bromine
  - Oxidation with potassium permanganate
- Amines
  - IR and NMR spectroscopy
- Presence of aromaticity
  - Ignition
  - Reaction with aluminum chloride/chloroform
- Carboxylic acids
  - Neutralization equivalent
- Esters
  - Ferric hydroxamate test
  - Hydrolysis
- Presence of halides
  - Beilstein test
- Phenols
  - Reaction with bromine/water
  - Reaction with ferric chloride

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**SAFETY INFORMATION**

Wear gloves while conducting any functional-group test.

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**25.1****Alcohols****Chromic Acid Oxidation\***

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**SAFETY INFORMATION**

**Chromic acid** solutions are very toxic, corrosive, and a suspected carcinogen. Wear gloves and avoid contact with skin, eyes, and clothing. If you spill any on your skin, wash it off immediately with copious amounts of water.

\*Bordwell, F. G.; Wellman, K. M. J. *Chem. Educ.* **1962**, 39, 308–310.

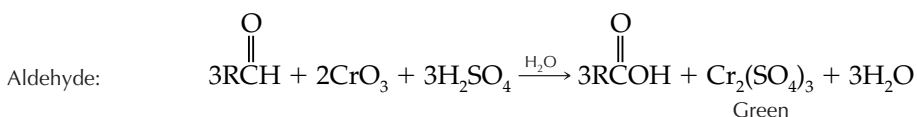
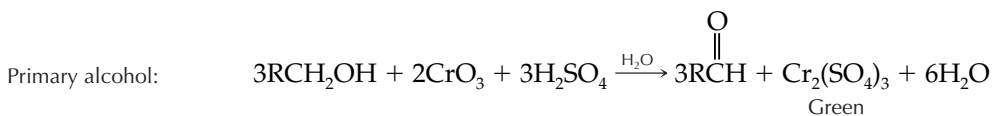
*Positive test: A primary or secondary alcohol will reduce the orange-red chromic acid/sulfuric acid reagent to an opaque green or blue suspension of Cr(III) salts in 2–5 s.*

*To the instructor: The chromic acid reagent is prepared by slowly pouring, with stirring, 25 mL of concentrated sulfuric acid into a solution of 25 g of chromic acid (CrO<sub>3</sub>) in 75 mL of water. (Safety Precaution: Prepare this solution in a hood. CrO<sub>3</sub> dust is a suspected carcinogen.)*

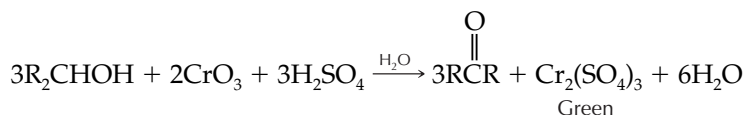
**PROCEDURE:** Add 1 drop or 30 mg of the unknown or reference compound to 1 mL of reagent-grade acetone in a test tube. Then add a drop of the chromic acid/sulfuric acid reagent directly into the solution. Shake the mixture. A primary or secondary alcohol will reduce the orange-red chromic acid/sulfuric acid reagent to an opaque green or blue suspension of Cr(III) salts in 2–5 s. 1-Butanol, 2-butanol, and 2-methyl-2-propanol (*tert*-butyl alcohol) can be used as reference compounds.

**CLEANUP:** The entire reaction mixture may be discarded in the chromium-waste container. Alternatively, the chromium-containing solution can be treated with 5 mL of 50% aqueous sodium bisulfite solution to reduce all the metal ion to green Cr(III). Chromic ion may be disposed of in a number of ways, and local regulations should of course be the basis for choice. Alternatives include placing the entire solution in the hazardous-waste container reserved for inorganic compounds. Another approach is to convert Cr<sup>+3</sup> to Cr(OH)<sub>3</sub> by treatment with excess ammonium hydroxide. The metal hydroxide precipitate is collected on filter paper and placed in the waste container intended for solid inorganic compounds. The filtrate from the latter procedure can be poured into the inorganic-waste container or down the sink, depending on local regulations.

Primary and secondary alcohols differ from tertiary alcohols in their reactions with oxidizing agents. On oxidation with Cr(VI), primary alcohols yield aldehydes, which are further oxidized to carboxylic acids:



Secondary alcohols react with chromic acid to yield ketones, which do not oxidize further under these conditions:



Tertiary alcohols are usually unreactive:

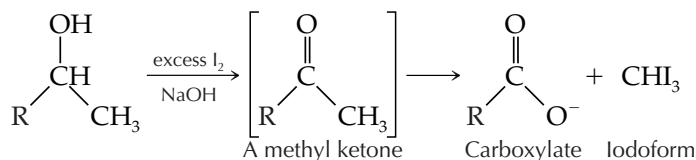


With a few tertiary alcohols, the sulfuric acid may catalyze an elimination reaction. The resulting alkene is oxidized, producing insoluble green Cr(III) salts.

Other functional groups can also be oxidized by the chromic acid reagent, for example, aldehydes, phenols, and many amines. Thus, other data must be used to discover whether or not these groups are present in your compound. For example, solubility tests are extremely useful in detecting a phenol or an amine. An aldehyde gives a solid 2,4-dinitrophenylhydrazone when reacted with the 2,4-dinitrophenylhydrazine reagent, whereas an alcohol does not. Thus a false positive test would be observed for these compounds with chromic acid.

### Iodoform Test

See Technique 25.2, Aldehydes and Ketones (p. 325), for directions on how to carry out the iodoform test. Its main use is for the identification of ketones with a methyl group attached to the carbonyl group. However, any alcohol that can be oxidized to such a ketone also gives a positive iodoform test:



### Lucas Test

#### SAFETY INFORMATION

The Lucas reagent contains **concentrated hydrochloric acid**, which is corrosive and emits toxic HCl vapors. Wear gloves and dispense the reagent in a hood.

*Positive test: Alkyl chloride formation is noted by the formation of an insoluble layer or emulsion. Tertiary alcohols form the second layer in less than a minute, secondary alcohols require somewhat longer (5–10 min), whereas primary alcohols are essentially unreactive.*

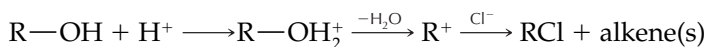
*To the instructor: The reagent is prepared by adding 136 g of anhydrous zinc chloride to 105 g of concentrated hydrochloric acid with cooling.*

**PROCEDURE:** Add 0.1 mL of the unknown or reference alcohol to a test tube and then add 1 mL of the hydrochloric acid/zinc chloride (Lucas) test reagent. Stir the mixture vigorously with a stirring rod or use a vortex mixer to ensure thorough mixing.

Alkyl chloride formation is noted by the formation of an insoluble layer or emulsion. Tertiary alcohols form the second layer in less than a minute, secondary alcohols require somewhat longer (5–10 min), whereas primary alcohols are essentially unreactive. The test is applicable only to alcohols that are soluble in water. 1-Butanol, 2-butanol, 2-methyl-2-propanol (*tert*-butyl alcohol), and 2-propene-1-ol (allyl alcohol) can be used as reference compounds.

**CLEANUP:** Pour the reaction mixture into a 100-mL beaker containing 20 mL of water. Add solid sodium carbonate until the acid is neutralized and the solution exhibits a basic reaction when tested with pH paper. (**Caution: Foaming.**) Collect the resulting zinc hydroxide by vacuum filtration. Discard the zinc hydroxide in the inorganic-waste or solid-waste container and wash the filtrate down the sink or pour it into the container for aqueous inorganic waste.

Primary, secondary, and tertiary alcohols differ from one another in their reactions with hydrochloric acid as a result of their abilities to produce stable carbocations, which react further to yield alkyl chlorides. The alkyl chlorides are insoluble in aqueous HCl solution. Because tertiary carbocations form far more easily than secondary carbocations, which, in turn, form more easily than primary carbocations, reactivity of alcohols with the hydrochloric acid/zinc chloride reagent is in the order tertiary > secondary > primary. However, any alcohol that can produce a carbocation easily forms an alkyl halide quickly. For example, primary alcohols such as benzyl alcohol or allyl alcohol form resonance-stabilized carbocations and therefore react more like secondary or tertiary alcohols. The presence of zinc chloride, a good Lewis acid, makes the reaction mixture even more acidic than HCl alone and enhances the formation of carbocations.



The more stable the carbocation, the greater the driving force for this reaction.

## 25.2

## Aldehydes and Ketones

### Reactions with 2,4-Dinitrophenyl- hydrazine

*Positive test: Formation of a large amount of yellow to red, insoluble 2,4-dinitrophenylhydrazone indicates a positive test.*

*To the instructor: Prepare the 2,4-dinitrophenylhydrazine reagent by carefully dissolving 8.0 g of 2,4-dinitrophenylhydrazine in 40 mL of concentrated sulfuric acid and adding 60 mL of water slowly while stirring the mixture to ensure complete dissolution. Add 200 mL of reagent-grade ethanol to this warm solution and filter the mixture if a solid precipitates.*

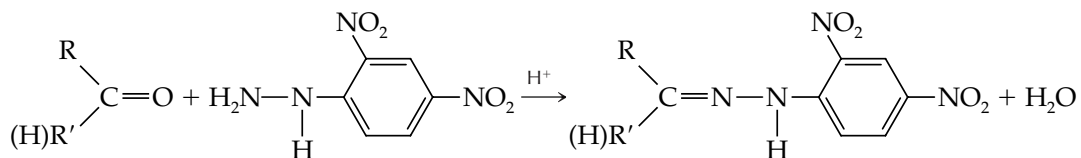
#### SAFETY INFORMATION

**2,4-Dinitrophenylhydrazine** is an irritant and stains the skin. The reagent solution used in this procedure contains sulfuric acid, which is corrosive. Wear gloves while carrying out this procedure.

**PROCEDURE:** Dissolve 20 mg of a solid unknown (1 or 2 drops of a liquid) in 0.5 mL of ethanol in a small test tube. Add 1 mL of the 2,4-dinitrophenylhydrazine test reagent. Shake the test tube vigorously. Formation of a large amount of yellow to red, insoluble 2,4-dinitrophenylhydrazone indicates a positive test. If no precipitate forms, heat the mixture to boiling for 30 s and shake the tube again. If there is still no precipitate, allow the tube to stand for 15 min. As a control, try the test on a known aldehyde and ketone. *Note:* The precipitate from this test may be collected on a Hirsch funnel and purified by the procedure described for the derivative preparation of 2,4-dinitrophenylhydrazones on page 341. Hence, it can serve as derivative of the unknown compound.

**CLEANUP:** Pour the test reaction mixture (or the filtrate, if you saved the precipitate) into the flammable-waste (organic-waste) container.

The reaction of 2,4-dinitrophenylhydrazine with an aldehyde or ketone in an acidic solution is a dependable and sensitive test. Carbonyl compounds react with 2,4-dinitrophenylhydrazine by nucleophilic attack at the carbonyl carbon atom followed by elimination of a molecule of water:



Most aromatic aldehydes and ketones produce red dinitrophenylhydrazones, whereas many nonaromatic aldehydes and ketones produce yellow products. If an orange precipitate forms, no definite conclusions can be drawn from the color.

The melting point of your derivative should not be confused with that of the starting reagent, 2,4-dinitrophenylhydrazine (mp 198°C, with decomposition).

### Oxidation of Aldehydes with Chromic Acid\*

#### SAFETY INFORMATION

**Chromic acid** solutions are very toxic and corrosive and are suspected carcinogens. Wear gloves and avoid contact with skin, eyes, and clothing. If you spill any on your skin, wash it off immediately with copious amounts of water.

*Positive test: A green or bluish green precipitate will appear within 1 min in the presence of an aldehyde.*

*To the instructor: The chromic acid reagent is prepared by slowly pouring, with stirring, 25 mL of concentrated sulfuric acid into a solution of 25 g of chromic acid (CrO<sub>3</sub>) in 75 mL of water. (Safety Precaution: Prepare this solution in a hood. CrO<sub>3</sub> dust is a suspected carcinogen.)*

**PROCEDURE:** Add 1 drop or 30 mg of the unknown or reference compound to 1 mL of reagent-grade acetone in a test tube. Then add 1 drop of the chromic acid/sulfuric acid reagent directly into the solution. Shake the mixture. A green or bluish green precipitate will appear within 1 min in the presence of an aldehyde. Aliphatic aldehydes give precipitates within 15 s, whereas aromatic aldehydes take 30–45 s. Acetone and other ketones will oxidize in this solution, but only after 2–3 min. Try the test with an aliphatic aldehyde, an aromatic aldehyde, a ketone, and a primary or secondary alcohol as reference compounds.

**CLEANUP:** The entire reaction mixture may be discarded in the chromium-waste container. Alternatively, the chromium-containing solution should be treated with 5 mL of 50% aqueous sodium bisulfite to reduce the metal ion to green Cr(III). Depending on local regulations, this solution can be placed in the inorganic-waste container or otherwise suitably disposed of (see p. 324).

\*Morrison, J. D. J. *Chem. Educ.* **1965**, *42*, 554.

A positive 2,4-dinitrophenylhydrazine test does not distinguish between an aldehyde and a ketone. This distinction can best be made by observing the rate of oxidation of the carbonyl compound with chromic acid. Aldehydes oxidize very easily, whereas ketones oxidize only slowly. Alcohols, phenols, and many amines can also be oxidized by the chromic acid reagent (see p. 324).

### Iodoform Test

*Positive test: A yellow precipitate of iodoform appears within 15 min.*

*Iodoform melts at 119°–121°C.*

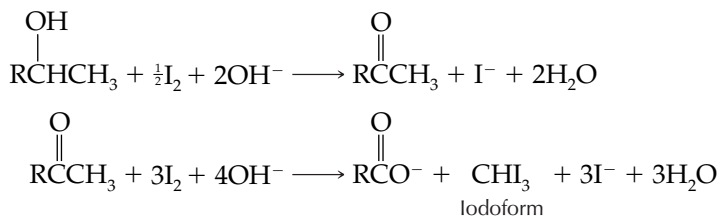
*To the instructor:  
Prepare the iodine/potassium iodide stock solution by adding 50 g of potassium iodide and 25 g of iodine to 200 mL of distilled water. Stir the mixture until it is a homogeneous solution.*

**PROCEDURE:** Place 75 mg or 3 drops of the unknown in a 25-mL Erlenmeyer flask and add 1 mL of water; then, for a water-insoluble compound, add 1,2-dimethoxyethane dropwise until the unknown dissolves. Add 1 mL of 2.5 M sodium hydroxide and the I<sub>2</sub>/KI stock solution dropwise until the red color of iodine persists after the reagents are thoroughly mixed. You have added enough when the reaction mixture is a dark red-brown color, almost as dark as the iodine/potassium iodide reagent itself.

Heat the mixture to 60°C in a water bath. Add more I<sub>2</sub>/KI solution, if necessary, to maintain a definite red color for 2 min while heating at 60°C. Then discharge the excess iodine color by adding, with shaking, a few drops of 2.5 M NaOH and 5 mL of water. With a positive test, a yellow precipitate of iodoform appears within 15 min. Filter the product, wash it with water, dry it, and determine its melting point. Try the test with acetone, 3-pentanone, and ethanol as reference compounds.

**CLEANUP:** Place all reaction mixtures in a beaker and add a few drops of acetone to consume any remaining iodine. (The solution should be colorless.) Collect any iodoform that forms by vacuum filtration; place the iodoform in the halogenated-waste container. Neutralize the aqueous filtrate to pH 7 before washing it down the sink or pouring it into the container for aqueous inorganic waste.

Ketones and alcohols with a methyl group directly adjacent to a carbonyl group or to a carbon atom bearing a hydroxyl group react with an alkaline solution of iodine to produce an easily identifiable canary yellow solid, iodoform:



Both reactions involve oxidation of the organic substrate by iodine. The mechanism of iodoform synthesis occurs through

a series of enolate anions, which are iodinated. In the final steps, hydroxide displaces the  $\text{Cl}_3^-$  anion through an addition-elimination pathway.

Only one aldehyde, acetaldehyde (ethanal), gives a positive iodoform test. Ethanol is the only primary alcohol that gives a positive iodoform test. Naturally, many ketones and secondary alcohols with the correct structural components also give a positive test.

### Tollens Test

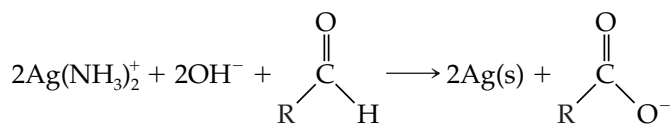
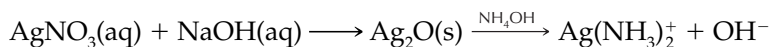
*Positive test: A silver mirror or colloidal silver appears in the test tube.*

**PROCEDURE:** Fresh reagent should be prepared each time the test is conducted. The reagent is prepared by placing 2 mL of a 5% aqueous solution of silver nitrate in a small test tube. A drop of 10% NaOH is added, producing brown silver oxide precipitate. This precipitate is dissolved by adding just enough dilute (2%) ammonia to dissolve the silver oxide precipitate. The test is carried out by adding a few drops of this reagent to a small amount (2 drops, or a microspatula full of solid) of unknown. Frequently, a silver mirror or colloidal silver appears instantly. If not, gently warm the tube for a few minutes in a  $75^\circ\text{C}$  water bath or a steam bath.

Control reactions should be carried out on the following reference compounds: acetone, benzaldehyde, formalin, and glucose.

**CLEANUP:** Combine all the reagents, whether used or unused, in a beaker. Add 6 M HCl until the precipitate stops forming. Collect the solid silver chloride by vacuum filtration and discard it in the container for solid inorganic waste. The filtrate should be neutralized with solid sodium carbonate before being washed down the sink or poured into the container for aqueous inorganic waste.

The preparation of Tollens reagent is based on the formation of a silver diamine complex that is water soluble in basic solution:



Tollens reagent gives a fast positive test with most simple aldehydes. Some  $\alpha$ -hydroxyketones, such as fructose, also give a positive test. The reactions are sometimes characterized by a brief induction period, probably due to the limited water solubility of the organic unknown and to the necessity of silver metal formation as an autocatalytic reagent.

## 25.3

## Alkenes

**Reaction with Bromine**

*Positive test: Alkenes react with bromine and the characteristic red-brown color of bromine disappears. For most alkenes, this reaction occurs so rapidly that the reaction solution never acquires the red color of the bromine until the alkene is completely brominated.*

*To the instructor: The Br<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub> solution should be replenished periodically because it has a limited shelf life.*

**Oxidation with Potassium Permanganate**

*Positive test: Alkenes are oxidized, thereby causing the purple color of the permanganate solution to be replaced within 2–3 min by a brown precipitate of manganese dioxide.*

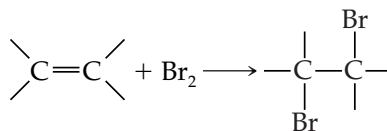
## SAFETY INFORMATION

**Bromine** solutions cause burns and emit toxic bromine vapors. Wear gloves and use the solution only in a hood.

**PROCEDURE:** Dissolve 30 mg or 2 drops of the unknown or reference alkene in 0.5 mL of dichloromethane. Add a 0.5 M solution of bromine in CH<sub>2</sub>Cl<sub>2</sub> dropwise with shaking after each drop is added. Alkenes react with bromine and the characteristic red-brown color of bromine disappears. For most alkenes, this reaction occurs so rapidly that the reaction solution never acquires the red color of the bromine until the alkene is completely brominated. Try this test on cyclohexane, cyclohexene, and acetophenone as reference reactions.

**CLEANUP:** The entire reaction mixture should be poured into the halogenated-waste container.

Almost all alkenes react quickly and smoothly with a dilute solution of Br<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> to form dibromoalkanes:



Very few other functional group classes interfere with this test. Although some compounds undergo free radical or ionic substitution under these conditions, hydrogen bromide gas (HBr) then evolves. Test for the presence of HBr by blowing with your breath lightly across the top of the test tube. If a fog is produced, then HBr is present. Phenols and some aldehydes and ketones may also be brominated under these conditions.

**PROCEDURE A:** Add 30 mg or 2 drops of an unknown or reference compound to 1 mL of acetone in a small test tube. Then add 1 drop of a 0.1 M aqueous solution of potassium permanganate and shake the test tube vigorously. Alkenes are oxidized, thereby causing the purple color of the permanganate solution to be replaced within 2–3 min by a brown precipitate of manganese dioxide. Try the test on an alkene, an aldehyde, and an alcohol.

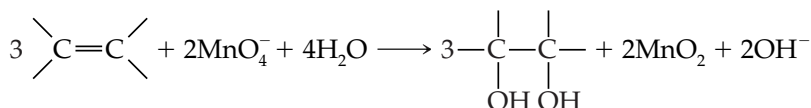
**CLEANUP:** Place the reaction mixtures in the inorganic-waste container.

*Positive test: Alkenes are oxidized, thereby causing the purple color of the permanganate solution to be replaced within 2–3 min by a brown precipitate of manganese dioxide.*

**PROCEDURE B:** Dissolve 800 mg of sodium chloride and 4 mg of potassium permanganate in 4 mL of distilled water in a 10-mL Erlenmeyer flask. Add 4 mL of toluene and stir for a few minutes. Allow the two layers to separate, and add 8 mg of tetrabutylammonium bromide to the mixture; stir until the toluene layer becomes a deep purple color as a result of the transfer of permanganate into this layer with a Pasteur pipet. Allow the layers to separate, then remove the toluene layer and place it in a clean 13 × 100 mm test tube. To this add 5–10 mg (or 1–2 drops) of unknown and reinitiate stirring. If the purple color turns brown within 5 min, this may be taken as a positive test result.

**CLEANUP:** Place the toluene solution in the container for flammable (organic) waste. Pour the aqueous phase into the container for inorganic waste.

The permanganate test for double bonds is generally superior to the bromine test because the manganese reagent adds hydroxyl groups to both simple alkenes and alkenes containing strongly electron-withdrawing substituents:



The phase-transfer catalysis of procedure B is superior to the reaction of procedure A in that the nonpolar layer (toluene in procedure B) normally contains the organic unknown and the catalyst greatly enhances transfer of ionic permanganate ions to that layer.

Because some aldehydes and alcohols may also be oxidized by potassium permanganate, both a positive permanganate oxidation test and a positive bromine addition test are used to identify a compound as an alkene.

## 25.4

### Amines

If an organic compound is a strong enough base to dissolve in 1.5 M HCl solution, we are justified in suspecting that it may be an amine. Many amines also have characteristic, pervasive odors either like that of ammonia or resembling the smell of fish. The Hinsberg test is the usual chemical test for classifying amines as primary, secondary or tertiary, but it often produces ambiguous results. Procedures for the Hinsberg test can be found in Ref. 1. Spectroscopic methods (IR and NMR) are more efficient than chemical tests for the classification of a compound as an amine. The characteristic IR absorption bands for amines are discussed in Technique 18.5.

**25.5****Presence of Aromaticity****Ignition Test**

*Positive test: Many alkanes and their substituted derivatives burn with a clean yellow or bluish flame, whereas most aromatic compounds burn with a smoky flame.*

**Reaction with Aluminum Chloride/ Chloroform**

*AlCl<sub>3</sub> is very hygroscopic. Keep the bottle tightly capped when not in use.*

*Positive test: A change in color of the aluminum chloride and the solution indicates a positive test.*

**SAFETY INFORMATION**

Carry out this test in an efficient hood. Do not wear gloves while using a Bunsen burner.

**PROCEDURE:** Place a small amount of the unknown (a few drops or a few milligrams) in a porcelain crucible cover. While holding the cover with tongs, bring it very near a Bunsen burner flame and allow the substance to ignite. Many alkanes and their substituted derivatives burn with a clean yellow or bluish flame, whereas most aromatic compounds burn with a smoky flame. Some halogenated compounds also burn with a smoky, sooty flame, but elemental analysis (see Ref. 1) easily distinguishes the two. Polyhalogenated compounds can be very difficult to ignite. Inorganic and organic salts always leave a residue upon burning or may not burn at all. The higher the oxygen content of a compound, the greater the propensity for the compound to burn with a colorless or blue flame.

**SAFETY INFORMATION**

Carry out this test in an efficient hood.  
**Chloroform** is volatile and toxic. Wear neoprene gloves and dispense the chloroform in a hood.

**PROCEDURE:** Place 1 mL of dry chloroform in a dry test tube; add 0.1 mL of a liquid or 75 mg of a solid unknown or reference compound; mix thoroughly and tilt the test tube to moisten the wall of the tube. Then add 0.25 g of anhydrous aluminum chloride so that some of the powder strikes the wetted side of the test tube. A change in color of the aluminum chloride and the solution indicates a positive test. Try the test with toluene, chlorobenzene, and hexane as reference compounds.

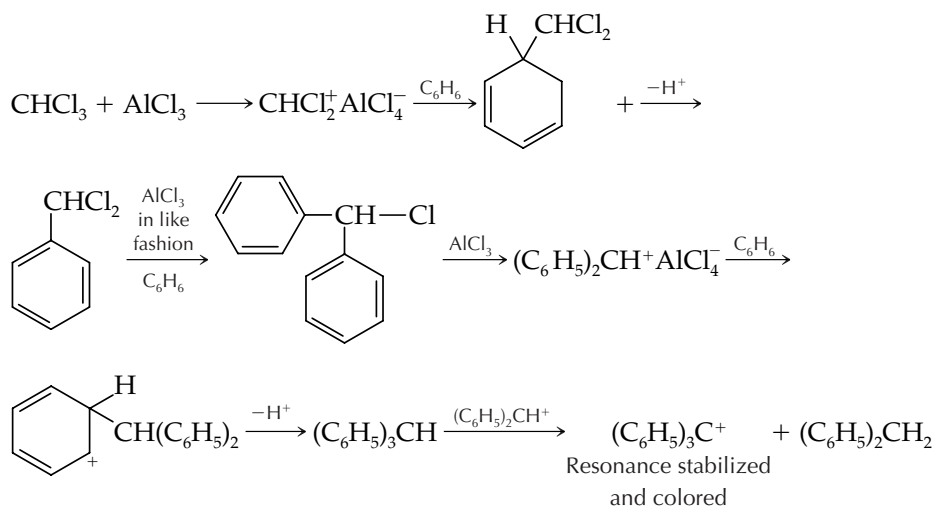
**CLEANUP:** Place the entire reaction mixture in the container for halogenated waste.

Aromatic compounds and their derivatives usually give characteristic colors when they come into contact with a mixture of aluminum chloride and chloroform. Generally, nonaromatic

compounds do not produce a color on contact with aluminum chloride. These color effects may be summarized as follows:

Compound class	Color
Benzene derivatives	Orange to red
Naphthalene	Blue
Biphenyl or phenanthrene	Purple
Anthracene	Green

The colors in this classification test result from Friedel-Crafts reactions between chloroform and the aromatic compounds. Stable, highly colored carbocation salts form on the aluminum chloride surface through alkylation and hydride-transfer reactions:



Compounds containing nitro groups and other electron-withdrawing substituents may not produce colors in this test.

## 25.6

### Carboxylic Acids

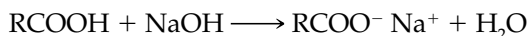
#### Neutralization Equivalent

**PROCEDURE:** Weigh at least two samples (three samples would be preferable to ensure better precision) of an unknown or reference carboxylic acid to three significant figures on a balance of milligram sensitivity. The size of the samples should be in the 200–300-mg range. Place the acid in a 125-mL Erlenmeyer flask. If the acid is water-soluble, dissolve the sample in 50 mL of distilled water. If the acid is not water-soluble, add 25 mL of water to the sample, followed by enough 95% ethanol to dissolve the sample. Add 2–3 drops of phenolphthalein indicator solution (use bromothymol blue

if the sample solution contains more than 50% ethanol). Titrate the acid solution with standardized 0.100 M sodium hydroxide to the indicator end point.

**CLEANUP:** Pour the titrated solution into the container for inorganic waste or other waste container, as directed by your instructor.

The neutralization equivalent test is based on the ability of NaOH to react stoichiometrically with the carboxyl group:



Identification of a carboxylic acid is aided by measuring the neutralization equivalent. In the case of carboxylic acids containing one carboxyl group, the neutralization equivalent and the molecular weight are the same. An acid that contains more than one carboxyl group gives a neutralization equivalent equal to the molecular weight divided by the number of acidic groups. Because it is desirable to know the neutralization equivalent of a carboxylic acid to three significant figures, it is important that you know the weight of the carboxylic acid sample that you titrate to the nearest mg.

Calculate the neutralization equivalent (N.E.) of the acid:

Milliequivalents acid = milliequivalents base  
used in the titration

Milliequivalents acid =  $M_{\text{NaOH}} \times (\text{mL of NaOH used})$

$$\text{N.E.} = \frac{\text{mg acid}}{M_{\text{NaOH}} \times (\text{mL of NaOH used})}$$

Molecular weight = (number of acid groups)  $\times$  (N.E.)

## 25.7

### Esters

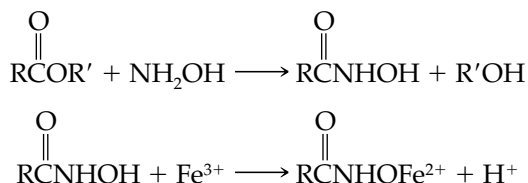
#### Hydroxamic Acid Test

*Positive test: A positive test is formation of a blue-red color.*

**PROCEDURE:** Place 50 mg or 2 drops of the unknown or reference compound along with 1 mL of 0.5 M hydroxylamine hydrochloride in methanol in a test tube. Add 2.5 M sodium hydroxide solution dropwise until the mixture is alkaline (use pH paper). Then add 3 drops more of the sodium hydroxide solution. Heat the reaction mixture just to boiling, cool the tube, and add 1.5 M hydrochloric acid dropwise with shaking until the pH of the mixture is 3. Add 2 or 3 mL more of methanol if a cloudy mixture results. Then add 1 drop of 0.7 M ferric chloride solution. A positive test is formation of a blue-red color. Try the test on one or two esters and on phenol as reference compounds.

**CLEANUP:** Place the entire reaction mixture in the container for inorganic waste.

Esters react with hydroxylamine in basic solution to form hydroxamic acids, which in turn react with ferric chloride in acidic solution to form bluish red ferric hydroxamates:



Ferric chloride reacts directly with phenols to give products of much the same color, and some phenols may interfere with this test. However, the acidic solution used here usually converts a ferric-phenolate complex into a free phenol, which is not deeply colored.

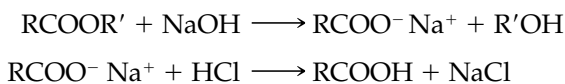
### Ester Hydrolysis

**PROCEDURE:** Place 1 g of the unknown or reference ester and 10 mL of 2.5 M sodium hydroxide in a 50-mL round-bottomed flask equipped with a reflux condenser. Reflux the mixture for 1 h, then extract the cooled product with two 20-mL portions of diethyl ether. After drying the ether solution, distill it to obtain the alcohol. Identify the alcohol.

Make the aqueous sodium hydroxide solution distinctly acidic with 1.5 M HCl and cool well. If a precipitate forms, collect the solid by vacuum filtration. If no precipitate forms, extract the solution with two 20-mL portions of diethyl ether. Dry the ether solution and distill it. Identify the carboxylic acid residue.

**CLEANUP:** Pour the recovered ether solutions into the container for flammable organic waste. Neutralize the aqueous filtrate with sodium carbonate before placing it in the container for aqueous inorganic waste or washing it down the sink.

Basic hydrolysis converts an ester into the carboxylate salt of the parent acid and the alcohol from which the ester was formed. Acidification of the carboxylate salt solution with HCl leads to the recovery of the parent acid.



Often you will find that either the carboxylic acid or the alcohol formed from the hydrolysis of an ester is extremely soluble in water and does not appear in the ether extract. This situation occurs with ethyl benzoate and 1-phenylethyl acetate, for example. Whereas the benzoic acid is easy to isolate, most of the ethanol remains in the water solution. Similarly, the 1-phenylethanol can be readily extracted

with ether, but this is not so for the acetic acid. In these cases, you may have to rely on a definite identification of the water-insoluble component and combine this evidence with the physical and spectral data for the unknown ester in order to reach a final answer.

## 25.8

### Beilstein Test

*Positive test:  
A blue-green flame  
indicates the presence  
of halogen.*

### Presence of Halides

#### SAFETY INFORMATION

Carry out this test in hood. Do not wear gloves while using a Bunsen burner.

**PROCEDURE:** Bend a small loop in the end of a 12-cm long copper wire. Embed the other end of the wire in a large cork. Holding the cork, place the loop in the upper tip of a Bunsen burner flame until the flame is no longer green. Allow the wire to cool. Dip the loop in the unknown compound so that some of the compound sticks to the copper surface. Place the wire in the flame. A blue-green flame indicates the presence of halogen. Try the test on a reference compound that contains halogen and one that doesn't contain halogen.

The Beilstein test is a quick preliminary check for halogens. Because the test is extremely sensitive to even trace impurities, your instructor may ask you to confirm a positive test by a sodium fusion procedure (see Ref. 1). The blue-green color is due to the emission of light from excited states of copper halide that has vaporized in the burner flame. Heating the copper wire before the test is carried out removes traces of sodium chloride that may be present on the wire from handling it with the fingers.

## 25.9

### Reaction with Bromine/Water

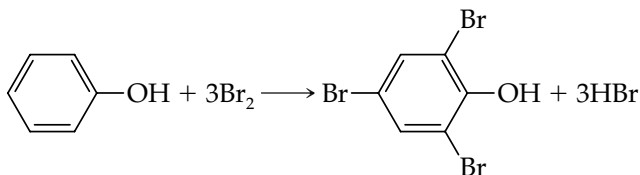
*Positive test:  
Disappearance of the  
orange-brown bromine  
color, accompanied by  
a precipitate, is  
a positive test.*

### Phenols

**PROCEDURE:** Add a saturated solution of bromine in water dropwise to 0.1 g of the unknown or reference phenol dissolved in 10 mL of water, shaking until the bromine color is no longer discharged. Disappearance of the orange-brown bromine color, accompanied by a precipitate, is a positive test. If the suspected phenol is insoluble in water, the test can be done in an ethanol/water mixture. Try the test with phenol and cyclohexene as reference compounds.

**CLEANUP:** Place the mixture in the container for halogenated waste.

Phenols are extremely reactive toward electrophilic substitution. For example, solid tribromophenol is formed almost immediately when bromine water is added to a solution of phenol in water:



### Reaction with Ferric Chloride

#### SAFETY INFORMATION

Carry out this test in an efficient hood.

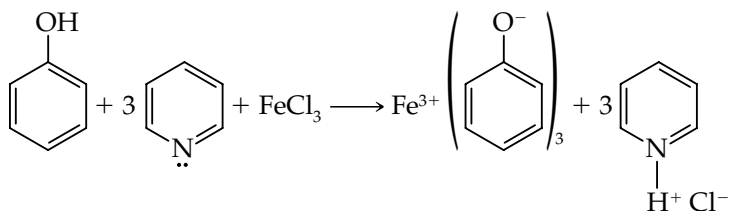
**Chloroform** is volatile and toxic. Wear neoprene gloves and dispense chloroform in a hood.

*Positive test: Most phenols react with ferric chloride to form red to blue ferric phenolate complexes.*

**PROCEDURE:** Suspend 30 mg or 1 drop of the suspected phenol in 1 mL of chloroform. Add 1 drop of pyridine (in the hood) and 3 drops of a 0.06 M solution of anhydrous ferric chloride in chloroform. Most phenols react with ferric chloride to form red to blue ferric phenolate complexes. Try the test on phenol and ethyl acetate as reference compounds.

**CLEANUP:** Place the entire mixture in the container for halogenated waste.

Because all phenols do not produce colored complexes under the test conditions, a negative test must be considered as an ambiguous result. Pyridine is a base which deprotonates the phenol to form phenolate ions. The color is produced by a coordination complex formed between iron(III) and three phenolate ions.



## SYNTHESIS OF SOLID DERIVATIVES

The last step in the identification of an unknown compound, the experiment that eliminates any remaining doubt, is the synthesis of a solid derivative whose melting point can be compared with the melting points of known compounds. The tables in the Appendix, as well as the references listed on page 355, contain lists of a large number of organic compounds and the melting points of their derivatives. Most of the physical constants of such organic compounds were compiled before the advent of infrared and NMR spectrometry, and modern spectrometric techniques have replaced their use in large part. In some cases, the physical properties of organic compounds and their derivatives can still be useful. For example, it would be difficult to be confident that an unknown compound was cholesterol, even if you possessed the infrared and NMR spectra of the compound, unless a sample of cholesterol or reference spectra were also available. Knowing that the phenylurethane of the unknown melts at 167°–168°C would remove a good deal of uncertainty about its identity.

For some functional groups, the synthesis of a derivative is straightforward. These are the ones we have included here. For others, the synthesis of a suitable derivative is quite involved and difficult, and we have omitted them. In these cases, you have to rely on more detailed spectral analyses, functional-group classifications, solubility data, and elemental analyses.

Your derivatives will probably melt a few degrees (2°–5°C) lower than those recorded in the literature, because the highest melting point obtained after repeated recrystallization is usually reported. The suggested recrystallization solvent for many of the derivatives is a mixture of ethanol and water. It is impossible to state an exact ratio of ethanol to water in each recrystallization because the compounds to be purified are so diverse in structure and solubility. Like most organic compounds, however, the derivatives are more soluble in ethanol than in water. The general procedure for recrystallizing a solid from a mixed solvent pair is discussed in Technique 9.2.

Derivatives have great importance in certain situations. For example, the isomers 1,3-dimethylaniline and 1,4-dimethylaniline have extremely similar IR and NMR spectra. Thus the preparation of derivatives with widely differing melting points is helpful. When choosing the specific derivative, very often the difference in melting points is the deciding factor. For example, if your list of possible unknowns includes both 1-propanol (bp 97°C) and 2-butanol (bp 99°C), you should choose the 1-naphthylurethane rather than the 3,5-dinitrobenzoate. The melting points are, respectively, 80°C and 97°C for the naphthylurethanes and 74°C and 75°C for the 3,5-dinitrobenzoates. The 3,5-dinitrobenzoates of 1-propanol and

2-butanol could not be distinguished from each other by a comparison of their melting points.

### Useful Solid Derivatives

Alcohols  
3,5-Dinitrobenzoates  
1-Naphthylurethanes  
Phenylurethanes  
Aldehydes and ketones  
2,4-Dinitrophenylhydrazones  
Semicarbazones  
Carboxylic acids  
Amides  
Anilides  
Toluidides  
Phenols  
1-Naphthylurethanes  
3,5-Dinitrobenzoates

## 26.1

### Alcohols

#### *3,5-Dinitrobenzoates*

#### SAFETY INFORMATION

**3,5-Dinitrobenzoyl chloride** is a strong irritant; wear gloves and avoid contact with skin, eyes, and clothing. This reagent is moisture-sensitive; recap the bottle quickly after use.

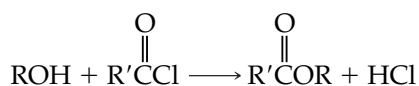
**Pyridine** is toxic and has an extremely unpleasant odor; dispense it in a hood.

**PROCEDURE:** Place 800 mg of 3,5-dinitrobenzoyl chloride, 0.20 mL (or 200 mg) of the unknown alcohol, 2.0 mL of dry pyridine, and a boiling stone in a 5-mL round-bottomed flask. Attach an air-cooled condenser and heat the mixture at reflux on an aluminum block or in a sand bath at 140°C for 15–20 min. Put 5 mL of water in a 10-mL Erlenmeyer flask and pour the reaction mixture slowly into the water. Cool the solution in an ice-water bath until the product precipitates. Scratching the walls of the flask with a stirring rod may be necessary to induce crystallization. Collect the crystals by vacuum filtration on a Hirsch funnel. Transfer the crystals to a small beaker and stir them thoroughly with 3 mL of 5% sodium carbonate solution to remove the excess 3,5-dinitrobenzoic acid that may be present. Again collect the solid by vacuum filtration on a Hirsch funnel

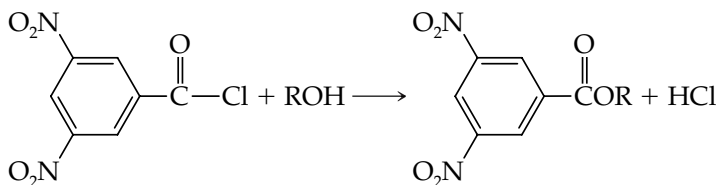
and wash it with 1 mL of cold water. Recrystallize the derivative from a mixture of ethanol and water.

**CLEANUP:** Acidify the sodium carbonate filtrate using HCl to obtain a pH of ~5. Use vacuum filtration to collect any 3,5-dinitrobenzoic acid that forms as a precipitate; place it in the container for solid organic waste. Neutralize the filtrate with solid sodium carbonate and place the resulting solution in the container for inorganic waste or wash it down the sink, as directed by your instructor. Place the filtrate from the recrystallization in the container for flammable (organic) waste.

Alcohols undergo reaction with carboxylic acids and some of their derivatives to form esters. An example is the reaction of an acyl chloride with an alcohol:



A useful derivative of an unknown alcohol is the 3,5-dinitrobenzoate ester, which is prepared through the reaction of the alcohol with 3,5-dinitrobenzoyl chloride:



The hydrogen chloride produced immediately undergoes reaction with the tertiary amine pyridine present in the reaction mixture. Hindered tertiary alcohols sometimes form esters quite slowly with 3,5-dinitrobenzoyl chloride. In such cases, it is advisable to heat the reaction mixture under reflux for 1–2 h.

### 1-Naphthylurethanes

#### SAFETY INFORMATION

**1-Naphthyl isocyanate** is a lachrymator (causes tears) and is moisture sensitive. Wear gloves and use it only in a hood.

**Hexane** (or petroleum ether) is extremely flammable. Heat it only on a steam bath or in a 70°C water bath.

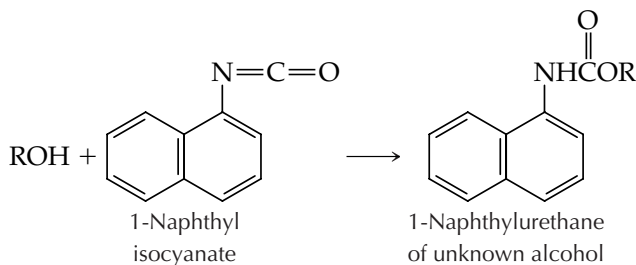
**PROCEDURE:** This reaction requires a dry alcohol. Place 0.5 mL of a liquid alcohol in a small test tube and dry it for 10 min with anhydrous sodium sulfate.

Place 0.2 g (or 5 drops) of dry unknown alcohol in a dry 4-in. test tube. Add 0.20 mL of 1-naphthyl isocyanate. A precipitate

usually forms spontaneously. If the reaction is not spontaneous, place a plug of cotton in the top of the test tube and warm the mixture in a 95°C water bath or on a steam bath for up to 15 min. When the reaction is complete, cool the test tube and add 3 mL of hexane (petroleum ether or ligroin may be substituted). Place a boiling stick or stone in the test tube and heat the mixture carefully in a 70°C water bath to dissolve the product. Gravity filter the hot solution through a small fluted filter paper to remove undissolved di-1-naphthylurea (mp = 297°C) that usually forms as a by-product. Cool the solution in an ice-water bath and collect the product by vacuum filtration on a Hirsch funnel. Further recrystallization is not usually necessary.

**CLEANUP:** Pour the filtrate into the container for flammable (organic) waste. Place the filter paper containing di-1-naphthylurea in the container for organic solid waste.

Most anhydrous alcohols react vigorously with 1-naphthyl isocyanate to form solid 1-naphthylurethanes:



### Phenylurethanes

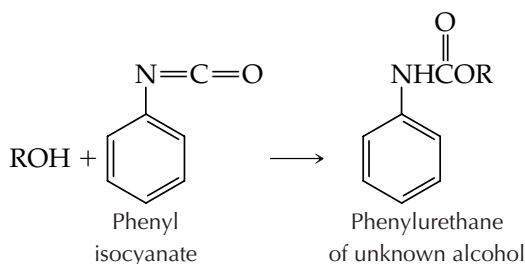
#### SAFETY INFORMATION

**Phenyl isocyanate** is toxic, corrosive, and moisture sensitive. Wear gloves and use it only in a hood.

**Hexane** is extremely flammable. Heat it only on a steam bath or in a 75°C water bath.

**PROCEDURE:** Follow the procedure described earlier for the preparation of 1-naphthylurethanes, except use 0.20 mL of phenyl isocyanate. (The melting point of the by-product, diphenylurea, is 240°C.)

Phenyl isocyanate reacts more slowly with alcohols than 1-naphthyl isocyanate does. Phenylurethanes may not form spontaneously if bulky substituents are present near the hydroxyl group of the alcohol.



## 26.2

## Aldehydes and Ketones

## 2,4-Dinitrophenylhydrazones

## SAFETY INFORMATION

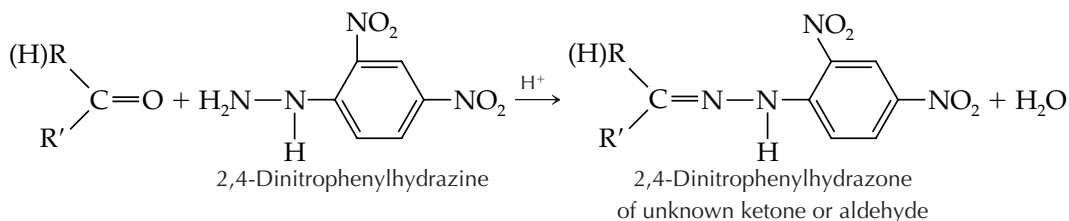
**2,4-Dinitrophenylhydrazine** is an irritant and stains the skin. The reagent solution used in this procedure contains sulfuric acid, which is corrosive. Wear gloves while carrying out this procedure.

*A thorough washing is necessary to remove all the sulfuric acid that may be clinging to the crystals. Any remaining acid will catalyze decomposition of the dinitrophenylhydrazone when you heat it, and the decomposition products lower and broaden the melting range.*

**PROCEDURE:** Dissolve 100 mg (or, with liquids, 3 drops) of the unknown carbonyl compound in 2 mL of reagent-grade ethanol and add 3 mL of the 2,4-dinitrophenylhydrazine reagent (see p. 325). A large quantity of crystals usually forms immediately; however, heating the reaction mixture in a water bath at 50°C for 2 min may be necessary to produce a derivative. Let the mixture stand at room temperature for 15–20 min before collecting the solid product by vacuum filtration on a Hirsch funnel. Wash the crystals with two or three 1-mL portions of cold ethanol. To do this, discontinue the suction, add the ethanol, and stir the crystals gently to wash them completely. Then apply suction again. After thorough washing, 2,4-dinitrophenylhydrazones often need no recrystallization. Determine the melting point. If recrystallization proves to be necessary, use ethanol as the solvent.

**CLEANUP:** Pour the filtrate into the container provided for flammable (organic) wastes.

The reaction between a carbonyl compound and 2,4-dinitrophenylhydrazine is written

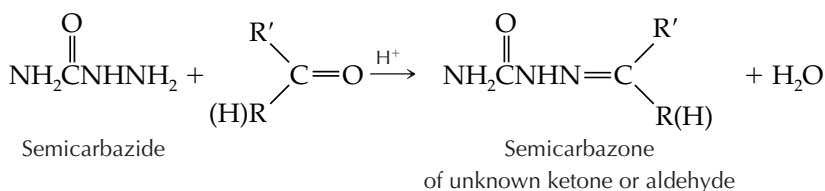


**Semicarbazones**

**PROCEDURE.** Dissolve 0.5 g of semicarbazide hydrochloride in a mixture of 4.0 mL of water and 7.0 mL of ethanol in a 25-mL round-bottomed flask. Add 0.80 g of sodium acetate trihydrate or 0.50 g of anhydrous sodium acetate to provide the proper pH for the formation of the semicarbazone. Add 250 mg of the unknown carbonyl compound and a boiling stone; fit the flask with a water-cooled condenser. Reflux the mixture on a steam bath or in a boiling-water bath for 30 min. Allow the solution to cool for a few minutes, add 3.0 mL of cold water, and cool the mixture in an ice-water bath. Scratch the inside of the flask with a stirring rod to induce crystallization of the semicarbazone. If crystallization still does not occur, evaporate at least half of the solvent on a steam bath and repeat the cooling process. Collect the crystals on a Hirsch funnel by vacuum filtration and recrystallize the product from an ethanol/water solvent.

**CLEANUP:** Dilute the filtrate from the reaction mixture with water and add enough 3 M HCl dropwise to make the solution slightly acidic (pH 5), then wash the solution down the sink or place it in the container for aqueous organic waste. Pour the filtrate from the recrystallization into the container for flammable (organic) waste.

Semicarbazones form readily from most aldehydes and ketones as highly crystalline solids.

**26.3****Carboxylic Acids: Amides, Anilides, Toluidides****Step 1: Preparation of the Acyl Chloride**

*The thionyl chloride must be pure; otherwise the procedure does not work well.*

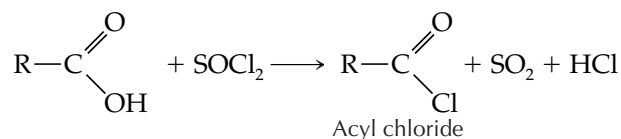
**SAFETY INFORMATION**

If **thionyl chloride** is spilled on the skin, serious burns can result. It is volatile and reacts with moisture in the atmosphere, forming hydrogen chloride and sulfur dioxide. Wear gloves. It should be dispensed in a hood and used in a hood, if possible. The bottle should be kept tightly capped when not in use.

*Piperidine, a cyclic secondary amine, serves as a catalyst.*

**PROCEDURE:** Place 250 mg of the unknown carboxylic acid, 0.30 mL of thionyl chloride, and 1 drop of piperidine in a 5- or 10-mL round-bottomed flask fitted with an air-cooled condenser and a drying tube filled with anhydrous calcium chloride. Heat the reaction mixture in a water bath at 50°–55°C for 25 min. Cool the solution in a bath of cold tap water. The acyl chloride solution is now ready for addition to the selected base, either ammonia, aniline, or 4-toluidine.

Synthesis of an amide, an anilide, or a toluidide begins with the preparation of the acyl chloride from the unknown carboxylic acid, using thionyl chloride:



## Step 2: Preparation of Amides

### SAFETY INFORMATION

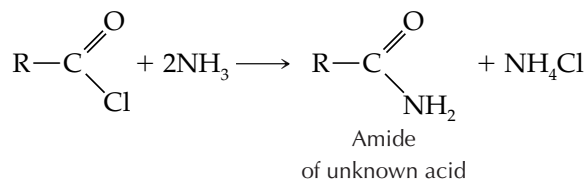
The addition of an **acyl chloride** solution to cold **concentrated ammonia** can cause a violent reaction when the thionyl chloride hydrolyzes to hydrochloric acid. Carry out the addition dropwise with stirring. Work in a hood.

*This procedure does not work well for an unknown carboxylic acid that is water-soluble because the amide is likely to be water-soluble also.*

**PROCEDURE:** Place 3 mL of concentrated ammonia solution in a 30-mL beaker and chill the solution in an ice-water bath. While stirring the ammonia solution with a glass rod, add the acyl chloride solution dropwise, using a Pasteur pipet. Stir the mixture until the reaction is complete. Collect the solid amide by vacuum filtration on a Hirsch funnel, and recrystallize it from an ethanol/water mixture.

**CLEANUP:** Dilute the filtrate with water and neutralize it with 6 M HCl before flushing it down the sink or pouring it into the container for aqueous inorganic waste. Pour the filtrate from the recrystallization into the container for flammable (organic) wastes.

Amides are the most common solid derivatives of carboxylic acids and are prepared by the reaction of acyl chlorides with ammonia:



**Step 2: Preparation of Anilides or Toluidides**

**SAFETY INFORMATION**

**Aniline** and **4-toluidine** are very toxic and are readily absorbed through the skin. Measure aniline in a hood. Wear gloves while using either of these reagents.

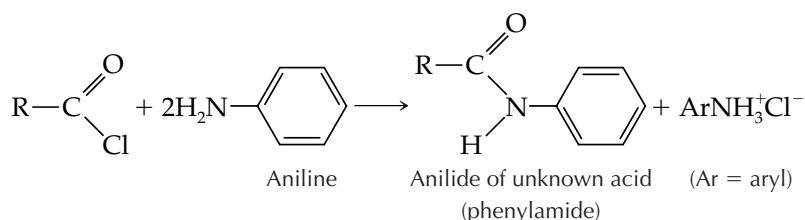
**Dichloromethane** is toxic, an irritant, absorbed through the skin, and harmful if inhaled. Use it only in a hood and wear neoprene gloves.

**PROCEDURE:** Place 5 mL of dichloromethane and 0.8 mL of aniline (or 0.9 g of 4-toluidine) in a 25-mL Erlenmeyer flask. While stirring the dichloromethane solution, add the acyl chloride dropwise, using a Pasteur pipet. Rinse the reaction flask with a few drops of dichloromethane and add this rinse to the Erlenmeyer flask. The reaction is quite vigorous and a thick slurry should form. Allow the mixture to stand for 5 min, then add 7 mL of ice-cold water and stir thoroughly to mix the layers; the solid should dissolve.

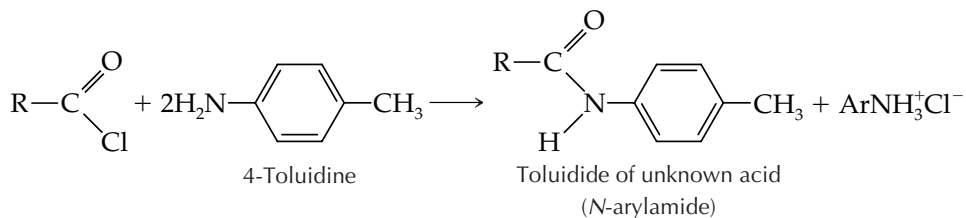
Pour the two-phase mixture into a 15-mL centrifuge tube. Transfer the lower organic phase to another 15-mL centrifuge tube, using a Pasteur pipet. Wash the organic layer successively with 2 mL of water, 2 mL of 10% HCl (to remove the excess amine), then 2 mL of water [see Technique 4.5b]. Dry the organic layer with anhydrous calcium chloride. Transfer the dried solution to a 10-mL Erlenmeyer flask. Working in a hood, evaporate the dichloromethane on a steam bath or with a stream of nitrogen or air. Recrystallize the product from ethanol or an ethanol/water solution.

**CLEANUP:** Combine the aqueous phases from the extractions and adjust the pH to 10 with 5% NaOH. Transfer the solution to a screw-capped centrifuge tube and extract the aqueous phase with 2 mL of ether. Remove the lower aqueous phase and adjust the pH to 7 with 5% HCl before washing the solution down the sink or pouring it into the container for aqueous inorganic waste. Pour the ether solution and the filtrate from the recrystallization into the container for flammable (organic) waste. Place the calcium chloride pellets in the inorganic-waste container.

Anilides are formed by the reaction of acyl chlorides with aniline:



Toluidides are analogous compounds containing a methyl group in the para position of the aromatic ring.



## 26.4

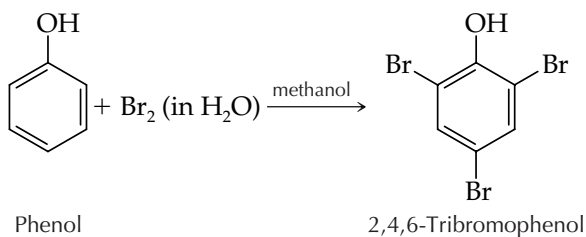
### Phenols

#### *Bromo Derivatives*

**PROCEDURE:** Dissolve 0.1 g of the unknown phenol in 1 mL of methanol in a 50-mL Erlenmeyer flask and add 1 mL of water. Slowly add a saturated solution of bromine in water, a few milliliters at a time, until the bromine color persists. Shake the flask after each addition. Filter the solid product and wash it well with water. Recrystallize it from a methanol/water solvent mixture.

**CLEANUP:** Pour the filtrate from the reaction mixture and the recrystallization into the container for halogenated waste.

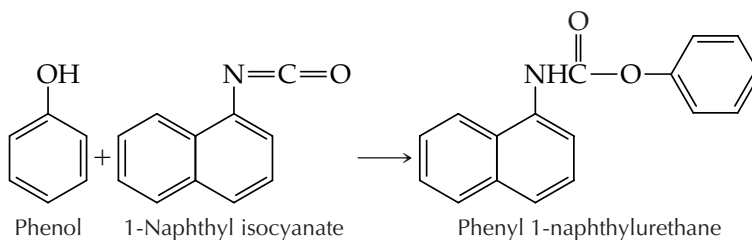
The bromination of phenol is a typical example of this reaction:



#### *1-Naphthylurethanes*

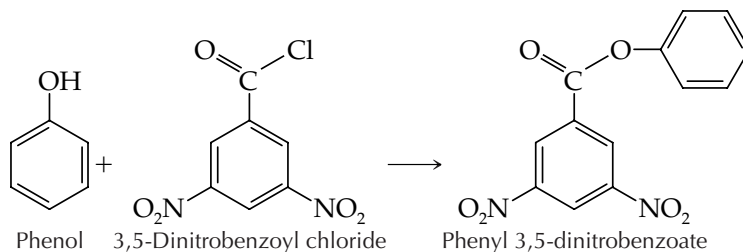
**PROCEDURE:** Follow the procedure used for alcohols (p. 339), except add 1 drop of pyridine to the reaction mixture.

The reaction of phenol and 1-naphthyl isocyanate is



**3,5-Dinitrobenzoates** **PROCEDURE:** Follow the procedure used for alcohols (p. 338).

Phenyl 3,5-dinitrobenzoate, for example, forms by this reaction:



## TECHNIQUE

# 27

## SEPARATION OF MIXTURES

The practicing chemist is usually faced with a mixture of products and unreacted starting materials rather than a single easily purified unknown. In fact, you have already separated many mixtures as you isolated and purified products in the experiments you have done.

When faced with a mixture of compounds whose separate identities you want to know, you need to discover first of all how many compounds there are in the mixture. Then you must develop a method for their separation before you can begin to use the identification tests we have already discussed.

The science of mixture separation continues to be improved every day. When an organic chemist considers a separation, the first question to be addressed is whether a preparative or an analytical separation is necessary. For an analytical separation, merely enough of each compound (just a milligram or so) to determine the presence and identity of all components is often sufficient. The use of analysis as a means of determining a mixture's composition is not a viable alternative unless the chemist already has a good idea about the identity of all the components (after using many of the techniques described in this section). The analysis can be carried out more readily when a pure sample of each component is in hand. Where the preparative approach is necessary, it is normally appropriate to separate much larger amounts of compound, and it is usually desirable to isolate between 100 mg and 1 g of each component, if possible.

In the early part of your experimental work, obtain an infrared spectrum of the test mixture. This spectrum can be a big help in deciding what procedures to use for separating the compounds. Initially, try your separation methods on small amounts of the unknown mixture before you commit the bulk of your sample. Separation of components from a mixture is, in part, a trial-and-error process.

**27.1****Techniques of Separation**

There are many useful techniques for the separation of mixtures. Only some of these techniques are available in the educational laboratory, but it is worthwhile to learn about the procedures of the research scientist at the same time. Following are the techniques we cover in this text.

Thin-layer chromatography (TLC)

Extraction

Distillation

Liquid chromatography (LC)

High-performance liquid chromatography (HPLC)

Gas chromatography (GC)

Mass spectrometry (MS)

We summarize the strengths and weaknesses of each of the seven techniques to familiarize you with situations to which the techniques may best lend themselves. Full descriptions appear elsewhere, as the cross-references indicate.

***Thin-Layer  
Chromatography  
[Technique 15]***

Thin-layer chromatography (TLC) is the technique most frequently used by an organic chemist to investigate mixtures. It requires only small amounts of compounds, and with practice it is easily modified (by varying the choice of solvent) to resolve even very complex mixtures. Silica gel is a relatively gentle absorbent; thus TLC does not harm most sensitive compounds. Elevated temperatures are not required, as is the case for distillation or gas chromatography. TLC is also a companion technique: For example, before examining a sample by means of GC, a TLC procedure is often carried out to be sure that the compound is sufficiently pure and will not foul the GC column. Moreover, TLC analysis is frequently run on fractions taken from column chromatography to determine the number of components in a sample and often the identity of the components. "Thick"-layer chromatography can be carried out on substances when a preparative-scale TLC separation is desired. Special large chromatographic plates are used for this procedure, thereby ensuring the separation of enough material to allow the recovery of individual compounds.

***Extraction  
[Technique 8]***

Because extractions are frequently used to purify the products of organic synthesis, the equipment (separatory funnels and so on) is commonly available. Extraction requires fairly large amounts of compound (at least several hundred milligrams). Specific solubility properties such as the polarity characteristics and the acid-base chemistry of the organic compounds of interest must be considered. Extraction does not harm most organic compounds, so long as they can tolerate 5–10% solutions of strong acids or bases. Elevated temperatures are not required. TLC procedures can be performed before and after subjecting a sample to acid extraction. Mechanical

losses, however, can be fairly substantial. The details of a typical extraction carried out on a mixture of simple organic compounds are described in Technique 27.3.

**Distillation**  
[Technique 11]

Because distillation is frequently used to purify the products of organic synthesis, the equipment (condensers, adapters, and so on) is normally readily available. Distillation requires fairly large amounts of compound (at least a few grams for a miniscale distillation). All components of the mixture must be reasonably stable with respect to heat. Vacuum distillation can be used for thermally sensitive compounds of modest thermal stability, but it is very inefficient. Mechanical losses can be fairly substantial in any distillation. One can run TLC procedures before distillation and on each fraction obtained from the distillation.

**Liquid  
Chromatography**  
[Technique 17]

Liquid or column chromatography is frequently used when the sample is thermally sensitive enough to prohibit preparative-scale separation by either distillation or gas chromatography. TLC is often used to identify useful solvent systems for column chromatography, although the separations are not normally as good on a column as they are on thin-layer plates. Columns require substantial amounts of compound (100 mg, and often much more), and TLC must be used to monitor the identity of the samples as they come off the column. Compounds with close ratio-to-front factor ( $R_f$ ) values are frequently not easily separable by means of column chromatography. Because silica gel is a gentle adsorbent, compound stability is not normally an issue. Elevated temperatures are not required. Special techniques such as flash chromatography [Technique 17.9] use pressure-driven liquids forced through very small particles of adsorbent to carry out improved separations.

**High-Performance  
Liquid  
Chromatography**  
[Technique 17.10]

HPLC is similar to flash chromatography in that pressure is used to drive mixtures through adsorbents of an especially small particle size. HPLC is used when high speed is needed and especially when the sample is thermally sensitive. TLC is often used to decide what solvent system might work as the mobile phase. Although HPLC separations are frequently excellent as an analytical technique, an expensive, elaborate instrument is required, especially when doing preparative-scale separations. Sample sizes akin to that used for TLC (milligrams) or even smaller amounts are usually sufficient for analytical work. Elevated temperatures are not required.

**Gas Chromatography**  
[Technique 15]

In all the preceding techniques, the samples are in the liquid phase. In gas chromatography, the sample is in the gaseous phase and components are separated by adhesion to a stationary liquid adsorbent. Thus, significant thermal stability and vapor pressure are required of all components in the mixture. Sample sizes akin to those used for TLC and HPLC (milligrams or microliters) or even smaller amounts are usually sufficient. Preparative-scale procedures can be carried out on specially adapted instruments. The analytical procedure itself is usually quite fast (a matter of minutes).

**Mass Spectrometry**  
**[Technique 20]**

One particularly powerful method allows the acquisition of the mass spectra for compounds separated by gas chromatography in a simple and straightforward manner. The instrument used in this method links a gas chromatograph directly to a mass spectrometer; the method is thus designated GC-MS. To obtain a mass spectrum of each component of a mixture, a tiny amount of the mixture is dissolved in a solvent such as methanol or ether and the solution is injected into the gas chromatograph. A time delay before the mass spectrometer begins to operate is built into the procedure so that the solvent can exit the gas chromatograph before MS data is collected. This delay means that low-boiling-point organic compounds are not observed. A mass spectrum is recorded for each GC peak, so the molecular ion and fragmentation peaks can be interpreted by the methods discussed in Technique 20.

**27.2****Assaying the Number of Compounds**

If you have a mixture of solids, run TLC chromatograms on the mixture. Ethyl acetate is a developing solvent of medium polarity and would be a good initial choice if you are using silica gel TLC plates. A general method of selecting a TLC developing solvent is discussed in Technique 15.5.

**Liquid-Solid Samples**

With a mixture that is part liquid and part solid, vacuum filtration is a natural first step. Gas-liquid chromatography is the method of choice for analyzing the number of compounds in a liquid. However, there may be solids dissolved in the liquid portion of a liquid-solid mixture that will plug the GC column and never reach the detector. Most solids are not volatile enough to pass through standard GC columns at the column temperatures normally used. TLC analysis at least gives a rough idea of the purity of a sample that you are considering for GC analysis.

To determine whether the liquid portion of your mixture contains any solids in solution, place a few drops of the liquid on a watch glass in the hood. Allow the liquid to evaporate and observe whether a solid residue remains. The only ambiguity in this analysis occurs with liquid amines, which often react with carbon dioxide from the air to form solid carbonates and ureas.

**Do not put any liquid that contains dissolved solids through a gas-liquid chromatograph.** First find a method for separating out the dissolved solids. Only when a solid compound has already been identified and is known to be volatile can an exception be made to this rule.

**Liquid Samples**

If you are given a homogeneous liquid mixture, place a few drops of it on a watch glass in the hood. Allow the liquid to evaporate and observe whether a solid residue remains. When a solid is present, treat the mixture as a liquid-solid mixture.

If no solid is present, analyze the liquid mixture by gas-liquid chromatography. It is easiest to distill a small amount of the liquid first to gain some idea of its volatility; see the discussion on microscale distillation in Technique 11.3b or 11.3c. This preliminary distillation allows you to choose an appropriate GC column and working temperature. Initially, choose a column temperature from 20°C to 75°C below the point at which the liquid boils. If the mixture boils over a wide temperature range, you may have to do GC analyses at several different temperatures.

---

## 27.3

### Separating the Mixture

Filtration, distillation, extraction, and chromatography are the primary separation techniques. We have already discussed the use of filtration for separating solids from liquids. For separating liquids from one another, distillation can be an effective method. If this method looks like a feasible approach for your unknown, try it out on a small amount (1–2 mL) of the sample. Remember that it is difficult to separate liquids that boil within 50°C of one another by using simple fractionating columns. In addition, you must be aware of the possibility that two liquid compounds may undergo reaction with each other at the elevated temperatures of a distillation. A reaction is especially likely if you heat an alcohol and a carboxylic acid or an amine and a carboxylic acid or one of its derivatives. If no solids are present in solution, check the purity of the mixture by GC both before and after the distillation. If a distillation has produced an 80:20 mixture from a 50:50 mixture of two volatile liquids, a second and even a third distillation are probably warranted.

#### *Extraction*

Extraction techniques provide one of the best ways to separate a mixture of compounds. Extraction can take advantage of the chemical nature of the compounds to be separated. Both the polarity and the acid-base properties of the test compounds can be exploited for this purpose.

**Extraction with Water.** Because most organic compounds are insoluble in water, it is unlikely that an entire mixture will be soluble. However, there is a chance that one of its components may be soluble in water, especially if O—H stretching vibrations appear in the infrared spectrum. When one of the components is soluble in water, this behavior is the basis of an excellent separation method.

Determining the water solubility of one component of a mixture is not always easy. Even with a positive result, there will still be two layers present. Use a 10-mL graduated cylinder to test the solubility of the component. Add 0.5 mL of the mixture and then a few milliliters of water. Shake the liquids together and allow them to separate again; then carefully check the volume of the organic layer. You should be able to see whether more than 0.1 mL of the

mixture has dissolved in the water. If in doubt, add another measured quantity of the mixture and check to see how much has been extracted into the water layer overall.

If one component is soluble in water and the others insoluble, extraction of the mixture by means of a separatory funnel permit you to separate the water-soluble component. Separating that component from the water requires distillation. Remember, however, that some water-soluble compounds form azeotropic mixtures with water. If this is the case, you may have to add a low-boiling-point solvent, such as dichloromethane or diethyl ether, to the distillate and dry the solution with anhydrous magnesium sulfate. If a drying agent is added directly to a small volume of liquid, a large percentage of the liquid may be lost as it clings to the solid particles. After filtration and distillation of the low-boiling-point solvent, the water-soluble component that remains can be identified by the usual methods. [See Technique 8.7 for the methods of drying a solution.]

**Extraction with Acid or Base.** One of the best methods for separating a mixture of compounds is extraction with acid or base. Acidic or basic compounds can be converted to water-soluble salts by neutralization with 2.5 M NaOH and 1.5 M HCl, respectively. In this way, a carboxylic acid can be separated from an ester and an alcohol, a phenol from an aryl halide, an amine from an amide, and so forth.

Consider the case of a water-soluble carboxylic acid and an ester. If you shake a few milliliters of 2.5 M NaOH solution with your unknown mixture, the carboxylic acid dissolves in the aqueous layer as the carboxylate salt. After separation of the organic and aqueous layers, the aqueous layer can be acidified with 6 M HCl solution. A solid carboxylic acid precipitates and can be filtered. A liquid carboxylic acid can be distilled or extracted with diethyl ether and isolated as discussed earlier.

A water-insoluble amine can be extracted with 1.5 M HCl solution. After separation of the layers, the aqueous mixture can be made strongly alkaline with 2.5 M NaOH solution. The amine can be recovered as a residue by extraction with ether, drying, and distillation of the solvent.

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## 27.4

### Model Extraction Procedure

The following model extraction procedure can be used to separate four classes of organic compounds: a stronger organic acid (a carboxylic acid), a weaker acid (a phenol), a base (an amine), and a neutral compound.

Assume that a mixture (total weight 5–20 g) is composed of benzoic acid, phenol, 1-amino-4-methylbenzene (*p*-methylaniline), and methoxybenzene (anisole). The task of analyzing a mixture of, respectively, a strong organic acid, a weak acid, a base, and a neutral compound represents a typical situation for separation by extraction, as shown in the flow diagram in Figure 27.1.

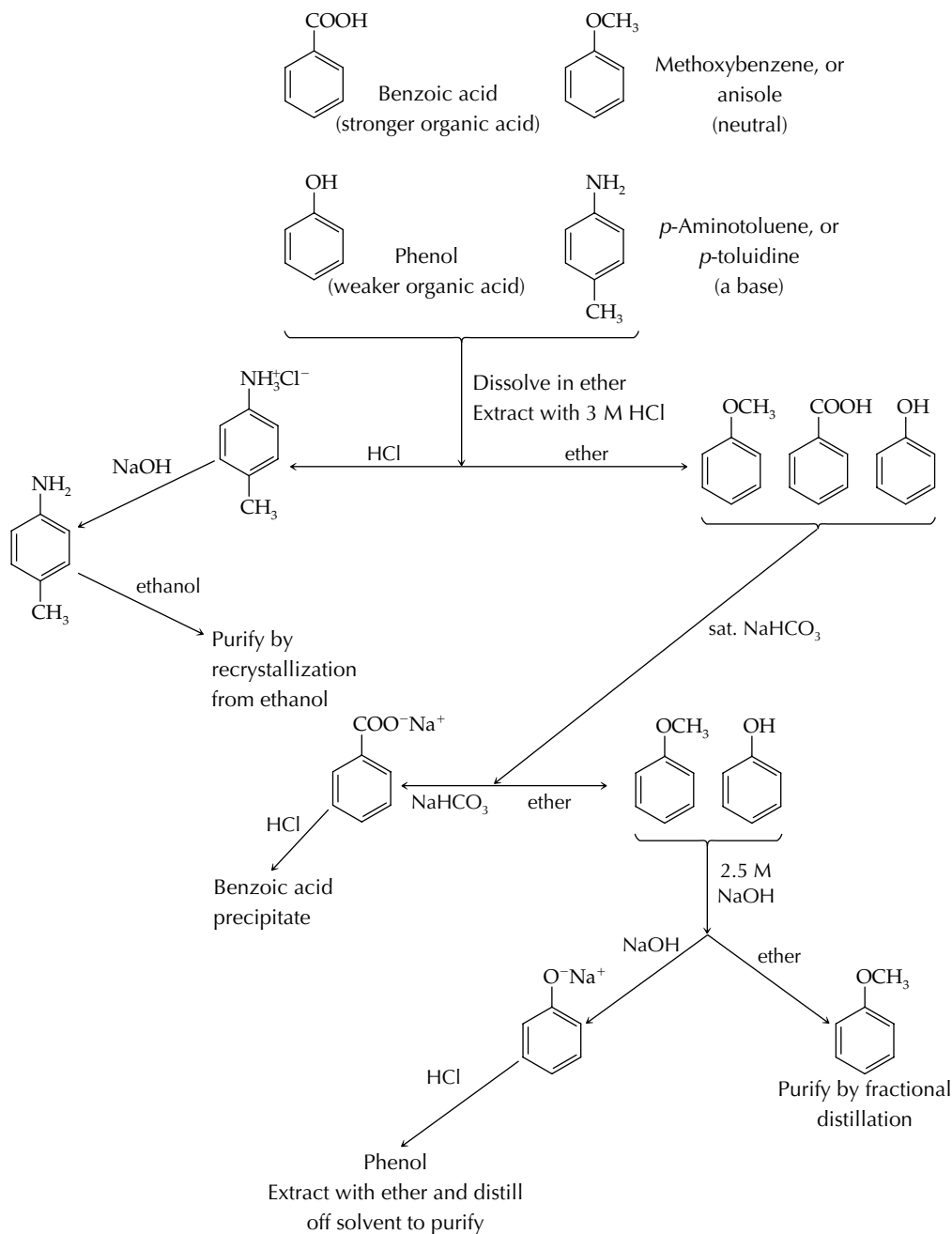


FIGURE 27.1 Extraction of organic compounds with acids and bases.

### Extraction with 3 M HCl Solution

Dissolve the entire mixture in 100 mL of ether (filter off any solids). In a separatory funnel, extract [Technique 8.2] this solution with  $2 \times 35\text{-mL}$  portions of 3 M HCl. The aqueous layer contains 1-amino-4-methylbenzene hydrochloride, which can be treated with ammonia (until the solution is no longer acidic as determined

with pH paper); as a result, the amine will precipitate out. The solid amine can be recrystallized from ethanol for purification.

**Extraction with Saturated  $\text{NaHCO}_3$  Solution**

Extract the remaining ether layer twice with 35-mL portions of saturated sodium bicarbonate solution. By this means the stronger acid, benzoic, is removed from the ether solution. Treat the sodium benzoate in the water layer with 3 M HCl solution until the water layer is no longer basic; this step precipitates the benzoic acid (mp 121°C), which can be recrystallized from hot water.

**Extraction with 2.5 M NaOH Solution**

The ether solution now contains only phenol (a weak acid) and methoxybenzene, which is neutral. Extract this solution with  $2 \times 35$  mL portions of 2.5 M NaOH, and treat the water layer, which now contains sodium phenoxide, with 3 M HCl until it is no longer basic as tested with pH paper.

Neutralization with HCl regenerates (reprotonates) the phenol, which can be recovered from the aqueous solution by extraction with  $2 \times 35$ -mL portions of ether followed by evaporation of the ether.

The ether layer remaining from the NaOH extractions now contains only methoxybenzene, which can be recovered by first distilling off the ether (bp 35°C) and then the methoxybenzene (bp 154°C).

Remember that infrared spectrometry, as well as many of the procedures for making derivatives, **requires dry reagents**. After you have done aqueous extractions, always remove any water in the organic phase with a small amount of a drying agent.

**Chromatographic Techniques.** Numerous chromatographic techniques may be helpful in separating a mixture of unknowns. Liquid or column chromatography [Technique 17] is the most important one. If you have a particularly difficult separation, in which distillation and extraction methods are of no avail, consider column chromatography. This is a powerful technique, but it is often time-consuming to develop a chromatographic separation from scratch. Recall that TLC is a good way to determine the mobile phase (solvent) and stationary phase (adsorbent) that could work with column chromatography. Gravity columns, however, do not yield as clean a separation as suggested by a simple TLC test. Try to maximize the TLC separation by seeking a large difference between the  $R_f$  values of the components of interest before performing column chromatography. Analyze all fractions collected from the column by TLC and combine the fractions containing the same compound. Recover the individual compounds by evaporation of the solvent on a rotary evaporator [see Technique 8.9].

**Identity of Individual Components**

After separating a mixture, identify the individual components. Treat the individual compounds as separate unknowns. Use methods based on solubility, physical constants, and spectral properties. Perform classification tests and prepare derivatives to complete the identification of the individual compounds in your mixture.

## 28

**SUMMARY OF IDENTIFICATION  
PROCEDURE FOR AN  
UNKNOWN COMPOUND**

1. **Purity**  
Estimate purity: color (one color? off-color? decomposition?), appearance (crystallinity of solid? solid and liquid?, mp of solids, bp of liquids), TLC, GC  
Ignition test: residue? soot? flame color?  
Improve purity: distillation, recrystallization, chromatography
2. **Physical properties**  
Solid or liquid? color? bp or mp? odor (hazardous)?
3. **Solubility**  
Determine classification as directed in Technique 23.  
Suggest functional-group classes.  
Make list of compounds from tables by functional group (mp/bp).
4. **IR and NMR analysis**  
Refine list of compounds (identify compound?).  
Assign IR and NMR absorptions.
5. **Chemical tests for functional groups**  
Choose tests found in Technique 25.
6. **Derivative**  
Choose product that differentiates proposed structures.

## 29

**SUMMARY OF THE ANALYSIS  
OF A MIXTURE OF UNKNOWN  
COMPOUNDS**

1. **Preliminary procedures**  
Note color, appearance, pH.  
Take advantage of easy separations (filtration, etc.).
2. **Assay the number of compounds in mixture.**  
TLC, GC (only with instructor's permission), IR, and NMR of mixture
3. **Carry out separation.**  
Decision based on conclusions from 1 and 2  
Distillation, chromatography, or extraction

4. **Monitor success.**

Use TLC (or GC, with permission) to determine whether fractions contain one compound.

5. **Identification**

Use TLC (or GC), mp, bp results already determined.

Use procedures summarized in Technique 28 to identify each compound in mixture.

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## Questions

- Hexanoic (caproic) acid is only slightly soluble in water but is readily soluble (with stirring or shaking) in both 0.6 M NaHCO<sub>3</sub> and 2.5 M NaOH. Conversely, methanoic (formic acid) is readily soluble in both water and the two alkaline reagents. Explain.
- Picric acid (2,4,6-trinitrophenol) is slightly soluble in water but is readily soluble (with stirring or shaking) in both 0.6 M NaHCO<sub>3</sub> and 2.5 M NaOH. Conversely, 2-ethylphenol is insoluble in both water and 0.6 M NaHCO<sub>3</sub> but soluble in 2.5 M NaOH. Explain.
- Both *p*-ethylaniline and triethylamine are only slightly soluble in water but both are readily soluble with stirring in 1.5 M HCl. In contrast, triphenylamine shows virtually no solubility in either water or 1.5 M HCl. Explain.
- Match each one of the five compounds (1–5 on the right) with one of the following sets of IR bands (a–e on the left) selected from the IR spectra of the five compounds. All except the last two bands are strong, and the band at 3373 cm<sup>-1</sup> is exceptionally broad.
 

a. 1715 cm <sup>-1</sup>	1. acetophenone
b. 3373 cm <sup>-1</sup>	2. 2-butanone
c. 3008, 2940, 741 cm <sup>-1</sup>	3. octylamine
d. 1685 cm <sup>-1</sup>	4. phenol
e. 3372, 3290 cm <sup>-1</sup>	5. <i>o</i> -xylene
- The <sup>1</sup>H NMR spectrum of a compound of molecular formula C<sub>3</sub>H<sub>6</sub>Cl<sub>2</sub> shows only two multiplets, a triplet at 3.72 ppm and a quintet at 2.23 ppm. The high-field:low-field integration ratio is 2:1. Deduce the structure of the organic halide and explain the NMR signals.

6. A compound of bp  $204^{\circ}\text{C}$  is water-insoluble and is insoluble in 2.5 M NaOH and 1.5 M HCl as well. The compound does dissolve in concentrated  $\text{H}_2\text{SO}_4$ . The original compound produces both a positive iodoform test and a positive 2,4-dinitrophenylhydrazine test. Deduce the structure and name of the compound and write reactions for all positive chemical tests.
7. A compound of bp  $152^{\circ}\text{--}153^{\circ}\text{C}$  is water-insoluble and insoluble in 2.5 M NaOH, 1.5 M HCl, and concentrated  $\text{H}_2\text{SO}_4$ . The original compound reacts negatively to a 2,4-dinitrophenylhydrazine test. The  $^1\text{H}$  NMR spectrum produces the following signals: 1.25 ppm, 6H, d; 2.9 ppm, 1H, septet; 7.1–7.4 ppm, 5H, m. The proton-decoupled  $^{13}\text{C}$  NMR spectrum shows singlets at 22, 34.5, 126, 127, 129, and 149 ppm. The IR spectrum shows four peaks between  $2980\text{--}2800\text{ cm}^{-1}$  and three peaks in the  $3100\text{--}3000\text{ cm}^{-1}$  region. Deduce the structure and name of the compound and assign all spectral absorptions.
8. A compound of mp  $150^{\circ}\text{C}$  is water-insoluble and also insoluble in 1.5 M HCl. The compound does dissolve in 2.5 M NaOH, in 0.6 M  $\text{NaHCO}_3$ , and in concentrated  $\text{H}_2\text{SO}_4$ . Elemental analysis by sodium fusion indicates the presence of only bromine. The original compound gives a negative 2,4-dinitrophenylhydrazine test. Treatment with aluminum chloride produces an intense color. When treated with thionyl chloride, followed by ammonia, the compound forms an amide that melts at  $154^{\circ}\text{C}$ . Deduce the structure and name of the compound and write out all chemical reactions.
9. A compound of mp  $150^{\circ}\text{C}$  is water-insoluble and also insoluble in 1.5 M HCl. The compound does dissolve in 2.5 M NaOH, in 0.6 M  $\text{NaHCO}_3$ , and in concentrated  $\text{H}_2\text{SO}_4$ . Elemental analysis by sodium fusion reveals no elements. The original compound is acidic as tested with pH paper and gives a positive 2,4-dinitrophenylhydrazine test. Treatment with aluminum chloride gives rise to an intense color. When treated with thionyl chloride, followed by ammonia, the compound forms an amide derivative that melts at  $166^{\circ}\text{C}$ . Deduce the structure and name of the compound and write out all chemical reactions.
10. The compound on which the tests in Question 6 are carried out produces 2,4-dinitrophenylhydrazones of different melting points ( $240^{\circ}\text{C}$ ,  $250^{\circ}\text{C}$ ), depending on the conditions of the derivatization procedure. Suggest a reason for this behavior.