

## Experiment 51

### Identification of Unknowns

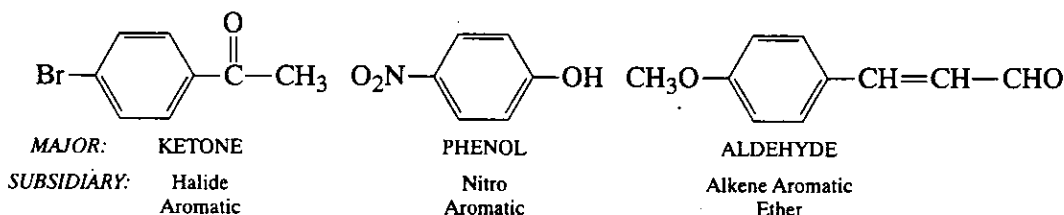
Qualitative organic analysis, the identification and characterization of unknown compounds, is an important part of organic chemistry. Every chemist must learn the appropriate methods for establishing the identity of a compound. In this experiment, you will be issued an unknown compound, and will be asked to identify it through chemical and spectroscopic methods. Your instructor may give you a general unknown or a specific unknown. With a **general unknown**, you must first determine the class of compound to which the unknown belongs, that is, identify its main functional group; then you must determine the specific compound in that class that corresponds to the unknown. With a **specific unknown**, you will know the class of compound (ketone, alcohol, amine, and so on) in advance, and it will be necessary to determine only whatever specific member of that class was issued to you as an unknown. This experiment is designed so that the instructor can issue several general unknowns or as many as six successive specific unknowns, each having a different main functional group.

Although there are well over a million organic compounds that an organic chemist might be called on to identify, the scope of this experiment is necessarily limited. In this textbook, just over 300 compounds are included in the tables of possible unknowns given for the experiment (see Appendix 1). Your instructor may wish to expand the list of possible unknowns, however. In such a case, you will have to consult more extensive tables, such as those found in the work compiled by Rappoport (see References). In addition, the experiment is restricted to include only seven important functional groups:


|                  |          |
|------------------|----------|
| Aldehydes        | Amines   |
| Ketones          | Alcohols |
| Carboxylic acids | Esters   |
| Phenols          |          |

Even though this list of functional groups omits some of the important types of compounds (alkyl halides, alkenes, alkynes, aromatics, ethers, amides, mercaptans, nitriles, acid chlorides, acid anhydrides, nitro compounds, and so on), the methods introduced here can be applied equally well to other classes of compounds. The list is sufficiently broad to illustrate all the principles involved in identifying an unknown compound.

In addition, although many of the functional groups listed as being excluded will not appear as the major functional group in a compound, several of them will frequently appear as secondary, or subsidiary, functional groups. Three examples of this are presented here.



The groups included that have subsidiary status are

|     |        |                  |        |   |             |
|-----|--------|------------------|--------|---|-------------|
| -Cl | Chloro | -NO <sub>2</sub> | Nitro  | C=C   | Double Bond |
| -Br | Bromo  | -C≡N             | Cyano  | C≡C   | Triple Bond |
| -I  | Iodo   | -OR              | Alkoxy |  | Aromatic    |

The experiment presents all the chief chemical and spectroscopic methods of determining the main functional groups, and it includes methods for verifying the presence of the subsidiary functional groups as well. It will usually not be necessary to determine the presence of the subsidiary functional groups to identify the unknown compound correctly. *Every* piece of information helps the identification, however, and if these groups can be detected easily, you should not hesitate to determine them. Finally, complex bifunctional compounds are generally avoided in this experiment; only a few are included.

## HOW TO PROCEED

Fortunately, we can detail a fairly straightforward procedure for determining all the necessary pieces of information. This procedure consists of the following steps:

### Part One: Chemical Classification

1. Preliminary classification by physical state, color, and odor
2. Melting-point or boiling-point determination; other physical data
3. Purification, if necessary
4. Determination of solubility behavior in water and in acids and bases
5. Simple preliminary tests: Beilstein, ignition (combustion)
6. Application of relevant chemical classification tests

### Part Two: Spectroscopy

7. Determination of infrared and NMR spectra

### Part Three: Optional Procedures

8. Elemental analysis, if necessary
9. Preparation of derivatives
10. Confirmation of identity

Each of these steps is discussed briefly in the following sections.

## PRELIMINARY CLASSIFICATION

Note the physical characteristics of the unknown, including its color, its odor, and its physical state (liquid, solid, crystalline form). Many compounds have characteristic colors or odors, or they crystallize with a specific crystal structure. This information can often be found in a handbook and can be checked later. Compounds with a high degree of conjugation are frequently yellow to red. Amines often have a fishlike odor. Esters have a pleasant fruity or floral odor. Acids have a sharp and pungent odor. A part of the training of every good chemist includes cultivating the ability to recognize familiar or typical odors. As a note of caution, many compounds have distinctly unpleasant or nauseating odors. Some

have corrosive vapors. Sniff any unknown substance with the greatest caution. As a first step, open the container, hold it away from you, and using your hand, carefully waft the vapors toward your nose. If you get past this stage, a closer inspection will be possible.

## MELTING-POINT OR BOILING-POINT DETERMINATION

The single most useful piece of information to have for an unknown compound is its melting point or boiling point. Either piece of data will drastically limit the compounds that are possible. The electric melting-point apparatus gives a rapid and accurate measurement (see Technique 6, Section 6.7, and 6.8). To save time, you can often determine two separate melting points. The first determination can be made rapidly to get an approximate value. Then you can determine the second melting point more carefully.

The boiling point is easily obtained by a simple distillation of the unknown (Technique 8, Section 8.4), by reflux (Technique 6, Section 6.11), or by a micro boiling-point determination (Technique 6, Section 6.10). The simple distillation has the advantage in that it also purifies the compound. A Hickman head should be used if a simple distillation is performed, and you should be sure the thermometer bulb is fully immersed in the vapor of the distilling liquid. For an accurate boiling-point value, distill the liquid rapidly. You must distill more than 0.75 mL of liquid.

If the solid is high-melting ( $>200^{\circ}\text{C}$ ), or the liquid high-boiling ( $>200^{\circ}\text{C}$ ), a thermometer correction may be needed (Technique 6, Sections 6.12 and 6.13). In any event, allowance should be made for errors of as large as  $\pm 5^{\circ}\text{C}$  in these values.

## PURIFICATION

If the melting point of a solid has a wide range (*ca*  $5^{\circ}\text{C}$ ), it should be recrystallized and the melting point redetermined.

If a liquid was highly colored before distillation, if it yielded a wide boiling-point range, or if the temperature did not hold constant during the distillation, it should be redistilled to determine a new temperature range. A reduced-pressure distillation is in order for high-boiling liquids or for those that show any sign of decomposition on heating.

Occasionally column chromatography may be necessary to purify solids that have large amounts of impurities and do not yield satisfactory results on crystallization.

Acidic or basic impurities that contaminate a neutral compound may often be removed by dissolving the compound in a low-boiling solvent, such as  $\text{CH}_2\text{Cl}_2$  or ether, and extracting with 5%  $\text{NaHCO}_3$  or 5%  $\text{HCl}$ , respectively. Conversely, acidic or basic compounds can be purified by dissolving them in 5%  $\text{NaHCO}_3$  or 5%  $\text{HCl}$ , respectively, and extracting them with a low-boiling organic solvent to remove impurities. After neutralization of the aqueous solution, the desired compound can be recovered by extraction.

## SOLUBILITY BEHAVIOR

Tests on solubility are described fully in Experiment 51A. They are extremely important. Determine the solubility of small amounts of the unknown in water, 5%  $\text{HCl}$ , 5%  $\text{NaHCO}_3$ , 5%  $\text{NaOH}$ , concentrated  $\text{H}_2\text{SO}_4$ , and organic solvents. This information reveals whether a compound is an acid, a base, or a neutral substance. The sulfuric acid test reveals whether a neutral compound has a functional group that contains an oxygen, a nitrogen, or a sulfur atom that can be protonated. This information allows you to eliminate or to choose various functional-group possibilities. The solubility tests must be made on *all* unknowns.

## PRELIMINARY TESTS

The two combustion tests, the Beilstein test (Experiment 51B) and the ignition test (Experiment 51C) can be performed easily and quickly, and they often give valuable information. It is recommended that they be performed on all unknowns.

## CHEMICAL CLASSIFICATION TESTS

The solubility tests usually suggest or eliminate several possible functional groups. The chemical classification tests listed in Experiments 51D to 51I allow you to distinguish among the possible choices. Choose only those tests that the solubility tests suggest might be meaningful. Time will be wasted performing unnecessary tests. There is no substitute for a firsthand, thorough knowledge of these tests. Study each of the sections carefully until you understand the significance of each test. Also, it will be helpful to actually try the tests on *known* substances. In this way, it will be easier to recognize a positive test. Appropriate test compounds are listed for many of the tests. When you are performing a test that is new to you, it is always good practice to run the test separately on both a known substance and the unknown *at the same time*. This practice lets you compare results directly.

Once the melting or boiling point, the solubilities, and the main chemical tests have been made, it will be possible to identify the class of compound. At this stage, with the melting point or boiling point as a guide, it will be possible to compile a list of possible compounds. Inspection of this list will suggest additional tests that must be performed to distinguish among the possibilities. For instance, one compound may be a methyl ketone and the other may not. The iodoform test is called for to distinguish the two possibilities. The tests for the subsidiary functional groups may also be required. These tests are described in Experiments 51B and 51C. These tests should also be studied carefully; there is no substitute for firsthand knowledge about these either.

Do not perform the chemical tests either haphazardly or in a methodical, comprehensive sequence. Instead, use the tests selectively. Solubility tests automatically eliminate the need for some of the chemical tests. Each successive test will either eliminate the need for another test or dictate its use. You should also examine the tables of unknowns carefully. The boiling point or the melting point of the unknown may eliminate the need for many of the tests. For instance, the possible compounds may simply not include one with a double bond. Efficiency is the key word here. Do not waste time performing nonsensical or unnecessary tests. Many possibilities can be eliminated on the basis of logic alone.

How you proceed with the following steps may be limited by your instructor's wishes. Many instructors may restrict your access to infrared and NMR spectra until you have narrowed your choices to a few compounds *all within the same class*. Others may have you determine these data routinely. Some instructors may want students to perform elemental analysis on all unknowns; others may restrict it to only the most essential situations. Most unknowns can be identified without either spectroscopy or elemental analysis. Again, some instructors may require derivatives as a final confirmation of the compound's identity; others may not wish to use them at all.

## SPECTROSCOPY

Spectroscopy is probably the most powerful and modern tool available to the chemist for determining the structure of an unknown compound. It is often possible to determine structure through spectroscopy alone. On the other hand, there are also situations for which

spectroscopy is not of much help and the traditional methods must be relied on. For this reason, you should not use spectroscopy to the exclusion of the more traditional tests but rather as a confirmation of those results. Nevertheless, the main functional groups and their immediate environmental features can be determined quickly and accurately with spectroscopy.

## ELEMENTAL ANALYSIS

Elemental analysis—which allows you to determine the presence of nitrogen, sulfur, or a specific halogen atom (Cl, Br, I) in a compound—is often useful; however, other information often renders these tests unnecessary. A compound identified as an amine by solubility tests obviously contains nitrogen. Many nitrogen-containing groups (for instance, nitro groups) can be identified by infrared spectroscopy. Finally, it is not usually necessary to identify a specific halogen. The simple information that the compound contains a halogen (any halogen) may be enough information to distinguish between two compounds. A simple Beilstein test provides this information.

## DERIVATIVES

One of the principal tests for the correct identification of an unknown compound comes in trying to convert the compound by a chemical reaction to another known compound. This second compound is called a **derivative**. The best derivatives are solid compounds, because the melting point of a solid provides an accurate and reliable identification of most compounds. Solids are also easily purified through crystallization. The derivative provides a way of distinguishing two otherwise very similar compounds. Usually they will have derivatives (both prepared by the same reaction) that have different melting points. Tables of unknowns and derivatives are listed in Appendix 1. Procedures for preparing derivatives are given in Appendix 2.

## CONFIRMATION OF IDENTITY

A rigid and final test for identifying an unknown can be made if an “authentic” sample of the compound is available for comparison. One can compare infrared and NMR spectra of the unknown compound with the spectra of the known compound. If the spectra match, peak for peak, then the identity is probably certain. Other physical and chemical properties can also be compared. If the compound is a solid, a convenient test is the mixed melting point (Technique 6, Section 6.4). Thin-layer or gas-chromatographic comparisons may also be useful. For thin-layer analysis, however, it may be necessary to experiment with several different development solvents to reach a satisfactory conclusion about the identity of the substance in question.

Although we cannot be complete in this experiment in terms of the functional groups covered, or the tests described, the experiment should provide a good introduction to the methods and the techniques chemists use to identify unknown compounds. Textbooks that cover the subject more thoroughly are listed in the References. You are encouraged to consult these for more information, including specific methods and classification tests.

## REFERENCES

**Comprehensive Textbooks**

- Cheronis, N. D., and Entrikin, J. B. *Identification of Organic Compounds*. New York: Wiley-Interscience, 1963.
- Pasto, D. J., and Johnson, C. R. *Laboratory Test for Organic Chemistry*. Englewood Cliffs, NJ: Prentice-Hall, 1979.
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**Spectroscopy**

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- Silverstein, R. M., and Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed. New York: John Wiley & Sons, 1998.

**Extensive Tables of Compounds and Derivatives**

- Rappoport, Z., ed. *Handbook of Tables for Organic Compound Identification*. Cleveland: Chemical Rubber Co., 1967.

## Experiment 51A

### Solubility Tests

Solubility tests should be performed on *every unknown*. They are extremely important in determining the nature of the main functional group of the unknown compound. The tests are very simple and require only small amounts of the unknown. In addition, solubility tests reveal whether the compound is a strong base (amine), a weak acid (phenol), a strong acid (carboxylic acid), or a neutral substance (aldehyde, ketone, alcohol, ester). The common solvents used to determine solubility types are

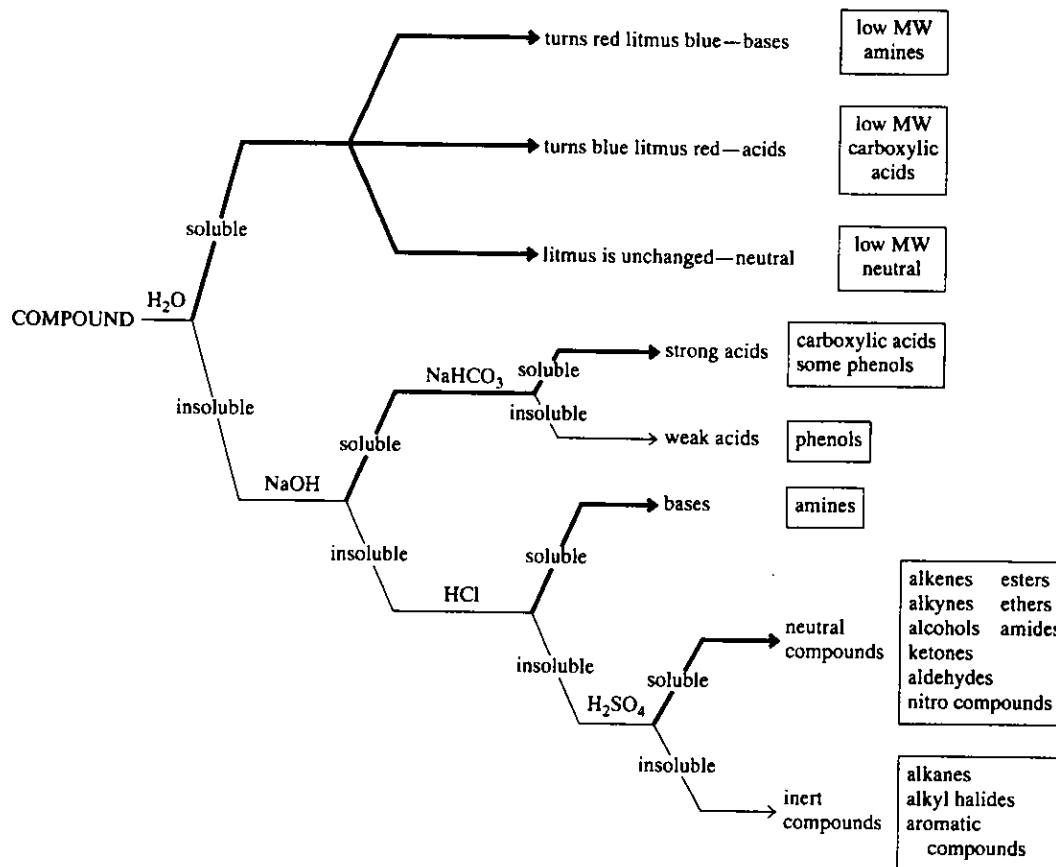
|                       |   |
|-----------------------|---|
| 5% HCl                | Concentrated H <sub>2</sub> SO <sub>4</sub> |
| 5% NaHCO <sub>3</sub> | Water                                       |
| 5% NaOH               | Organic solvents                            |

The solubility chart on page 434 indicates solvents in which compounds containing the various functional groups are likely to dissolve. The summary charts in Experiments 51D through 51I repeat this information for each functional group included in this experiment. In this section, the correct procedure for determining whether a compound is soluble in a test solvent is given. Also given is a series of explanations detailing the reasons that

compounds having specific functional groups are soluble in only specific solvents. This is accomplished by indicating the type of chemistry or the type of chemical interaction that is possible in each solvent.

### WASTE DISPOSAL

Dispose of all aqueous solutions in the container designated for aqueous waste. Any remaining organic compounds must be disposed of in the appropriate organic waste container.



Solubility chart for compounds containing various functional groups.

## SOLUBILITY TESTS

### Procedure

Place about 1 mL of the solvent in a small test tube. Add one drop of an unknown liquid from a Pasteur pipet or a few crystals of an unknown solid from the end of a spatula, directly into the solvent. Gently tap the test tube with your finger to ensure mixing, and then observe whether any mixing lines appear in the solution. The disappearance of the liquid or solid or the appearance of

the mixing lines indicates that solution is taking place. Add several more drops of the liquid or a few more crystals of the solid to determine the extent of the compound's solubility. A common mistake in determining the solubility of a compound is testing with a quantity of the unknown too large to dissolve in the chosen solvent. Use small amounts. It may take several minutes to dissolve solids. Compounds in the form of large crystals need more time to dissolve than powders or very small crystals. In some cases, it is helpful to pulverize a compound with large crystals using a mortar and pestle. Sometimes gentle heating helps, but strong heating is discouraged, as it often leads to reaction. When colored compounds dissolve, the solution often assumes the color.

Using the preceding procedure, determine the solubility of the unknown in each of the following solvents: water, 5% HCl, 5% NaHCO<sub>3</sub>, 5% NaOH, and concentrated H<sub>2</sub>SO<sub>4</sub>. With sulfuric acid, a color change may be observed rather than solution. A color change should be regarded as a positive solubility test. Solid unknowns that do not dissolve in any of the test solvents may be inorganic substances. To eliminate this possibility, determine the solubility of the unknown in several organic solvents, such as ether. If the compound is organic, a solvent that will dissolve it can usually be found.

If a compound is found to dissolve in water, the pH of the aqueous solution should be estimated with pH paper or litmus. Compounds soluble in water are usually soluble in *all* the aqueous solvents. If a compound is only slightly soluble in water, it may be *more* soluble in another aqueous solvent. For instance, a carboxylic acid may be only slightly soluble in water but very soluble in dilute base. It often will not be necessary to determine the solubility of the unknown in every solvent.

### Test Compounds

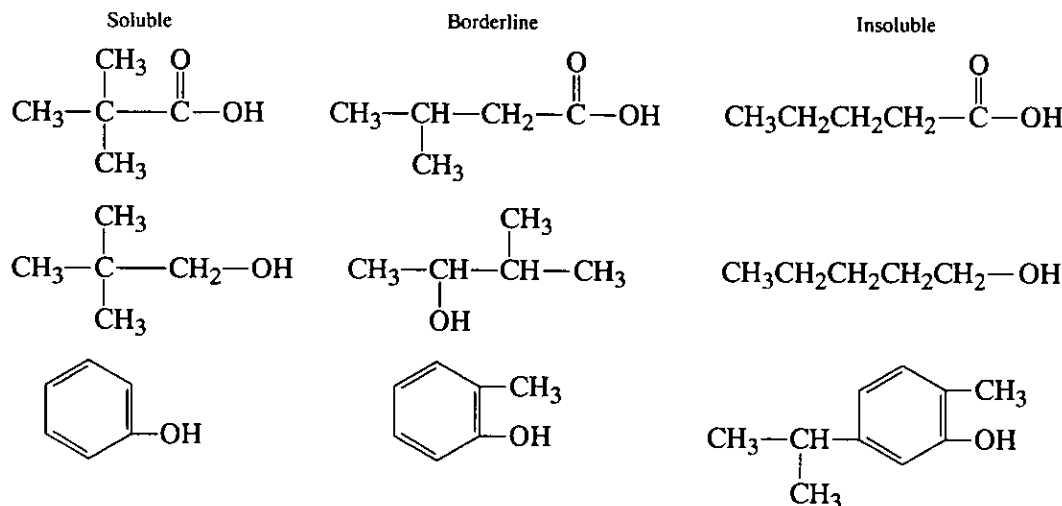
Five solubility unknowns can be found on the supply shelf. The five unknowns include a base, a weak acid, a strong acid, a neutral substance with an oxygen-containing functional group, and a neutral substance that is inert. Using solubility tests, distinguish these unknowns by type. Verify your answer with the instructor.

**Solubility in Water.** Compounds that contain four or fewer carbons and also contain oxygen, nitrogen, or sulfur are often soluble in water. Almost any functional group containing these elements will lead to water solubility for low-molecular-weight (C<sub>4</sub>) compounds. Compounds having five or six carbons and any of those elements are often insoluble in water or have borderline solubility. Branching of the alkyl chain in a compound lowers the intermolecular forces between its molecules. This is usually reflected in a lowered boiling point or melting point and a greater solubility in water for the branched compound than for the corresponding straight-chain compound. This occurs simply because the molecules of the branched compound are more easily separated from one another. Thus, *t*-butyl alcohol would be expected to be more soluble in water than *n*-butyl alcohol.

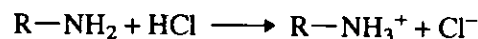
When the ratio of the oxygen, nitrogen, or sulfur atoms in a compound to the carbon atoms is increased, the solubility of that compound in water often increases. This is due to the increased number of polar functional groups. Thus, 1,5-pentanediol would be expected to be more soluble in water than 1-pentanol.

As the size of the alkyl chain of a compound is increased beyond about four carbons, the influence of a polar functional group is diminished, and the water solubility begins to decrease. A few examples of these generalizations are given here.

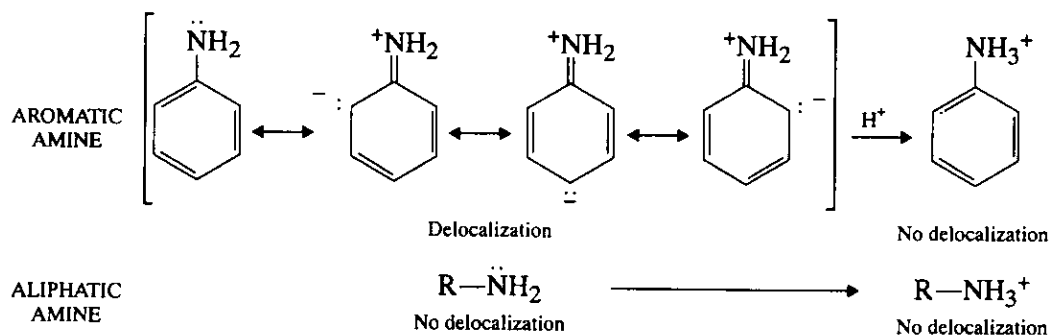




**Solubility in 5% HCl.** The possibility of an amine should be considered immediately if a compound is soluble in dilute acid (5% HCl). Aliphatic amines ( $\text{RNH}_2$ ,  $\text{R}_2\text{NH}$ ,  $\text{R}_3\text{N}$ ) are basic compounds that readily dissolve in acid because they form hydrochloride salts that are soluble in the aqueous medium:



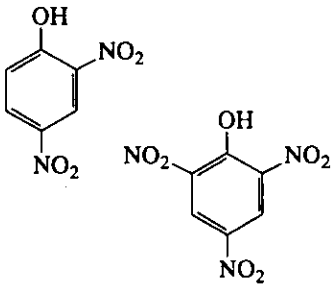
The substitution of an aromatic (benzene) ring Ar for an alkyl group R reduces the basicity of an amine somewhat, but the amine will still protonate, and it will still generally be soluble in dilute acid. The reduction in basicity in an aromatic amine is due to the resonance delocalization of the unshared electrons on the amino nitrogen of the free base. The delocalization is lost on protonation, a problem that does not exist for aliphatic amines. The substitution of two or three aromatic rings on an amine nitrogen reduces the basicity of the amine even further. Diaryl and triaryl amines do not dissolve in dilute HCl because they do not protonate easily. Thus,  $\text{Ar}_2\text{NH}$  and  $\text{Ar}_3\text{N}$  are insoluble in dilute acid. Some amines of very high molecular weight, such as tribromoaniline ( $MW = 330$ ), may also be insoluble in dilute acid.



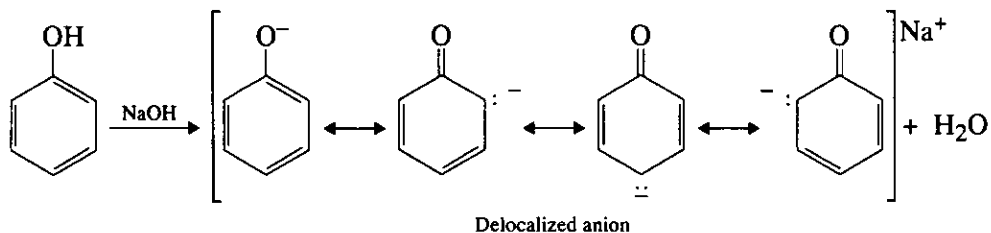
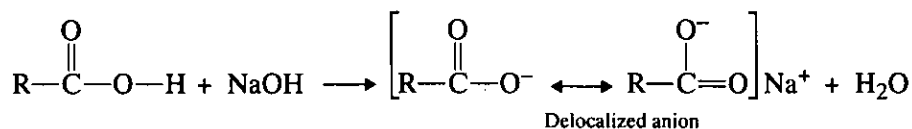
**Solubility in 5%  $\text{NaHCO}_3$  and 5%  $\text{NaOH}$ .** Compounds that dissolve in sodium bicarbonate, a weak base, are strong acids. Compounds that dissolve in sodium hydroxide, a strong base, may be either strong or weak acids. Thus, one can distinguish weak and strong acids by determining their solubility in both strong ( $\text{NaOH}$ ) and weak ( $\text{NaHCO}_3$ ) base. The classification of some functional groups as either weak or strong acids is given in the table on page 437.

In this experiment, carboxylic acids ( $\text{p}K_a \sim 5$ ) are generally indicated when a compound is soluble in both bases, while phenols ( $\text{p}K_a \sim 10$ ) are indicated when it is soluble in  $\text{NaOH}$  only.

Compounds dissolve in base because they form sodium salts that are soluble in the aqueous medium. The salts of some high-molecular-weight compounds are not soluble, however, and precipitate. The salts of the long-chain carboxylic acids, such as myristic acid  $C_{14}$ , palmitic acid  $C_{16}$ , and stearic acid  $C_{18}$ , which form soaps, are in this category. Some phenols also produce insoluble sodium salts, and often these are colored due to resonance in the anion.

| Strong Acids<br>(soluble in both NaOH and $\text{NaHCO}_3$ )   | Weak Acids<br>(soluble in NaOH but not $\text{NaHCO}_3$ )  |
|--|--|
| Sulfonic acids $\text{RSO}_3\text{H}$<br>Carboxylic acids $\text{RCOOH}$<br><i>Ortho</i> - and <i>para</i> -substituted<br>di- and trinitrophenols<br> | Phenols $\text{ArOH}$<br>Nitroalkanes $\text{RCH}_2\text{NO}_2$<br>$\text{R}_2\text{CHNO}_2$<br>$\beta$ -Diketones<br>$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$<br>$\beta$ -Diesters<br>$\text{RO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}$<br>Imides<br>$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$<br>Sulfonamides $\text{ArSO}_2\text{NH}_2$<br>$\text{ArSO}_2\text{NHR}$ |

Both phenols and carboxylic acids produce resonance-stabilized conjugate bases. Thus, bases of the appropriate strength may easily remove their acidic protons to form the sodium salts.

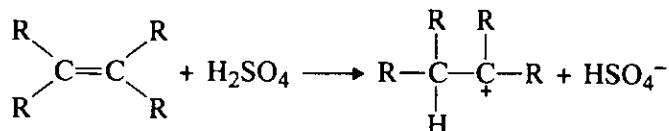
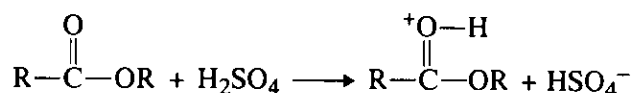
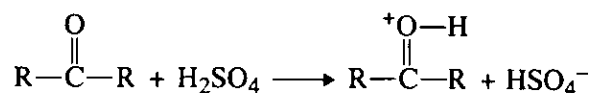
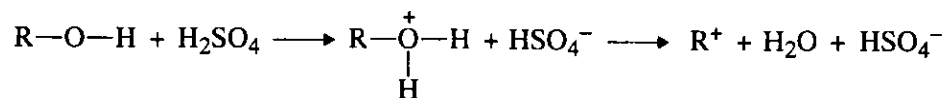


In phenols, substitution of nitro groups in the *ortho* and *para* positions of the ring increases the acidity. Nitro groups in these positions provide additional delocalization in the conjugate anion. Phenols that have two or three nitro groups in the *ortho* and *para* positions often dissolve in *both* sodium hydroxide and sodium bicarbonate solutions.

**Solubility in Concentrated Sulfuric Acid.** Many compounds are soluble in cold concentrated sulfuric acid. Of the compounds included in this experiment, alcohols, ketones, aldehydes, and esters are in this category. Other compounds that also dissolve include

alkenes, alkynes, ethers, nitroaromatics, and amides. Because several different kinds of compounds are soluble in sulfuric acid, further chemical tests and spectroscopy will be needed to differentiate among them.

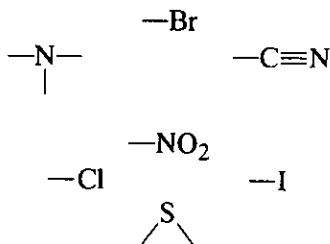
Compounds that are soluble in concentrated sulfuric acid but not in dilute acid are extremely weak bases. Almost any compound containing a nitrogen, an oxygen, or a sulfur atom can be protonated in concentrated sulfuric acid. The ions produced are soluble in the medium.



**Inert Compounds.** Compounds not soluble in concentrated sulfuric acid or any of the other solvents are said to be *inert*. Compounds not soluble in concentrated sulfuric acid include the alkanes, most simple aromatics, and the alkyl halides. Some examples of inert compounds are hexane, benzene, chlorobenzene, chlorohexane, and toluene.

## Experiment 51B

### Tests for the Elements (N, S, X)



Except for amines (Experiment 51G), which are easily detected by their solubility behavior, all compounds issued in this experiment will contain heteroelements (N, S, Cl, Br, or I) only as *secondary* functional group. These will be subsidiary to some other important functional group. Thus, no alkyl or aryl halides, nitro compounds, thiols, or thioethers will be issued. However, some of the unknowns may contain a halogen or a nitro group. Less frequently, they may contain a sulfur atom or a cyano group.

Consider as an example *p*-bromobenzaldehyde, an **aldehyde** that contains bromine as a ring substituent. The identification of this compound would hinge on whether the investigator could identify it as an aldehyde. It could probably be identified *without* proving the existence of bromine in the molecule. That information, however, could make the identification easier. In this experiment, methods are given for identifying the presence of a halogen or a nitro group in an unknown compound. Also given is a general method (sodium fusion) for detecting the principal heteroelements that may exist in organic molecules.

Classification Tests

| Halides   | Nitro Groups      | N, S, X (Cl, Br, I) |
|---|-------------------|---------------------|
| Beilstein test<br>Silver nitrate<br>Sodium iodide/acetone | Ferrous hydroxide | Sodium fusion       |

#### WASTE DISPOSAL

Dispose of all solutions containing silver into a waste container designated for this purpose. Any other aqueous solutions should be disposed of in the container designated for aqueous waste. Any remaining organic compounds must be disposed of in the appropriate organic waste container under the hood. This is particularly true of any solution containing benzyl bromide, which is a lachrymator.

### TESTS FOR A HALIDE

#### Beilstein Test

**Procedure.** Bend a small loop in the end of a short length of copper wire. Heat the loop end of the wire in a Bunsen burner flame. After cooling, dip the wire directly into a small sample of the unknown. If the unknown is a solid and won't adhere to the copper wire, place a small amount of the substance on a watch glass, wet the copper wire in distilled water, and place the wire into the sample on the watch glass. The solid should adhere to the wire. Now heat the wire in the Bunsen burner flame again. The compound will first burn. After the burning, a green flame will be produced if a halogen is present.

**Test Compounds.** Try this test on bromobenzene and benzoic acid.

Halogens can be detected easily and reliably by the Beilstein test. It is the simplest method for determining the presence of a halogen, but it does not differentiate among chlorine, bromine, and iodine, any one of which will give a positive test. However, when the identity of the unknown has been narrowed to two choices, of which one has a halogen and one does not, the Beilstein test will often be enough to distinguish between the two.

A positive Beilstein test results from the production of a volatile copper halide when an organic halide is heated with copper oxide. The copper halide imparts a blue-green color to the flame.

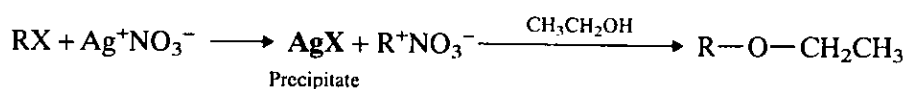
This test can be very sensitive to small amounts of halide impurities in some compounds. Therefore, use caution in interpreting the results of the test if you obtain only a weak color.

### Silver Nitrate Test

**Procedure.** Add one drop of a liquid or five drops of a concentrated ethanolic solution of a solid unknown to 2 mL of a 2% ethanolic silver nitrate solution. If no reaction is observed after 5 minutes at room temperature, heat the solution in a hot water bath at about 100°C and note whether a precipitate forms. If a precipitate forms, add two drops of 5% nitric acid and note whether the precipitate dissolves. Carboxylic acids give a false test by precipitating in silver nitrate, but they dissolve when nitric acid is added. Silver halides, in contrast, do not dissolve in nitric acid.

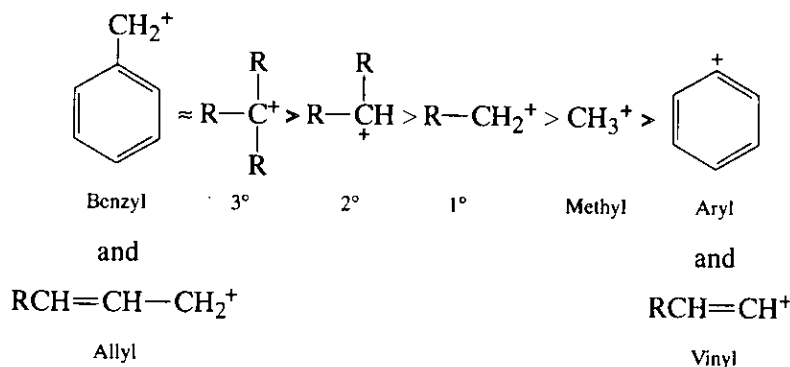
**Test Compounds.** Apply this test to benzyl bromide ( $\alpha$ -bromotoluene) and bromobenzene. Discard all waste reagents in a suitable waste container in the hood, because benzyl bromide is a lachrymator.

This test depends on the formation of a white or off-white precipitate of silver halide when silver nitrate is allowed to react with a sufficiently reactive halide.



The test does not distinguish among chlorides, bromides, and iodides but does distinguish **labile** (reactive) halides from halides that are unreactive. Halides substituted on an aromatic ring will not usually give a positive silver nitrate test; however, alkyl halides of many types will give a positive test.

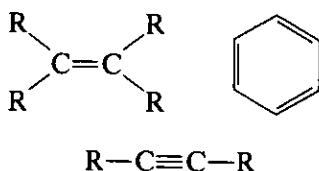
The most reactive compounds are those able to form stable carbocations in solution and those equipped with good leaving groups ( $\text{X} = \text{I}, \text{Br}, \text{Cl}$ ), Benzyl, allyl, and tertiary halides react immediately with silver nitrate. Secondary and primary halides do not react at room temperature but react readily when heated. Aryl and vinyl halides do not react at all, even at elevated temperatures. This pattern of reactivity fits the stability order for various carbocations quite well. Compounds that produce stable carbocations react at higher rates than those that do not.



The fast reaction of benzylic and allylic halides is a result of the resonance stabilization that is available to the intermediate carbocations formed. Tertiary halides are more reactive than secondary halides, which are in turn more reactive than primary or methyl halides because alkyl substituents are able to stabilize the intermediate carbocations by an electron-releasing effect. The methyl carbocations have no alkyl groups and are the least stable of all carbocations mentioned thus far. Vinyl and aryl carbocations are extremely unstable because the charge is localized on an  $\text{sp}^2$ -hybridized carbon (double-bond carbon) rather than on one that is  $\text{sp}^3$ -hybridized.

## Experiment 51C

### Tests for Unsaturation



The unknowns to be issued for this experiment have neither a double bond nor a triple bond as their *only* functional group. Hence, simple alkenes and alkynes can be ruled out as possible compounds. Some of the unknowns may have a double or a triple bond, however *in addition* to another more important functional group. The tests described allow you to determine the presence of a double bond or a triple bond (unsaturation) in such compounds.

Classification Tests

| Unsaturation   | Aromaticity   |
|--|---------------|
| Bromine-carbon tetrachloride<br>Potassium permanganate | Ignition test |

#### WASTE DISPOSAL

Test reagents that contain bromine should be discarded into a special waste container designated for this purpose. Methylene chloride and carbon tetrachloride must be placed in the organic waste container designated for the disposal of halogenated organic wastes. Dispose of all other aqueous solutions in the container designated for aqueous waste. Any remaining organic compounds must be disposed of in the appropriate organic waste container.

### TESTS FOR SIMPLE MULTIPLE BONDS

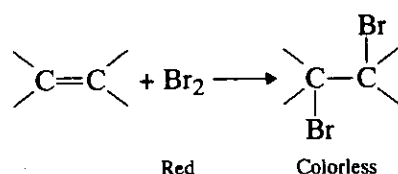
#### Bromine in Carbon Tetrachloride or Methylene Chloride

**Procedure.** Dissolve 50 mg of a solid unknown or two drops of a liquid unknown in 1 mL of carbon tetrachloride (or 1,2-dimethoxyethane). Add a 2% (by volume) solution of bromine in carbon tetrachloride, dropwise, and shake it until the bromine color persists. The test is positive if more than five drops of the bromine solution are needed so that the color remains for 1 minute. Usually, many drops of the bromine solution will be needed if unsaturation is present. Hydrogen bromide should not be evolved. If hydrogen bromide gas is evolved, you will note a "fog" while you blow across the mouth of the test tube. The HBr can also be detected by a moistened piece of litmus or pH paper. If hydrogen bromide is evolved, the reaction is a **substitution reaction** (see discussion below) and not an **addition reaction**, and a double or triple bond is probably not present.

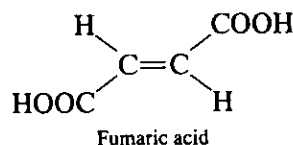
**Methylene Chloride.** Even though carbon tetrachloride is used in very small quantities in this test, it poses certain health hazards (see p. 17), and another solvent may be preferable. Methylene chloride (dichloromethane) can be substituted for carbon tetrachloride. Certain problems arise, however, because methylene chloride slowly reacts with bromine, presumably by a light-induced free-radical process, to produce HBr. After about 1 week, the color of a 2% solution of bromine in methylene chloride fades noticeably, and the odor of the HBr can be detected in the reagent. Although the decolorization tests still work satisfactorily, the presence of HBr makes it difficult to distinguish between addition and substitution reactions. A freshly prepared solution of bromine in methylene chloride must be used to make this distinction. Deterioration of the reagent can be forestalled by storing it in a brown glass bottle. Most other substitute solvents also present problems. Ethers, for instance, react slowly in the same way as methylene chloride, and hydrocarbons, such as hexane, are not general enough solvents to be able to dissolve all the possible test compounds.

**Test Compounds.** Try this test with cyclohexene, cyclohexane, toluene, and acetone.

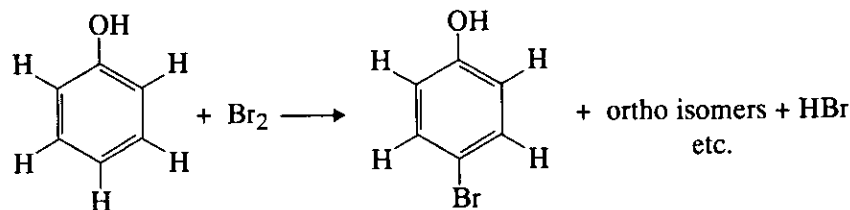
A successful test depends on the addition of bromine, a red liquid, to a double or a triple bond to give a colorless dibromide:



Not all double bonds react with bromine-carbon tetrachloride solution. Only those that are electron-rich are sufficiently reactive nucleophiles to initiate the reaction. A double bond that is substituted by electron-withdrawing groups often fails to react or reacts slowly. Fumaric acid is an example of a compound that fails to give the reaction.



Aromatic compounds either do not react with bromine-carbon tetrachloride reagent or they react by **substitution**. Only the aromatic rings that have activating groups as substituents ( $-\text{OH}$ ,  $-\text{OR}$ , or  $-\text{NR}_2$ ) give the substitution reaction.



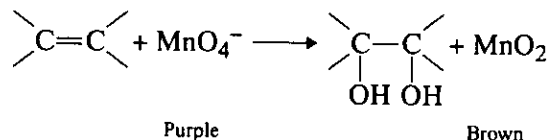
Some ketones and aldehydes react with bromine to give a **substitution product**, but this reaction is slow except for ketones that have a high enol content. When substitution occurs, not only is the bromine color discharged, but hydrogen bromide gas is also evolved.

### Potassium Permanganate (Baeyer Test)

**Procedure.** Dissolve 25 mg of a solid unknown or two drops of a liquid unknown in 2 mL of water or 95% ethanol (1,2-dimethoxyethane may also be used). Slowly add a 1% aqueous solution (weight/volume) of potassium permanganate, drop by drop while shaking, to the unknown. In a positive test, the purple color of the reagent is discharged, and a brown precipitate of manganese dioxide forms, usually within 1 minute. If alcohol was the solvent, the solution should not be allowed to stand for more than 5 minutes, because oxidation of the alcohol will begin slowly. Because permanganate solutions undergo some decomposition to manganese dioxide on standing, any small amount of amount of precipitate should be interpreted with caution.

**Test Compounds.** Try this test on cyclohexene and toluene.

This test is positive for double and triple bonds but not for aromatic rings. It depends on the conversion of the purple ion  $\text{MnO}_4^-$  to a brown precipitate of  $\text{MnO}_2$  following the oxidation of an unsaturated compound.



Other easily oxidized compounds also give a positive test with potassium permanganate solution. These substances include aldehydes, some alcohols, phenols, and aromatic amines. If you suspect that any of these functional groups are present, you should interpret the test with caution.

## Spectroscopy

### Infrared

#### Double Bonds (C=C)

C=C stretch usually occurs near 1680–1620  $\text{cm}^{-1}$ . Symmetrical alkenes may have no absorption.

C—H stretch of vinyl hydrogens occurs  $>3000 \text{ cm}^{-1}$ , but usually not higher than 3150  $\text{cm}^{-1}$ .

C—H out-of-plane bending occurs near 1000–700  $\text{cm}^{-1}$  (see Appendix 3).

#### Triple Bonds (C≡C)

C≡C stretch usually occurs near 2250–2100  $\text{cm}^{-1}$ . The peak is usually sharp. Symmetrical alkynes show no absorption.

C—H stretch of terminal acetylenes occurs near 3310–3200  $\text{cm}^{-1}$ .

## Nuclear Magnetic Resonance

Vinyl hydrogens have resonance near 5–7 ppm and have coupling values as follows:  $J_{trans} = 11\text{--}18 \text{ Hz}$ ,  $J_{cis} = 6\text{--}15 \text{ Hz}$ ,  $J_{geminal} = 0\text{--}5 \text{ Hz}$ . Allylic hydrogens have resonance near 2 ppm. Acetylenic hydrogens have resonance near 2.8–3.0 ppm.

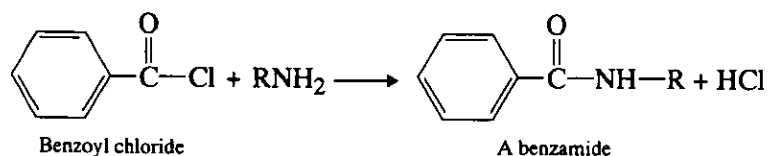
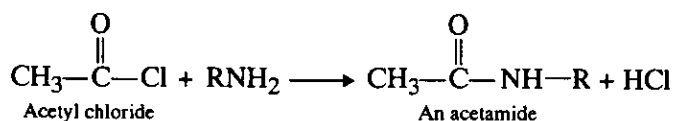


## Nuclear Magnetic Resonance

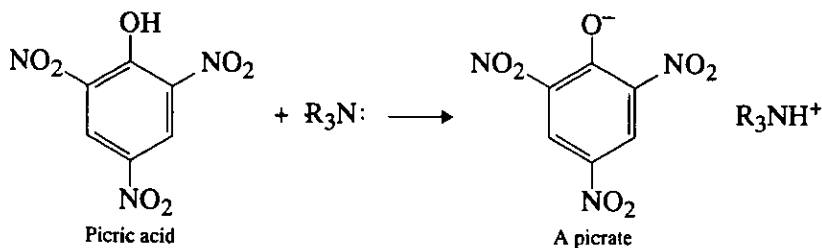
The resonance position of amino hydrogens is extremely variable. The resonance may also be very broad (quadrupole broadening). Aromatic amines give resonances near 7 ppm due to the aromatic ring hydrogens.

## Derivatives

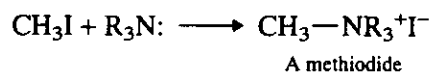
The derivatives of amines that are most easily prepared are the acetamides and the benzamides. These derivatives work well for both primary and secondary amines but not for tertiary amines.



The most general derivative that can be prepared is the picric acid salt, or picrate, of an amine. This derivative can be used for primary, secondary, and tertiary amines.



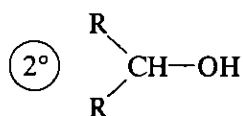
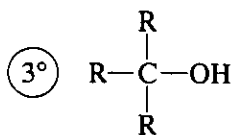
For tertiary amines, the methiodide salt is often useful.



Procedures for preparing derivatives from amines can be found in Appendix 2.

## Experiment 51H

### Alcohols



Alcohols are neutral compounds. The only other classes of neutral compounds used in this experiment are the aldehydes and ketones and the esters. Alcohols and esters usually do not give a positive 2,4-dinitrophenylhydrazine test; aldehydes and ketones do. Esters do not react with acetyl chloride or with Lucas reagent, as alcohols do, and they are easily distinguished from alcohols on this basis. Primary and secondary alcohols are easily oxidized; esters and tertiary alcohols are not. A combination of the Lucas test and the chromic acid test will differentiate among primary, secondary, and tertiary alcohols.

| Solubility Characteristics |                    |      |                                |       | Classification Tests |
|----------------------------|--------------------|------|--------------------------------|-------|----------------------|
| HCl                        | NaHCO <sub>3</sub> | NaOH | H <sub>2</sub> SO <sub>4</sub> | Ether | Acetyl chloride      |
| (-)                        | (-)                | (-)  | (+)                            | (+)   | Lucas test           |
| Water: <C <sub>6</sub> (+) |                    |      |                                |       | Chromic acid test    |
| >C <sub>6</sub> (-)        |                    |      |                                |       | Iodoform test        |

#### WASTE DISPOSAL

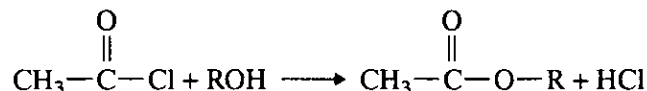
Any solution containing chromium must be disposed of by placing it in a waste container specifically identified for the disposal of chromium wastes. Dispose of all other aqueous solutions in the container designated for aqueous waste. Any remaining organic compounds must be disposed of in the appropriate organic waste container.

### CLASSIFICATION TESTS

#### Acetyl Chloride

**Procedure.** Cautiously add about 10–15 drops of acetyl chloride, drop by drop, to about 0.5 mL of the liquid alcohol contained in a small test tube. Evolution of heat and hydrogen chloride gas indicates a positive reaction. Adding water will sometimes precipitate the acetate.

Acid chlorides react with alcohols to form esters. Acetyl chloride forms acetate esters.



Usually the reaction is exothermic, and the heat evolved is easily detected. Phenols react with acid chlorides somewhat as alcohols do. Hence, phenols should be eliminated as possibilities before this test is attempted. Amines also react with acetyl chloride to evolve heat (see Experiment 51G). This test does not work well with solid alcohols.

#### Lucas Test

**Procedure.** Place 2 mL of Lucas reagent in a small test tube, and add three to four drops of the alcohol. Stopper the test tube, and shake it vigorously. Tertiary (3°), benzylic, and allylic alcohols give an immediate cloudiness in the solution as the insoluble alkyl halide separates from the aqueous solution. After a short time, the immiscible alkyl halide will form a separate layer.

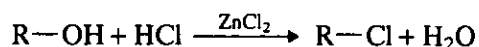
Secondary (2°) alcohols produce a cloudiness after 2-5 minutes. Primary (1°) alcohols dissolve in the reagent to give a clear solution. Some secondary alcohols may have to be heated slightly to encourage reaction with the reagent.

**Note:** This test works only for alcohols that are soluble in the reagent. This often means that alcohols with more than six carbon atoms cannot be tested.

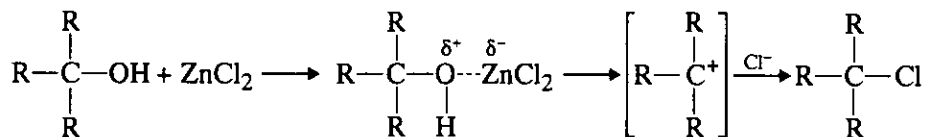
**Test Compounds.** Try this test with a 1-butanol (*n*-butyl alcohol), 2-butanol (*sec*-butyl alcohol), and 2-methyl-2-propanol (*t*-butyl alcohol).

**Reagent.** Cool 10 mL of concentrated hydrochloric acid in a beaker, using an ice bath. While still cooling and while stirring, dissolve 16 g of anhydrous zinc chloride in the acid.

This test depends on the appearance of an alkyl chloride as an insoluble second layer when an alcohol is treated with a mixture of hydrochloric acid and zinc chloride (Lucas reagent):



Primary alcohols do not react at room temperature; therefore, the alcohol is seen simply to dissolve. Secondary alcohols react slowly, whereas tertiary, benzylic, and allylic alcohols react instantly. These relative reactivities are explained on the same basis as the silver nitrate reaction, which is discussed in Experiment 51B. Primary carbocations are unstable and do not form under the conditions of this test, hence no results are observed for primary alcohols.



The Lucas test does not work well with solid alcohols.

### Chromic Acid Test

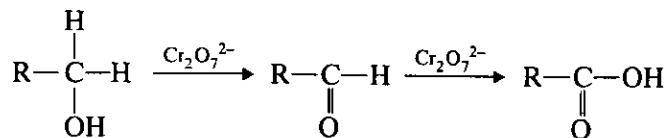
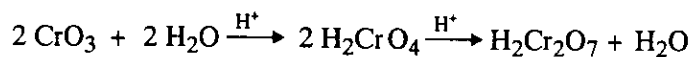
**Procedure.** Dissolve one drop of a liquid or about 10 mg of a solid alcohol in 1 mL of *reagent-grade* acetone. Add one drop of the chromic acid reagent, and note the result that occurs within 2 seconds. A positive test for a primary or a secondary alcohol is the appearance of a blue-green color. Tertiary alcohols do not produce the test result within 2 seconds, and the solution remains orange. To make sure that the acetone solvent is pure and does not give a positive test result, add one drop of chromic acid to 1 mL of acetone that does not have an unknown dissolved in it. The orange color of the reagent should persist for *at least* 3 seconds. If it does not, a new bottle of acetone should be used.

**Test Compounds.** Try this test with 1-butanol (*n*-butyl alcohol), 2-butanol (*sec*-butyl alcohol), and 2-methyl-2-propanol (*t*-butyl alcohol).

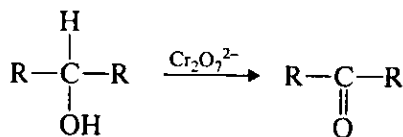
**CAUTION:** Many compounds of chromium(VI) are suspected carcinogens (see p. 19) and should be handled with care. Avoid contact.

**Reagent.** Dissolve 1 g of chromic oxide  $\text{CrO}_3$  in 1 mL of concentrated sulfuric acid. Carefully add the mixture to 3 mL of water.

This test is based on the reduction of chromium(VI), which is orange, to chromium(III), which is green, when an alcohol is oxidized by the reagent. A change in color of the reagent from orange to green represents a positive test. Primary alcohols are oxidized by the reagent to carboxylic acids; secondary alcohols are oxidized to ketones.



Primary alcohols



Secondary alcohol

Although primary alcohols are first oxidized to aldehydes, the aldehydes are further oxidized to carboxylic acids. The ability of chromic acid to oxidize aldehydes but not ketones is taken advantage of in a test that uses chromic acid to distinguish between aldehydes and ketones (Experiment 51D). Secondary alcohols are oxidized to ketones, but no further. Tertiary alcohols are not oxidized at all by the reagent, hence this test can be used to distinguish primary and secondary alcohols from tertiary alcohols. Unlike the Lucas test, this test can be used with all alcohols regardless of molecular weight and solubility.

### Iodoform Test

Alcohols with the hydroxyl group at the 2-position of the chain give a positive iodoform test. See the discussion in Experiment 51D, Aldehydes and Ketones.

### Spectroscopy

#### Infrared

**O—H stretch.** A medium to strong, and usually broad, absorption comes in the region  $3600\text{--}3200 \text{ cm}^{-1}$ . In dilute solutions or with little hydrogen bonding, there is a sharp absorption near  $3600 \text{ cm}^{-1}$ . In more concentrated solutions, or with considerable hydrogen bonding, there is a broad absorption near  $3400 \text{ cm}^{-1}$ . Sometimes both bands appear.

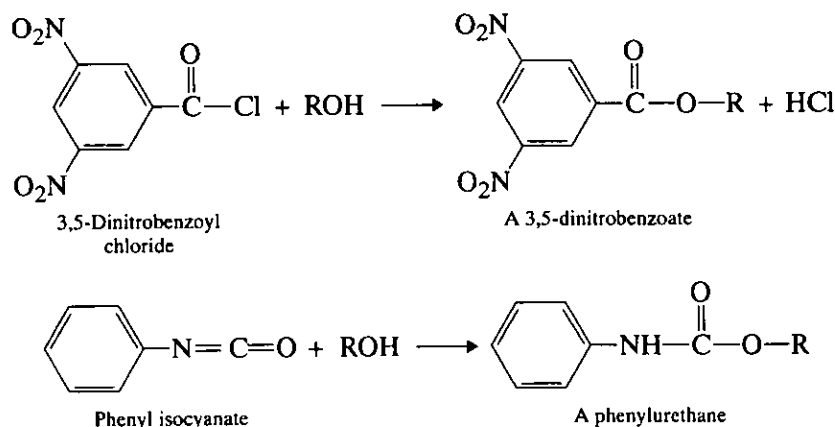
**C—O stretch.** There is a strong absorption in the region  $1200\text{--}1500 \text{ cm}^{-1}$ . Primary alcohols absorb nearer  $1050 \text{ cm}^{-1}$ ; tertiary alcohols and phenols absorb nearer  $1200 \text{ cm}^{-1}$ . Secondary alcohols absorb in the middle of this range.

## Nuclear Magnetic Resonance

The hydroxyl resonance is extremely concentration-dependent, but it is usually found between 1 and 5 ppm. Under normal conditions, the hydroxyl proton does not couple with protons on adjacent carbon atoms.

## Derivatives

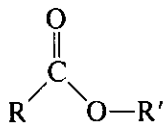
The most common derivatives for alcohols are the 3,5-dinitrobenzoate esters and the phenylurethanes. Occasionally the  $\alpha$ -naphthylurethanes (Experiment 51F) are also prepared, but these latter derivatives are more often used for phenols.



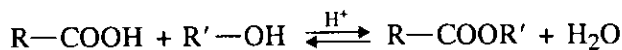
Procedures for preparing these derivatives are given in Appendix 2.

## Experiment 51I

### Esters



Esters are formally considered "derivatives" of the corresponding carboxylic acid. They are frequently synthesized from the carboxylic acid and the appropriate alcohol:



Thus esters are sometimes referred to as though they were composed of an acid part and an alcohol part.

Although esters, like aldehydes and ketones, are neutral compounds that have a carbonyl group, they do not usually give a positive 2,4-dinitrophenylhydrazine test result. The two most common tests for identifying esters are the basic hydrolysis and ferric hydroxamate tests.