
*Identification of
Organic Substances*

Identification of Unknowns

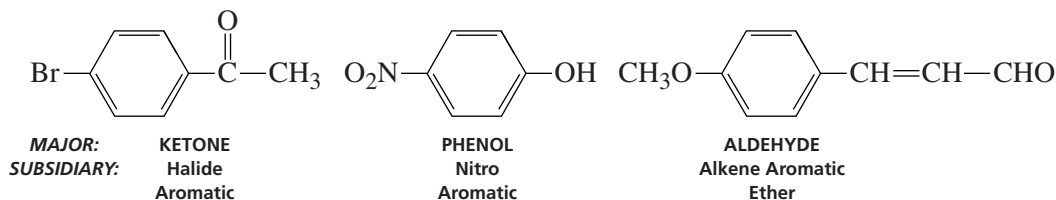
Qualitative organic analysis, the identification and characterization of unknown compounds, is an important part of organic chemistry. Every chemist must learn the appropriate methods for establishing the identity of a compound. In this experiment, you will be issued an unknown compound and will be asked 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 millions of organic compounds that an organic chemist might be called on to identify, the scope of this experiment is necessarily limited. In this textbook, about 500 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 ₂	Nitro	$\text{C}=\text{C}$	Double Bond
—Br	Bromo	—C≡N	Cyano	$\text{C}\equiv\text{C}$	Triple Bond
—I	Iodo	—OR	Alkoxy		Aromatic

The experiment presents all of 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—Option 1

Fortunately, we can detail a fairly straightforward procedure for determining all of 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
7. Inspection of tables for possible structure(s) of unknown; elimination of unlikely compounds

Part Two: Spectroscopy

8. Determination of infrared and NMR spectra

Part Three: Optional Procedures

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

Each of these steps is discussed briefly starting on page 449.

Green Chemistry Method: How to Proceed—Option 2

At the option of your instructor, another approach may be taken in determining the structure of unknowns in the organic laboratory. This approach makes minimal use of classification tests but retains the solubility tests as the main way of determining functional groups and spectroscopy as a way of determining the detailed structure of an unknown. Elimination of classification tests described in Part One, number 6, tremendously reduces the waste generated in the laboratory. It also eliminates the use of many of the toxic and potentially dangerous reagents that are a standard part of the traditional classification tests. This approach is, therefore, a “Green” approach to solving structures of organic compounds.

Although classification tests can be useful in determining the identity of an unknown compound, spectroscopic methods have become the principal means by which an organic chemist identifies unknown substances. The technology and instrumentation available has almost obviated the need for classification tests, because valuable information can be discovered simply by obtaining infrared and NMR spectra. Option 2 relies heavily on the spectroscopic results; if acetone- d_6 or DMSO- d_6 are used as NMR spectroscopy solvents, this becomes a more environmentally sound approach.

The ability to use IR and NMR spectroscopy and evaluate spectra inherently requires a logical sequence of steps in the identification of an unknown. By relying on these techniques, students learn the techniques and higher-order thinking skills that they would be required to know and use for a career in chemistry. This approach more closely simulates the types of structure-proof methods that one would find in a modern research or industrial laboratory. Students can still learn how to go through the logical steps used in the classification tests by practicing these methods in a more environmentally friendly scenario through the use of computer simulations.

The procedure for determining the structure of a compound using the environmentally friendly approach is fairly straightforward and 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. Inspection of tables for possible structure(s) of unknowns

Part Two: Spectroscopy

7. Determination of infrared and NMR (proton and ^{13}C , if available) spectra
8. Confirmation of structure

In many cases, the type of compound and functional group should be discovered after completing Part One. Spectroscopy (Part Two) will be used *principally* to confirm the structural assignment and to provide further information toward identifying the unknown. Your instructor may not allow you to obtain spectroscopic information (infrared or NMR) until you have completed Part One. Show your test results to your instructor for approval. Once this part has been completed, you should have narrowed the list of possible compounds to a few likely candidates, *all containing the same functional group*. In other words, you should have determined the principal functional group. You *must* obtain approval from the instructor to perform spectroscopy.

The functional groups that may be included in the unknowns are listed on the first page of this experiment. Tables of possible compounds are listed in the Appendix 1 of this book.

1. PRELIMINARY CLASSIFICATION

Note the physical characteristics of the unknown, including its color, odor, and 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.

2. 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 9, Sections 9.5 and 9.7). 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. Because some of the unknown solids contain traces of impurities, you may find that your observed melting point is lower than the values found in the tables in Appendix 1. This is especially true for low-melting compounds ($<50^{\circ}\text{C}$). For these low-melting compounds, it is a good idea to look at compounds in the tables in Appendix 1 that have melting points above your observed melting-point range. The same advice may apply to other solid compounds issued to you as unknowns.

The boiling point is easily obtained by a simple distillation of the unknown (see Technique 14, Section 14.3) by reflux (see Technique 13, Section 13.2), by a microboiling-point determination (see Technique 13, Section 13.2), or by Vernier LabPro interface method (see Technique 13, Section 13.5). The simple distillation has the advantage in that it also purifies the compound. The smallest distilling flask available should be used if a simple distillation is performed, and you should be sure that the thermometer bulb is fully immersed in the vapor of the distilling liquid. The liquid should be distilled rapidly to determine an accurate boiling-point value. The microboiling-point method requires the least amount of unknown, but the refluxing method is more reliable and requires much less liquid than that required for distillation.

When inspecting the tables of unknowns in Appendix 1, you may find that the observed boiling point that you determined is lower than the value for the corresponding compound listed in the tables. This is especially true for compounds boiling above 200°C . It is less likely, but not impossible, that the observed boiling point of your unknown will be higher than the value given in the table. Thus, your strategy should be to look for boiling points of compounds in the tables that are nearly equal to or above the value you obtained, within a range of about $\pm 5^{\circ}\text{C}$. For high-boiling liquid compounds ($>200^{\circ}\text{C}$), you may need to apply a thermometer correction (see Technique 13, Section 13.3).

3. PURIFICATION

If the melting point of a solid has a wide range (about 5°C), the solid 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 CH₂Cl₂ or ether, and extracting with 5% NaHCO₃ or 5% HCl, respectively. Conversely, acidic or basic compounds can be purified by dissolving them in 5% NaHCO₃ or 5% HCl, respectively, and extracting them with a low-boiling organic solvent to remove impurities. After the aqueous solution has been neutralized, the desired compound can be recovered by extraction.

4. SOLUBILITY BEHAVIOR

Tests on solubility are described fully in Experiment 55A. They are extremely important. Determine the solubility of small amounts of the unknown in water, 5% HCl, 5% NaHCO₃, 5% NaOH, concentrated H₂SO₄, 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.

5. PRELIMINARY TESTS

The two combustion tests, the Beilstein test (Experiment 55B) and the ignition test (Experiment 55C), can be performed easily and quickly, and they often give valuable information. It is recommended that they be performed on all unknowns.

6. CHEMICAL CLASSIFICATION TESTS

The solubility tests usually suggest or eliminate several possible functional groups. The chemical classification tests listed in Experiments 55D to 55I 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 is essential 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.

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 in Appendix 1 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. Again, some instructors may require derivatives as a final confirmation of the compound's identity; others may not wish to use them at all.

7. INSPECTION OF TABLES FOR POSSIBLE STRUCTURES

Once the melting or boiling point, the solubilities, and the main chemical classification tests have been made, you should be able to identify the class of compound (aldehyde, ketone, and so on). At this stage, with the melting point or boiling point as a guide, you can compile a list of possible compounds from one of the appropriate tables in Appendix 1. It is very important to draw out the structures of compounds that fit the solubility, classification tests, and melting point or boiling point that were determined. If necessary, you can look up the structures in the *CRC Handbook*, *The Merck Index*, or the *Aldrich Handbook*. Remember that the boiling point or melting point recorded in the table may be higher than what you obtained in the laboratory (see Section 2 above).

The short list that you developed by inspection of the tables in Appendix 1 and the structures drawn should suggest that some additional tests may be needed 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 55B and 55C. These tests should also be studied carefully; there is no substitute for firsthand knowledge about these tests.

8. 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 the structure through spectroscopy alone. On the other hand, there are also situations for which spectroscopy may not be 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.

9. 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 may render 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.

10. DERIVATIVES

One of the principal tests for the correct identification of an unknown compound is 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.

11. 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 mixture melting point (see Technique 9, Section 9.4). 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.

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Extensive Tables of Compounds and Derivatives

- Rappoport, Z., Ed. *Handbook of Tables for Organic Compound Identification*, 3rd ed.; CRC Press: Boca Raton, FL, 1967.

55A

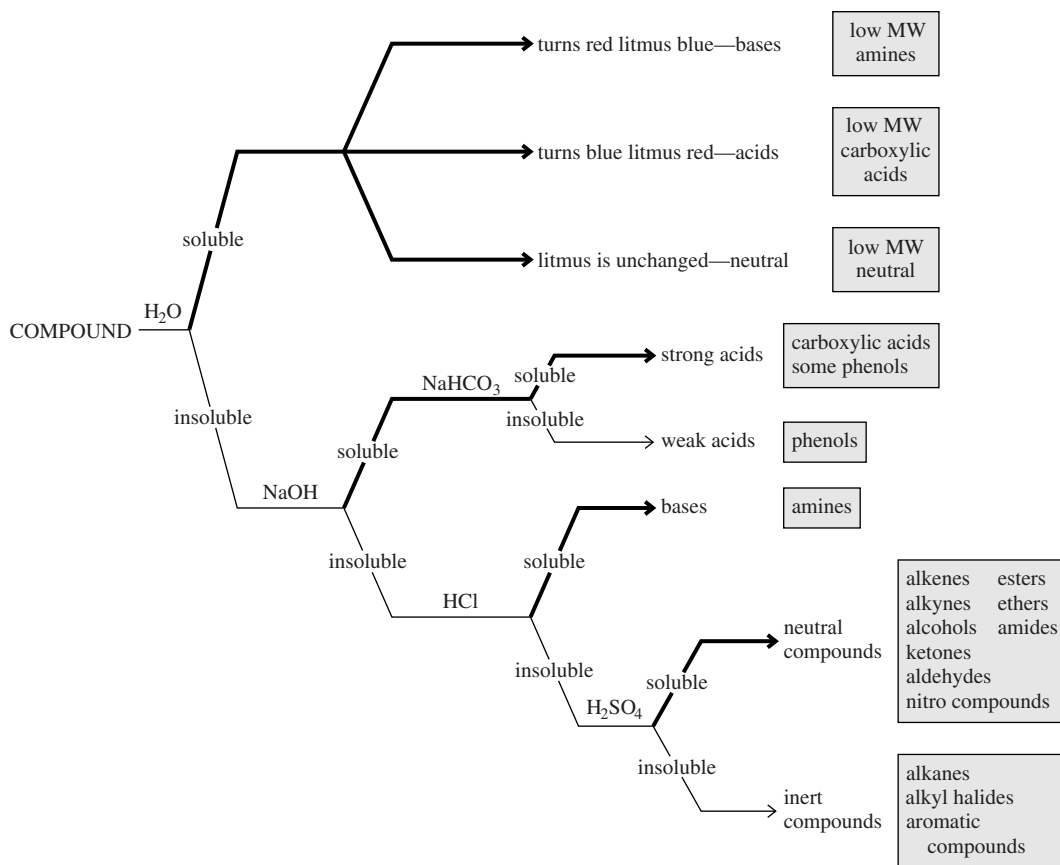
EXPERIMENT 55A

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 ₂ SO ₄
5% NaHCO ₃	Water
5% NaOH	Organic solvents

The solubility chart given in the next page indicates solvents in which compounds containing the various functional groups are likely to dissolve. The summary charts in Experiments 55D through 55I 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 only in specific solvents. This is accomplished by indicating the type of chemistry or the type of chemical interaction that is possible in each solvent.



Solubility chart for compounds containing various functional groups.

SUGGESTED 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 TESTS

Procedure. Place about 2 mL of the solvent in a small test tube. Add 1 drop of an unknown liquid from a Pasteur pipet or a few crystals of an unknown solid using 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 only small amounts of the unknown. 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 use a mortar and pestle to pulverize a compound with large crystals. 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% NaHCO₃, 5% NaOH, and concentrated H₂SO₄. With sulfuric acid, a color change may be observed rather than solution. A color change should be regarded as a positive solubility test. Unknown solids 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, carboxylic acid may be only slightly soluble in water but very much 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. A general discussion of solubility behavior is provided in Technique 10, Section 10.2.

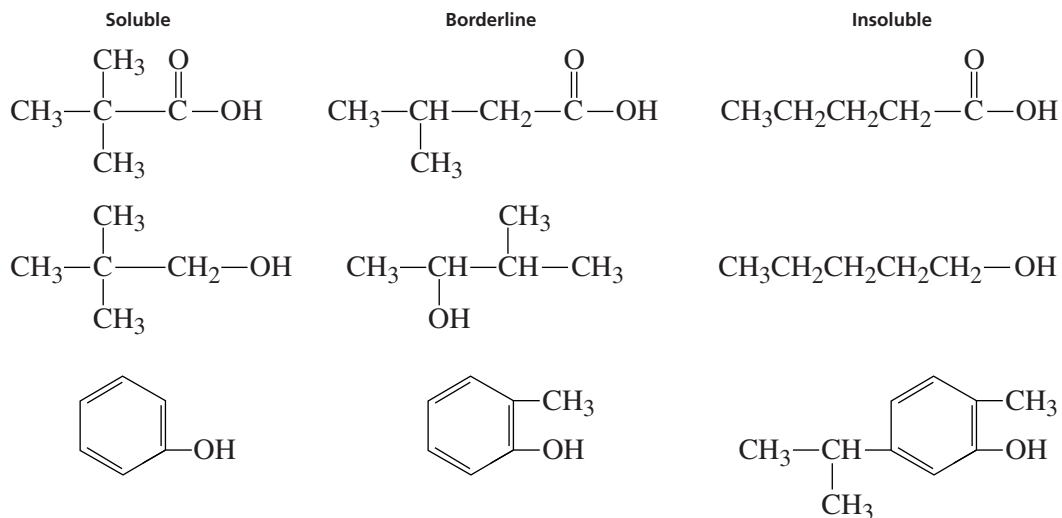
Discussion

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 (C₄) 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.

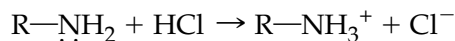
When the ratio of the oxygen, nitrogen, or sulfur atoms in a compound to the carbon atoms is increased, the solubility of that compound in water often increases. This is due to the increased number of polar functional groups. Thus, 1,5-pentanediol would be expected to be more soluble in water than 1-pentanol.

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.

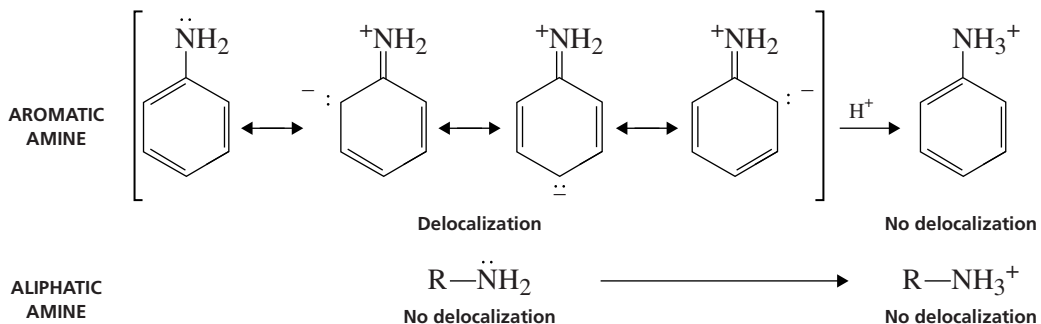


Solubility in 5% HCl

The possibility of an amine should be considered immediately if a compound is soluble in dilute acid (5% HCl). Aliphatic amines (RNH_2 , R_2NH , R_3N) 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, Ar_2NH and Ar_3N are insoluble in dilute acid. Some amines of very high molecular weight, such as tribromoaniline ($MW=330$), may also be insoluble in dilute acid.



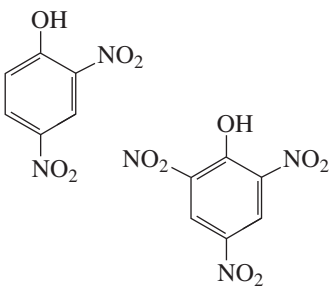
Solubility in 5% NaHCO_3 and 5% NaOH

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

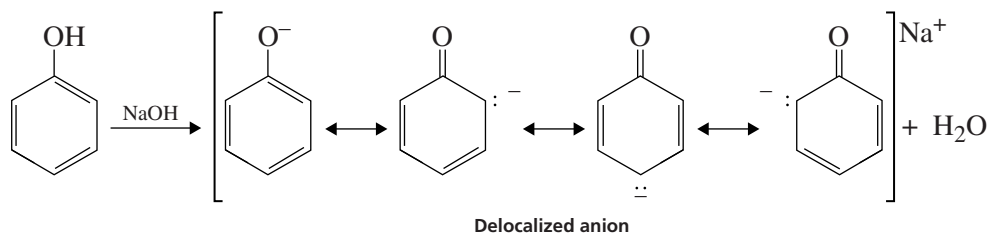
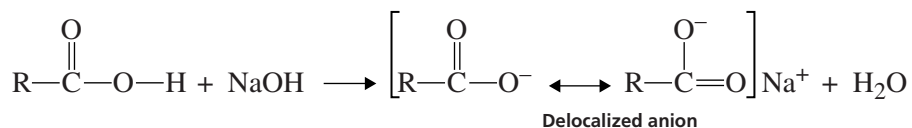
(NaOH) and weak (NaHCO_3) base. The classification of some functional groups as either weak or strong acids is given in the table below.

In this experiment, carboxylic acids ($\text{p}K_a \sim 5$) are generally indicated when a compound is soluble in both bases, and phenols ($\text{p}K_a \sim 10$) are indicated when it is soluble in 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, belong to this category. Some phenols also produce insoluble sodium salts, and often these are colored due to resonance in the anion.

Strong Acids (Soluble in Both NaOH and NaHCO_3)	Weak Acids (Soluble in NaOH but Not in NaHCO_3)
Sulfonic acids RSO_3H Carboxylic acids RCOOH <i>ortho</i> - and <i>para</i> -substituted di- and trinitrophenols 	Phenols ArOH Nitroalkanes RCH_2NO_2 R_2CHNO_2 <i>β</i> -Diketones $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$ <i>β</i> -Diesters $\text{RO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}$ Imides $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$ Sulfonamides ArSO_2NH_2 ArSO_2NHR

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

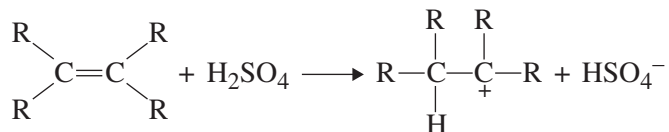
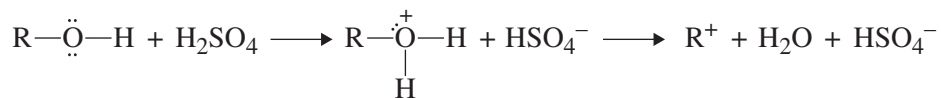


In phenols, substitution of nitro groups in the *ortho* and *para* positions of the ring increases acidity. Nitro groups in these positions provide additional delocalization in the conjugate anion. Phenols that have two or three nitro groups in the *ortho* and *para* positions often dissolve in *both*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

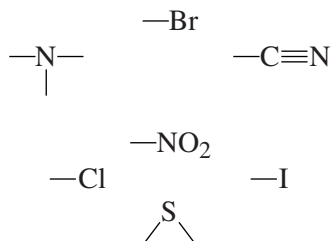
Solubility in Concentrated Sulfuric Acid

Many compounds are soluble in cold, concentrated sulfuric acid. Of the compounds included in this experiment, alcohols, ketones, aldehydes, and esters belong to this category. These compounds are described as being "neutral." 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, the most simple aromatics, and the alkyl halides. Some examples of inert compounds are hexane, benzene, chlorobenzene, chlorohexane, and toluene.

55B**EXPERIMENT 55B***Tests for the Elements (N, S, X)*

Except for amines (Experiment 55G), 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 groups. 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	Ferrous hydroxide	Sodium fusion
Silver nitrate		
Sodium iodide/acetone		

SUGGESTED 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. Adjust the air and gas mixture so that the flame of a Bunsen burner or microburner is blue. Bend the end of a piece of copper wire so that a small closed loop is created. Heat the loop end of the wire in the flame until it glows brightly. After the wire has cooled, dip the wire directly into a 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. Again heat the wire in the Bunsen burner flame. The compound will first burn. After the burning, a green flame will be produced if a halogen is present. You should hold the wire in the flame either just above the tip of the flame or at its outside edge near the bottom of the flame. You will need to experiment to find the best position to hold the copper wire to obtain the best result.

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

Discussion

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.

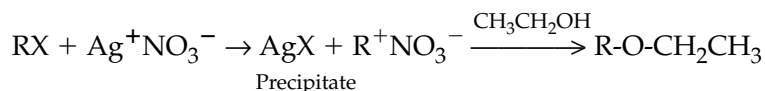
Silver Nitrate Test

Procedure. Add 1 drop of a liquid or 5 drops of a concentrated ethanolic solution of the unknown solid 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 2 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 (α -bromotoluene) and bromobenzene. Discard all waste reagents in a suitable waste container in the hood because benzyl bromide is a lachrymator.

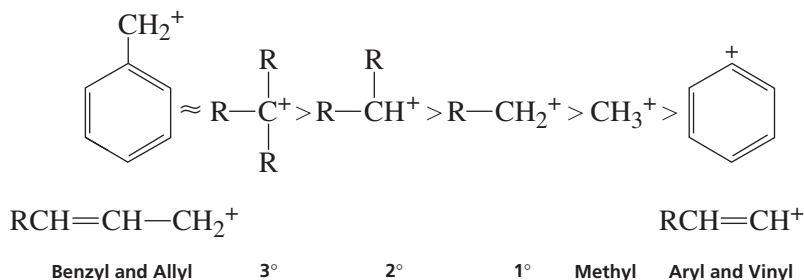
Discussion

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 ($X = \text{I}, \text{Br}, \text{Cl}$). 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 sp^2 -hybridized carbon (double-bond carbon) rather than one that is sp^3 -hybridized.

Sodium Iodide in Acetone

Procedure. This test is described in Experiment 19.

Test Compounds. Apply this test to benzyl bromide (α -bromotoluene), bromobenzene, and 2-chloro-2-methylpropane (*tert*-butyl chloride).

DETECTION OF NITRO GROUPS

Although nitro compounds will not be issued as distinct unknowns, many of the unknowns may have a nitro group as a secondary functional group. The presence of a nitro group, and hence nitrogen, in an unknown compound is determined most easily by infrared spectroscopy. However, many nitro compounds give a positive result in the following test. Unfortunately, functional groups other than the nitro group may also give a positive result. You should interpret the results of this test with caution.

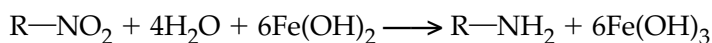
Ferrous Hydroxide Test

Procedure. Place 1.5 mL of freshly prepared 5% aqueous ferrous ammonium sulfate in a small test tube, and add about 10 mg of a solid or 5 drops of a liquid compound. Mix the solution well, and then add first 1 drop of 2 M sulfuric acid and then 1 mL of 2 M potassium hydroxide in methanol. Stopper the test tube and shake it vigorously. A positive test is indicated by the formation of a red-brown precipitate, usually within 1 minute.

Test Compound. Apply this test to 2-nitrotoluene.

Discussion

Most nitro compounds oxidize ferrous hydroxide to ferric hydroxide, which is a red-brown solid. A precipitate indicates a positive test.

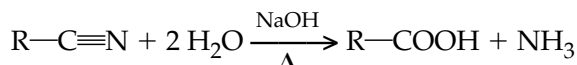


Infrared Spectroscopy

The nitro group gives two strong bands near 1560 cm^{-1} and 1350 cm^{-1} . See Technique 25 for details.

DETECTION OF A CYANO GROUP

Although nitriles will not be given as unknowns in this experiment, the cyano group may be a subsidiary functional group whose presence or absence is important to the final identification of an unknown compound. The cyano group can be hydrolyzed in a strong base by heating vigorously to give carboxylic acid and ammonia gas:



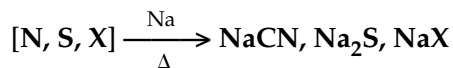
The ammonia gas can be detected by its odor or by using moist pH paper. However, this method is somewhat difficult, and the presence of a nitrile group is confirmed most easily by infrared spectroscopy. No other functional groups (except some $\text{C}\equiv\text{C}$) absorb in the same region of the spectrum as $\text{C}\equiv\text{N}$.

Infrared Spectroscopy

$\text{C}\equiv\text{N}$ stretch is a sharp band of medium intensity near 2250 cm^{-1} . See Technique 25 for details.

Sodium Fusion Tests (Detection of N, S, And X) (Optional)

When an organic compound containing nitrogen, sulfur, or halide atoms is fused with sodium metal, there is a reductive decomposition of the compound, which converts these atoms to the sodium salts of the inorganic ions CN^- , S^{2-} , and X^- .



When the fusion mixture is dissolved in distilled water, the cyanide, sulfide, and halide ions can be detected by standard qualitative inorganic tests.

CAUTION

Always remember to manipulate the sodium metal with a knife or a forceps. Do not touch it with your fingers. Keep sodium away from water. Destroy all waste sodium with 1-butanol or ethanol. Wear safety glasses.

PREPARATION OF STOCK SOLUTION**General Method**

Procedure. Using a forceps and a knife, take some sodium from the storage container, cut a small piece about the size of a small pea (3 mm on a side), and dry it on a paper towel. Place this small piece of sodium in a clean, dry, small test tube (10 mm × 75 mm). Clamp the test tube to a ring stand, and heat the bottom of the tube with a microburner until the sodium melts and its metallic vapor can be seen to rise about a third of the way up the tube.

The bottom of the tube will probably have a dull red glow. Remove the burner and *immediately* drop the sample directly into the tube. Use about 10 mg of a solid placed on the end of a spatula or 2–3 drops of a liquid. Be sure to drop the sample directly down the center of the tube so that it touches the hot sodium metal and does not adhere to the side of the test tube. If the fusion is successful, there will usually be a flash or a small explosion. If the reaction is not successful, heat the tube to red heat for a few seconds to ensure complete reaction.

Allow the test tube to cool to room temperature, and then carefully add 10 drops of methanol, a drop at a time, to the fusion mixture. Using a spatula or a long glass rod, reach into the test tube and stir the mixture to ensure complete reaction of any excess sodium metal. The fusion will have destroyed the test tube for other uses. Thus, the easiest way to recover the fusion mixture is to crush the test tube into a small beaker containing 5–10 mL of *distilled* water. The tube is easily crushed if it is placed in the angle of a clamp holder. Tighten the clamp until the tube is securely held near its bottom and then—standing back from the beaker and holding the clamp at its opposite end—continue tightening the clamp until the test tube breaks and the pieces fall into the beaker. Stir the solution well, heat until it boils, and then filter it by gravity through a fluted filter (see Technique 8, Figure 8.3). Portions of this solution will be used in the tests to detect nitrogen, sulfur, and the halogens.

Alternative Method

Procedure. With some volatile liquids, the previous method will not work. The compounds volatilize before they reach the sodium vapors. For such compounds, place 4 or 5 drops of the pure liquid in a clean, dry test tube, clamp it, and cautiously add the small piece of sodium metal. If there is any reaction, wait until it subsides. Then heat the test tube to red heat, and continue according to the instructions in the second paragraph of the preceding procedure.

Nitrogen Test

Procedure. Using pH paper and a 10% sodium hydroxide solution, adjust the pH of about 1 mL of the stock solution to pH 13. Add 2 drops of saturated ferrous ammonium sulfate solution and 2 drops of 30% potassium fluoride solution. Boil the solution for about 30 seconds. Then acidify the hot solution by adding 30% sulfuric acid dropwise until the iron hydroxides dissolve. Avoid using excess acid. If nitrogen is present, a dark blue (not green) precipitate of Prussian blue $\text{NaFe}_2(\text{CN})_6$ will form, or the solution will assume a dark blue color.

Reagents. Dissolve 5 g of ferrous ammonium sulfate in 100 mL of water. Dissolve 30 g of potassium fluoride in 100 mL of water.

Sulfur Test

Procedure. Acidify about 1 mL of the test solution with acetic acid, and add a few drops of a 1% lead acetate solution. The presence of sulfur is indicated by a black precipitate of lead sulfide (PbS).

CAUTION



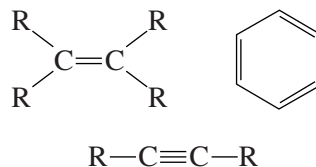
Many compounds of lead(II) are suspected carcinogens (see Technique 1, Section 1.4) and should be handled with care. Avoid contact.

Halide Tests

Procedure. Cyanide and sulfide ions interfere with the test for halides. If such ions are present, they must be removed. To accomplish this, acidify the solution with dilute nitric acid and boil it for about 2 minutes. This will drive off any HCN or H₂S that is formed. When the solution cools, add a few drops of a 5% silver nitrate solution. A *voluminous* precipitate indicates a halide. A faint turbidity *does not* mean a positive test. Silver chloride is white. Silver bromide is off-white. Silver iodide is yellow. Silver chloride will readily dissolve in concentrated ammonium hydroxide, whereas silver bromide is only slightly soluble.

Differentiation of Chloride, Bromide, and Iodide

Procedure. Acidify 2 mL of the test solution with 10% sulfuric acid, and boil it for about 2 minutes. Cool the solution and add about 0.5 mL of methylene chloride. Add a few drops of chlorine water or 2–4 mg of calcium hypochlorite.¹ Check to be sure that the solution is still acidic. Then stopper the tube, shake it vigorously, and set it aside to allow the layers to separate. An orange to brown color in the methylene chloride layer indicates bromine. Violet indicates iodine. No color or a *light* yellow indicates chlorine.

55C EXPERIMENT 55C*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–methylene chloride	Ignition test
Potassium permanganate	

¹Clorox, the commercial bleach, is a permissible substitute for chlorine water, as is any other brand of bleach, provided that it is based on sodium hypochlorite.

SUGGESTED WASTE DISPOSAL

Test reagents that contain bromine should be discarded into a special waste container designated for this purpose. Methylene chloride 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.

TEST FOR SIMPLE MULTIPLE BONDS

Bromine in Methylene Chloride

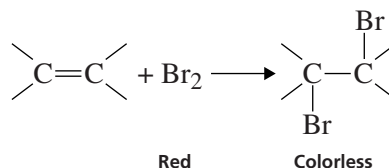
Procedure. Dissolve 50 mg of the unknown solid or 4 drops of the unknown liquid in 1 mL of methylene chloride (dichloromethane) or in 1,2-dimethoxyethane. Add a 2% (by volume) solution of bromine in methylene chloride, dropwise, with shaking. If you find that the red color remains after adding 1 or 2 drops of the bromine solution, the test is negative. If the red color disappears, continue adding the bromine in methylene chloride until the red bromine color remains. The test is positive if more than 5 drops of the bromine solution were added, with discharge of the red color of bromine. If the red color disappears, try adding more drops of the bromine solution to see how many drops are necessary before the red color persists. Usually, many drops of the bromine solution will be decolorized when an isolated double bond is present. Hydrogen bromide should not be evolved. If hydrogen bromide gas is evolved, you will note a “fog” when 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 following discussion) and not an **addition reaction**, and a double or triple bond is probably not present.

Reagent. The classic method for running this test is to use bromine dissolved in carbon tetrachloride. Because of the toxic nature of this solvent, methylene chloride has been substituted for carbon tetrachloride. The instructor must prepare this reagent because of the danger associated with the very toxic bromine vapor. Be sure to work in an efficient fume hood. Dissolve 2 mL of bromine in 100 mL of methylene chloride (dichloromethane). The solvent will undergo a light-induced, free-radical substitution producing hydrogen bromide over a period of time. After about 1 week, the color of the 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.

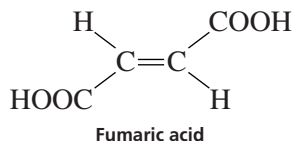
Test Compounds. Try this test with cyclohexene, cyclohexane, toluene, and acetone.

Discussion

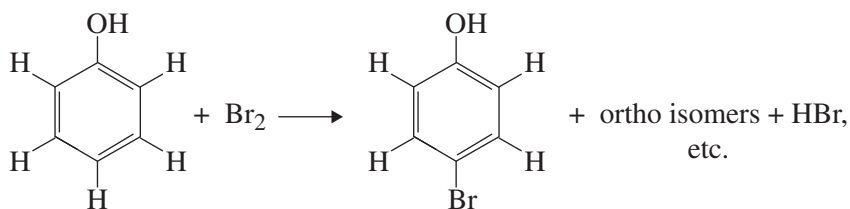
A successful test depends on the addition of bromine, a red liquid, to a double or a triple bond to give a colorless dibromide:



Not all double bonds react with the bromine 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 the bromine 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.

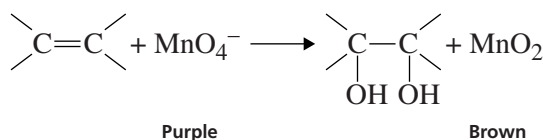
Potassium Permanganate (Baeyer Test)

Procedure. Dissolve 25 mg of the unknown solid or 2 drops of the unknown liquid in 2 mL of 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 precipitate should be interpreted with caution.

Test Compounds. Try this test on cyclohexene and toluene.

Discussion

This test is positive for double and triple bonds but not for aromatic rings. It depends on the conversion of the purple ion MnO_4^- to a brown precipitate of 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 is present, you should interpret the test with caution.

Spectroscopy

Infrared

Double Bonds (C=C)

C=C stretch usually occurs near 1680–1620 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 cm^{-1} .

C—H out-of-plane bending occurs near 1000–700 cm^{-1} .

See Technique 25 for details.

Triple Bonds (C≡C)

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

C—H stretch of terminal acetylenes occurs near 3310–3200 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. See Technique 26 for details on proton NMR. Carbon NMR is described in Technique 27.

TESTS FOR AROMATICITY

None of the unknowns to be issued for this experiment will be simple aromatic hydrocarbons. All aromatic compounds will have a principal functional group as a part of their structure. Nevertheless, in many cases it will be useful to be able to recognize the presence of an aromatic ring. Although infrared and nuclear magnetic spectroscopy provide the most reliable methods of determining aromatic compounds, often they can be detected by a simple ignition test.

Ignition Test

Procedure. Working in a hood, place a small amount of the compound on a spatula and place it in the flame of a Bunsen burner. Observe whether a sooty flame results. Compounds giving the sooty yellow flame have a high degree of unsaturation and may be aromatic. This test should be interpreted with care because some nonaromatic compounds may produce soot. If in doubt, use spectroscopy to more reliably determine the presence or absence of an aromatic ring.

Test Compounds. Try this test with ethyl benzoate and benzoin.

Discussion

The presence of an aromatic ring will usually lead to the production of a sooty yellow flame in this test. In addition, halogenated alkanes and high-molecular weight aliphatic compounds may produce a sooty yellow flame. Aromatic compounds with high oxygen content may burn cleaner and produce less soot even though the compound contains an aromatic ring.

This is actually a test to determine the ratio of carbon to hydrogen, and oxygen in an unknown substance. If the carbon-to-hydrogen ratio is high and if little or no oxygen is present, you will observe a sooty flame. For instance, acetylene, C_2H_2 (a gas), will burn with a sooty flame unless mixed with oxygen. When the carbon-to-hydrogen ratio is nearly equal to one, you will be very likely to see a sooty flame.

Spectroscopy

Infrared

$C=C$ aromatic-ring double bonds appear in the $1600\text{--}1450\text{ cm}^{-1}$ region. There are often four sharp absorptions that occur in pairs near 1600 cm^{-1} and 1450 cm^{-1} , which are characteristic of an aromatic ring.

Special ring absorptions: There are often weak ring absorptions around $2000\text{--}1600\text{ cm}^{-1}$. These are frequently obscured, but when they can be observed, the relative shapes and numbers of these peaks can often be used to ascertain the type of ring substitution.

$=C-H$ stretch, aromatic ring: The aromatic $C-H$ stretch always occurs at a higher frequency than 3000 cm^{-1} .

$=C-H$ out-of-plane bending peaks appear in the region $900\text{--}690\text{ cm}^{-1}$. The number and position of these peaks can be used to determine the substitution pattern of the ring.

See Technique 25 for details.

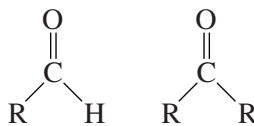
Nuclear Magnetic Resonance

Hydrogens attached to an aromatic ring usually have resonance near 7 ppm. Monosubstituted rings not substituted by anisotropic or electronegative groups often give a single resonance for all of the ring hydrogens. Monosubstituted rings with anisotropic or electronegative groups usually have the aromatic resonances split into two groups integrating either 3:2 or 2:3. A nonsymmetric, *para*-disubstituted ring has a characteristic four-peak splitting pattern (see Technique 26). Carbon NMR is described in Technique 27.

55D

EXPERIMENT 55D

Aldehydes and Ketones



Compounds containing the carbonyl functional group >C=O , where it has

only hydrogen atoms or alkyl groups as substituents, are called aldehydes, RCHO , or ketones, RCOR' . The chemistry of these compounds is primarily due to the chemistry of the carbonyl functional groups. These compounds are identified by the distinctive reactions of the carbonyl function.

Solubility Characteristics	Classification Tests
HCl NaHCO ₃ NaOH H ₂ SO ₄ Ether (-) (-) (-) (+) (+)	Aldehydes and ketones 2,4-Dinitrophenylhydrazine
Water: < C ₅ and some C ₆ (+) > C ₅ (-)	Aldehydes only Methyl ketones Tollens reagent Iodoform test Chromic acid
	Compounds with high enol content Ferric chloride test

SUGGESTED WASTE DISPOSAL

Solutions containing 2,4-dinitrophenylhydrazine or derivatives formed from it should be placed in a waste container designated for these compounds. Any solution containing chromium must be disposed of in a waste container specifically identified for the disposal of chromium wastes. Dispose of all solutions containing silver by acidifying them with 5% hydrochloric acid and then placing them in a waste container designated for this purpose. 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

Most aldehydes and ketones give a solid, yellow to red precipitate when mixed with 2,4-dinitrophenylhydrazine. However, only aldehydes will reduce chromium(VI) or silver(I). By this difference in behavior, you can differentiate between aldehydes and ketones.

2, 4- Dinitrophenylhydrazine

Procedure. Place 1 drop of the liquid unknown in a small test tube and add 1 mL of the 2,4-dinitrophenylhydrazine reagent. If the unknown is a solid, dissolve about 10 mg (estimate) in a minimum amount of 95% ethanol or di(ethylene glycol) diethyl ether before adding the reagent. Shake the mixture vigorously. Most aldehydes and ketones will give a yellow to red precipitate immediately. However, some compounds will require up to 15 minutes, or even *gentle* heating, to give a precipitate. A precipitate indicates a positive test.

Test Compounds. Try this test on cyclohexanone, benzaldehyde, and benzophenone.

CAUTION

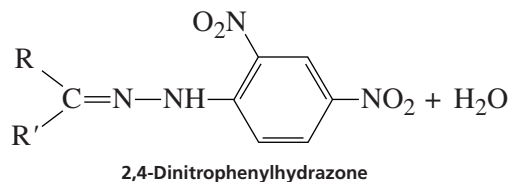
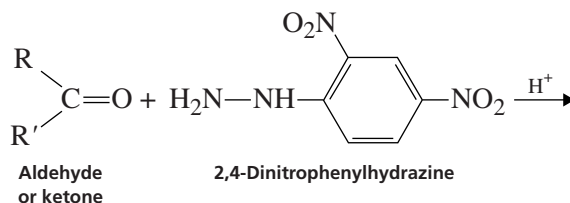


Many derivatives of phenylhydrazine are suspected carcinogens (see Technique 1, Section 1.4) and should be handled with care. Avoid contact.

Reagent. Dissolve 3.0 g of 2,4-dinitrophenylhydrazine in 15 mL of concentrated sulfuric acid. In a beaker, slowly add, with mixing, 23 mL of water until the solid dissolves. Add 75 mL of 95% ethanol to the warm solution, while stirring. After thorough mixing, filter the solution if any solid remains. This reagent needs to be prepared fresh each time.

Discussion

Most aldehydes and ketones give a precipitate, but esters generally do not give this result. Thus, an ester usually can be eliminated by this test. The color of the 2,4-dinitrophenylhydrazone (precipitate) formed is often a guide to the amount of conjugation in the original aldehyde or ketone. Unconjugated ketones, such as cyclohexanone, give yellow precipitates, whereas conjugated ketones, such as benzophenone, give orange to red precipitates. Compounds that are highly conjugated give red precipitates. However, the 2,4-dinitrophenylhydrazine reagent is itself orange-red, and the color of any precipitate must be judged cautiously. Occasionally, compounds that are either strongly basic or strongly acidic precipitate the unreacted reagent.



Some allylic and benzylic alcohols give this test result because the reagent can oxidize them to aldehydes and ketones, which subsequently react. Some alcohols may be contaminated with carbonyl impurities, either as a result of their method of synthesis (reduction) or as a result of their becoming air-oxidized. A precipitate formed from small amounts of impurity in the solution will be formed in small amounts. With some caution, a test that gives only a slight amount of precipitate can usually be ignored. The infrared spectrum of the compound should establish its identity and identify any impurities present.

Tollens Test

Procedure. The reagent must be prepared immediately before use. To prepare the reagent, mix 1 mL of Tollens solution A with 1 mL of Tollens solution B. A precipitate of silver oxide will form. Add enough dilute (10%) ammonia solution (dropwise) to the mixture to dissolve the silver oxide *just barely*. The reagent so prepared can be used immediately for the following test.

Dissolve 1 drop of a liquid aldehyde or 10 mg (approximate) of a solid aldehyde in the minimum amount of di(ethylene glycol) diethyl ether. Add this solution, a little at a time, to the 2–3 mL of reagent contained in a small test tube. Shake the solution well. If a mirror of silver is deposited on the inner walls of the test tube, the test is positive. In some cases, it may be necessary to warm the test tube in a warm water bath.

Test Compounds. Try the test on benzaldehyde, butanal (butyraldehyde), and cyclohexanone.

CAUTION



The reagent should be prepared immediately before use and all residues disposed of immediately after use. Dispose of any residues by acidifying them with 5% hydrochloric acid and then placing them in a waste container designated for this purpose. On standing, the reagent tends to form silver fulminate, a *very explosive* substance. Solutions containing the mixed Tollens reagent should never be stored.

Reagents. *Solution A:* Dissolve 3.0 g of silver nitrate in 30 mL of water. *Solution B:* Prepare a 10% sodium hydroxide solution.

Discussion

Most aldehydes reduce ammoniacal silver nitrate solution to give a precipitate of silver metal. The aldehyde is oxidized to a carboxylic acid:



Ordinary ketones do not give a positive result in this test. The test should be used only if it has already been shown that the unknown compound is either an aldehyde or a ketone.

Chromic Acid Test: Alternative Test

CAUTION



Many chromium (VI) compounds are suspected carcinogens. If you would like to run this test, talk to your instructor first. Most often, the Tollens test will easily distinguish between aldehydes and ketones, and you should do that test first. If you run the chromic acid test, be sure to wear gloves to avoid contact with this reagent.

Procedure. Dissolve 1 drop of a liquid or 10 mg (approximate) of a solid aldehyde in 1 mL of *reagent-grade* acetone. Add several drops of the chromic acid reagent, a drop at a time, while shaking the mixture. A positive test is indicated by a green precipitate and a loss of the orange color in the reagent. With aliphatic aldehydes, RCHO, the solution turns cloudy within 5 seconds, and a precipitate appears within 30 seconds. With aromatic aldehydes, ArCHO, it generally takes 30–120 seconds for a precipitate to form, but with some it may take even longer. In some cases, however, you may find that some of the original orange color may remain, together with a green or brown precipitate. This should be interpreted as a positive test. In a negative test, a nongreen precipitate may form in an orange solution.

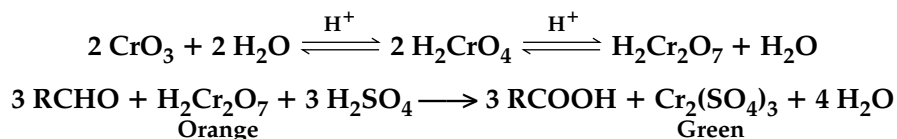
In performing this test, make sure that the acetone used for the solvent does not give a positive test with the reagent. Add several drops of the chromic acid reagent to a few drops of the reagent acetone contained in a small test tube. Allow this mixture to stand for 3–5 minutes. If no reaction has occurred by this time, the acetone is pure enough to use as a solvent for the test. If a positive test resulted, try another bottle of acetone.

Test Compounds. Try the test on benzaldehyde, butanal (butyraldehyde), and cyclohexanone.

Reagent. Dissolve 20 g of chromium trioxide (CrO_3) in 60 mL of cold water in a beaker. With stirring, slowly and carefully add 20 mL of concentrated sulfuric acid to the solution. This reagent should be prepared fresh each time.

Discussion

This test has as its basis on the fact that aldehydes are easily oxidized to the corresponding carboxylic acid by chromic acid. The green precipitate is due to chromous sulfate.



Primary and secondary alcohols are also oxidized by this reagent (see Experiment 55H). Therefore, this test is not useful in identifying aldehydes *unless* a positive identification of the carbonyl group has already been made. Aldehydes give a 2,4-dinitrophenylhydrazine test result, whereas alcohols do not.

There are numerous other tests used to detect the aldehyde functional group. Most are based on an easily detectable oxidation of the aldehyde to a carboxylic acid. The most common tests are the Tollens, Fehling's, and Benedict's tests. Only the Tollens test is described in this book. The Tollens test is often more reliable than the chromic acid test for aldehydes.

Iodoform Test

Procedure. Prepare a 60–70°C water bath in a beaker. Using a Pasteur pipet, add 6 drops of a liquid unknown to a 15-mm x 100-mm or 15-mm x 125-mm test tube. Alternatively, 0.06 g of the unknown solid may be used. Dissolve the unknown liquid or solid compound in 2 mL of 1,2-dimethoxyethane. Add 2 mL of 10% aqueous sodium hydroxide solution, and place the test tube in the hot-water bath. Next add 4 mL of iodine–potassium iodide solution in 1-mL portions to the test tube. *Cork* the test tube and shake it after adding each portion of iodine reagent. Heat the mixture in the hot-water bath for about 5 minutes, shaking the test tube occasionally. It is likely that some or all of the dark color of the iodine reagent will be discharged.

If the dark color of the iodine reagent is still apparent following heating, add 10% sodium hydroxide solution until the dark color of the iodine reagent has been discharged. Shake the mixture in the test tube (corked) during the addition of sodium hydroxide. Care need not be taken to avoid adding excess sodium hydroxide.

After the dark iodine color of the solution has been discharged, fill the test tube with water to within 2 cm of the top. Cork the test tube and shake it vigorously. Allow the tube to stand for at least 15 minutes at room temperature. The appearance of a pale yellow precipitate of iodoform, CHI_3 , constitutes a positive test, indicating that the unknown is a methyl ketone

or a compound that is easily oxidized to a methyl ketone, such as a 2-alkanol. Other ketones will also decolorize the iodine solution, but they will not give a precipitate of iodoform *unless* there is an impurity of a methyl ketone present in the unknown.

The yellow precipitate usually settles out slowly onto the bottom of the test tube. Sometimes, the yellow color of iodoform is masked by a dark substance. If this is the case, cork the test tube and shake it vigorously. If the dark color persists, add more sodium hydroxide solution, and shake the test tube again. Then allow the tube to stand for at least 15 minutes. If there is some doubt as to whether the solid is iodoform, collect the precipitate on a Hirsch funnel and dry it. Iodoform melts at 119–121°C.

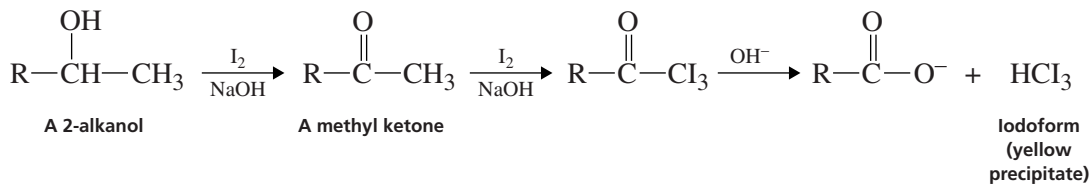
You may find on some occasions that methyl ketone gives only a yellow coloration to the solution rather than a distinct yellow precipitate. You should be cautious about drawing any conclusions from this result. Therefore, you should depend on proton NMR to confirm the presence of a methyl group attached directly to a carbonyl group (singlet at about 2 ppm).

Test Compounds. Try the test on 2-heptanone, 4-heptanone (dipropyl ketone), and 2-pentanol.

Reagents. The iodine reagent is prepared by dissolving 20 g of potassium iodide and 10 g of iodine in 100 mL of water. The aqueous sodium hydroxide solution is prepared by dissolving 10 g of sodium hydroxide in 100 mL of water.

Discussion

The basis of this test is the ability of certain compounds to form a precipitate of iodoform when treated with a basic solution of iodine. Methyl ketones are the most common types of compounds that give a positive result in this test. However, acetaldehyde, CH_3CHO , and alcohols with the hydroxyl group at the 2-position of the chain also give a precipitate of iodoform. 2-Alkanols of the type described are easily oxidized to methyl ketones under the conditions of the reaction. The other product of the reaction, besides iodoform, is the sodium or potassium salt of a carboxylic acid.



Ferric Chloride Test

Procedure. Some aldehydes and ketones, those that have a high **enol content**, give a positive ferric chloride test, as described for phenols in Experiment 55F.

Spectroscopy

Infrared

The carbonyl group is usually one of the strongest-absorbing groups in the infrared spectrum, with a very broad range: $1800\text{--}1650\text{ cm}^{-1}$. The aldehyde functional group has *very characteristic* C—H stretch absorptions: two sharp peaks that lie *far outside* the usual region for —C—H , =C—H or ≡C—H .

Aldehydes

C=O stretch at approximately
 1725 cm^{-1} is normal.
 1725–1685 cm^{-1} .*

C—H stretch (aldehyde—CHO)
 has two weak bands at about
 2750 cm^{-1} and 2850 cm^{-1} .

See Technique 25 for details.

Ketones

C=O stretch at approximately
 1715 cm^{-1} is normal.
 1780–1665 cm^{-1} .*

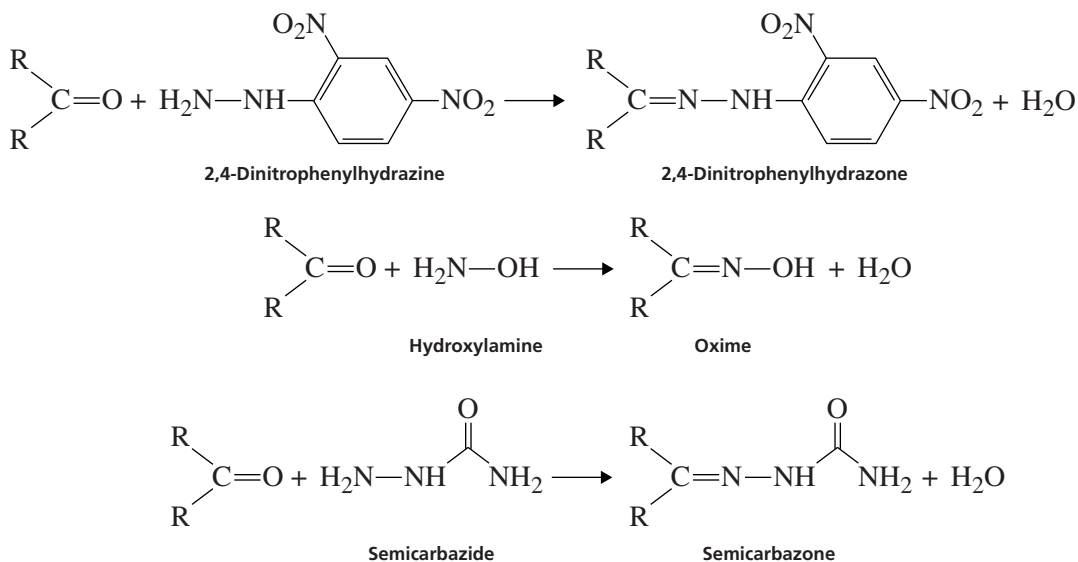
Nuclear Magnetic Resonance

Hydrogens alpha to a carbonyl group have resonance in the region between 2 ppm and 3 ppm. The hydrogen of an aldehyde group has a characteristic resonance between 9 ppm and 10 ppm. In aldehydes, there is coupling between the aldehyde hydrogen and any alpha hydrogens ($J = 1\text{--}3$ Hz).

See Technique 26 for details on proton NMR. Carbon NMR is described in Technique 27.

Derivatives

The most common derivatives of aldehydes and ketones are 2,4-dinitrophenylhydrazones, oximes, and semicarbazones. Procedures for preparing these derivatives are given in Appendix 2.

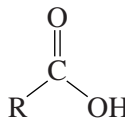


***Conjugation** moves the absorption to lower frequencies. **Ring strain** (cyclic ketones) moves the absorption to higher frequencies.

55E

EXPERIMENT 55E

Carboxylic Acids



Carboxylic acids are detectable mainly by their solubility characteristics. They are soluble in *both* dilute sodium hydroxide and sodium bicarbonate solutions.

Solubility Characteristics					Classification Tests
HCl (-)	NaHCO ₃ (+)	NaOH (+)	H ₂ SO ₄ (+)	Ether (+)	pH of an aqueous solution
Water: < C ₆ (+)					Sodium bicarbonate
> C ₆ (-)					Silver nitrate
					Neutralization equivalent

SUGGESTED 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.

CLASSIFICATION TESTS

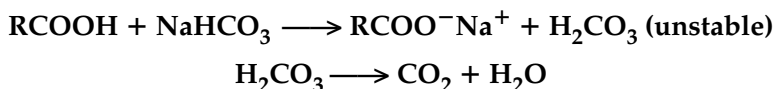
pH of an Aqueous Solution

Procedure. If the compound is soluble in water, simply prepare an aqueous solution and check the pH with pH paper. If the compound is an acid, the solution will have a low pH.

Compounds that are insoluble in water can be dissolved in ethanol (or methanol) and water. First, dissolve the compound in the alcohol, and then add water until the solution *just* becomes cloudy. Clarify the solution by adding a few drops of the alcohol, and then determine its pH using pH paper.

Sodium Bicarbonate

Procedure. Dissolve a small amount of the compound in a 5% aqueous sodium bicarbonate solution. Observe the solution carefully. If the compound is an acid, you may see bubbles of carbon dioxide form. In some cases with solids, the evolution of carbon dioxide may not be that obvious.



Silver Nitrate

Procedure. Acids may give a false silver nitrate test, as described in Experiment 55B.

Neutralization Equivalent (Optional)

Procedure. Accurately weigh (to three significant figures) approximately 0.2 g of the acid and place in a 125-mL Erlenmeyer flask. Dissolve the acid in about 50 mL of water or aqueous ethanol (the acid need not dissolve completely, because it will dissolve as it is titrated). Titrate the acid using a solution of sodium hydroxide of known molarity (about 0.1 M) and a phenolphthalein indicator.

Calculate the neutralization equivalent (NE) from the equation

$$\text{NE} = \frac{\text{mg acid}}{\text{molarity of NaOH} \times \text{mL of NaOH added}}$$

The NE is identical to the equivalent weight of the acid. If the acid has only one carboxyl group, the neutralization equivalent and the molecular weight of the acid are identical. If the acid has more than one carboxyl group, the neutralization equivalent equals the molecular weight of the acid divided by the number of carboxyl groups, that is, the equivalent weight. The NE can be used much like a derivative to identify a specific acid.

Some phenols are not sufficiently acidic to behave much like carboxylic acids. This is especially true of those substituted with electron-withdrawing groups at the *ortho* and *para* ring positions. These phenols, however, can usually be eliminated either by the ferric chloride test (see Experiment 55F) or by spectroscopy (phenols have no carbonyl group).

Spectroscopy**Infrared**

C=O stretch is very strong and often broad in the region between 1725 cm^{-1} and 1690 cm^{-1} .

O—H stretch has a very broad absorption in the region between 3300 cm^{-1} and 2500 cm^{-1} ; it usually overlaps the CH stretch region.

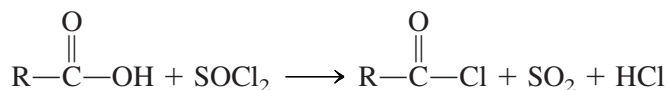
See Technique 25 for details.

Nuclear Magnetic Resonance

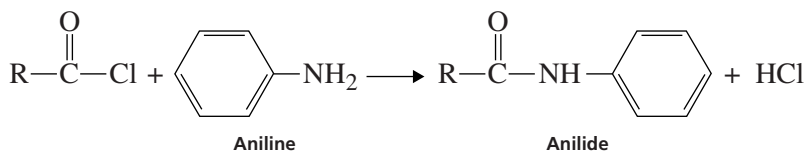
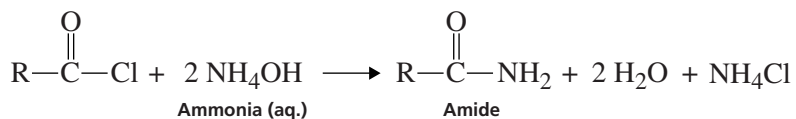
The acid proton of a —COOH group usually has resonance near 12.0 ppm. See Technique 26 for details. Carbon NMR is described in Technique 27.

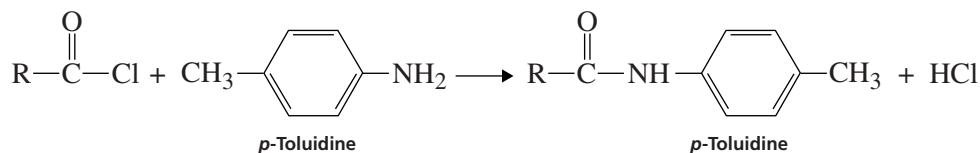
Derivatives

Derivatives of acids are usually amides. They are prepared via the corresponding acid chloride:



The most common derivatives are the amides, the anilides, and the *p*-toluidides.



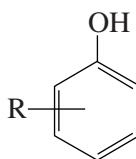


Procedures for the preparation of these derivatives are given in Appendix 2.

55F

EXPERIMENT 55F

Phenols



Like carboxylic acids, phenols are acidic compounds. However, except for the nitro-substituted phenols (discussed in the section covering solubilities), they are not as acidic as carboxylic acids. The $\text{p}K_{\text{a}}$ of a typical phenol is 10, whereas the $\text{p}K_{\text{a}}$ of a carboxylic acid is usually near 5. Hence, phenols are generally not soluble in the weakly basic sodium bicarbonate solution, but they dissolve in sodium hydroxide solution, which is more strongly basic.

Solubility Characteristics

Classification Tests

HCl	NaHCO ₃	NaOH	H ₂ SO ₄	Ether
(-)	(-)	(+)	(+)	(+)

Colored phenolate anion
Ferric chloride

Water: Most are insoluble, although phenol itself and the nitrophenols are soluble.

Ce(IV) Test
Bromine/water

SUGGESTED 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.

CLASSIFICATION TESTS

Sodium Hydroxide Solution

With phenols that have a high degree of conjugation possible in their conjugate base (phenolate ion), the anion is often colored. To observe the color, dissolve a small amount of the phenol in 10% aqueous sodium hydroxide solution. Some phenols do not give a color. Others have an insoluble anion and give a precipitate. The more acidic phenols, such as the nitrophenols, tend more toward colored anions.

Ferr Chloride

Procedure. Add about 50 mg of the unknown solid (2 mm or 3 mm off the end of a spatula) or 5 drops of the liquid unknown to 1 mL of water. Stir the mixture with a spatula so that as much as possible of the unknown dissolves in water. Add several drops of a 2.5% aqueous solution of ferric chloride to the mixture. Most water-soluble phenols produce an intense red, blue, purple, or green color. Some colors are transient, and it may be necessary to observe the solution carefully just as the solutions are mixed. The formation of a color is usually immediate, but the color may not last over any great period. Some phenols do not give a positive result in this test, so a negative test must not be taken as significant without other adequate evidence.

Test Compound. Try this test on phenol.

Discussion

The colors observed in this test result from the formation of a complex of the phenols with Fe(III) ion. Carbonyl compounds that have a high enol content also give a positive result in this test. The ferric chloride test works best with water-soluble phenols. A more reliable test, especially for water insoluble phenols, is the Ce(IV) test.

Cerium(IV) Test

Add 3 mL of 1,2-dimethoxyethane to 0.5 mL of Cerium(IV) reagent in a dry test tube. Gently shake the solution to thoroughly mix it, and then add 4 drops of a liquid compound to be tested. If you have a solid, you can directly add a few milligrams of the solid to the solution. Enough will dissolve to test if an —OH group is present. Gently shake the mixture, and look for an immediate color change from a yellow-orange solution to a red-orange or a deep red color indicating the presence of a phenol. The unsubstituted phenol, C₆H₅-OH, forms a dark-brown precipitate. Other phenols should yield a deep-red solution.

Test Compounds. Try this test on β-naphthol (2-naphthol).

Reagent. Prepare 2 M nitric acid solution by diluting 12.8 mL of concentrated nitric acid to 100 mL with water. Dissolve 8 g of ceric ammonium nitrate [Ce(NH₄)₂(NO₃)₆] in 20 mL of the dilute nitric acid solution.

Discussion

The Ce(IV) test provides a more reliable way of detecting the presence of the hydroxyl group in water-insoluble phenols than the ferric chloride test. Since alcohols also give a color change with this reagent, you will first need to distinguish between alcohols and phenols by determining the solubility behavior of your compound. Phenols should be soluble in sodium hydroxide, whereas alcohols will not dissolve in aqueous sodium hydroxide.

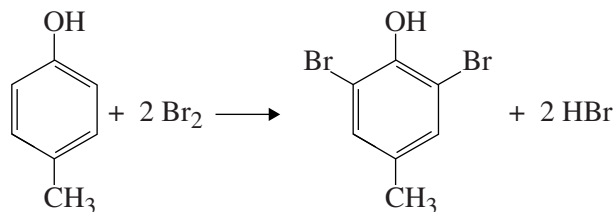
Bromine Water

Procedure. Prepare a 1% aqueous solution of the unknown, and then add a saturated solution of bromine in water to it, drop by drop while shaking, until the bromine color is no longer discharged. A positive test is indicated by the precipitation of a substitution product at the same time that the bromine color of the reagent is discharged.

Test Compound. Try this test on a 1% aqueous phenol solution.

Discussion

Aromatic compounds with ring-activating substituents give a positive test with bromine in water. The reaction is an aromatic substitution reaction that introduces bromine atoms into the aromatic ring at the positions *ortho* and *para* to the hydroxyl group. All available positions are usually substituted. The precipitate is the brominated phenol, which is generally insoluble because of its large molecular weight.



Other compounds that give a positive result with this test include aromatic compounds that have activating substituents other than hydroxyl. These compounds include anilines and alkoxyaromatics.

Spectroscopy

Infrared

O—H stretch is observed near 3400 cm^{-1} .

C—O stretch is observed near 1200 cm^{-1} .

The typical aromatic ring absorptions between 1600 cm^{-1} and 1450 cm^{-1} are also found. Aromatic C—H is observed near 3100 cm^{-1} .

See Technique 25 for details.

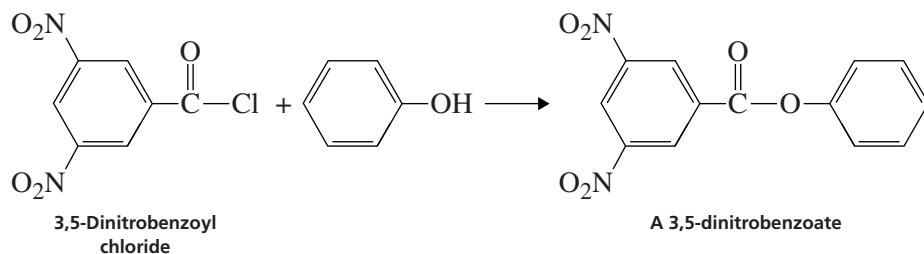
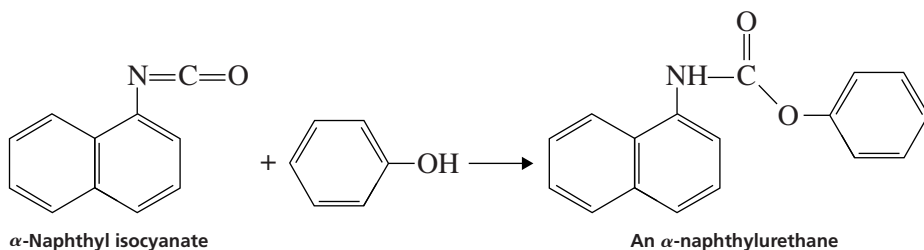
Nuclear Magnetic Resonance

Aromatic protons are observed near 7 ppm. The hydroxyl proton has a resonance position that is concentration dependent.

See Technique 26 for details. Carbon NMR is described in Technique 27.

Derivatives

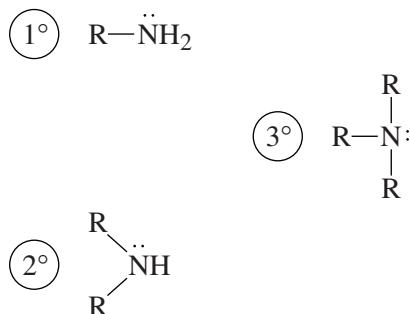
Phenols form the same derivatives as alcohols (see Experiment 55H). They form urethanes on reaction with isocyanates. Phenylurethanes are used for alcohols, and the α -naphthylurethanes are more useful for phenols. Like alcohols, phenols yield 3,5-dinitrobenzoates.



The bromine–water reagent yields solid bromo derivatives of phenols in several cases. These solid derivatives can be used to characterize an unknown phenol. Procedures for preparing these derivatives are given in Appendix 2.

55G EXPERIMENT 55G

Amines



Amines are detected best by their solubility behavior and their basicity. They are the only basic compounds that will be issued for this experiment. Hence, once the compound has been identified as an amine, the main problem that remains is to decide whether it is primary (1°), secondary (2°), or tertiary (3°). This can usually be decided either by the nitrous acid tests or by infrared spectroscopy.

Solubility Characteristics					Classification Tests
HCl	NaHCO ₃	NaOH	H ₂ SO ₄	Ether	pH of an aqueous solution
(+)	(-)	(-)	(+)	(+)	Hinsberg test
Water: < C ₆ (+)					Nitrous acid test
> C ₆ (-)					Acetyl chloride

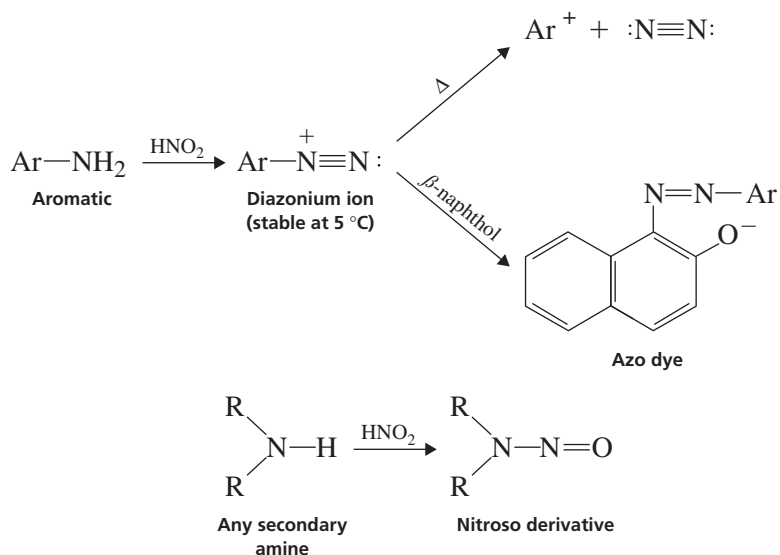
SUGGESTED WASTE DISPOSAL

Residues from the nitrous acid test should be poured into a waste container containing 6 M hydrochloric acid. 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.

CLASSIFICATION TESTS

Nitrous Acid Test

Procedure. Dissolve 0.1 g of an amine in 2 mL of water to which 8 drops of concentrated sulfuric acid have been added. Use a large test tube. Often, a considerable amount of solid

**Hinsberg Test**

A traditional method for classifying amines is the **Hinsberg test**. A discussion of this test can be found in the comprehensive textbooks listed prior to Section 55A. We have found that infrared spectroscopy is a more reliable method for distinguishing between primary, secondary, and tertiary amines.

pH of an Aqueous Solution

Procedure. If the compound is soluble in water, simply prepare an aqueous solution and check the pH with pH paper. If the compound is an amine, it will be basic and the solution will have a high pH. Compounds that are insoluble in water can be dissolved in ethanol–water or 1,2-dimethoxyethane–water.

Acetyl Chloride

Procedure. Primary and secondary amines give a positive acetyl chloride test result (liberation of heat). This test is described for alcohols in Experiment 55H. Cautiously add dropwise the acetyl chloride to the liquid amine. This reaction can be very exothermic and violent! When the test mixture is diluted with water, primary and secondary amines often give a solid acetamide derivative; tertiary amines do not.

Test Compounds. Try this test with aniline and butylamine.

Spectroscopy**Infrared**

N—H stretch. Both aliphatic and aromatic primary amines show two absorptions (doublet due to symmetric and asymmetric stretches) in the region 3500–3300 cm^{-1} . Secondary amines show a single absorption in this region. Tertiary amines have no N—H bonds.

N—H bend. Primary amines have a strong absorption at 1640–1560 cm^{-1} . Secondary amines have an absorption at 1580–1490 cm^{-1} .

Aromatic amines show bands typical for the aromatic ring in the region 1600–1450 cm^{-1} .

Aromatic C—H is observed near 3100 cm^{-1} .

See Technique 25 for details.

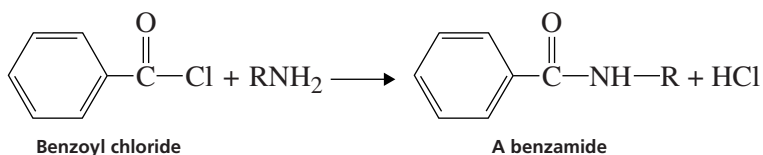
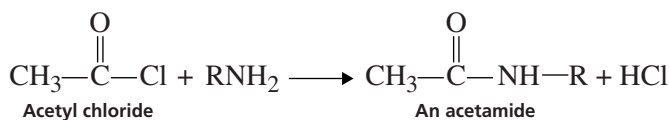
Nuclear Magnetic Resonance

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.

See Technique 26 for details. Carbon NMR is described in Technique 27.

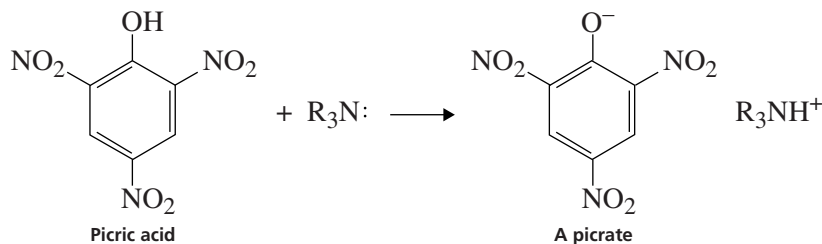
Derivatives

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.

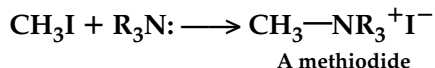


The most general derivative that can be prepared is the picric acid salt, or picrate, of an amine. This derivative can be used for primary, secondary, and tertiary amines.

Great care must be taken when working with saturated solutions of picric acid. Picric acid may detonate when heated above 300 °C! It is also known to explode when heated rapidly. For this reason, it is strongly recommended that you check with your instructor before preparing this derivative.



For tertiary amines, the methiodide salt is often useful.



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

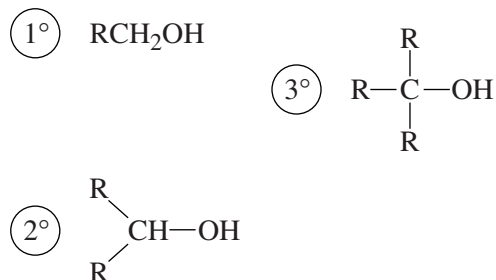
55H

EXPERIMENT 55H

Alcohols

Alcohols are neutral compounds. The only other classes of neutral compounds used in this experiment are the aldehydes, ketones, and esters. Alcohols and esters usually do not give a positive 2,4-dinitrophenylhydrazine test; aldehydes and ketones do. Esters do not react with Ce(IV) or 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 ₃	NaOH	H ₂ SO ₄	Ether	Cerium(IV) test
(-)	(-)	(-)	(+)	(+)	Acetyl chloride
Water: < C ₆ (+)					Lucas test
> C ₆ (-)					Chromic acid test
					Iodoform test

SUGGESTED 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

Cerium (IV) Test

Procedure for Water-Soluble or Partially Soluble Compounds. Add 3 mL of water to 0.5 mL of Cerium(IV) reagent in a test tube. Gently shake the solution to thoroughly mix it, and then add 4 drops of the compound to be tested. Gently shake the mixture and look for an immediate color change from a yellow-orange solution to a red-orange or deep red color indicating the presence of an —OH group in an alcohol or phenol. Phenol forms a dark-brown precipitate.

Test Compounds. Try this test on 1-butanol, 2-pentanol, 2-methyl-2-butanol, phenol, butanal, cyclohexanone, and ethyl acetate.

Procedure for Water-Insoluble Compounds. Add 3 mL of 1,2-dimethoxyethane to 0.5 mL of Cerium(IV) reagent in a dry test tube. Gently shake the solution to thoroughly mix it, and then add 4 drops of a liquid compound to be tested. If you have a solid, you can directly add a few milligrams of the solid to the solution. Enough will dissolve to test if an —OH group

is present. Gently shake the mixture, and look for an *immediate color change* from a yellow-orange solution to a reddish-brown color indicating the presence of an alcohol or phenol.

Test Compounds. Try this test 1-octanol, β -naphthol (2-naphthol), and benzoic acid.

Reagent. Prepare 2 M nitric acid solution by diluting 12.8 mL of concentrated nitric acid with 100 mL of water. Dissolve 8 g of ceric ammonium nitrate $[\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6]$ in 20 mL of the dilute nitric acid solution.

Discussion

Primary, secondary, and tertiary alcohols and phenols form 1:1 colored complexes with Ce(IV) and are an excellent way to detect hydroxyl groups. However, this is limited to compounds with no more than 10 carbon atoms. Unfortunately, the test cannot distinguish between primary, secondary, and tertiary alcohols. The Lucas test or chromium oxide test will have to be used for this purpose. Esters, ketones, carboxylic acids, and simple aldehydes do not change the color of the reagent and give a negative test with the Ce(IV) reagent. Thus, esters and other neutral compounds can be distinguished from alcohols by this test. Amines produce a flocculent white precipitate with the reagent. Cerium solutions can oxidize alcohols, but this usually occurs when the solution is heated or when the alcohol is in contact with the reagent for long periods.

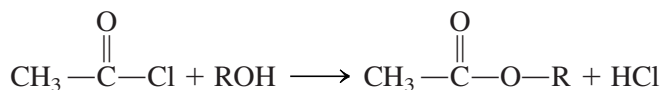
Acetyl Chloride

Procedure. Cautiously add about 5–10 drops of acetyl chloride, drop by drop, to about 0.25 mL of the liquid alcohol contained in a small test tube. Evolution of heat and hydrogen chloride gas indicates a positive reaction. Check for the evolution of HCl with a piece of wet blue litmus paper. Hydrogen chloride will turn the litmus paper red. Adding water will sometimes precipitate the acetate.

Test Compounds. Try this test with 1-butanol.

Discussion

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 55G). This test does not work well with solid alcohols.

Lucas Test

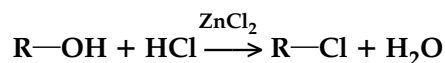
Procedure. Place 2 mL of Lucas reagent in a small test tube, and add 3–4 drops of the alcohol. Stopper the test tube and shake it vigorously. Tertiary (3°), benzylic, and allylic alcohols give an immediate cloudiness in the solution as the insoluble alkyl halide separates from the aqueous solution. After a short time, the immiscible alkyl halide may 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 (no cloudiness). 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.

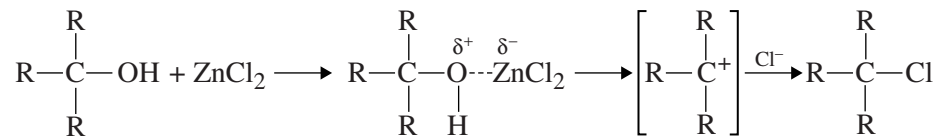
Test Compounds. Try this test with 1-butanol (*n*-butyl alcohol), 2-butanol (*sec*-butyl alcohol), and 2-methyl-2-propanol (*t*-butyl alcohol).

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 55B. 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 or liquid alcohols containing six or more carbon atoms.

Chromic Acid Test: Alternative Test

CAUTION



Many chromium(VI) compounds are suspected carcinogens. If you would like to run this test, talk to your instructor first. The Lucas test will distinguish between 1°, 2°, and 3° alcohols, and you should do that test first. If you run the chromic acid test, be sure to wear gloves to avoid contact with this reagent.

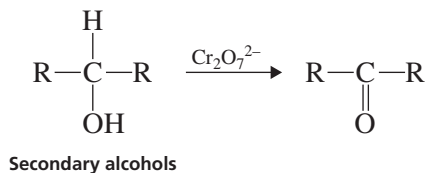
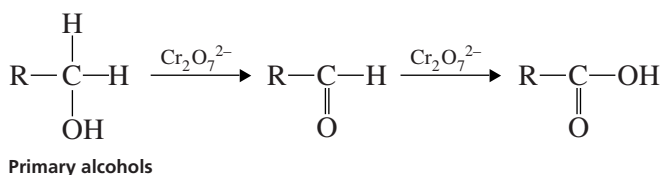
Procedure. Dissolve 1 drop of a liquid or about 10 mg of a solid alcohol in 1 mL of *reagent-grade* acetone. Add 1 drop of the chromic acid reagent, and note the result that occurs within 2 seconds. A positive test for a primary or a secondary alcohol is the appearance of a blue-green color. Tertiary 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 1 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).

Reagent. Dissolve 20 g of chromium trioxide (CrO_3) in 60 mL of cold water in a beaker. Add a magnetic stir bar to the solution. With stirring, slowly and carefully add 20 mL of concentrated sulfuric acid to the solution. This reagent should be prepared fresh each term.

Discussion

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.



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 (see Experiment 55D). 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 55D.

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 cm^{-1} . In more concentrated solutions, or with considerable hydrogen bonding, there is a broad absorption near 3400 cm^{-1} . Sometimes both bands appear.

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

See Technique 25 for details.

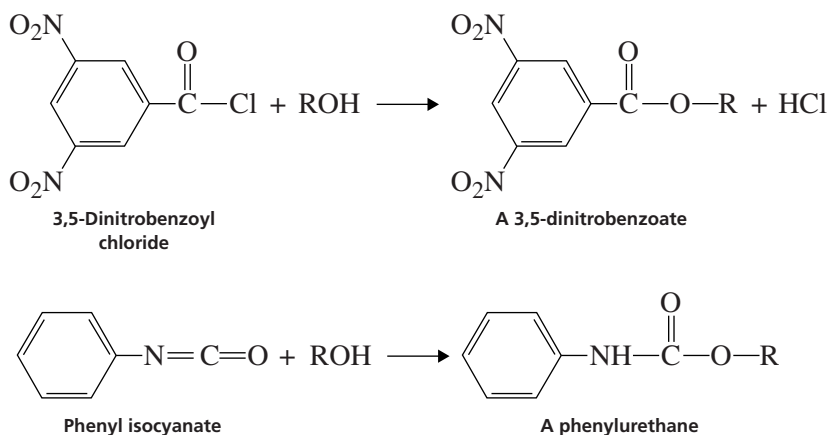
Nuclear Magnetic Resonance

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

See Technique 26 for details. Carbon NMR is described in Technique 27.

Derivatives

The most common derivatives for alcohols are the 3,5-dinitrobenzoate esters and the phenylurethanes. Occasionally, the α -naphthylurethanes (Experiment 55F) are also prepared, but these latter derivatives are more often used for phenols.

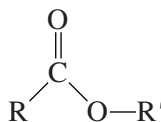


Procedures for preparing these derivatives are given in Appendix 2.

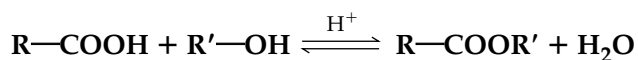
55I

EXPERIMENT 55I

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.

Solubility Characteristics					Classification Tests
HCl	NaHCO ₃	NaOH	H ₂ SO ₄	Ether	Ferric hydroxamate test
(-)	(-)	(-)	(+)	(+)	Basic hydrolysis
Water: < C ₄ (+)					
> C ₅ (-)					

SUGGESTED WASTE DISPOSAL

Solutions containing hydroxylamine or derivatives formed from it should be placed in a beaker containing 6 M hydrochloric acid. Dispose of any 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

Ferric Hydroxamate Test

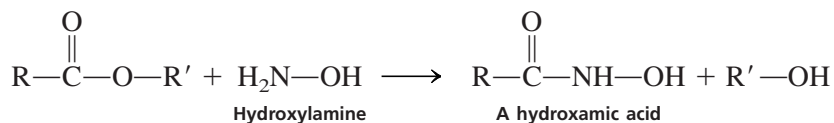
Procedure. Before starting, you must determine whether the compound to be tested already has enough enolic character in acid solution to give a positive ferric chloride test. Dissolve 1 or 2 drops of the unknown liquid or a few crystals of the unknown solid in 1 mL of 95% ethanol, and add 1 mL of 1 M hydrochloric acid. Add 1 or 2 drops of 5% ferric chloride solution. If a burgundy, magenta, or reddish-brown color appears, the ferric hydroxamate test cannot be used. It contains enolic character (see Experiment 55F).

If the compound did not show enolic character, continue as follows. Dissolve 5 or 6 drops of a liquid ester, or about 40 mg of a solid ester, in a mixture of 1 mL of 0.5 M hydroxylamine hydrochloride (dissolved in 95% ethanol) and 0.4 mL of 6 M sodium hydroxide. Heat the mixture till it boils for a few minutes. Cool the solution and then add 2 mL of 1 M hydrochloric acid. If the solution becomes cloudy, add 2 mL of 95% ethanol to clarify it. Add a drop of 5% ferric chloride solution, and note whether a color is produced. If the color fades, continue to add ferric chloride until the color persists. A positive test should give a deep burgundy, magenta, or reddish-brown color.

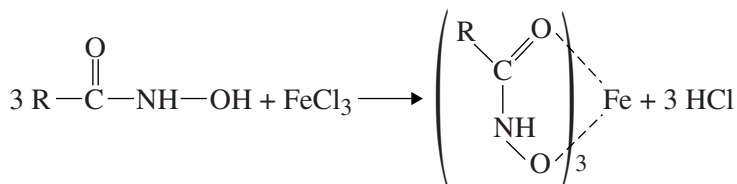
Test Compound. Try this test with ethyl butanoate.

Discussion

On being heated with hydroxylamine, esters are converted to the corresponding hydroxamic acids.



The hydroxamic acids form strong, colored complexes with ferric ion.



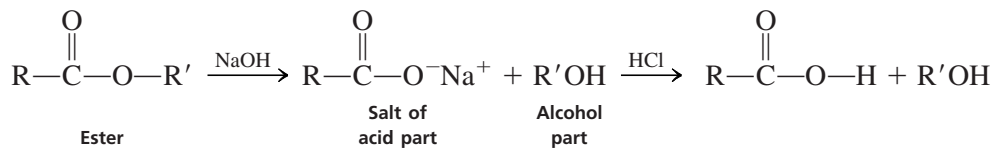
Basic Hydrolysis (Optional)

Procedure. Place 0.7 g of the ester in a 10-mL round-bottom flask with 7 mL of 25% aqueous sodium hydroxide. Add a boiling stone and attach a water condenser. Use a small amount of stopcock grease to lubricate the ground-glass joint. Boil the mixture for about 30 minutes. Stop the heating, and observe the solution to determine whether the oily ester layer has disappeared or whether the odor of the ester (usually pleasant) has disappeared. Low-boiling esters (below 110°C) usually dissolve within 30 minutes if the alcohol part has a low molecular weight. If the ester has not dissolved, reheat the mixture to reflux for 1–2 hours. After that time, the oily ester layer should have disappeared, along with the characteristic odor. Esters with boiling points up to 200°C should hydrolyze during this time. Compounds remaining after this extended period of heating are either unreactive esters or are not esters at all.

For esters derived from solid acids, the acid part can, if desired, be recovered after hydrolysis. Extract the basic solution with ether to remove any unreacted ester (even if it appears to be gone), acidify the basic solution with hydrochloric acid, and extract the acidic phase with ether to remove the acid. Dry the ether layer over anhydrous sodium sulfate, decant, and evaporate the solvent to obtain the parent acid from the original ester. The melting point of the parent acid can provide valuable information in the identification process.

Discussion

This procedure converts the ester to its separate acid and alcohol parts. The ester dissolves because the alcohol part (if small) is usually soluble in the aqueous medium, as is the sodium salt of the acid. Acidification produces the parent acid.



All derivatives of carboxylic acids are converted to the parent acid on basic hydrolysis. Thus, amides, which are not covered in this experiment, would also dissolve in this test, liberating the free amine and the sodium salt of the carboxylic acid.

Spectroscopy

Infrared

The ester–carbonyl group (C=O) peak usually indicates a strong absorption, as is the absorption of the carbonyl–oxygen link (C–O) to the alcohol part. C=O stretch at approximately 1735 cm^{-1} is normal.¹ C–O stretch usually gives two or more absorptions, one stronger than the others, in the region $1280\text{--}1051\text{ cm}^{-1}$.

See Technique 25 for details.

Nuclear Magnetic Resonance

Hydrogens that are alpha to an ester carbonyl group have resonance in the region 2–3 ppm. Hydrogens alpha to the alcohol oxygen of an ester have resonance in the region 3–5 ppm.

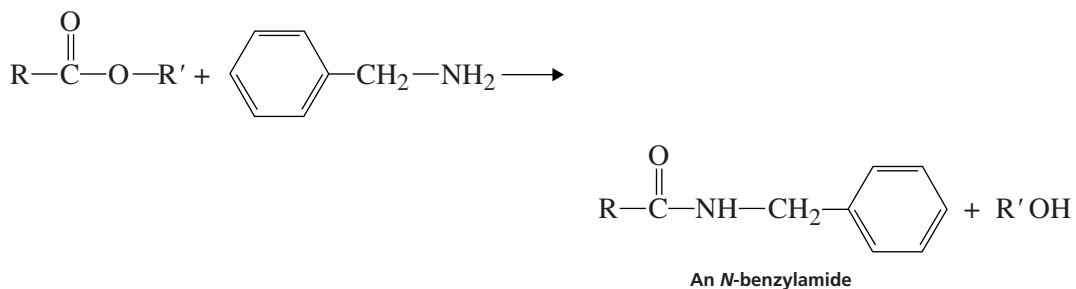
See Technique 26 for details. Carbon NMR is described in Technique 27.

Derivatives

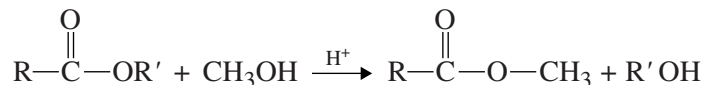
Esters present a double problem when trying to prepare derivatives. To characterize an ester completely, you need to prepare derivatives of *both* the acid part and the alcohol part.

Acid Part

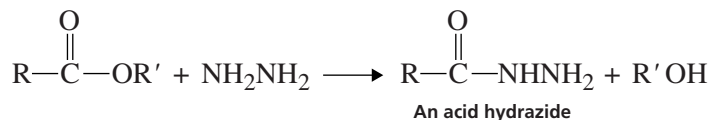
The most common derivative of the acid is the *N*-benzylamide derivative.



The reaction does not proceed well unless R⁺ is methyl or ethyl. For alcohol portions that are larger, the ester must be transesterified to a methyl or an ethyl ester before preparing the derivative.



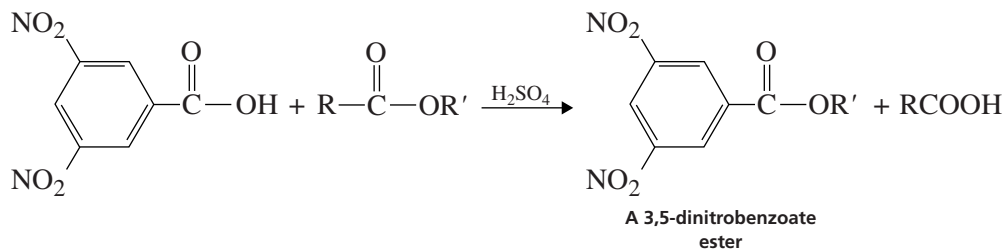
Hydrazine also reacts well with methyl and ethyl esters to give acid hydrazides.



¹Conjugation with the carbonyl group moves the carbonyl absorption to lower frequencies. Conjugation with the alcohol oxygen raises the carbonyl absorption to higher frequencies. Ring strain (lactones) moves the carbonyl absorption to higher frequencies.

Alcohol Part

The best derivative of the alcohol part of an ester is the 3,5-dinitrobenzoate ester, which is prepared by an acyl interchange reaction.



Most esters are composed of very simple acid and alkyl portions. For this reason, spectroscopy is usually a better method of identification than is the preparation of derivatives. Not only is it necessary to prepare two derivatives with an ester, but all esters with the same acid portion, or all those with the same alcohol portion, give identical derivatives of those portions.