

Identification of Unknown Organic Compounds

Introduction

The identification and characterization of the structures of unknown substances are an important part of organic chemistry. Although it is often possible to establish the structure of a compound on the basis of spectra alone (IR, NMR, etc.), the spectra typically must be supplemented with other information about the compound: physical state and properties (melting point, boiling point, solubility, odor, color, etc.), elemental analysis, and confirmatory tests for functional groups.

In this experiment you will carry out several qualitative tests that will allow you to identify functional groups in organic molecules. You will then apply what you have learned by characterizing unknown organic compounds in terms of their functional group and solubility behavior. The functional groups you will examine include amines, alcohols, carboxylic acids, alkenes, alkanes, and alkyl halides.

Solubility and Functional Group Tests

Each functional group has a particular set of chemical properties that allow it to be identified. Some of these properties can be demonstrated by observing solubility behavior, while others can be seen in chemical reactions that are accompanied by color changes, precipitate formation, or other visible effects.

1. Solubility Tests

The solubility of an organic compound in water, dilute acid, or dilute base can provide useful information about the presence or absence of certain functional groups. A flowchart showing the sequence of solubility tests along with the appropriate conclusions is shown in **Figure 1**.

Solubility in water: Most organic compounds are not soluble in water, except for low molecular-weight amines and oxygen-containing compounds. Low molecular-weight compounds are generally limited to those with fewer than five carbon atoms.

- Carboxylic acids with fewer than five carbon atoms are soluble in water and form solutions that give an acidic response ($\text{pH} < 7$) when tested with litmus paper.
- Amines with fewer than five carbons are also soluble in water, and their solutions give a basic response ($\text{pH} > 7$) when tested with litmus paper.
- Ketones, aldehydes, and alcohols with fewer than five carbon atoms are soluble in water and form neutral solutions ($\text{pH} = 7$).

Solubility in NaOH: Solubility in 6M NaOH is a positive identification test for acids. A carboxylic acid that is insoluble in pure water will be soluble in base due to the formation of the sodium salt of the acid as the acid is neutralized by the base.

Solubility in HCl: Solubility in 6M HCl is a positive identification test for bases. Amines that are insoluble in pure water will be soluble in acid due to the formation of an ammonium chloride salt.

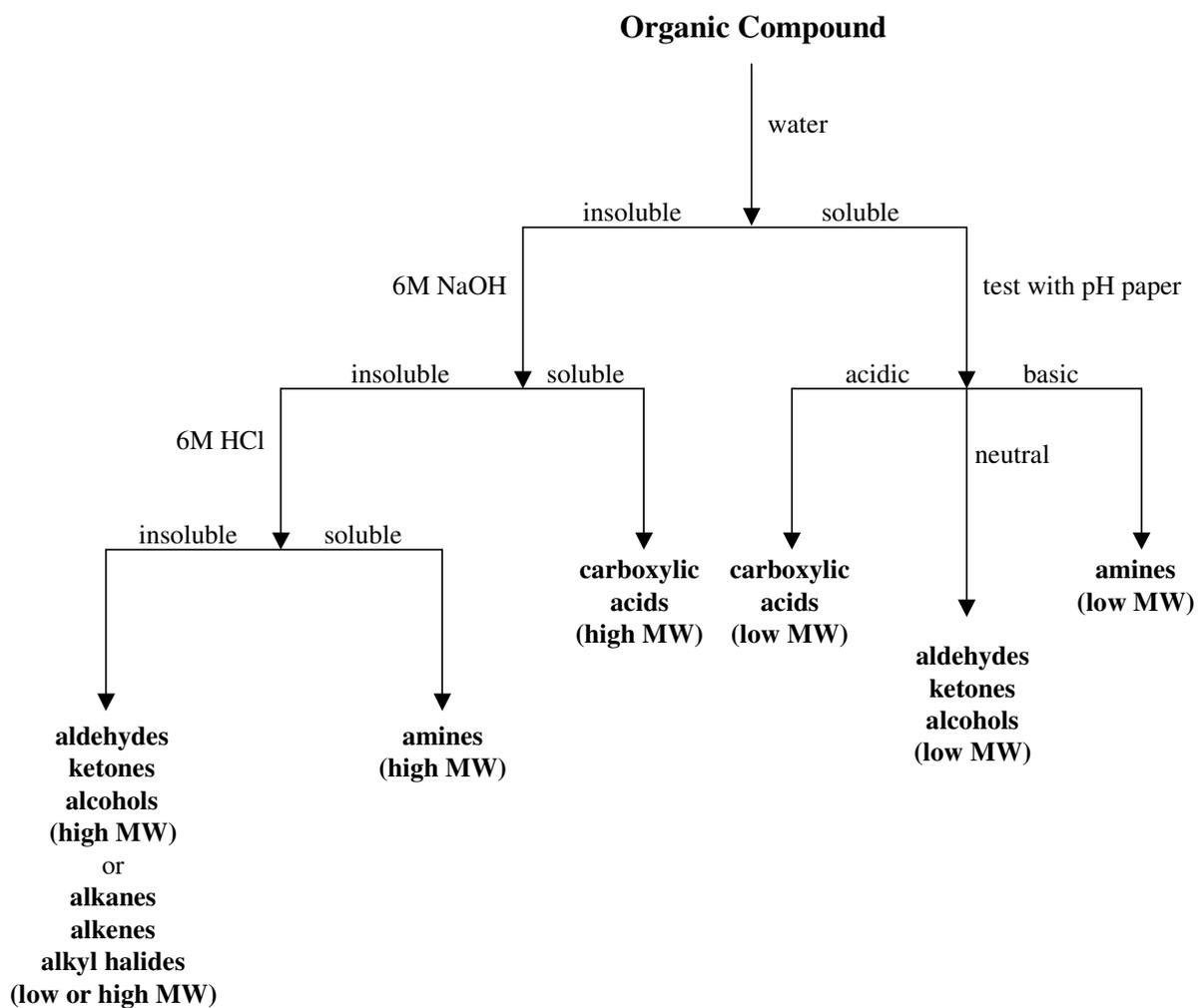


Figure 1. The Solubility Test Flowchart

2. Silver Nitrate Test for Alkyl Halides and Carboxylic Acids

The reaction of an alkyl halide with silver nitrate in ethanol will result in the formation of a white or yellow silver halide precipitate that is insoluble in nitric acid. This reaction quite often proceeds slowly, and occasionally slight warming is necessary.



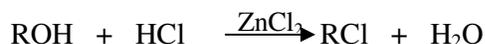
It is important to check if the precipitate is soluble in dilute nitric acid. Carboxylic acids form insoluble silver salts that precipitate, but these dissolve in nitric acid whereas the silver halides do not.

3. Beilstein Test for Halides

Halogens can be detected easily and reliably by the Beilstein test. It is the simplest method for determining the presence of a halogen, but does not differentiate among chlorine, bromine, and iodine. 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.

4. Lucas Test for Alcohols

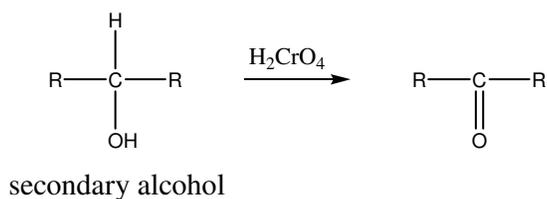
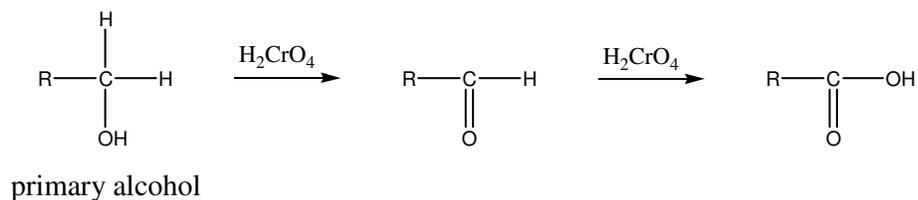
This test depends on the appearance of an alkyl chloride as an insoluble second layer when an alcohol is treated with a mixture of hydrochloric acid and zinc chloride (Lucas reagent):



Primary alcohols do not react at room temperature; therefore, the alcohol is seen simply to dissolve. Secondary alcohols will react slowly, whereas tertiary, benzylic, and allylic alcohols react instantly.

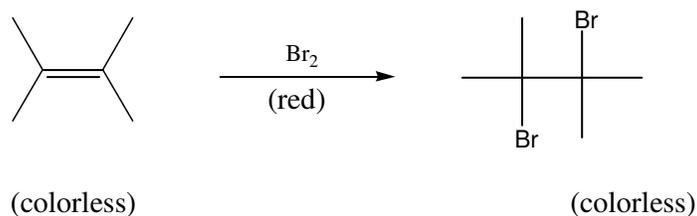
5. Chromic Acid Test for Alcohols

This test is based on the reduction of chromium(IV), 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. Tertiary alcohols are not oxidized at all by the reagent. Hence, this reaction can be used to distinguish tertiary alcohols from primary and secondary alcohols. Unlike the Lucas test, this test can be used with all alcohols, regardless of molecular weight and solubility.



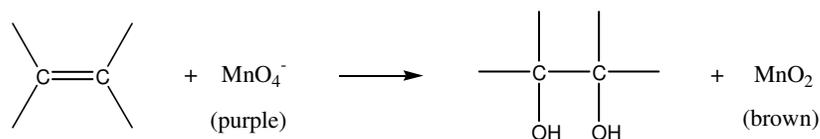
6. Bromination Test for Alkenes

Bromine readily adds across the carbon-carbon double bond of an alkene to produce a dibromoalkane. A red solution of bromine in methylene chloride will quickly become colorless as the addition reaction with the alkene takes place. The general equation describing the test is:



7. Potassium Permanganate Test for Alkenes

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 include aldehydes, some alcohols, phenols, and aromatic amines.

I. Lucas Test

- **Equipment**

Three small screw top vials, pipettes w/ bulbs, overhead projector.

- **Reagents**

1-butanol, 2-butanol, 2-methyl-2-propanol, Lucas reagent (16 g anhydrous zinc chloride dissolved in 10 mL concentrated hydrochloric acid).

- **Presentation**

1. Add 5 drops of an alcohol to a vial.
2. Repeat step one with the other two alcohols and separate vials.
3. Add three squeezes of the Lucas reagent to the primary alcohol vial, screw the lid on, shake vigorously, and lay the vial on its side on the center of the overhead projector.
4. Repeat step 2 for the secondary alcohol and then the tertiary alcohol.

- **Hazards**

Vapors of these three alcohols are mildly irritating to eyes, nose, throat, and are toxic upon inhalation. Liquid contact with eyes is irritating and may produce burns. Repeated contact with skin may dry (defat) and crack skin.

Hydrochloric acid can irritate the skin. Hydrochloric acid vapors are extremely irritating to the eyes and respiratory system. Therefore, it should be handled only in well-ventilated area.

- **Discussion**

The tertiary alcohol will react immediately to produce an insoluble alkyl halide. This makes the contents of the vial cloudy and the vial will appear black on the screen. The secondary alcohol reacts more slowly to produce the corresponding alkyl halide. The time varies from

approximately 1-3 minutes depending upon the temperature. The screen image will initially appear clear, but will gradually darken to black. The primary alcohol will not react, so its screen image is clear and remains so.

- **References**

1. Pavia, Lampman, Kriz, *Introduction to Organic Laboratory Techniques*, 2nd edition, Saunders College pub., **1982**, p. 427.
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II. Chromic Acid Test

- **Equipment**

Three 50 mL beakers w/ stir rods, pipettes w/ bulbs, overhead projector.

- **Reagents**

1-butanol, 2-butanol, 2-methyl-2-propanol, chromic acid (1 g chromium (VI) oxide dissolved in 1 mL of concentrated sulfuric acid and this diluted with 3 mL of DI water).

- **Presentation**

1. Add enough of the three alcohols to separate beakers to cover the bottoms.
2. Place the beakers on the overhead projector.
3. Add ~2 drops of the chromic acid solution (enough to give the mixture a definite yellow color) to a beaker and stir the contents.
4. Repeat step three for the other two beakers.

- **Hazards**

Vapors of these three alcohols are mildly irritating to eyes, nose, throat, and are toxic upon inhalation. Liquid contact with eyes is irritating and may produce burns. Repeated contact with skin may dry (defat) and crack skin.

Because sulfuric acid is both a strong acid and a powerful dehydrating agent, it must be handled with great care. The dilution of concentrated sulfuric acid is a highly exothermic process and releases sufficient heat

to cause burns. Therefore, when preparing dilute solutions from the concentrated acid, always add the acid to the water, slowly, with stirring and cooling the receiving beaker.

Both chromic oxide (VI) and chromic acid are powerful oxidizing agents and suspected human carcinogens. Contact with solid chromic anhydride may result in severe burns of eyes with possible permanent vision loss. Skin contact with solid chromic anhydride or with concentrated solutions of chromic acid causes burns with potential for major skin damage.

- **Discussion**

Primary and secondary alcohols will be oxidized to carboxylic acids and ketones respectively. The tertiary alcohol will not react. When the alcohol is oxidized, the Cr^{6+} (yellow/orange) is reduced to Cr^{3+} (blue/green). Therefore the appearance of a blue green color is indicative of a primary or secondary alcohol. The beakers that have reactions take place may become opaque from a variety of precipitates. The colors can still be viewed from the side.

- **References**

1. Pavia, Lampman, Kriz, *Introduction to Organic Laboratory Techniques*, 2nd edition, Saunders College pub., 1982, p. 427.

Lucas Test for Primary, Secondary, and Tertiary Alcohols
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1-butanol, 2-butanol, and 2-methyl-2-propanol are treated with a solution of ZnCl_2 in concentrated aqueous HCl.

Three test tubes contain a solution of zinc chloride (ZnCl_2) in concentrated aqueous hydrochloric acid (HCl). The primary alcohol 1-butanol, the secondary alcohol 2-butanol, and the tertiary alcohol 2-methyl-2-propanol are added to separate test tubes. Immediately the tertiary alcohol forms a cloudy solution as the alcohol is converted to the water insoluble alkyl chloride by a $\text{S}_{\text{N}}1$ reaction. The primary alcohol, 1-butanol, does not react. The secondary alcohol, 2-butanol, reacts after about 6.5 minutes.

Discussion

In sequence, 1-butanol, 2-butanol, and 2-methyl-2-propanol are treated with a solution of ZnCl_2 in concentrated aqueous HCl. Immediately the tertiary alcohol forms a cloudy solution as the alcohol is converted to the water insoluble alkyl chloride by a $\text{S}_{\text{N}}1$ reaction. The secondary alcohol, 2-butanol, reacts after about 6.5 minutes. The primary alcohol, 1-butanol, does not react.

