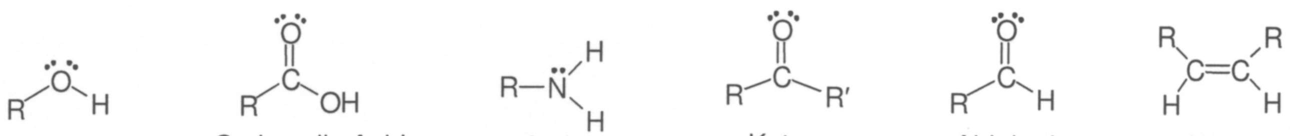
11. *Identification of an Unknown Organic Compound*

What you will accomplish in this experiment

This make-up lab provides you with the opportunity to:

- Identify the functional group of an unknown compound.
- Use a synthesis reaction to prepare a *"derivative"* of your organic compound.
- Purify the derivative by recrystallization.
- Determine the melting point of your recrystallized derivative.
- Use the melting point of the derivative to determine the identity of the unknown organic compound.

Your unknown compound will contain one of the following organic functional groups:



Alcohol	Carboxylic Acid	Amine	Ketone	Aldehyde	Alkene
ROH	RCOOH	RNH_2	RCOR	RCHO	RCH=CHR

The abbreviation "R" is used above to indicate an alkyl or aryl group. For example, a generic alcohol might have the formula R-OH. When the "R group" is a four-carbon chain, the alcohol becomes $CH_3CH_2CH_2CH_2OH$, 1-butanol.

Concepts you need to know to be prepared

You'll start by performing a sequence of simple diagnostic tests to determine the *presence of* (or indicate the *absence of*) particular organic functional groups.

The complete sequence is shown in the flow diagram at the top of the next page.

This diagram will serve you in several ways:

- It's a summary of the procedure that you'll follow in identifying your *unknown* compound as one of the organic functional groups, and as being *low* molecular weight (short carbon chain) or *high* molecular weight (longer carbon charin).
- It can order your thoughts as you read the discussion of each diagnostic test, and help you to understand the significance of that test.
- It can enhance your appreciation for and enjoyment of this experiment. Your role is that of organic chemist and detective: you'll use the flow chart to *sleuth out* the identity of your unknown's functionality.

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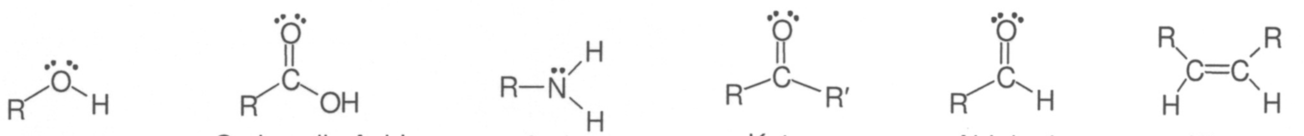

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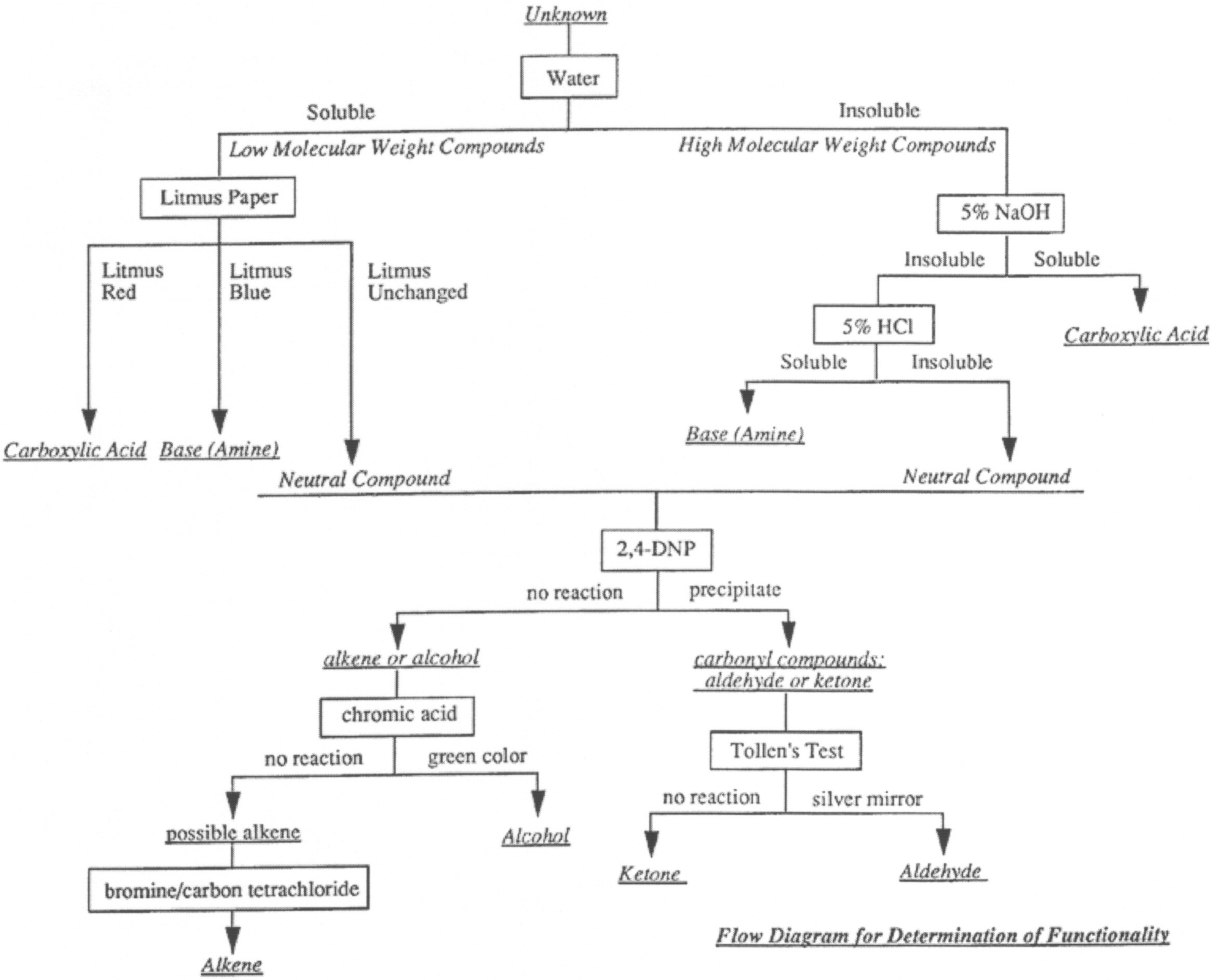
Discussion of Chemical Tests



Flow Diagram for Determination of Functionality

1. Water Solubility: Diagnosis of a Low Molecular Weight (Short Carbon Chain) Compound

Most organic compounds are insoluble or only slightly soluble in water. Water solubility is uncommon, and when observed, is an indication of a *LOW molecular weight* (*short carbon chain*) compound (fewer than five carbon atoms) with a polar functional group. Obviously, water solubility will *increase* with the number of polar functional groups present on the carbon chain.

If a low molecular weight compound is water-soluble, then the compound *might also* contain an ionizable carboxylic acid or amine functional group. The aqueous solution can be tested with litmus paper to diagnose the presence (or absence) of an acid or amine group.

A. *Acidic Response to Litmus: Diagnosis of a Low Molecular Weight Carboxylic Acid*

Carboxylic acids *donate* a proton to water, creating an acidic solution which will turn *blue* litmus paper *red.*

$$RCOOH \quad + \quad H_2O \rightleftharpoons RCOO^{\ominus} \quad + \quad H_3O^{\oplus}\ .$$

Carboxylic Acid — Blue Litmus turns Red

B. *Basic Response to Litmus: Diagnosis of a Low Molecular Weight Amine*

Amines are the organic derivatives of ammonia (NH_3), and like ammonia, they are weak bases. Amines *accept* a proton from water, creating a basic solution which will turn *red* litmus paper *blue.*

$$R\ddot{N}H_2 \quad + \quad H_2O \rightleftharpoons RNH_3^{\oplus} \quad + \quad \overset{\ominus}{O}H$$

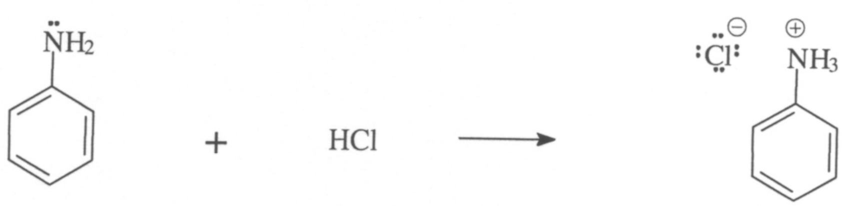
Amine — Red Litmus turns Blue

If an unknown compound is water soluble, but tests neutral to litmus, then the compound contains neither the carboxylic acid nor the amine functional group, and will require further testing to determine its functional group (see the Flow Chart).

2. *Solubility in 5% Hydrochloric Acid: Diagnosis of a High Molecular Weight Amine*

An *amine* with five or more carbon atoms, though *insoluble* in *water*, will be *soluble* in a 5% *HCl* solution because of the acid-base reaction to form the ammonium chloride salt.

For example, aniline, a six-carbon water-insoluble amine, reacts with hydrochloric acid to form the water-soluble aniline chloride salt.

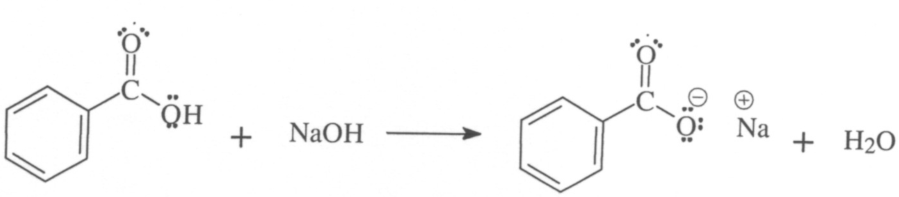


water insoluble — water soluble

3. *Solubility in 5% Sodium Hydroxide: Diagnosis of a High Molecular Weight Carboxylic Acid*

A *carboxylic acid* with five or more carbon atoms, though *insoluble* in *water*, will be *soluble* in a 5% *NaOH* solution because of the acid-base reaction to form the sodium carboxylate salt.

For example, benzoic acid, a seven-carbon water-insoluble carboxylic acid, reacts with sodium hydroxide to form the water-soluble sodium benzoate salt.



water insoluble — water soluble

Because only six organic families will be investigated in this experiment, once the carboxylic acids and amines have been eliminated as possible functional groups, the only remaining families are the aldehydes, ketones, alkenes and alcohols.

Thus, if the unknown compound does NOT dissolve in either 5% NaOH or 5 % HCl, it is a "NEUTRAL" compound (containing a non-ionizable functional group: aldehyde, ketone, alcohol, or alkene) of HIGH molecular weight (long carbon chain).

4. Reaction with 2, 4-Dinitrophenylhydrazine (2,4-DNP): Diagnosis of Aldehyde or Ketone

Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to form the corresponding orange or red-orange hydrazone precipitate.

If R' = alkyl = ketone
If R' = hydrogen = aldehyde

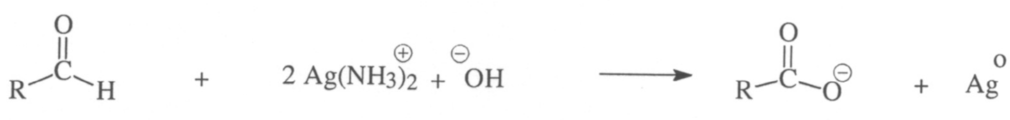
2,4-DNP

orange precipitate

If the hydrazone precipitate is observed, the organic compound contains an *aldehyde* or *ketone* functional group, and an additional test is required to distinguish between the two carbonyl families.

5. Tollen's Test: Diagnosis of Aldehyde

A positive result for the Tollen's silver mirror test (a shiny coating of silver on the bottom of the reaction test tube), indicates the presence of an aldehyde functional group. (If the results are inconclusive, the chromic acid test can *also* be used: aldehydes can be oxidized, and give a positive result, while ketones do not.)



Tollen's Reagent

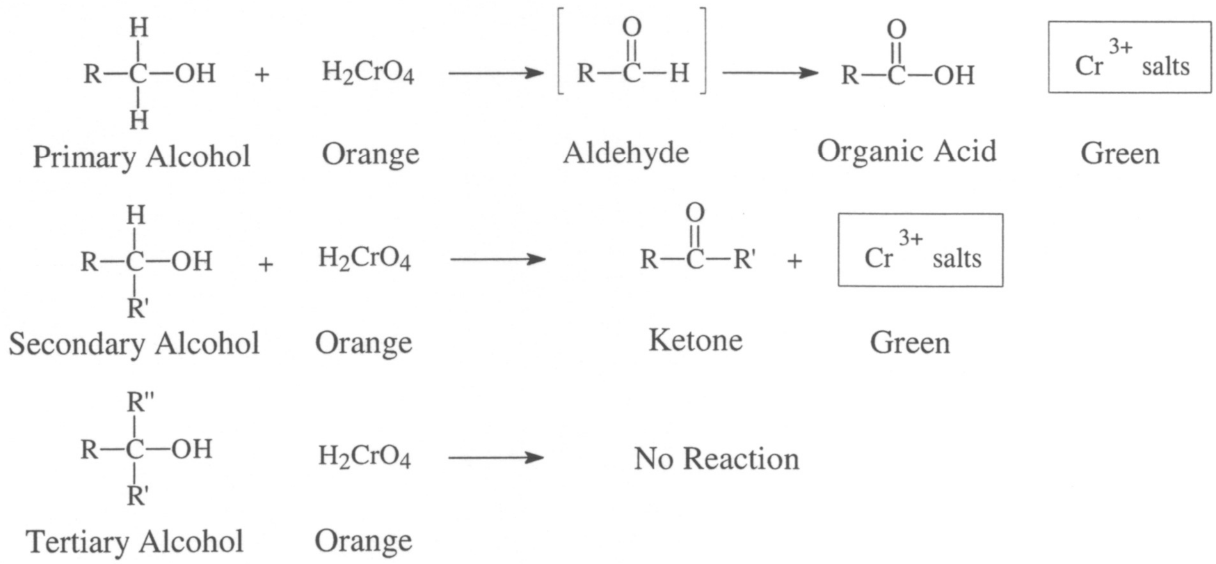
Reduced Silver

If NO precipitate is obtained in the 2,4-DNP test, then the unknown functional group has been narrowed down to one of two organic families: alkene or alcohol.

6. Oxidation with Chromic Acid: Diagnosis of Alcohol

If the organic compound is a primary or secondary alcohol, it should react with chromic acid. The chromium (VI) salts are orange in color; after oxidizing the alcohols, the green chromium (III) salts remain. This change in color is a positive test result.

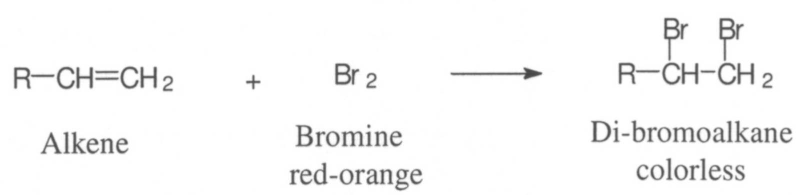
The oxidation product of a primary alcohol is the organic acid, while oxidation of a secondary alcohol yields the ketone. A tertiary alcohol will not react with the chromic acid, and thus the solution will remain orange. If the flow chart has been followed properly, and the compound does not react with bromine or with chromic acid, then the compound is a tertiary alcohol.



7. Decolorization of Bromine: Diagnosis of Alkene

Finally, if the compound is an alkene, the halogen bromine should add across the carbon-carbon double bond to form the corresponding dibromoalkane.

As you're already aware, molecular bromine has a red-orange color, while alkenes and dibromoalkanes are colorless. Rapid decolorization of bromine is a positive indication of an alkene. You must take care, however, not to add too much bromine, or the compound will be stoichiometrically "swamped;" meaning that the red-orange color will remain due to an excess of un-reacted bromine.



Procedure that you will follow

You and your lab partner should *each* have your own unknown compound. Follow the procedure below (and the flow chart on page 2) to track your progress in identifying the *functional group* and *molecular weight* (low or high) of your *unknown*.

Part ONE: Identifying the Functional Group and Molecular Weight (Low or High) of the Unknown Organic Compound

1. Water Solubility: Diagnosis of a Low Molecular Weight (Short Carbon Chain) Compound

In a small, *clean* test tube add 10 drops of distilled water to 5 drops of the compound. Agitate the tube to ensure complete mixing, and record your observations. A liquid that is insoluble in water will form a second phase, so you should observe whether there is one layer or two.

Visualization of two liquid phases in a few drops of mixture can be difficult; holding the test tube nearly horizontally should make the liquid-liquid interface readily observable. Do not be confused by the refraction of light at the meniscus near the top of the liquid. You can compare your sample with a test tube containing only water. Be sure to ask your lab instructor if the results are in question.

IF the compound is *water-soluble*, it is a *LOW molecular weight (SHORT carbon chain)* compound, and the solution should be tested with litmus paper to determine if the compound is a carboxylic acid, amine, or non-ionizable *"NEUTRAL"* compound (aldehyde, ketone, alkene, or alcohol).

Touch a clean glass stirring rod to the solution, and then to the litmus paper. Record your observations. If the solution tests *acidic* to litmus, then the compound is a *LOW molecular weight CARBOXYLIC ACID.* If the solution tests *basic* to litmus, then the compound is a *LOW molecular weight AMINE.* If the solution tests *neutral* to litmus, then you should proceed to the 2,4-DNP Test.

ONLY if the compound is INSOLUBLE in water:

2. Solubility in 5% Hydrochloric Acid: Diagnosis of a High Molecular Weight Amine

In a small, clean test tube add 10 drops of 5% HCl solution to 5 drops of the compound. Agitate the tube to ensure complete mixing, and record your observations.

If the compound is *soluble*, then it is a *HIGH molecular weight AMINE.* If the compound is *insoluble*, then you should proceed to the 5% NaOH Test.

3. Solubility in 5% Sodium Hydroxide: Diagnosis of a High Molecular Weight Carboxylic Acid

In a small, clean test tube add 10 drops of 5% NaOH solution to 5 drops of the compound. Agitate the tube to ensure complete mixing, and record your observations.

If the compound is *soluble*, then it is a *HIGH molecular weight CARBOXYLIC ACID.* If the compound is insoluble, then you should proceed to the 2,4-DNP Test.

4. Reaction with 2, 4-Dinitrophenylhydrazine (2,4-DNP): Diagnosis of Aldehyde or Ketone

Add 10 drops of the 2,4-DNP test reagent to a small, clean test tube. Add 2-3 drops of the compound, and agitate the test tube to ensure mixing. This reaction *may take several minutes* to reach completion. Record your observations.

If an orange-red precipitate forms, the compound contains a *CARBONYL GROUP*, and you should proceed to the Tollen's Test to distinguish between an *aldehyde* and *ketone*. If no precipitate forms, the compound has *NO CARBONYL GROUP*, and you should proceed to the Chromic Acid Test.

5. Tollen's Test: Diagnosis of Aldehyde

Place 20 drops of the 5% aqueous silver nitrate solution (5% $AgNO_3$) into a *VERY CLEAN* test tube. (Dirty test tubes prevent the silver from depositing on the glass walls. Your lab instructor will provide *new* test tubes for this reaction.)

Add 1 drop of 5% NaOH and mix well. Note that a brown precipitate of silver oxide will form. Add 5% ammonia solution (5% NH_3) to the tube dropwise with vigorous mixing. Keep adding the NH_3 (dropwise, with mixing) until the precipitate *just* redissolves. (Larger pieces of the brown solid may remain near the bottom of the test tube.) It is *essential* that you *do not add too much NH_3*, so monitor the status of the precipitate closely.

After preparing this Tollen's reagent, add the *smallest possible amount* of the compound (*less* than *ONE* drop) and mix thoroughly. If no reaction occurs at room temperature, heat the mixture in a slightly warm water bath (40-60 °C, *NO hotter*) for several minutes.

Notes on the Tollen's Test: Using too much of the compound can cause the mirror to not form. Using too much ammonia can cause the mirror to not form. Using too warm a water bath may volatilize the compound being tested. Often the heat of your hand is enough to trigger the formation of the silver mirror, so do not allow the water bath to overheat.

A positive Tollen's Test (formation of a mirror) indicates that the carbonyl group is an *ALDEHYDE.* A negative test indicates the carbonyl group is a *KETONE.*

Do *NOT* return test tubes used for the Tollen's reaction to the general storage area. After rinsing the tubes into the Tollen's waste container, place the test tubes in a special beaker marked for Tollen's test tubes only.

6. Oxidation with Chromic Acid: Diagnosis of Alcohol

Place five drops of the compound into a small, *clean* test tube and add 1 drop of the chromic acid reagent. (Remember that chromic acid is a strong oxidizing agent that can react with a number of different functional groups – your test tube *must* be *clean* and free of organic residue.) Agitate the tube to mix thoroughly. Record your observations.

If the color of the chromic acid reagent (orange) remains, you should proceed to the Bromine test. A green color indicates that the compound is a *PRIMARY or SECONDARY ALCOHOL.*

7. Decolorization of Bromine: Diagnosis of Alkene

Place two drops of the compound into a small, clean test tube. Add the bromine (in methylene chloride) test solution *dropwise*. Watch closely to see whether the red-orange bromine color disappears. A positive test result for alkenes is the nearly instantaneous decolorization of bromine. Only two drops of an alkene should be able to rapidly decolorize 15 to 20 drops of a saturated solution of bromine in methylene chloride.

Note that if too much bromine has been added, a false negative may be observed due to the presence of excess reactant.

If the red-orange color of bromine disappears, then the compound has an *ALKENE* functional group. If the color remains, the compound is most likely to be a *TERTIARY ALCOHOL.*

Part TWO: Preparing a Derivative of the Unknown Organic Compound

When you believe that you've correctly identified your unknown compound's *functional group* and *molecular weight,* ask your Lab Instructor to confirm your identification.

At that time, your Lab Instructor will provide you with a set of written instructions for synthesizing a derivative of your unknown compound, as well as a list of possible substances and the melting points of their derivatives.

Following those instructions, you'll perform a simple chemical reaction to make a solid derivative compound, isolate that solid by centrifugation, and then recrystallize the derivative from an appropriate solvent.

After recrystallization, you'll determine the melting point of the derivative compound, identify it from a list provided by your TA, and thus identify the original unknown compound from which the derivative was made.