

Identification of an Unknown Carbonyl

Updated August 2013

You will be given an aldehyde or ketone, and your task is to determine its identity using spectroscopy and wet chemistry techniques. No one else in the lab should have the same unknown that you have! It might be any of the aldehydes or ketones listed in the tables in Shriner, et al, *The Systematic Identification of Organic Compounds*. Copies of this book are available in the laboratory and copies of the tables are also available in Dr. Moody's folder in the student U: drive.

NOTE: you do not have to prepare a Physical Properties table for this lab because of the huge number of reagents that we will use; all other pre-lab preparations ARE still required. For your reactions (and mechanisms), you should write them for "generic" aldehydes or ketones, using "R" as an alkyl group where appropriate.

To determine the ID of your carbonyl unknown, you must do all of the following:

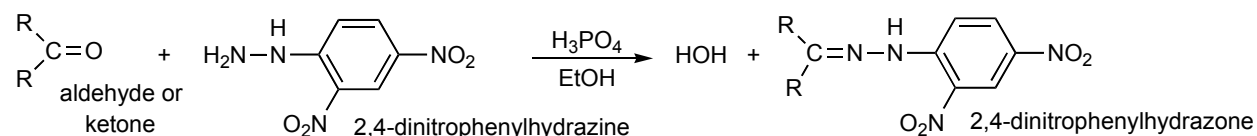
- Make general observations about the unknown: color, solid or liquid state, odor, solubility, etc.
- Take various spectra: IR and NMR, both ^1H and ^{13}C . For the NMR: you prepare the sample; someone else will run the NMR instrument. Remember to use a deuterated solvent and to label the NMR tubes correctly.
- Determine the bp (if liquid) OR mp (if solid). To determine a bp, many students prefer to distill their material using a Hickman still head to simultaneously get the bp and to purify some of the material. (See the Figure on page 147 in Padias.) See also the method described on pp. 54-55 in Padias.
- Prepare TWO derivatives: a 2,4-dinitrophenylhydrazone and a semicarbazone, and measure their mp's.
- Run FOUR classification tests: Tollens' test, chromic acid test, Schiff's test, and iodoform test. For each of these tests, you should run your unknown, a known positive, and a known negative substance to see clearly the category of your unknown.

You have two lab periods to do ALL of these things. You may do them in any order that you like. As a summary, compile all your data in a table and explain your approach and rationale for determining the structure of your unknown. Your lab grade will depend on performing all of the work above, your rationale, and the correct identification (name and structure) of your unknown.

Derivative Procedures.

As you will see, measuring boiling points of liquids accurately is more challenging than measuring mp's of solids. Conversion of your unknown (especially if it is a liquid) to a solid derivative thus gives you a more reliable physical measurement that is related to the structure of the original unknown. Use these two procedures to make your solid derivatives, measure their mp's, and compare them to the literature values that are readily available in the reference tables.

D-1. Preparation of 2,4-Dinitrophenylhydrazones



Add 4 drops of your unknown to about 4 mL of a 0.1 M stock solution of 2,4-dinitrophenylhydrazine in phosphoric acid. Warm the reaction mixture for a few minutes in a water bath, and then allow to crystallize. After 10 min of cooling, if no precipitate has formed, add water dropwise to encourage formation of the solid. Collect the solid by suction filtration, and wash the crystals with a large amount of water to remove the phosphoric acid. Test the pH of the wash water by touching a piece of pH paper to the liquid that is at the tip of the Hirsch funnel, and if it is still acidic, wash then with more water. Let the product air dry in the suction apparatus under vacuum for at least 15 minutes.

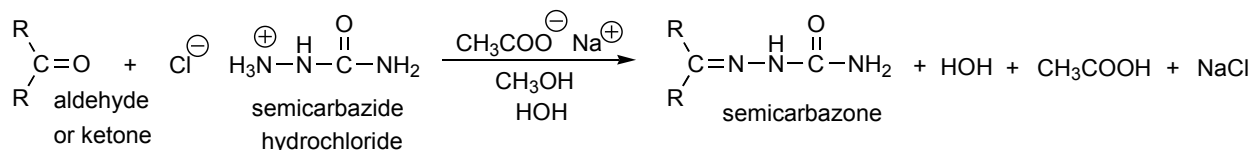
Recrystallize from hot ethanol. Occasionally, a high-molecular-weight derivative will not dissolve in a reasonable quantity (5 mL) of ethanol. In that case, boil the sample for a few minutes even though it does not dissolve. Then allow the hot suspension to cool slowly so that further crystallization can proceed as in a normal recrystallization. The boiling ethanol treatment removes impurities so that a reasonably accurate melting point can be obtained on the isolated material.

Cleaning Up

The filtrate from the preparation of the 2,4-dinitrophenylhydrazone should have very little 2,4-dinitrophenylhydrazine in it, so after dilution with water and neutralization with sodium carbonate it can be flushed down the drain.

D-2. Preparation of Semicarbazones

Semicarbazide (mp 96°C) is not very stable in the free form and is used as the crystalline hydrochloride (mp 173°C). Since this salt is insoluble in methanol or ethanol and does not react readily with typical carbonyl compounds in alcohol-water mixtures, a basic reagent such as sodium acetate is added to liberate free semicarbazide.



Add 10 drops of the unknown to 0.5 mL of a stock solution of semicarbazide hydrochloride (which should contain 0.5 mmol of the reagent). Add enough methanol (~1 mL or more) to make a homogeneous solution. It might help to warm this solution gently in your hot water bath. When the sample is dissolved, add about 20 drops (~1 mL) of saturated aqueous sodium acetate and warm the solution gently in a hot water bath for a few minutes. Remove the mixture from the water bath and allow it to cool slowly to room temperature. It may be necessary to scratch the inside of the test tube in order to induce crystallization. Cool the tube further in ice, collect the product by suction filtration, and wash it with water followed by a small amount of ice cold methanol. Recrystallize the product from ethanol or ethanol/water.

Cleaning Up

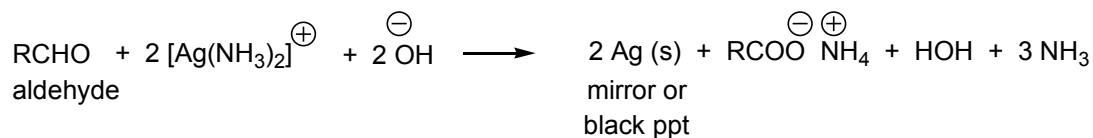
Combine the filtrate from the reaction and the mother liquor from the crystallization, dilute with water, make very slightly acidic with dilute hydrochloric acid, and flush the mixture down the drain.

Classification Tests

Test reactions are useful to quickly check for the presence of particular functional groups, since they result in an obvious visible color change, a precipitate, or some other visible difference when the functional group is present. For each of these tests, you should perform the reaction with a known positive, a known negative, and your unknown to be confident that you know what you are learning about your unknown.

The first three procedures below are simple ways to determine the presence of an aldehyde by a chemical test. Each of the three tests rely on the ability of an aldehyde to oxidize readily. When the aldehyde is oxidized, the corresponding oxidizing agent either changes color or precipitates, indicating the presence of an aldehyde in your unknown. If all three tests are negative, then you likely have a ketone.

T-1. Tollens' Test



Cleaning the test tubes. Clean four reaction tubes by adding 5-10 mL of 3 M sodium hydroxide solution to each and heating them in a water bath while preparing the Tollens' reagent.

Preparing the Tollens' Reagent. Put 5 mL of water into a 4-in test tube and mark the height of the solution. Pour out the water and add 1.0 mL of 0.03 M aqueous silver nitrate solution and 0.5 mL of 3 M sodium hydroxide; you will see a pale gray precipitate which is silver oxide (Ag_2O). Add 0.25 mL of 2.8 % ammonia solution (0.1 mL of concentrated ammonium hydroxide diluted to 1 mL). Stopper the tube and shake it. Repeat the addition of 0.25 mL portions of the 2.8% ammonia until *almost all* of the precipitate dissolves (at most 1.5 mL of the ammonium hydroxide solution); then dilute the solution to your 5 mL mark with distilled water.

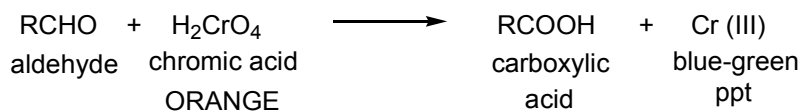
Carrying out the Tollens' Test. Empty the cleaned tubes of sodium hydroxide solution, rinse them with distilled water and add 0.5 mL of Tollens' reagent to each. Add one drop (no more) of the substance to be tested by allowing it to run down the inside of the inclined reaction tube. As in all these tests, compare the results produced by a known aldehyde, a known ketone, and the unknown compound. Set the tubes aside for a few minutes without agitating the contents. If no reaction occurs, warm the mixture briefly on a water bath.

Destroying the Tollens' Reagent. At the end of the reaction promptly destroy excess Tollens' reagent with a few drops of nitric acid (wear gloves). The Tollens' Reagent can form an explosive fulminate on standing, so do not delay destroying it once you are done with the tests! A drop of nitric acid also can be used to remove silver mirrors from the test tubes.

Cleaning Up

Clean up uses nitric acid, so you might want to wear gloves. Place all solutions used in this experiment in a beaker (including the unused ammonium hydroxide, sodium hydroxide solution used to clean out the tubes, Tollens' reagent from all tubes). Remove any silver mirrors from reaction tubes with a few drops of nitric acid and add it to the beaker. Make the mixture acidic with nitric acid to destroy unreacted Tollens' reagent, then neutralize the solution with sodium carbonate, and add some sodium chloride solution to precipitate silver chloride (about 40 mg). The whole mixture can be flushed down the drain or the silver chloride collected by suction filtration and the filtrate flushed down the drain. Place the silver chloride in the non-hazardous solid waste container.

T-2. Chromic Acid Test



Chromic acid can cause burns and unsightly stains, so you might want to wear gloves. If you come in contact with it, wash with water.

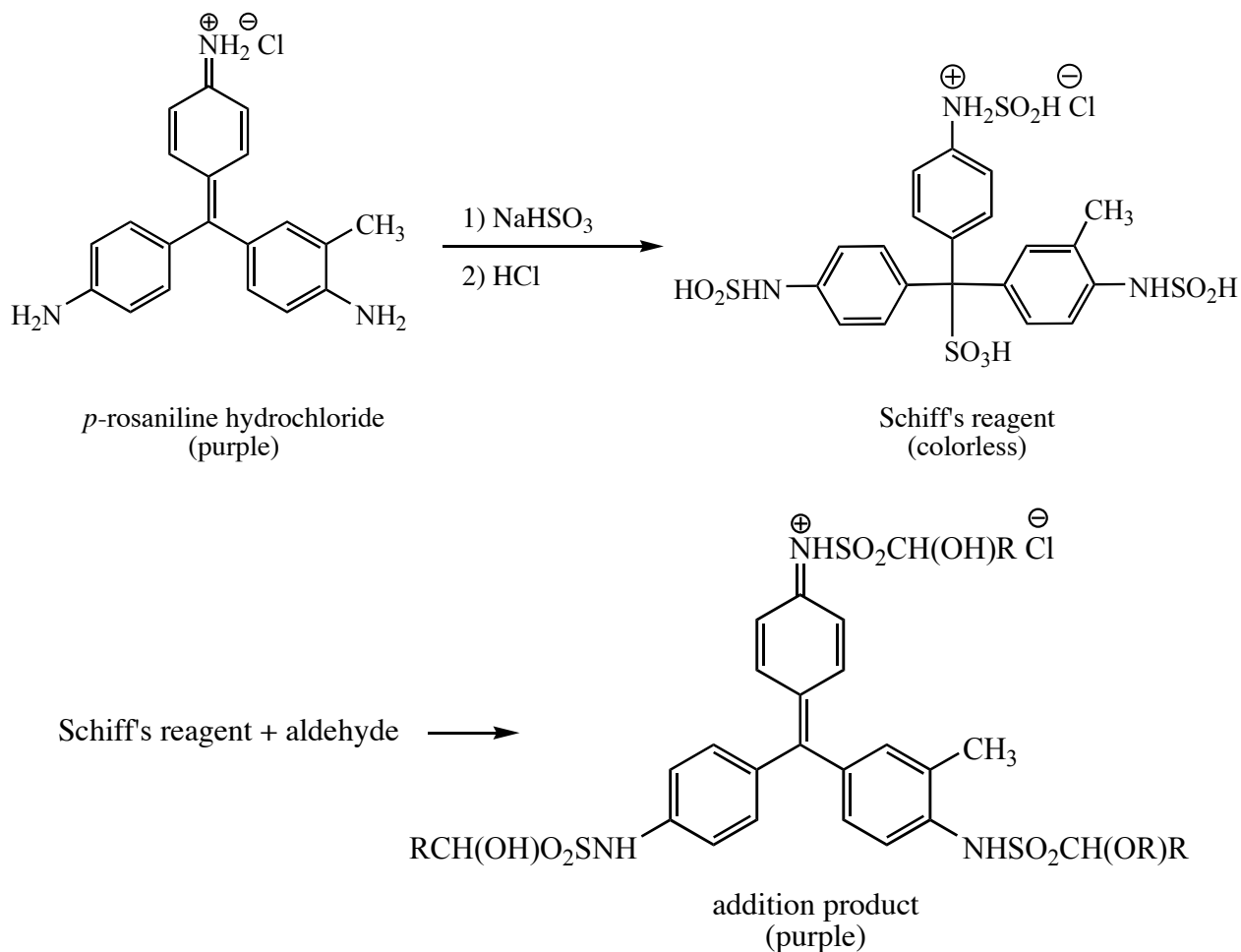
Add a few drops or about 10 mg (the tip of a spatula) of your unknown to 1 mL of *reagent-grade* acetone (from a glass bottle, not from a plastic squirt bottle!). Add a few drops of

the chromic acid reagent to the acetone solution, and gently shake the tube to mix the contents. If the orange color disappears and a green or blue-green precipitate forms, this is a positive test for an aldehyde. Generally a positive test occurs almost immediately, but some aldehydes take up to a minute. If your color change takes longer than a minute, this does not indicate a positive test. As in all these tests, compare the colors produced by a known aldehyde, a known ketone, and the unknown compound.

Cleaning Up

Add sodium sulfite to the aqueous solution of chromium salts in order to destroy excess Cr^{6+} . Make the solution slightly basic, to form chromium hydroxide, and isolate this salt by vacuum filtration. Place the filter paper and the filter cake in the container for heavy metals; flush the filtrate down the drain.

T-3. Schiff's Test



Wear gloves for this one! If you do not wear gloves, and are even slightly careless, your fingers will turn magenta from the aldehydes in your skin.

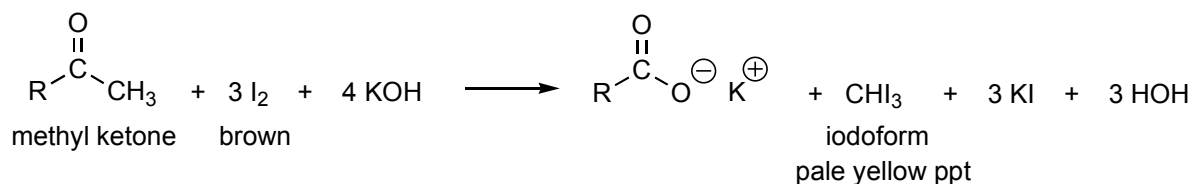
Add 2 drops of the unknown to 1 ml of the Schiff's reagent solution. A magenta color will appear within 10 min if an aldehyde is present. As in all these tests, compare the colors produced by a known aldehyde, a known ketone, and the unknown compound.

Cleaning Up

Neutralize the solution with sodium carbonate and flush it down the drain. The amount of *p*-rosaniline in this mixture is negligible (1 mg).

T-4. Iodoform Test

Unlike the previous tests, the iodoform test will determine the presence of a methyl ketone. If your previous three tests were positive, you will likely have a negative iodoform test. If the previous tests were all negative, you could still have a negative iodoform test, since again, it is only positive for a ketone that has a methyl group on it!



If your unknown is water soluble, dissolve a few drops (or about 15 mg if it is a solid) in 0.5 mL of water in a test tube, add 0.5 mL of 3 M sodium hydroxide, and then slowly add 0.75 mL of the iodine/potassium iodide solution. If a methyl ketone is present, the brown color of the iodine reagent will disappear and iodoform will precipitate as fluffy yellow solid. As in all these tests, compare the mixtures produced by a known aldehyde, a known ketone, and the unknown compound.

If the substance to be tested is insoluble in water, dissolve it in 0.5 mL of 1,2-dimethoxyethane, proceed as above, and at the end dilute with 2.5 mL of water.

Cleaning Up

Combine all reaction mixtures in a beaker, add a few drops of acetone to destroy any unreacted iodine in potassium iodide reagent, remove the iodoform by suction filtration, and place it in the halogenated organic waste container. The filtrate can be flushed down the drain after neutralization (if necessary).