Identification of an Unknown Carbonyl

Updated January 2019

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 large 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:

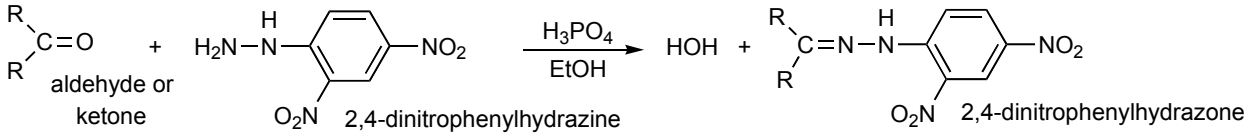
- Make general observations about the unknown: color, solid or liquid state, odor, solubility, etc.
- Take various spectra: IR and NMR, both ^{1}H and ^{13}C. For the NMR: you prepare the sample; someone else will run the NMR instrument. Remember to use a deuterated solvent and to label your NMR tubes' locations in the NMR sample rack correctly.
- Prepare TWO derivatives: a 2,4-dinitrophenylhydrazone and a semicarbazone, and measure their mp's.
- Run TWO classification tests: 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 to see clearly the category of your unknown.
- Determine the boiling point (bp, if unknown is a liquid) OR melting point (mp, if it is a solid). To determine a bp, see pages 54-55 of Padias (3e). Alternativley, you can distill your material using a Hickman still head to simultaneously get the bp and to purify some of the material.

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 accruately 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 (the derivative's mp) 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



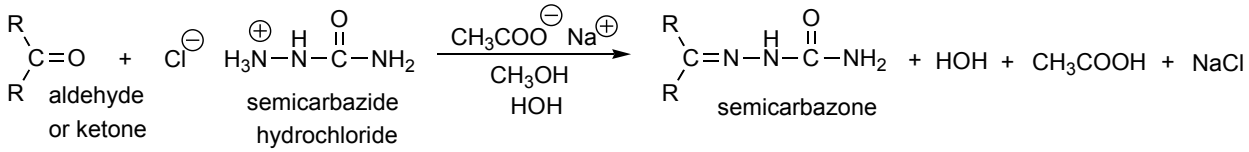
Add 4 drops of your unknown to about 4 mL of a 0.1 M stock solution of 2,4-dinitrophenylhydrazine in phosphoric acid. Warm the reaction mixture for a few minutes in a water bath, and then allow to crystallize. After 10 min of cooling, if no precipitate has formed, add water dropwise to encourage formation 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 are 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 resonably accurate melting point can be obtained on the isolated material.

2,4-DNP Cleaning Up

The filtrate from the preparation of the 2,4-dinitrophenylhydrazone should go in the liquid organic hazardous waste, since there may be some leftover unknown in it.

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.

Semicarbazone Cleaning Up

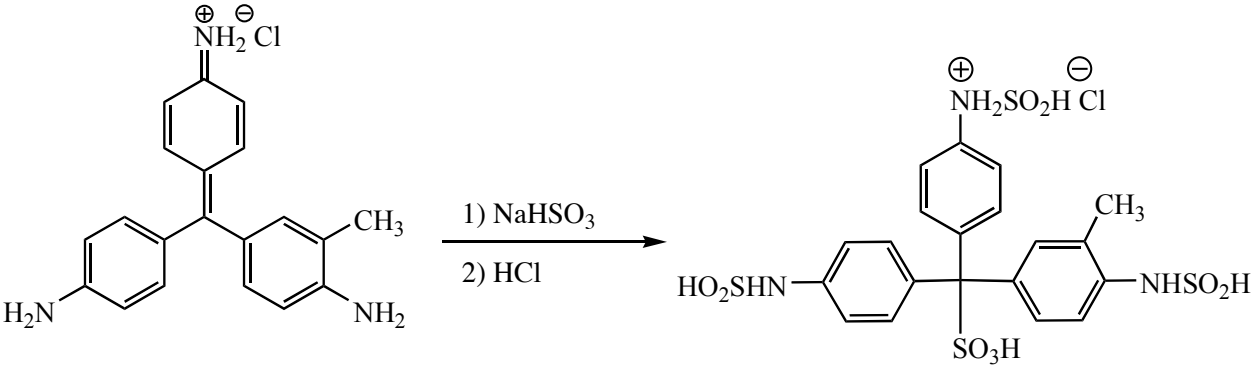
Both the filtrate from the reaction and the mother liquor from the crystallization should go in the liquid organic hazardous waste, since there may be some leftover unknown in it. Unused semicarbazide reagent should go to the liquid organic hazardous waste if it isn't needed.

Classification Test Procedures

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.*

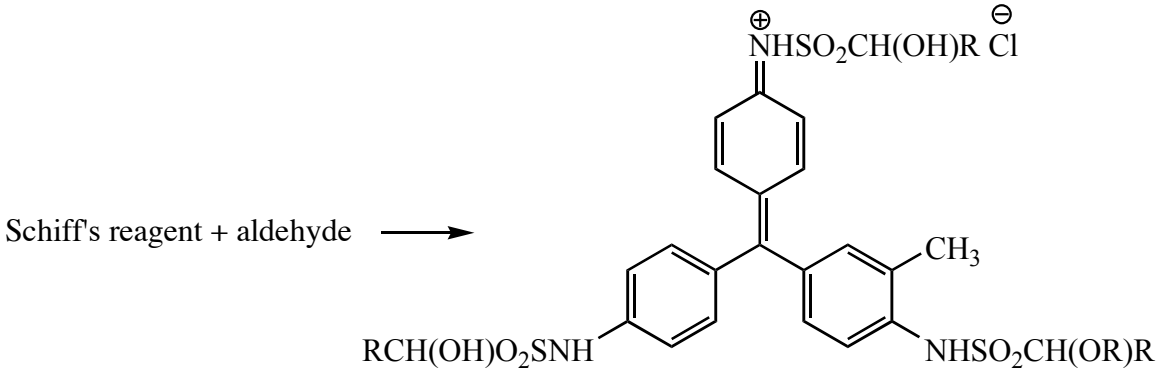
T-1. Schiff's Test

The Schiff's test is one of many simple ways to detect the presence of an aldehyde. Most of these 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. When an aldehyde reacts with the colorless Schiff's reagent, making the test positive, the color of the solution changes to magenta or purple.



p-rosaniline hydrochloride (purple)

Schiff's reagent (colorless)



addition product (purple)

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

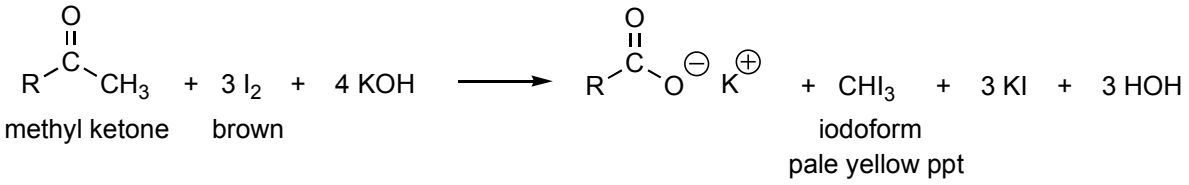
Add 2 drops of the unknown to 1 ml of the Schiff's reagent solution. A magenta color will appear within 10 min if an aldehyde is present. Be sure to compare the colors produced by a known aldehyde, a known ketone, and your unknown compound.

Schiff's Test Cleaning Up

Neutralize the solution with sodium carbonate and put it in the liquid organic hazardous waste, since there may be some leftover unknown in it.

T-2 Iodoform Test

The iodoform test will determine the presence of a methyl ketone. If your Schiff's tests is positive, you will likely have a negative iodoform test. If it was negative, you could still have a negative iodoform test, since again, it is only positive for a ketone that has a methyl group attached to 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.

Iodoform Cleaning Up

Combine all reaction mixtures in a beaker, add a few drops of acetone to destroy any unreacted iodine in potassium iodide reagent, and put all of this mixture in the liquid organic hazardous waste, since there may be some leftover unknown in it.