CH242 EXPERIMENT #2

CHEMICAL AND SPECTROSCOPIC IDENTIFICATION OF UNKNOWN ORGANIC COMPOUNDS

Background

In this lab you will be given a series of unknown compounds, either in pure form or as a mixture of two compounds. Your task is to separate the components (if necessary) and, using an assortment of instrumental and wet chemical methods, unambiguously establish the chemical identity of your unknown compounds.

- Unknown 1 will be a pure (single) compound of relatively simple structure.
- Unknowns 2 and 3 will be supplied to you as a mixture, which will require separation prior to structure identification.
- Unknown 4 will be a pure (single) compound of more complex structure.

Instrumental Methods **(required for all unknowns unless otherwise indicated):** ^{1}H NMR, ^{13}C NMR (optional for unknowns 2 & 3), IR, and MS.

Mandatory Wet Chemical Methods For Unknown 1: Attempt all the available functional group tests and prepare an appropriate derivative for your unknown (see below for more details on derivative preparation). In addition, determine the melting point of your unknown if it is a solid.

Mandatory Wet Chemical Methods For Unknowns 2 and 3: Attempt all the available functional group tests for each unknown. In addition, determine the melting point of each unknown that is a solid.

Wet Chemical Methods For Unknown 4: Wet chemical methods are NOT required, but may be used to aid/confirm your spectroscopic analysis. In addition, determine the melting point of your unknown if it is a solid.

1. Procedural Guidelines for the separation of unknowns 2 and 3 (supplied as a mixture):

You will need to develop a procedure for the separation of unknowns 2 and 3 based on the following information: One of the components in your mixture is either a carboxylic acid or a phenol. Your second component is **not** a carboxylic acid or a phenol and also does not contain any functional group more acidic than water.

We also strongly recommend that you use an extraction procedure based on the above information in order to separate your compounds. Further, we recommend that you purify all solid unknowns by recrystallization.

Very important!!! Some liquid unknowns may be sufficiently volatile to be lost if left on the rotary evaporator for a long time. If your unknown is a liquid, make sure that you keep an eye on it while on the rotary evaporator!

2. Make sure to record the physical characteristics of each unknown. Include characteristics such as color, odor, whether it is solid or liquid.

3. Determine the melting point for all solids. Take care that an accurate measurement is made and that you report your value as a range. *This becomes an important clue to the identity of your unknown.*

Functional group tests

Each of the tests below gives qualitative (yes/no) information regarding the presence of a certain functional group(s). You should always run a known compound along with your unknown to make sure that the test itself is working properly.

1. Test for alkenes or alkynes: The red/brown color of a bromine solution should disappear (the solution goes clear) if an alkene or alkyne is present. *The disappearance of color is a <u>positive</u> test – the presence of an alkene or alkyne. There are some exceptions to this test – you will need to understand the mechanism of the chemical reaction that occurs to understand the exceptions!*

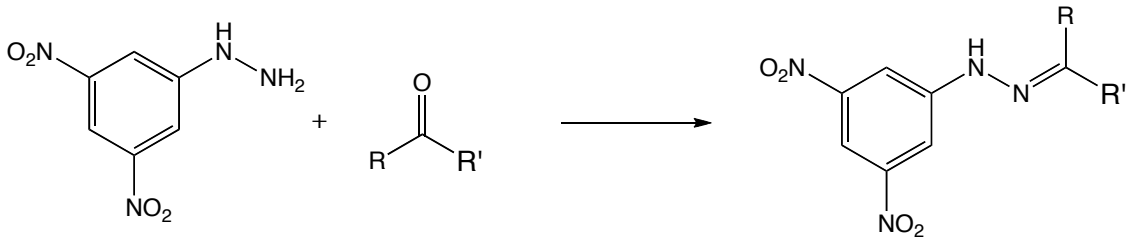
CAUTION! Avoid getting bromine on your skin. Do not breathe vapors.

Procedure: Dissolve a drop (or a few crystals) of your unknown in 1 mL of dichloromethane. Add a drop of bromine solution. Observe!

2. Test for aldehydes and ketones

a. 2,4-dinitrophenylhydrazones are brightly colored solids that can be formed from ketones or aldehydes. A positive test is the immediate formation of a yellow to red precipitate.

CAUTION! Contains sulfuric acid. Handle with care.

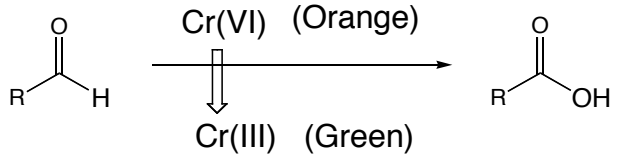


2,4-dinitrophenylhydrazine (2,4-D) *a 2,4-dinitrophenylhydrazone*

Procedure: Dissolve a small amount of your compound in a minimum amount of 95% ethanol, then add a small amount of the 2,4-dinitrophenylhydrazine (2,4-DNP) solution. Observe!

b. Chromic acid oxidation. This test differentiates between aldehydes and ketones. Aldehydes react to give an immediate green precipitate, but ketones do not. The first step is the formation of a chromate ester, followed by an elimination reaction. For the reaction to proceed there must be a hydrogen atom on the carbon bearing the oxygen atom. *Note: primary and secondary alcohols also react with chromic acid – see the* ***Alcohols*** *section.*

CAUTION! Strongly acidic. Chromium reagents are strong oxidizing agents and toxic. Handle with care.



Procedure: Add a small amount of your unknown to acetone in one of the wells of a spot plate. SLOWLY add a few drops of the chromic acid reagent (Jones Reagent). Observe!

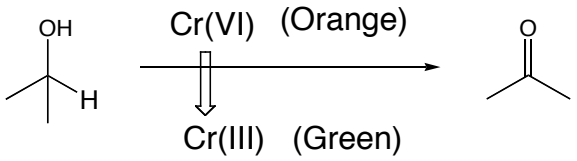
3. Test for phenols

A colored (gray-purple) complex is formed in a reaction with ferric chloride. A brown, ferric chloride colored, solution or precipitate is NOT a positive test. Note: this test is much less reliable than the others listed.

Procedure: *Dissolve a few drops (or crystals) of unknown in dichloromethane. Add a drop of pyridine and a couple of drops of iron (III) solution.*

4. Test for alcohols

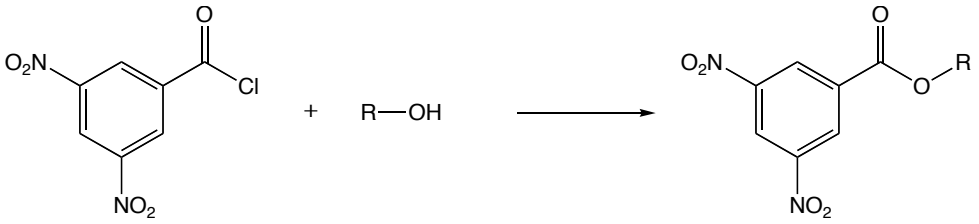
Chromic acid will oxidize primary and secondary alcohols. Tertiary alcohols do not react (the procedure and more details are given in section **2b**, above).



Preparation of Derivatives (Unknown 1 only)

1. Alcohols and Phenols

A 3,5-dinitrobenzoate derivative usually provides a solid compound having a characteristic melting point.



Place about 800 mg of 3,5-dinitrobenzoyl chloride in approximately 2.0 mL of dry pyridine. Add about 200 mg or 0.20 mL of alcohol or phenol, and a boiling stone in a 5-mL conical vial. Attach a condenser and at reflux on aluminum block for15-20 minutes. Put 5.0 mL of water in a 10-mL Erlenmeyer flask and pour the reaction mixture slowly into the water. Cool the solution in an ice/water bath until the product precipitates. Collect the crystals by vacuum filtration. Remove any 3,5-dinitrobenzoic acid by washing

with 5% sodium carbonate solution, and then remove any inorganic materials by washing with water. Recrystallize the derivative from ethanol-water.[1]

If after 10 minutes of stirring no product has crystallized, isolate your product via an extractive workup) containing CH_2Cl_2 and 5% sodium bicarbonate, followed by washing with 1M HCl.

2. Aldehydes and Ketones

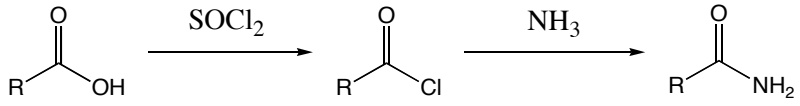
Prepare a 2,4-dinitrophenylhydrazone. Most aromatic aldehydes and ketones tend to yield a red dinitrophenylhydrazones product, while many nonaromatic aldehydes and ketones produce a yellow derivative. If the color of the precipitate is orange, no definite conclusion can be drawn from the color.[1]

Dissolve 100 mg or 3 drops of liquid aldehyde or ketone in 2.0 mL of regent grade ethanol. Add 3.0 mL of the 2,4-DNP reagent. You should see the immediate formation of a large amount of precipitate. If you do not see any precipitate, heat the mixture in a 50° C water bath for about 2 minutes. Allow the mixture to stand at room temperature for 15-20 minutes. Collect the crystals by vacuum filtration. Wash the solid thoroughly with cold ethanol. 2,4-dinitrophenylhydrozones usually do not need to be purified by recrystallization. If recrystallization is needed, use an ethanol-water mixture.[1]

3. Carboxylic Acids

Prepare an amide derivative.

CAUTION! Thionyl chloride is a lachrymator. It reacts violently with water to give HCl.



Add about 0.5g of the acid to about 1.0 mL of thionyl chloride and 1 drop of piperidine in a 5-mL conical vial fitted with a reflux condenser and a drying tube filled with calcium chloride. Heat the reaction mixture in a 50-55°C water bath for 25 minutes. Cool the mixture in a bath of cold tap water. Place 5 mL of concentrated ammonia (ammonium hydroxide) solution in a 30-mL beaker in an ice/water bath. While stirring the ammonia solution with a glass stirring rod, add the acyl chloride solution dropwise using a Pasteur pipet. Stir the mixture until the all the acyl chloride has been added. Collect the solid amide derivative by vacuum filtration and then recyrstallize the solid from ethanol/water.[1]

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[1] *Experimental Organic Chemistry*, Mohrig, J. R., etal, W.H. Freeman and Company, NY, 1998.

4. Esters

Esters are often formed by the reaction of a carboxylic acid and an alcohol. To characterize an ester, it is necessary to first hydrolyze the ester into its components. If the resulting acid and alcohol are not appreciably water soluble, they can be separated and then characterized by instrumental analysis. The following procedure, however, is designed for you to isolate only the acid component of your unknown. You should be able to identify the alcohol component by reviewing the ^{1}H NMR you performed on the original ester.

Place about 1 g of your ester and 10 mL of 2.5M NaOH into a 50 mL round bottomed flask equipped with a reflux condenser. Be sure to lubricate the ground glass joints of the apparatus before you begin. Heat the mixture at reflux for about one hour. Allow the mixture to cool to room temperature, and then acidify with 1.5M HCl. If a precipitate forms, collect it by vacuum filtration. If no precipitate forms, isolate your product by extraction with ether.

Prelab Questions

Due at the beginning of your laboratory period the week of February 22nd

1. You have an unknown that is either an alcohol or a phenol. Using the following ^{1}H NMR data, is the unknown an alcohol or a phenol? Briefly explain your answer.
Observed resonances: doublet at 1.3 ppm, septet at 2.8 ppm, doublet at 3.7 ppm, and a singlet at 4.1 ppm.

2. You have an unknown organic compound that is either a ketone or an aldehyde. What signal in a ^{1}H NMR spectrum could you use to distinguish between these compounds?

3. You have been given the task of identifying the contents of two unlabeled bottles. One of the bottles contains allyl alcohol and the other bottle contains 1-butanol. Suggest at least two means of identifying the contents of the bottles using wet chemical tests.

4. You and your partner made a big mistake!! You accidentally put your carboxylic acid component into the waste container in your hood. You have already added both fluorenone and 3-nitroaniline into the same waste container. Not wanting to tell your instructor of your mistake, you ask your TA what you should do. Your TA thinks that

you can extract the waste mixture and recover your acid. Is the TA is correct? Clearly explain why or why not.

5. For **each** of the following pairs of compounds, describe a set (a set is two different tests) of wet chemical tests that could distinguish one compound from the other:

a) Vanillin from Tylenol b) Menthol from Terpineol c) Limonene from β-Ionone

Laboratory Report

For each unknown compound, complete the two-page laboratory report form supplied below (yes, you will need to make several copies). Make sure your analysis ***unambiguously*** (very important!) identifies each compound structure. No other "report" is required for this experiment.

Laboratory Report for Experiment #2

Names_____ and _____

Laboratory Section_____ Date_____

Unknown Code: _____

Physical Characteristics

1. Solid or liquid

   Color

   Odor

2. Melting point (report your value as a range). Does this match the literature? Why/why not?

Functional Group Tests, if conducted:

Negative tests:

Inferences:

Positive tests:

Inferences:

Derivative results, if required: Does your derivative match the literature compound? Why/why not?

NMR (attach copies of the ^{1}H and ^{13}C NMR spectra)
Fully analyze the signals on the submitted copies, and summarize below:

IR (attach a copy of the IR spectrum)
Fully analyze the important signals on the submitted copy, and summarize below:

MS (attach a copy of the MS)
Fully analyze the important signals below:

My Unknown Is: _____