CH 242 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 containing 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(s).

Unknown #1 will be a pure (single) compound of relatively simple structure.

Unknown #2 will be a mixture of two compounds, which will require separation prior to structure identification.

Unknown #3 will be a pure compound of more complex structure. You are required to record and analyze the following data for each unknown compound:

Mandatory Instrumental Methods **(<u>All Unknowns</u>):** ^{1}H NMR, ^{13}C NMR (required for unknowns #1 & #3 only), IR, and MS (either direct MS or GC/MS).

Mandatory Wet Chemical Methods <u>For Unknown #1</u>: Report at least one confirmatory functional group test <u>and prepare an appropriate derivative</u> for your unknown (see below for more details on derivative preparation). In addition, you will need to determine the melting point of your unknown if it is a solid.

Mandatory Wet Chemical Methods <u>For Unknown Mixture #2</u>: Report at least one confirmatory functional group test for each unknown. In addition, you will need to determine the melting point of each unknown that is a solid.

Mandatory Wet Chemical Methods <u>For Unknown #3</u>: Wet chemical methods are NOT required, but may be used to aid/confirm your spectroscopic analysis. In addition, you will need to determine the melting point of your unknown if it is a solid.

Unknown #1 and compounds in unknown mixture#2 will contain only one "major" functional group (amine, alcohol, ketone, carboxylic acid, aldehyde, etc.). For example, you will not have an alcohol that also contains an aldehydic functional group elsewhere in the molecule. For our purposes, however, halides, carbon-carbon double and triple bonds, and aromatic rings are not considered unique functional groups, so you might have an alcohol that also contains a halide and/or a phenyl group as substituents, for instance. Furthermore, unknown mixtures will not contain two acids (or a phenol and an acid), two bases, or two neutral compounds. Unknown #3 will likely have multiple functional groups.

Separation Protocol – This section applies to Unknown #2 only!

Step 1: Dissolve the mixture in 25 mL of dichloromethane and pour into a 125 mL separatory funnel. Extract the organic solution three times with 15 mL portions of 5% NaOH and separate the layers after each extraction. Set aside the organic layer. Combine the aqueous extracts, cool in an ice-water bath and carefully add 6M HCl until the solution is strongly acidic. You may then proceed as follows depending on the outcome of acidification.

(a) If a solid precipitate forms, filter and recrystallize from a suitable solvent. Meanwhile, proceed to step 3. OR
(b) If an oily material is produced, extract the acidified solution with three 10 mL portions of dichloromethane. Combine the organic layers, dry over anhydrous Na_2SO_4, decant, and remove the solvent by distillation or using a rotary evaporator. *Note: some liquid unknowns may be low boiling and could be lost if left on the rotary evaporator too long. If your unknown is a liquid, make sure it is high-boiling before placing it on the rotary evaporator!* Meanwhile, proceed to step 3. OR
(c) If no precipitate or oily material is produced, go to step 2 below.

Step 2: Extract the organic layer, that you set aside in step 1, three times with 15 mL portions of 5% HCl and separate the layers after each extraction. Combine the aqueous extracts, cool in an ice-water bath and carefully add 5% NaOH until the solution is strongly basic. You may then proceed as follows depending on the outcome of basification.

(a) If a solid precipitate forms, filter and recrystallize from a suitable solvent.
Meanwhile, proceed to step 3. OR

(b) If an oily material is produced, extract the basified solution with three 10 mL portions of dichloromethane. Combine the organic layers, dry over anhydrous Na_2SO_4, decant, and remove the solvent. Meanwhile, proceed to step 3.

Step 3: Wash the organic layer remaining after the acid or base extraction with two 10 mL portions of water followed by one 10 mL portion of brine**.** Dry the organic layer over anhydrous Na_2SO_4, decant, and remove the solvent.

A. For each unknown, record the following physical characteristics:

1. Solid or liquid

Color

Odor

2. Melting point (solid unknowns only). 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.

B. Available functional group tests (<u>Always</u> run a known compound along with your unknown to make sure that the test itself is working properly.):

1. 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.*

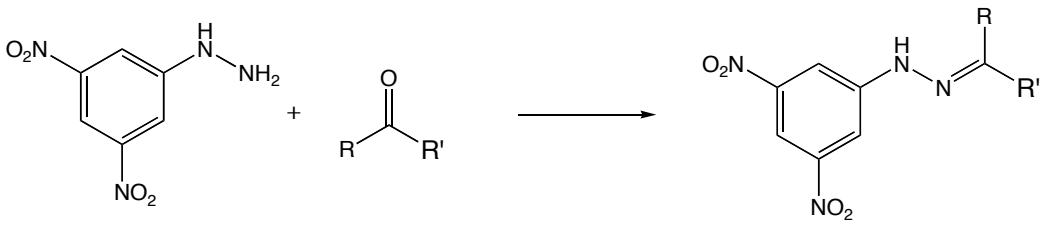
CAUTION! Avoid getting bromine on your skin. Do not breathe vapors.

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

2. Aldehydes and Ketones

a. Preparation of a 2,4-dinitrophenylhydrazone. A positive test is the immediate formation of a yellow to red precipitate.

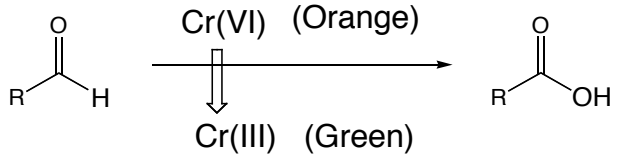
CAUTION! Contains sulfuric acid. Handle with care.



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-D) solution.

b. Chromic acid oxidation. This test differentiates between aldehydes and ketones. Aldehydes react to give an immediate green precipitate, but ketones do not react. 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 on the carbon bearing the oxygen atom (see **Alcohols** section as well).

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



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

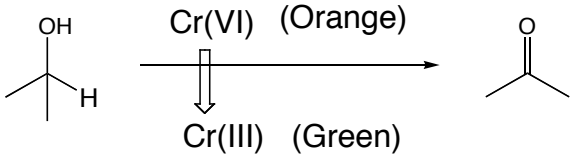
3. Phenols

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.

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. Alcohols

Chromic acid will oxidize primary and secondary alcohols. Tertiary alcohols do not react. See **3b**.

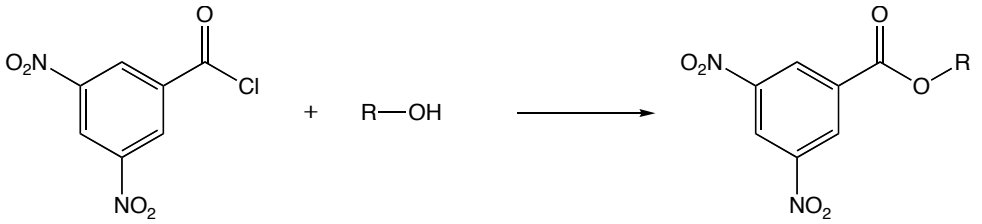


C. Preparation of Derivatives (Unknown #1 only):

Once you know the functional group in your compound, you need to characterize it by preparing a derivative.

1. Alcohols and Phenols

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



Place about 0.75 gram of 3,5-dinitrobenzoyl chloride in approximately 2 mL of dry pyridine. Add about 0.5g or 0.5 mL of alcohol or phenol, and heat for 30 minutes under reflux. Cool the mixture, and pour into a solution of 3 mL of 5% sodium bicarbonate, 3

mL of water, and some crushed ice. Stir vigerously, keeping the mixture cool until a product crystallizes. Collect and recrystallize from ethanol-water as described below. If after 10 minutes of stirring no product has crystallized, proceed with the following extractive workup: Pour the mixture into a separatory funnel (not the stir bar) containing 20 mL CH_2Cl_2 and 10 mL 5% sodium bicarbonate. Shake, venting frequently, and then retain the organic layer. Wash the organic layer with 1M HCl until the washings test below pH 2, then wash the organic layer with 20 mL of brine. Dry the organic layer over sodium sulfate, filter and concentrate using the rotary evaporator. Recrystallize the resulting product from ethanol-water as follows. Add enough hot ethanol to dissolve the compound; allow the solution to cool. If crystallization does not take place, add water a drop at a time until the solution becomes cloudy.

2. Aldehydes and Ketones

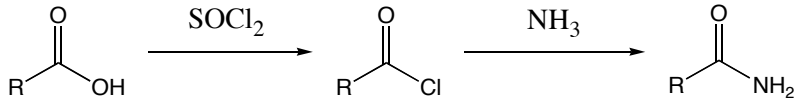
Prepare a 2,4-dinitrophenylhydrazone.

On a larger scale than your spot test (see 2a. of Functional Group Tests), prepare enough of the derivative to recrystallize and take its melting point. Ethanol-water is often used for recrystallization.

3. Carboxylic Acids

Prepare an amide derivative.

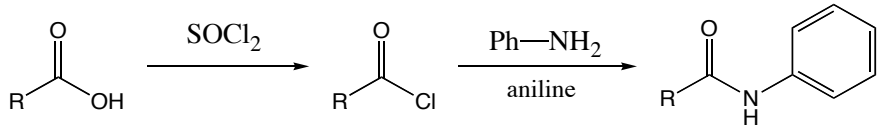
CAUTION! Thionyl chloride is a lachrymator. It reacts violently with water to give HCl.



Under your hood, add about 0.5g of the acid to about one mL of thionyl chloride. Heat under reflux for 30 minutes. Cool. Still under the hood, pour into a beaker containing about 5 mL of cold concentrated ammonia (ammonium hydroxide) solution. Note: Your product should be the solid material in your beaker, not the white solid (NH_4Cl) which may deposit on the glass above the solution. The product can be recrystallized from ethanol - water.

OR

Prepare an anilide derivative. On occasion, amide derivatives are difficult to prepare successfully. If you wish, you may try to prepare an anilide instead.



Follow the procedure for converting your acid into its acid chloride as outlined for the amide derivative. Cool the mixture and carefully and add to it 1 gm of aniline which has been dissolved in 25 mL of toluene. Warm for about 5 minutes on a hot plate, then

transfer to a separatory funnel. Wash this solution sequentially with 5 mL of water, 5 mL of 5% HCl, 5 mL of 5% NaOH, and finally with another 5 mL water. Dry the toluene layer over anhydrous Na_2SO_4 and evaporate to dryness. Recrystallize the resulting anilide from water or ethanol-water.

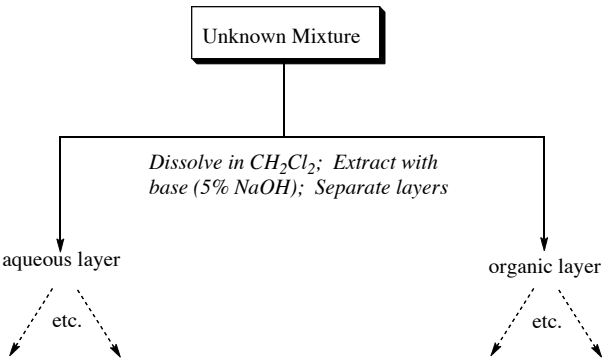
4. Esters

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}HNMR you performed on the original ester.

Place 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. Reflux the mixture for about one hour, allow it to cool, then add 6M HCl until the mixture is clearly acidic. If a precipitate forms, collect it by vacuum filtration. If no precipitate forms, extract the solution with two 20- mL portions of ether. Dry the ether solution with anhydrous Na_2SO_4, filter or decant the solution, and distill it to remove the ether. You may continue the distillation after the ether has been removed to determine the boiling point of your acid component.

PRELAB

(1) Prepare a flowchart that clearly outlines the separation protocol for a mixture of unknowns. For example:



(2) You have an unknown that is either a ketone or an aldehyde. What signal in a ^{1}H NMR spectrum could distinguish between these functional groups?

(3) You were given a mixture of unknowns containing a carboxylic acid and a phenol. How can you separate this mixture? Briefly explain your reasoning. *HINT: Carboxylic acids generally have a pK_a range of 3-6, and phenols a pK_a range of 9-11.*

Laboratory Report

For each unknown compound, complete the two page laboratory report form supplied below. Make sure your analysis ***unambiguously*** (very important!) identifies each compound structure.

Laboratory Report for Experiment #2 Name_____

Section_____

Date_____

UNKNOWN CODE: _____

A. Physical Characteristics

1. Solid or liquid

   Color

   Odor

2. Melting point (report your value as a range)

FUNCTIONAL GROUP TESTS (Required for unknowns #1 & #2)

Negative tests:

Inferences:

Positive tests:

Inferences:

DERIVATIVE (Required for unknown #1)

Results:

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 or GC-MS (attach a copy of the MS)

Fully analyze the important signals below:

MY UNKNOWN IS: _____