

LABORATORY SYLLABUS

INSTRUCTORS: Beatrice Ruhland, Ph.D.; Richard DiPietro, Ph.D.

TIMES: Monday/Wednesday: 8:00–12:30 PM; 4:30–9:00 PM;
Tuesday/Thursday: 8:00–12:30 PM; 4:30–9:00
Laboratories begin on **Monday, June 16**, and are held in DS 126

MATERIALS:

- This syllabus is available on Camino, for purchase from Copy Craft Printing, 341 Lafayette St. or from the Chemistry 31-33 laboratory site (<https://sites.google.com/a/scu.edu/organic-chemistry-laboratory/>)
- *Experimental Organic Chemistry* by Gilbert and Martin, SCU Custom Edition, 2011
- Bound laboratory notebook embossed with "Santa Clara University", Scientific Notebook Company (available from the bookstore)
- Safety splash goggles
- Laboratory coat (available from the bookstore)

COURSEMATE:

CourseMate is a website that contains valuable additional material associated with the course. If you don't already have the code required for access to the website, it is available from Lourdes Barretto in DS 113. **You must show her a receipt for purchase of the textbook to obtain your code.** The steps for accessing the website are as follows:

1. Go to www.cengagebrain.com
2. Click on "Sign up"
3. Complete the form
4. Type "gilbert" in the box, not the ISBN, because the custom version has an ISBN that is not in the system.
5. Enter to "Access Key" (code) provided to you by Lourdes.
6. Follow the rest of the instructions as prompted by the system.

LABORATORY GUIDELINES:

1. The laboratories in Daly Science 100 were modernized and redesigned in 1994, with safety as the primary concern. The main improvement in these labs was increasing the number of hoods so that each student has a workstation in a hood, two students per hood. This significant enhancement in safety protects everyone because many organic compounds are volatile and using a hood minimizes your exposure to fumes. Therefore, **virtually 100% of your chemical work should be performed in a fume hood.**
2. To do organic chemistry safely, you should treat all chemicals with respect; gloves should be worn unless otherwise directed by the instructor.
3. Because we are limited in space for each lab section, you may only attend your assigned laboratory time. To be granted an exception for special circumstances, you must request permission *from both your regular lab instructor and the lab instructor for the lab you wish to attend.* An e-mail to both instructors is the easiest method to achieve this; if you do not make a formal request to both instructors, you will not be admitted to another laboratory section.
4. Care of the organic laboratory is important because some 200 students share this organic facility each term, so we must regularly maintain this facility. It is important that you **clean your work area at the end of each lab period** as well as help with keeping the balances, instrument room, and other general use areas clean. **Inform the instructor of any spills and clean up the spill completely.**

COMMENTS:

Most students enjoy organic lab; it can be challenging, stimulating and rewarding. This is partly due to the relatively unstructured nature of the lab. After the first few technique experiments, you can work at your own pace and follow whatever sequence of steps seems best for your particular project. As a result, you are left to your own initiative to a much greater extent than in most labs you have taken. If you plan your work in advance and make a real effort to understand what you are doing, then even unexpected problems that always arise can be stimulating challenges.

NOTEBOOK:

Your laboratory notebook is the primary record of your lab work. Please look carefully at the guidelines on pages 16–17 of this syllabus before making entries in your notebook. Remember that a complete, well-organized notebook is critical for someone to be able to repeat your work and serves as the primary basis for your grade in the laboratory.

SCHEDULE:

Lab will start the first week of the term. Because we are limited in space for each laboratory section, you may only attend your assigned laboratory time. To be granted an exception for special circumstances, you must request permission *both from your regular laboratory instructor and from the laboratory instructor for the laboratory you wish to attend*. An e-mail to both instructors is the easiest method to achieve this; if you do not make a formal request to both instructors, you will not be admitted to another laboratory section. **The notebooks are due on the last regularly scheduled laboratory period of the term, and you must check out of your locker by then.**

SAFETY:

It is important to read the safety section in the laboratory textbook *carefully*, pages 16–23, on the front page of the book, *and* the back of your laboratory equipment check-in card before signing it. Critical points are highlighted below.

1. **Safety goggles and a lab coat must be worn in the laboratory at all times!**
2. **To prevent exposure of others to chemicals, do not wear your lab coat or gloves outside of Daly Science 100.**
3. **Required apparel for working in a teaching or research laboratory in the Department of Chemistry & Biochemistry at SCU:**
 - a. Laboratory coat.
 - b. Long pants.
 - c. Closed-toe shoes, ideally with a non-permeable upper component covering the foot.**Failure to meet these requirements will result in a student having to leave the laboratory until such time as any deficiencies have been addressed.**
4. Use of cell phones, radios, iPods, and the like is *not* permitted in laboratory.
5. Most organic solvents are flammable and should never be heated with an open flame. Hot plates or heating mantles are available for this purpose. **The instructor's permission is required to use an open flame in the laboratory.** Some solvents such as diethyl ether, *t*-butyl methyl ether and methanol have flash points so low that they can be ignited by the surface of a hot plate.
6. Be sure to handle organic chemicals carefully as many are toxic if absorbed through the skin or inhaled. **Gloves must be worn for all experiments.** Disposable gloves are provided in the laboratory. Change gloves when necessary. To avoid chemical contamination of the chemistry building, do not use gloved hands to handle objects outside the laboratory.

7. Substances with noxious or toxic vapors must be handled only in the fume hoods. **In general, you should perform all work at the fume hoods.**
8. Neatness in carrying out laboratory work is related to safety. It is important that each student help keep the laboratory clean and organized. Allow enough time for clean-up when planning your laboratory activities.
9. Report all accidents and spills to the instructor.
10. Use water to immediately wash off all chemicals that are accidentally spilled on your skin.
11. Know the locations of the safety showers, eyewash stations and fire extinguishers

WASTE DISPOSAL:

One of the most important practices in lab is the proper disposal of chemical wastes. The only substance allowed to go down the drain is uncontaminated water. The general rule is that **nothing should be poured into any sink or placed in the garbage cans**. There are containers in the lab for the various kinds of waste materials generated: aqueous waste, basic aqueous waste, acidic aqueous waste, solid organic waste, organic solvent waste (non-halogenated), halogenated organic waste, and contaminated glass. Be absolutely positive that you are putting the proper materials in the containers. Useful directions for waste disposal are provided with each experimental procedure provided in the textbook, and there is a handout that specifies where to put the waste you generate as a result of performing experiments. Remember that anything with **WATER** in it is an aqueous waste and must go in one of the containers so labeled. It is also extremely important that you enter into the appropriate logbook the identity and amount of each substance added to each container. **If you are unsure of which container to use, ask one of the lab instructors.**

ACADEMIC INTEGRITY:

You are expected to uphold the university policy on academic integrity. In the context of the laboratory, you may help each other understand and complete various procedures. However, **all work recorded in your notebook must be your own**. If your instructor ever tells you to include data from a fellow student, that data should be clearly referenced. Giving or receiving unauthorized aid in any form can result in course failure. See your instructor if further clarification is needed.

FORMAT:

Roughly the first half of this session's laboratory will be devoted to learning important laboratory techniques. During the second half, these techniques will be applied in two synthetic reactions and separating, purifying and identifying two components in an unknown mixture. The overall scheme of the lab and some of the specific procedures to be followed are contained in this syllabus; other procedures can be found in the lab text. In addition, this syllabus, worksheets, and other information such as the grading template for the experiments are available on the Chem 31 lab Canvas or Google site webpages. The grading template is also found on page 26 of this syllabus.

Lab lectures describing important details of each experiment will be held during the regular laboratory time at the beginning of the lab. It is therefore very important that you are on time to lab so that you get the vital information to complete the experiment. It is also very important that you come prepared for lab and know exactly what you are to accomplish that day in lab. Because you may not attend other laboratory sections it is important that you make the most of your time in lab.

Data, observations, conclusions, and results for all experimental work should be included in your notebook. Pay close attention to the syllabus and the experimental procedures for any specific data or analyses that are requested. All but one of the experiments also asks you to answer specific questions, and these answers should also be written directly in the notebook at the end of the appropriate

experiment. **Notebooks are due on your last scheduled laboratory period for the session.** If you have any questions about when to turn in your notebook, please see your instructor. Please note that a grade cannot be issued for the course unless you have completed the laboratory and turned in a notebook, so be sure to submit your notebook to your laboratory instructor on time.

DESK EQUIPMENT:

The apparatus that you use in organic chemistry laboratory is likely to be unfamiliar to you, based on your prior laboratory experience. To assist you in recognizing the various items in your desk, assembling the apparatus for various experimental procedures, and showing the steps involved in some of the techniques you will be using, references to relevant web videos are provided. Viewing them *prior* to coming into the laboratory will make it easier for you to perform the assigned experiments.

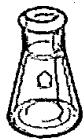
A figure showing some of the apparatus in your desk is provided on page 5 of this syllabus. When checking into the laboratory, be certain that your glassware is clean and is not chipped or cracked. Show any dirty or damaged glassware to your instructor to determine whether it needs to be replaced. In addition, return any excess equipment to the bin near the door leading to the stockroom.

Approximate Laboratory Schedule: Experiments to complete each laboratory meeting or session

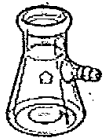
Session	Experiments	Reading in Text and Exercises
1AB	Purification by Distillation	Distillation: Secs. 4.3 and 4.4, pp. 131–134, and 135–143 Experimental Procedures: Simple distillation: Syllabus p. 7; Fractional distillation p. 11 Exercises: 1bc,3 (p. 135); 2ab,6,7 (p. 143)
	Analysis by GC	Gas Chromatography: Sec. 6.4, pp. 196–207 Experimental Procedure: Syllabus p. 7-8
	Analysis by IR Spectroscopy	Infrared Spectroscopy: Sec. 8.2, pp. 240–256 Experimental Procedure: Syllabus p. 8
2AB	Purification by Recrystallization	Recrystallization: Secs. 2.7, 2.17, 3.2, and 3.3, pp. 38–41, 66–71, 94–101, 113–117 Thin-Layer Chromatography: Sec. 6.2, pp. 180–184 Experimental Procedures: Syllabus pp. 11–12 Exercises: 1cim,7,10 (pp. 110–111)
3	Monitoring a Reaction by TLC	Thin-Layer Chromatography: Sec. 6.2, pp. 180–184 Experimental Procedure: Sec. 17.4, p. 583 (microscale) and Syllabus p. 20,21 Exercises: 1,2 (Syllabus p. 21); 1,3 (p. 188)
4	Dehydration of Cyclohexanol	Sec. 10.3, pp. 348–352 Experimental Procedure: pp. 354–355 (microscale) Exercises: 3,26,28.32 [IR spectra only] (pp. 355, 358–359)
5	Bromination of Cinnamic Acid	Experimental Procedure: Syllabus pp. 21–24 Exercises: 1–3 (Syllabus p. 22)
6	Analysis of an Unknown Mixture: Separation and Purification	Secs. 2.21, 2.25, and 5.3, pp. 75–81, 87, 156–161 Experimental Procedure (modified): pp. 161–162 Should be syllabus pp. 13-15
7	Analysis of an Unknown Mixture: Identification	IR Spectroscopy: Sec. 8.2, pp. 240–256 ¹³ C Nuclear Magnetic Resonance Spectroscopy: Sec. 8.3, pp. 287–295 Tables of Compounds and Derivatives: Canvas

Organic Chemistry Lab

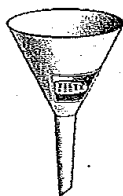
Glassware



Erlenmeyer
Flask



Filter
Flask



Hirsch
Funnel

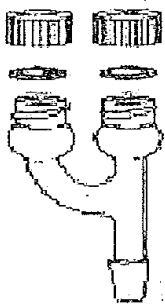


Short
Stem
Funnel

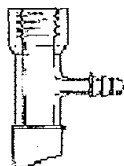


Centrifuge
Tube

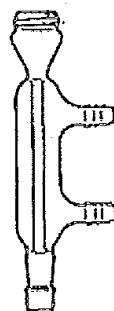
Microscale Kit



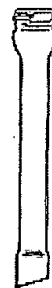
Claisen
Adapter



Thermometer
Adapter



Water
Jacket
Condenser



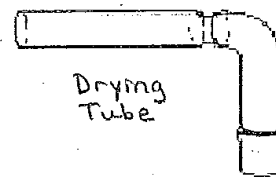
Air
Condenser



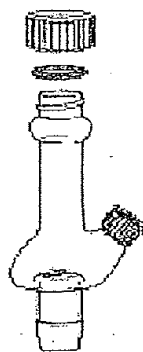
Spin vane
Stirrer



Stirring
Rod



Drying
Tube



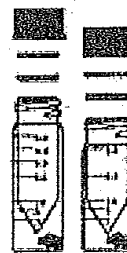
Hickman
Head



Craig Tube
& Plug



Round Bottom
Flask



5 mL conical vial
3 mL conical vial
0.1 mL conical vial



EXPERIMENTS:

1A. SEPARATION OF A BINARY MIXTURE BY SIMPLE DISTILLATION; ANALYSIS BY INFRARED (IR) SPECTROSCOPY AND GAS CHROMATOGRAPHY (GC)

Distillation is a common method for the separation of mixtures of liquids and the purification of liquids. In this experiment, we purposefully mix two liquids with very different boiling points and then practice separating them by a simple distillation. We then analyze the effectiveness of the separation by gas chromatography and infrared analysis. Read Section 4.3 (pp. 131–134) before starting this experiment.

Simple Distillation

Set up a simple distillation apparatus as shown on page 19 of this syllabus, using a 10-mL round-bottom flask containing a mixture of 3 mL of hexane and 3 mL of toluene. YouTube video showing set up: http://podcaster.gcsu.edu/podcastdata/GGC/Channel_6888/podcast_3336/3336.m4v. An arrangement using the air condenser rather than a water-cooled condenser should work fine. Equip the apparatus with a thermometer using the vacuum adapter to hold the thermometer in place. Make sure the thermometer bulb is positioned in the lower neck of the Hickman stillhead as described in the first paragraph on page 58 of the laboratory textbook. *Be sure to add a boiling stone to the distilling flask.* Heat the mixture by resting the round-bottom flask in the large well of an aluminum block supported by a stirring hotplate. The reservoir of the Hickman stillhead holds a little over 1 mL of distillate. As the reservoir approaches 3/4 full, record the temperature, uncap the side port of the Hickman stillhead and quickly remove the contents of the reservoir with a pipette. Reserve the liquid in a labeled vial. Be sure to recap the side port after removing a fraction! Continue collecting fractions in this manner until very little liquid remains in the round bottom flask. You will need to decide which fractions should be combined and used for gas chromatographic and infrared analysis. Usually, students save the first two and last two fractions. Be sure your samples are stored in tightly stoppered, labeled containers and placed in the refrigerator. Be sure to read the sections in the syllabus on gas chromatographic and infrared analysis; the lab instructor will assist you in these two procedures. Prepare a graph of temperature versus fraction number.

Gas Chromatography

Gas chromatography (GC) is a method to separate very small samples of liquids. Importantly, it also allows one to quantify the amount of each liquid in the sample. As a result, we can use GC to determine the effectiveness of the separation achieved in our distillations. See the next page for some information on the instrumentation and data associated with this technique.

The use of the gas chromatograph will be demonstrated, and the mole percent composition of the fractions saved for GC analysis from the distillation carried out above will be determined. Be sure to read Section 6.4 (pp. 196–207) before starting this part of the experiment and review the figures shown on the following page. YouTube video of gas chromatography: <http://www.youtube.com/watch?v=IJBctgHavoM&list=TLzbZ0JvilDzY>.

Make sure that the GC is turned on and running properly and that the chart recorder is on as well. Contact your instructor if you are unsure.

Now inject 2.5–3 μL of each of the appropriate fractions (usually just first and last fractions) saved from your distillation, waiting until the peaks for hexane and toluene appear for each GC trace on the recorder. Compare the GC traces you have obtained with the hexane and toluene standard sample GCs obtained by your instructor to confirm which peak is associated with each compound, hexane or toluene.

Measure the areas under the peaks manually as shown in Figure 6.19 (p. 204) or on page 9 of this syllabus, and determine the percentage of hexane and toluene for each of the fractions. All relevant data, calculations and conclusions must be clearly recorded in your notebook.

[The GC should be set up so that the column packing is 20% SE-30; oven temperature is 130–140 °C; helium gas flow of 30 mL/min; detector current of 100 milliamperes; and a chart speed of 0.5 in/min. You may be using new strip chart recorders, so other pertinent settings may be noted by your lab instructor.]

IR Spectroscopy

Infrared (IR) spectroscopy is a method for the identifying compounds, most often for the functional groups present in a sample. Examples of two IR spectra are provided on page 9 of this syllabus.

After learning how to use the IR spectrometers, acquire an IR spectrum for each of your saved fractions. Compare these spectra to the known spectra for pure hexane and toluene. Consider and comment on what conclusions are possible regarding identity and purity.

Directions for running IR spectra can be found in Section 8.2 of the laboratory textbook, and your laboratory instructor will also demonstrate the use of the instrument. In your reading, focus on the use of simple salt plates using "neat" (pure) liquid samples (Figure 8.4, p. 243). In this experiment, simply wipe the salt plates clean with a Kimwipe between samples. ***Never clean sodium chloride IR plates with water; they will dissolve!***

Gas Chromatography (GC)

Introduction to Organic Laboratory Techniques: A Microscale Approach, 4/e ■ Perla, Lampman, Kilo, Engel

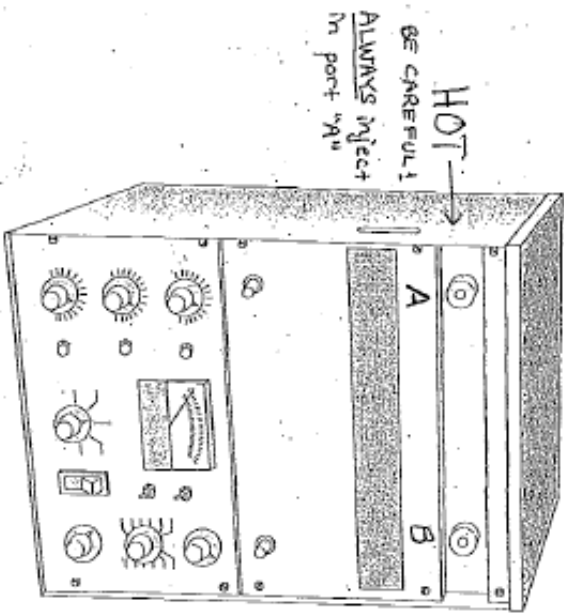
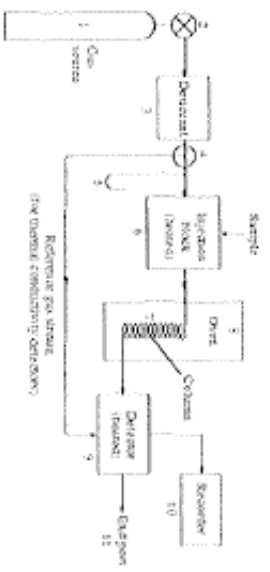


Figure 22.1. Gas chromatograph.

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Figure 6.13 Schematic diagram of apparatus for GLC

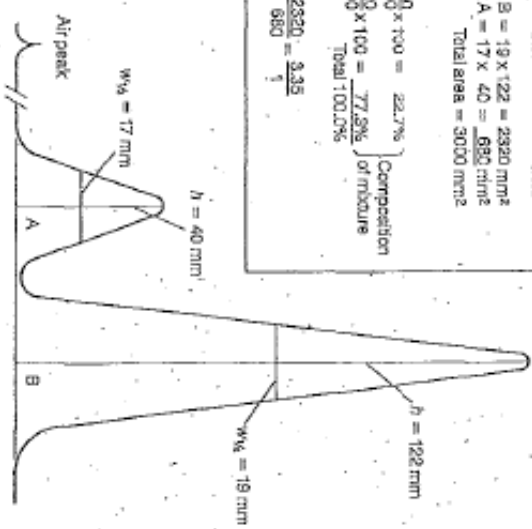


Do these calculations

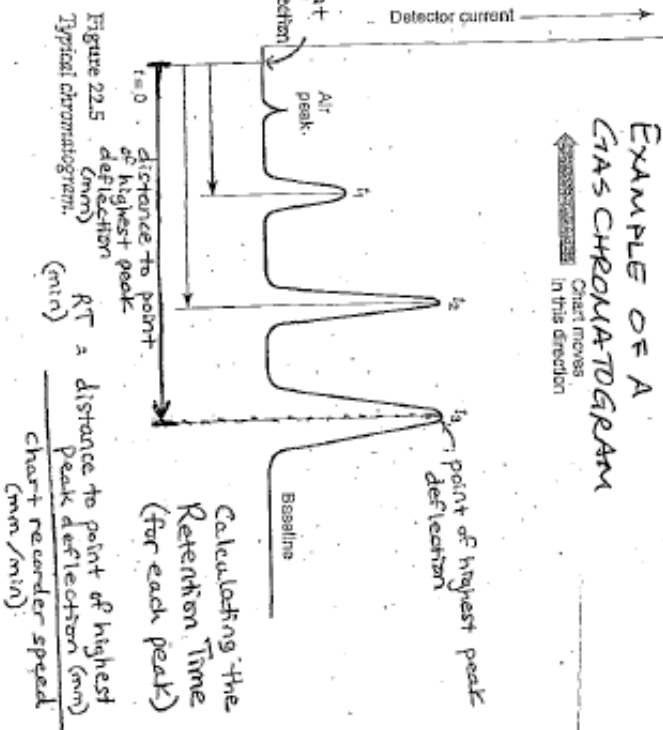
Area Peak B = $19 \times 122 = 2320 \text{ mm}^2$
 Area Peak A = $17 \times 40 = 680 \text{ mm}^2$
 Total Area = 3000 mm^2

$\%A = \frac{680}{3000} \times 100 = 22.7\%$
 $\%B = \frac{2320}{3000} \times 100 = 77.3\%$
 Total 100.0%

Ratio $\frac{B}{A} = \frac{2320}{680} = 3.39$



EXAMPLE OF A GAS CHROMATOGRAM



Example of an Infrared Spectrum

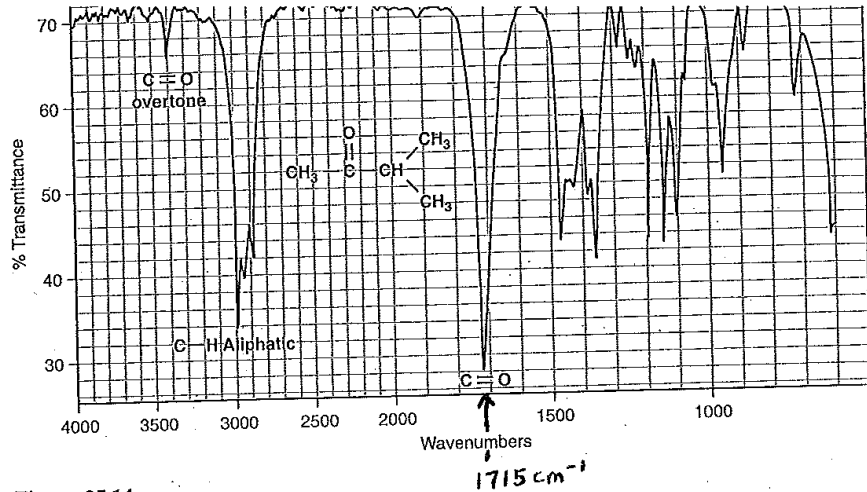


Figure 25.14
Infrared spectrum of methyl isopropyl ketone (neat liquid, salt plates).

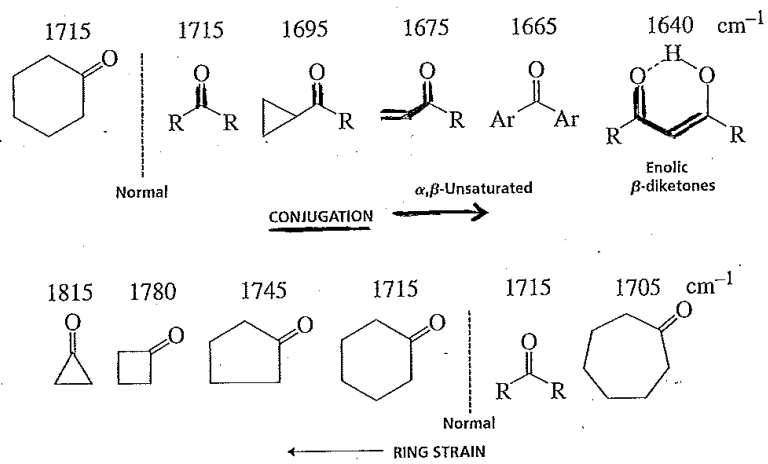


Figure 25.30
Effects of conjugation and ring strain on carbonyl frequencies in ketones.

IR Spectrum of a Conjugated Carbonyl-containing Compound:

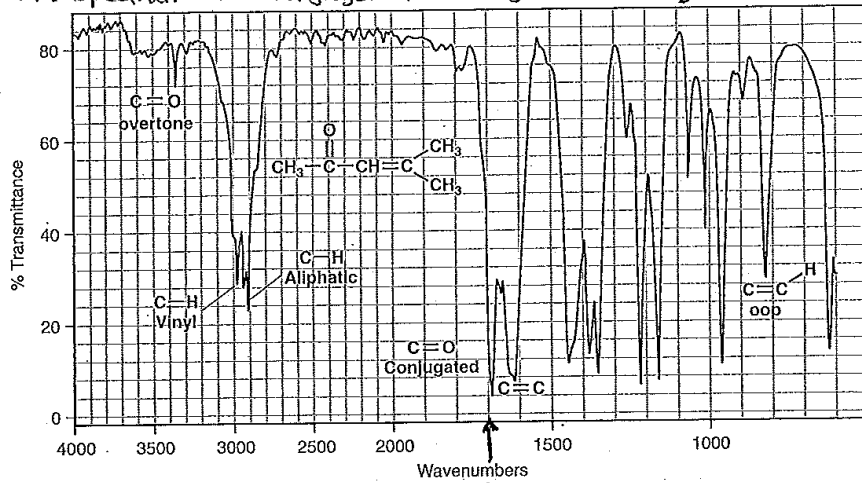


Figure 25.31
1675 cm^{-1}

1B. SEPARATION OF A BINARY MIXTURE BY FRACTIONAL DISTILLATION; ANALYSIS BY INFRARED SPECTROSCOPY AND GAS CHROMATOGRAPHY

This experiment mirrors Experiment 1A, but now *fractional* rather than *simple* distillation is used. An important part of your analysis is comparing and contrasting the results of this experiment with those of Experiment 1A.

Fractional Distillation

Read pages 135–143 before starting this experiment. YouTube video showing set up: http://podcaster.gcsu.edu/podcastdata/GGC/Channel_6888/podcast_3336/3336.m4v.

Set up the fractional distillation apparatus as shown on page 18 of this syllabus. Be sure to use a thermometer as in the simple distillation of Experiment 1A. Pack the fractionating column (the air condenser is used for this purpose) loosely with stainless steel sponge or copper ribbon as shown in the figure. Distill a fresh 6-mL mixture of hexane and toluene in a fashion similar to that used in Experiment 1A. Decide which fractions should be combined and used for gas chromatographic and infrared analysis. Be sure your samples are stored in tightly stoppered, labeled containers and placed in the refrigerator. Remember that these analyses should be carried out as soon as possible after the samples have been collected. Graph temperature versus fraction number.

Gas Chromatography and IR Spectroscopy

Carry out GC and IR spectral analyses for your fractions just as you did in Experiment 1A. See those sections above for the relevant details.

Comparative Analysis

Determine and discuss the relative efficiency of simple versus fractional distillation. Special emphasis should be given to comparisons of your respective plots of temperature vs. fraction number and the respective purities (as determined by GC analysis) of your fractions generated by simple (Exp. 1A) versus fractional (Exp. 1B) distillation.

2A. RECRYSTALLIZATION OF IMPURE SOLIDS

Recrystallization is a common method for the purification of solids. In this experiment, we will learn the basics of recrystallization by purifying a sample of acetanilide according to an optimized procedure provided in the syllabus. Subsequently, you will optimize your own procedure for the recrystallization of an impure sample of fluorene. The success of the purifications will be analyzed by taking melting point ranges and performing thin layer chromatography (TLC) for both the original and the purified samples. Be sure to read about filtration (pp. 66–71) and recrystallization (pp. 93–101) before performing any recrystallizations. YouTube video for recrystallization: <http://www.youtube.com/watch?v=genmtAjsDzA>; video for filtration with a Büchner or Hirsch funnel: <http://chem.illinois.edu/SABICstudio/237/vacuum-filtration.html>.

Semi-microscale Recrystallization of Acetanilide

Obtain a small sample of impure acetanilide in a melting point capillary to determine the melting point range. This capillary may be saved and its sample's melting point determined side-by-side with that of recrystallized acetanilide. Review the procedure under “2” on page 107 of the laboratory textbook, but instead of 100 mg, of acetanilide, weigh out a 150-mg sample of impure acetanilide and place it in a 10-mL Erlenmeyer flask. (Note – the sample need not be *exactly* 150 mg, but you should enter the exact amount you do use in your notebook. For many of these technique experiments, the amounts we use are not critical, but accurately reporting the amounts is always critical.) Add 4.0 mL of water, clamp the flask to a ring stand and heat to boiling using the proper well of the aluminum block heating setup. Heat the

solution until all of the solid dissolves. In this case, we have previously determined that 4.0 mL of water (the solvent) should be enough to dissolve 150 mg of sample (the solute), but ordinarily one does not know how much solvent will be necessary. If your sample is not fully dissolved, add additional small amounts of hot water until complete dissolution is reached. If any insoluble solids remain, they must be removed by filtration (ask your instructor).

Allow the flask to cool to room temperature. Then, place the Erlenmeyer flask in a small beaker of ice water to complete the crystallization.

Collect the crystals by vacuum filtration using a Hirsch funnel. With the vacuum still on, rinse the crystals with three 0.5-mL portions of ice-cold water. Use a clean micro-spatula to press the crystals as dry as possible on the funnel. Dry and weigh the crystals and determine percent mass recovery. Determine the melting point range of your crystals (laboratory textbook pp. 38–41) and also the melting point range of the impure acetanilide.

You may want to wait until the next laboratory period to weigh the crystals and determine their melting point because it can be especially difficult to remove the last traces of solvent from crystallized material, particularly if water is the solvent. Small traces of solvent can lower melting ranges substantially. Try drying a sample for a melting point by working a small sample of the solid on a piece of dry filter paper until the sample is a fine powder. You may also place your sample on a piece of filter paper (well labeled) under the heat lamp. Remember that the temperature under the lamp can melt some solids, so exercise caution when using the heat lamp with unknown samples.

Semi-Microscale Recrystallization of Fluorene

Carry out the recrystallization of a 300-mg. sample of fluorene (colorless) contaminated with 9-fluorenone (colored; look up its color). The eventual procedure will be identical to that used for acetanilide above, but initially you will have to determine which solvent will work best. Using the approach described on pp. 101–102 of the laboratory textbook and water, methyl alcohol, and toluene as trial solvents, experimentally determine the best proportion of solvent to solute for the recrystallization. YouTube video: <http://www.youtube.com/watch?v=genmtAjsDzA>. Make sure to include any observations or conclusions about the process in your notebook entries.

2B. ANALYSIS OF PURITY BY THIN-LAYER CHROMATOGRAPHY (TLC)

The impure and recrystallized samples of acetanilide and fluorene will be analyzed by thin-layer chromatography (TLC). The purified samples should show only one spot whereas the impure samples may show several. To understand this expectation, make sure you read about TLC on pages 180–184 of the laboratory textbook. YouTube video for TLC: http://www.youtube.com/watch?v=rpb_Qc4jMAc. Plastic-backed TLC plates of the proper size will be available for your use.

The choice of developing solvent is one of the most important factors for successful separations by TLC. Generally, the choice is made by experimenting with different solvents or combinations of solvents until one is found that separates all the components of the mixture to be analyzed. You will find a variety of eluting solvents pre-prepared in the eluting chambers available in the fume hood near the white board at the front of the room. Be certain to note the particular solvent or combination of solvents that you use for your analysis in your laboratory notebook.

A good general rule when testing the purity of a compound is to use a solvent in which the test compound has an R_f of 0.3–0.5. In this case, start by trying a 2:1 mixture of ethyl acetate:hexane as the developing solvent for the acetanilide samples and 2:1 hexane:methylene chloride as the developing solvent for the fluorene samples.

Obtain a TLC plate and spot the plate with solutions of the impure and recrystallized acetanilide samples as described in the “Setting Up” on pp.185 of the laboratory textbook. Prepare another plate in similar fashion with the fluorene samples. Remember that the spotting solution is prepared using a volatile solvent such as methylene chloride or acetone. Unlike the developing solvent, the choice of spotting solvent is not very critical; the criteria are simply that it adequately dissolves the sample and that it evaporates quickly.

After the solvent has evaporated from the spotted plate, develop it in the screw-cap jar serving as the developing chamber (Figure 6.3, p. 181), following the “Preparing and Developing a Plate” procedure (p. 185). Remember to keep the chamber you use *capped* while developing your TLC plate; otherwise, the solvent will evaporate! Be sure to stop development *before* the solvent reaches the end of the plate! Observe the spots by using a UV light and also by using iodine as the visualization reagent. Calculate the R_f value for the spots detected as described on page 183 of the textbook.

3. Monitoring a Reaction by Thin-Layer Chromatography (TLC)

The course of the reduction of a carbon-oxygen double bond will be monitored by TLC. Follow the procedure provided on p. 20 of this syllabus.

4. DEHYDRATION OF AN ALCOHOL: FORMATION OF CYCLOHEXENE

Follow the microscale procedure on pages 354–355 for the preparation of cyclohexene. YouTube video showing set up: http://podcaster.gcsu.edu/podcastdata/GGC/Channel_6888/podcast_3336/3336.m4v. Take an IR spectrum of your product, but not an NMR spectrum.

5. BROMINATION OF CINNAMIC ACID: SYNTHESIS OF 2,3-DIBROMO-3-PHENYLPROPANOIC ACID

Perform this experiment according to the supplemental procedure on pages 16–17 of this syllabus or on the Chem 31L Canvas page. Be sure to obtain and read the procedure at least one day before doing this experiment. When your product is dry, perform an IR and melting point analysis of the crude product. For additional fun, perform a TLC analysis comparing your product and the starting cinnamic acid to determine whether your reaction was successful. You first will have to determine what developing solvent separates the two compounds, which can be somewhat challenging because carboxylic acids tend to “streak” up the TLC plate (meaning they leave a long spot trailing from the baseline). A small amount of ethanol, methanol, or acetic acid added to the solvent mixture can solve this problem. Be sure your notebook entry includes the answer the questions at the end of the supplemental procedures.

6. ANALYSIS OF AN UNKNOWN MIXTURE

Introduction

A solution of two organic compounds dissolved in an organic solvent will be supplied. The experiment involves the separation of the two compounds from each other and from the solvent, the purification of each component, and the identification of each component. Importantly, you will use all of the techniques learned in the early experiments in order to complete this task.

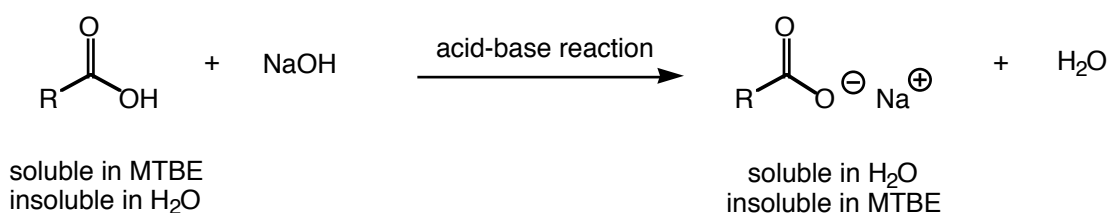
Specifically, you will be given a test tube containing two organic compounds dissolved in the organic solvent methyl *t*-butyl ether (*t*-BuOMe, also called MTBE). One of the organic compounds in the solution will be a neutral liquid: an aldehyde, ketone, alcohol or ester; the other compound will be a solid carboxylic acid. Both compounds are soluble in *t*-butyl methyl ether but insoluble in water. In order to identify the components of the mixture, you will have to separate the compounds from each other and from the solvent, purify each compound, determine the physical properties of each one and identify each one by comparing its physical and chemical properties with those of a limited selection of known compounds listed in the tables on the website for the textbook (www.cengage.com/login). In addition to being limited to compounds in these tables, the neutral unknowns will have only a single functional

group, *exclusive* of halogens, nitro groups, aromatic rings, and carbon-carbon multiple bonds. The acids will be carboxylic acids.

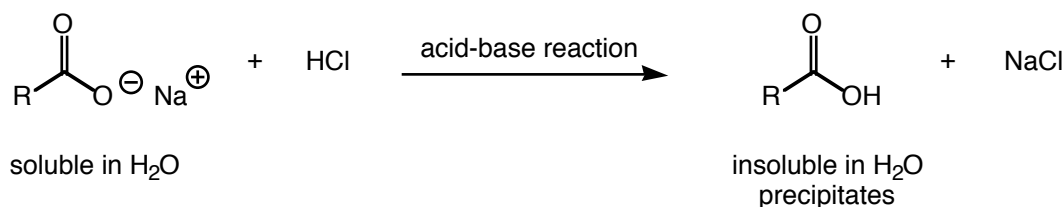
A good general description of the strategy involved can be found in the lab text on pages 156–161. **Also see the Extraction Flow-Chart in this syllabus (p. 25) for an outline of the sequence.**

Separation of the Acidic from the Neutral Unknown: Extraction

Although both unknowns are generally soluble in *t*-butyl methyl ether and insoluble in water, the acidic unknown is converted to a water-soluble, *t*-butyl methyl ether-insoluble salt by reaction with aqueous base (5% sodium hydroxide). The procedure involves the extraction of the acidic unknown from the *t*-butyl methyl ether solution using aqueous base. Because *t*-butyl methyl ether and water are immiscible, separation of the two liquid layers can be carried out mechanically; the lower aqueous layer will contain the acidic unknown in the form of a water-soluble salt, and the upper *t*-butyl methyl ether layer will contain the neutral liquid. (densities: H₂O, *d* = 1.000 g/mL; *t*-BuOMe, *d* = 0.740 g/mL).



After the two layers have been separated, the acid is recovered by acidification with HCl after which the carboxylic acid precipitates from water as shown below.



Before starting this part of the experiment, you should read pages 75–81 and 156–161 of the laboratory textbook.

Select an unknown, *being sure to record the unknown number in your notebook*. Each unknown contains approximately 0.5 g of the solid carboxylic acid and 2 mL of the liquid neutral compound dissolved in about 4 mL of *t*-butyl methyl ether. Place the solution in your centrifuge tube and add 3 mL of 5% NaOH solution (dilute, aqueous base). If you have a solid in your unknown sample vial, wash the solid into the centrifuge tube with an extra 1 mL of 5% NaOH and continue. Cork the tube and shake it gently for 30 seconds. Allow the phases to separate completely so that you can see two distinct layers. The aqueous phase should be the bottom layer. (When unsure if a phase is aqueous or organic, add a drop of water and see in which phase it dissolves.) Next, using a Pasteur pipette with a 2-mL rubber bulb attached, squeeze the bulb and insert the pipette into the centrifuge tube so that the tip touches the bottom. With experience, you should be able to judge how much to squeeze the bulb to draw in the desired volume of liquid. Pipette out the lower water layer and store it in a clean 50-mL beaker. Leave the remaining ether layer in the centrifuge tube. The above process is considered one extraction cycle.

The *t*-butyl methyl ether layer in the centrifuge tube must be extracted *twice* more using fresh 3-mL portions of aqueous base. After each extraction, combine all aqueous layers in the 50-mL beaker. A final extraction with 3 mL of water should be performed and the rinse water added to the combined 9 mL of

aqueous extract in the 50-mL beaker. The *t*-butyl methyl ether solution should be placed in a 10-mL Erlenmeyer flask and a few micro-spatulafuls of anhydrous sodium sulfate (Na_2SO_4) added as a drying agent to remove traces of water. Read page 87 in the laboratory textbook for further details.

The combined aqueous layers (the three 3-mL NaOH portions and the 3-mL water wash) that contain the salt of the organic acid are made acidic by adding enough 10% HCl (a dilute aqueous acid) so that the solution turns blue litmus paper red, or records a pH below 7. The addition of the aqueous hydrochloric acid converts the salt of the unknown to the free acid. Because the organic acid itself (in contrast to its salt) is insoluble in water, it precipitates from the solution. You can actually use the cessation of precipitation as a guide to when acidification is complete. The solid is then isolated by vacuum filtration using a Hirsch funnel.

The liquid unknown may be separated from the *t*-butyl methyl ether solution by distillation. *t*-Butyl methyl ether has a boiling point of 55 °C; the unknowns all boil above 90 °C; consequently, a simple distillation is efficient enough to separate them. When the *t*-butyl methyl ether solution has dried (wait a minimum of 15 minutes), use a dry Pasteur pipette or a dry filter-tip pipette to remove the solution from the drying agent and transfer the solution to a dry 10-mL round-bottom flask. Use simple distillation (but use a water-jacketed condenser rather than an air condenser) to remove the volatile *t*-butyl methyl ether. The residue in the 10-mL round-bottom flask is the neutral liquid unknown.

Purification of the Unknowns

The liquid unknown may then be purified by simple distillation. Transfer the liquid neutral compound to an appropriate sized conical vial and perform a simple distillation of this residue using the apparatus portrayed in Figure 2.38 of the textbook. Insert a thermometer inside of the condenser so that the bulb is positioned in the neck of the Hickman stillhead. Wrap the top of the vial and the neck of the stillhead with aluminum foil in order to insulate the apparatus. You may combine any fractions that boil at the relatively constant temperature range that will be achieved. This temperature is the boiling point of your liquid unknown; make sure to record it in your lab notebook. The purity of the distilled liquid should then be determined by gas chromatography. You should see only one peak if the liquid is pure.

The solid unknown is to be purified by recrystallization. You will have to find an appropriate solvent (Section 3.2, p. 101). Solvent selection can be very time consuming so here are some tips. Carboxylic acids are rather polar, so for most of them a solvent like methanol, ethanol or water works well. Test your compound in test tubes with these three solvents using very small amounts of material. (Recall the procedure you used to determine the solvent for the fluorene recrystallization.) You may find you need to perform a mixed solvent recrystallization, about which you should ask your instructor.

Once your solid is recrystallized and dried, check its purity by performing a TLC (ask your instructor about choices for a developing solvent) and obtaining a melting point. Because you don't know the melting point of your unknown (and it may be anywhere between about 110 °C and 250 °C) the most efficient way to determine the melting point is the following. Fill *two* melting point capillaries and determine an *approximate* melting point on one sample by allowing the temperature of the apparatus to increase relatively rapidly, say 20–30 °C/minute. The melting point obtained will be *below* the true one because the measured temperature lags behind the actual temperature of the apparatus. After getting a rough idea of the melting point of your unknown, allow the apparatus to cool somewhat and then get an accurate melting point for your second sample by having the temperature of the apparatus increase by only about 2 °C/minute.

At this point, report the melting point of the solid unknown and the boiling point of the liquid unknown to your lab instructor. If your melting or boiling point is off by more than ± 10 °C, you will be required to recrystallize again or re-distill. Alternatively, you may be able to obtain an accurate boiling point using the microscale boiling point method described in Section 2.21 and on page 131. If your sample is less than

95% pure by GC or shows two or more spots on the TLC, you will also be required to re-distill or recrystallize again.

Spectroscopy: Functional Group Determination and Compound Identification

Very simply, IR spectra will be used in two ways: to verify the presence of a particular functional group and to verify the identity of the unknowns. A typical spectrum is shown on the next page, and the effect of conjugation on the location of the absorption for a carbonyl peak is outlined.

The presence of a particular functional group can be determined by comparing the absorption peaks in the IR spectrum of your unknown with those absorptions normally observed for a particular functional group. The usual absorptions for each functional group are described in Table 8.1 (p. 251). To identify the compound, you should attempt to interpret the major peaks as we have in class using an IR correlation tables (pp. 251–256). Also, the unknown spectrum can be compared with that of the suspected compound by visiting the following website: http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng

You will also be provided with the ^{13}C NMR spectra of your unknowns, which will allow you to determine the number of magnetically distinct carbon atoms in them. The spectra are found on Canvas. Consult with your instructor for assistance in interpreting the spectra of your unknowns.

For the liquid unknown, use IR spectroscopy to determine whether it is an aldehyde, ketone, alcohol, or ester. As part of the identification process, you will also compare the IR spectrum you have acquired with IR spectra of known compounds. Perform the IR analysis of your unknown liquid as you did for the liquid samples in Experiments 1 and 2. Rinse the salt plates with hexane (**not water!**) and dry them with a Kimwipe after using them.

No functional group determination is required for the solid unknown: the solid is a carboxylic acid. However, you need to acquire an IR spectrum for identification. Use the reflectance IR spectrometer that allows for the spectrum to be run directly on the solid unknown (rather than making a KBr pellet as described in your lab book). Your instructor can show you how to obtain a spectrum of your solid using this spectrometer. Check with your instructor after you have run the IR spectrum of the solid to determine the quality of this spectrum because some peaks look different in such spectra.

Compound Search

Compile a list of possible identities for each unknown. Fortunately, all the unknowns given to you will appear in one of the tables on the website for the textbook (www.cengage.com/login). There are separate tables for each functional group, and the compounds within each table are listed by increasing boiling/melting points. Consider as possibilities all compounds having boiling points or melting points within 5 °C of your experimentally determined value. Draw the structures of the possible compounds. Consider these structures seriously to determine how you may differentiate between them and look each up in reference books to find out how their physical properties may differ. With the limited techniques available at this point in the laboratory, you will need to focus on differences in secondary functional groups. You should also look up the reference IR spectrum for each possibility. Visit the following website for the spectra: http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng

Identification

After considering the possibilities and all of your data, you should draw conclusions about the identity of your unknown liquid and solid. Provide a thoughtful discussion of how you arrived at your conclusions, and make sure to provide both the name and a structural drawing for each compound. Briefly describe any difficulties you had with the process.

NOTEBOOK GUIDELINES

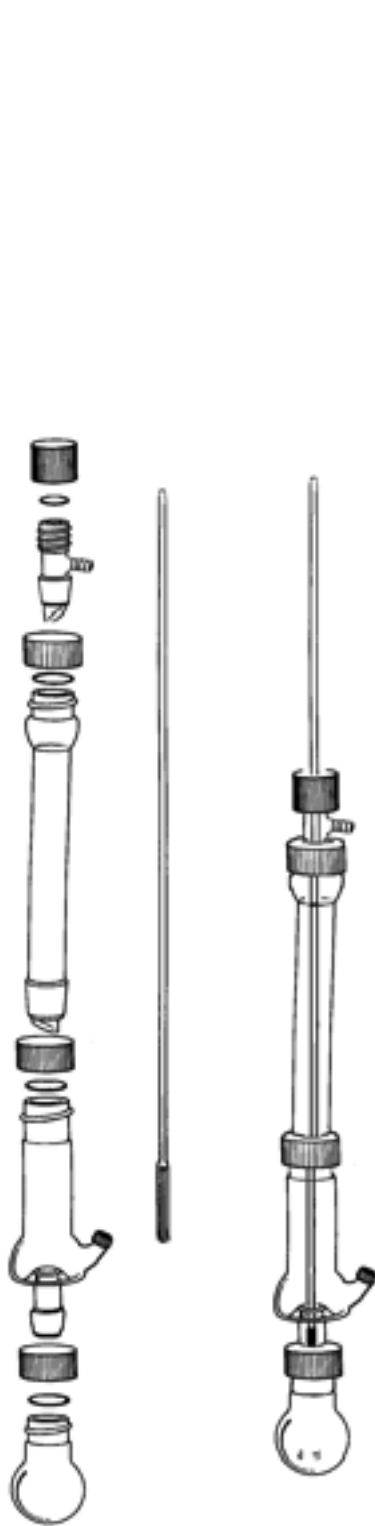
The guidelines are derived from those drawn up by the chemistry faculty for all lab courses. Please look at them carefully before making entries in your notebook. Remember that in addition to the specifics below, the goal of the notebook is for another person to be able to repeat your lab work precisely as you did it.

Data, conclusions and results for all experimental work should be included in the notebook. A running commentary of the experimental procedure should also be included with all observations made during the experiment. The term “running commentary” is used to highlight that you should write what you are doing as you do it; you should not record what the textbook or supplement tells you to do, but instead what you actually did and saw. Examples of appropriate styles for lab notes are available on Section 1.6 (pp. 7 and 11).

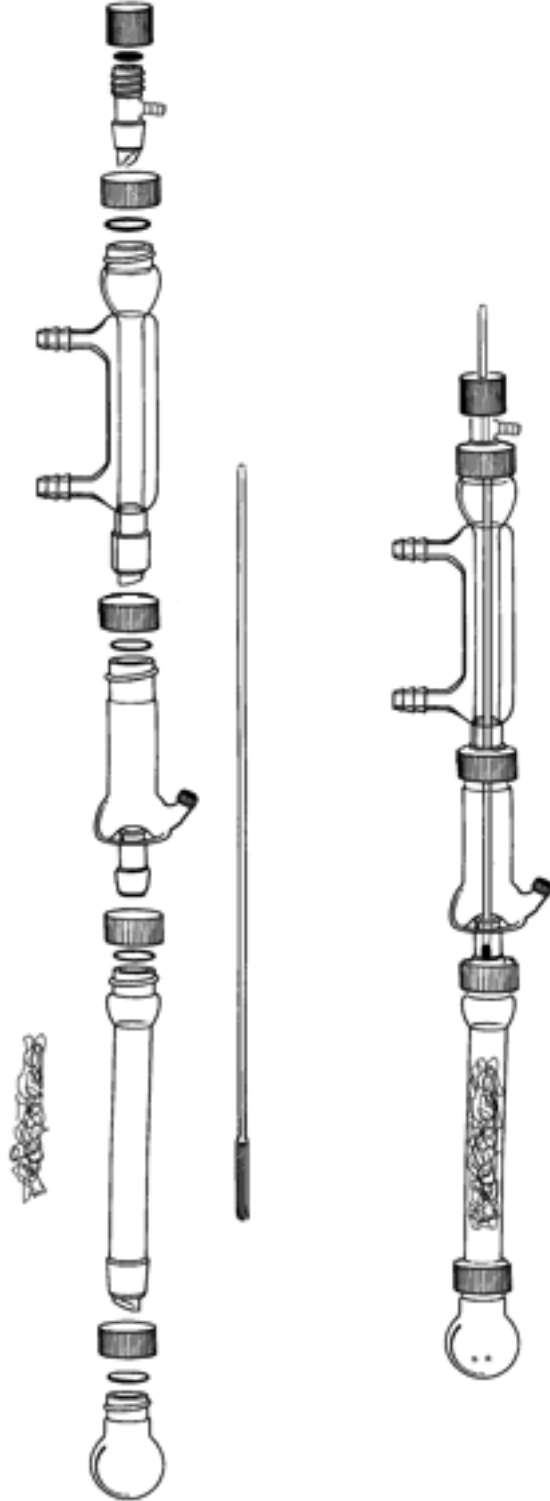
- 1) The notebook must be spiral-bound with at least 100 pages and pages that are consecutively numbered.
- 2) Pages must never be torn out or otherwise removed from the notebook.
- 3) The notebook should have a title page identifying you, the course name and number, and the lab instructor. The same notebook may be used for Chem 31, 32, and 33.
- 4) Reserve space at the beginning of the notebook for a Table of Contents. Entries in the Table of Contents should be identified by title and page numbers for all pages containing information relevant to that title.
- 5) Use a ballpoint pen for all entries in the notebook.
- 6) Any given page in your notebook should only include data for a single experiment. As a result, organize your notebook entries based on the experiment to which they correspond, not the date on which they were performed.
- 7) Each page in the notebook should be dated using an unambiguous notation like 15 October 2013. If a page includes work done for the same experiment on different days, date each entry separately.
- 8) If you need to continue an experiment onto another page, write the continuing page on the bottom of the initial page (cont'd on page xxx) and the page from which you are continuing at the top of the new one (cont'd from page xxx).
- 9) Cross out sections of pages you choose not to fill out. Do not leave blank spaces to be filled in later.
- 10) Graphs and spectral charts should be attached to notebook pages using glue or tape. **Each should be completely labeled.**
- 11) All entries should be legible and contain sufficient detail. For example:
 - use proper names for instruments and glassware: “10-mL Erlenmeyer flask” rather than just “flask”
 - indicate the specific concentration of reagents used: “6 M” or “0.1 M” rather than just “dilute”
 - indicate how precisely reagents were measured: graduated cylinder versus pipette.
 - record the sequence in which chemicals were mixed, the method and length of time for heating and/or stirring; note whether a heating mantle or hot plate was used.
 - completely record all observations like color changes, precipitates, gas evolution, etc.
 - display any calculations in full detail for ease of verification.
- 12) Draw a single line through mistakes. Erasing and over-writing are not acceptable methods for error correction.

13) At the end of each lab period sign and date your notebook and have the instructor sign it also.

Simple Distillation Setup



Fractional Distillation Setup



Reduction of 9-Fluorenone to 9-Fluoreinol: Monitoring a Reaction by TLC

You are to work with a partner on this experiment. YouTube video for TLC:

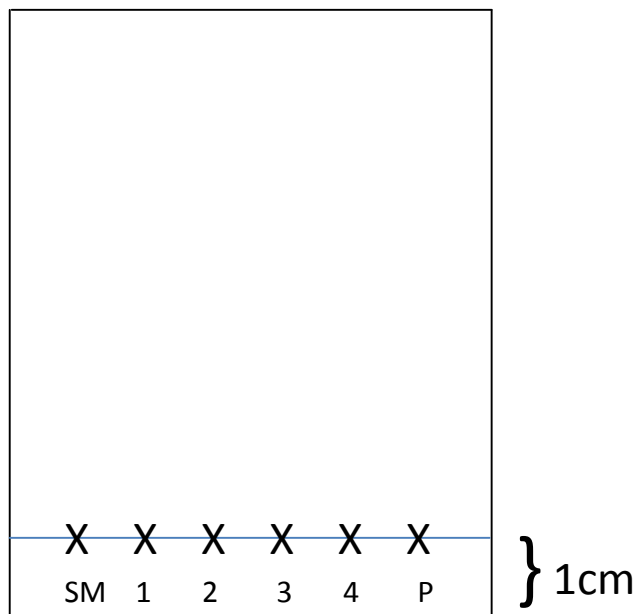
http://www.youtube.com/watch?v=rpb_Qc4jMAc

TLC can be used to monitor the progress of a chemical reaction. At various time intervals during a reaction, samples of the reaction mixture are taken and subjected to TLC analysis. At the start of the reaction, only the reactants show on the TLC plate. As the reaction progresses, the product starts to form and thus shows on the TLC plate. The product(s) spot increases in intensity while the reactant spot decreases in intensity as more and more of it is converted to product.

Preparation Follow the “Preparation” step of the microscale procedure on p. 583 of the textbook.

Apparatus A 5-mL conical vial, apparatus for magnetic stirring, aluminum block or clamp, seven capillary pipets.

Setting Up Take one large TLC plate having the dimensions of 7.5 cm × 7.5 cm. Use a lead pencil to draw a light line across the width of the plate ca. 1 cm from the bottom. Put six X's on the line as shown below. SM is for starting material, 9-fluorenone and P is for product, 9-fluoreinol. The remaining X's will be used for samples of the reaction mixture at the various time periods, namely 15, 30, 60, and 180 seconds.



Because of the short time between samplings, one member of a team will perform the reaction and the other will be the timekeeper and responsible for withdrawing samples from the reaction mixture and spotting the TLC plates. *A fresh capillary pipet must be used for each sampling.*

Quickly weigh 35 mg of sodium borohydride (NaBH₄) into a dry test tube, and stopper the tube immediately to avoid undue exposure of the hygroscopic reagent to atmospheric moisture.

Reduction Add 200 mg of 9-fluorenone and 4 mL of methanol to the conical vial and initiate magnetic stirring, holding the vial in place with an aluminum block or a clamp. Once dissolution is complete, dip a capillary in the solution and spot the TLC plate with it on the first X labeled SM, this is for spotting the starting material. Be sure the spot is not more than about 2 mm in diameter. Then add the NaBH₄ in one portion to the stirred solution and immediately begin to time the progress of the reaction. Spot the reaction mixture by using a new capillary each time at the following time intervals at 15 s, 30 s, 60 s and 120 s. *Be sure you know which sample has been spotted on which X of the plate!*

Analysis Develop the plates using dichloromethane as eluent and then allow them to dry. Visualize the results of the TLC separation by UV, using a pencil to circle the location of any spots that appear. Tape your plate in your lab notebook and record the results there as well.

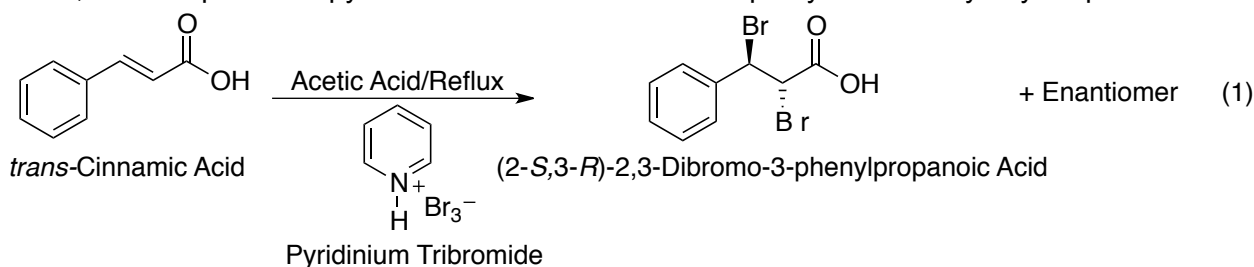
Exercises

1. Based on the TLC analyses, what evidence is there that the reaction did or did not go to completion?
2. What other evidence, if any, is there that indicates whether or not the reaction went to completion?

Bromination of Cinnamic Acid: Synthesis of 2,3-Dibromo-3-phenylpropanoic Acid (*aka* 2,3-Dibromo-3-phenylpropanoic Acid)

As we will learn in class, bromination of alkenes is a very facile reaction and is an easy experiment to do in a research laboratory. However, the challenge in this experiment is working with bromine, Br₂, which is a low-boiling, dense red liquid. Most introductory laboratory experiments substitute liquid bromine with a solid source of it, or generate bromine from less toxic compounds. All of these procedures have advantages and disadvantages with respect to the experimental process, yield, safety, waste generation, and cost or reagents. For less-experienced undergraduates in the laboratory, safety is the primary concern. Thus, we will use pyridinium tribromide, which is a solid and easy to handle, as our source of bromine.

The overall reaction is shown in Equation 1. The procedure for executing it is straightforward. You will reflux, i.e., heat the reaction mixture at its boiling point, a mixture of cinnamic acid and pyridinium tribromide in acetic acid as the solvent. The product is a solid and isolation by vacuum filtration will be done after cooling the reaction mixture and adding water. Thin-layer chromatography, melting point determination, and IR spectroscopy will be used to determine the purity and identity of your product.



Safety

Wear gloves while handling all compounds and dispense them in the hood. Cinnamic acid is an irritant, acetic acid is corrosive, and pyridinium tribromide is both corrosive and a lachrymator.

Procedure

1. Weigh 0.150 g of cinnamic acid and add it to a 5-mL round-bottom (RB) flask.
2. Add 2 mL of *glacial* acetic acid to the RB flask.
3. Add 0.385 g of pyridinium tribromide to the RB flask.
4. Add a stir bar to the reaction mixture.

5. Attach the water condenser onto the round bottom flask, and place the apparatus on the heating block. YouTube videos describing the apparatus and proper placement of the reaction flask on the stirring hotplate are found at:
http://podcaster.gcsu.edu/podcastdata/GGC/Channel_6888/podcast_10189/10189.m4v
http://podcaster.gcsu.edu/podcastdata/GGC/Channel_6888/podcast_15717/15717.m4v
6. Heat the reaction mixture at reflux (check the bp of *glacial* acetic acid) for 15 min. Reflux means that the mixture is heated to boiling and the vapours given off are cooled back to liquid, and fall back into the reaction vessel. The solids are not soluble in acetic acid at room temperature but should dissolve upon heating. Depending on the temperature in the laboratory, you may need to use water-cooling in your condenser. Check with your instructor about this.
7. Allow the reaction mixture to cool for 5 min.
8. Add 2.5 mL of deionized water to the RB flask.
9. Cool the reaction mixture in an ice-water bath for 15 min.
10. Collect the solid by vacuum filtration using a Hirsch funnel
11. After the product is dry, determine its weight, melting point and obtain its IR spectrum. Compare your melting point with the literature value of 200 °C
12. Assess the purity of your product by doing TLC of the product and cinnamic acid on the same TLC plate. Your laboratory instructor will assist you in determining the appropriate solvent for developing the plate.

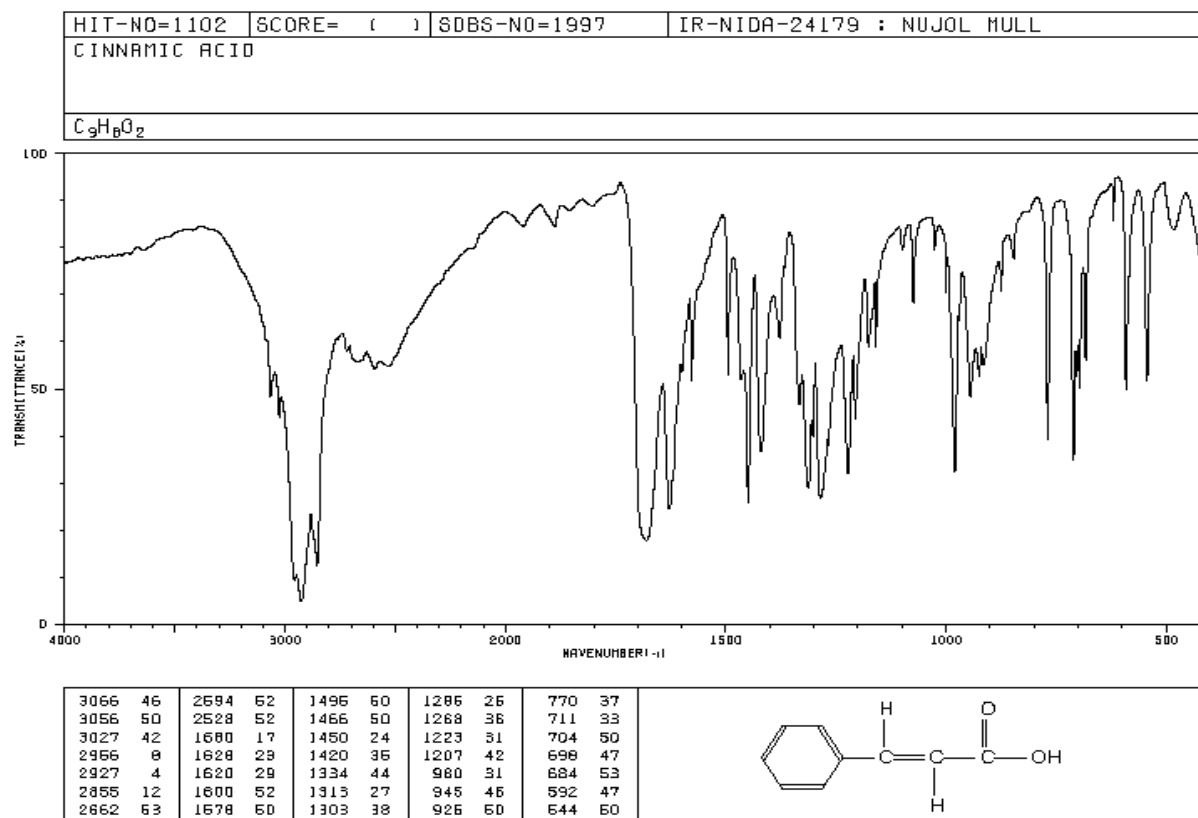
Exercises

1. Compare your IR spectrum with that of cinnamic acid as provided in **Figure 3**. Carefully examine the location of the carbonyl peak in the product as compared to cinnamic acid itself. Are the IR data consistent with your expectations?
2. Calculate the percent yield of your product, given the following molecular weights:

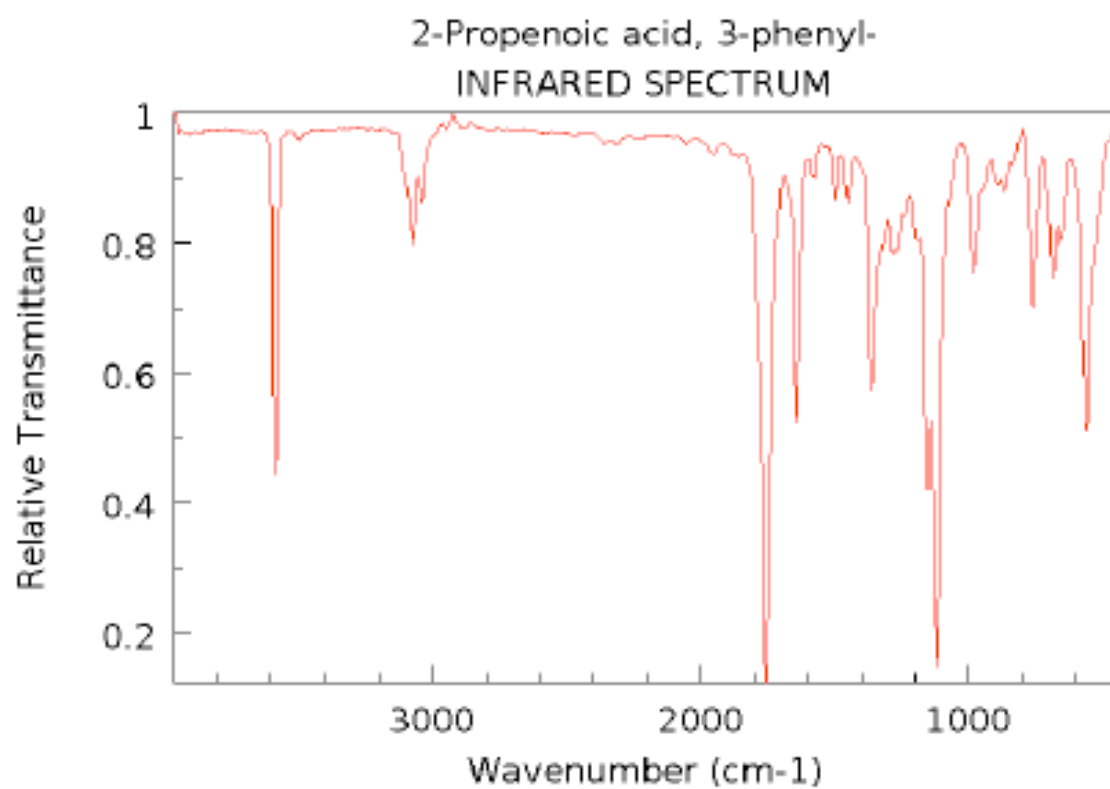
Cinnamic Acid	148.16 g/mol
Pyridinium tribromide	319.84 g/mol
2,3-Dibromo-3-phenylpropanoic Acid	307.97 g/mol
3. How many stereogenic centers are present in 2,3-dibromo-3-phenylpropanoic acid?

Figure 3. IR Spectra of Cinnamic Acid

Nujol mull:

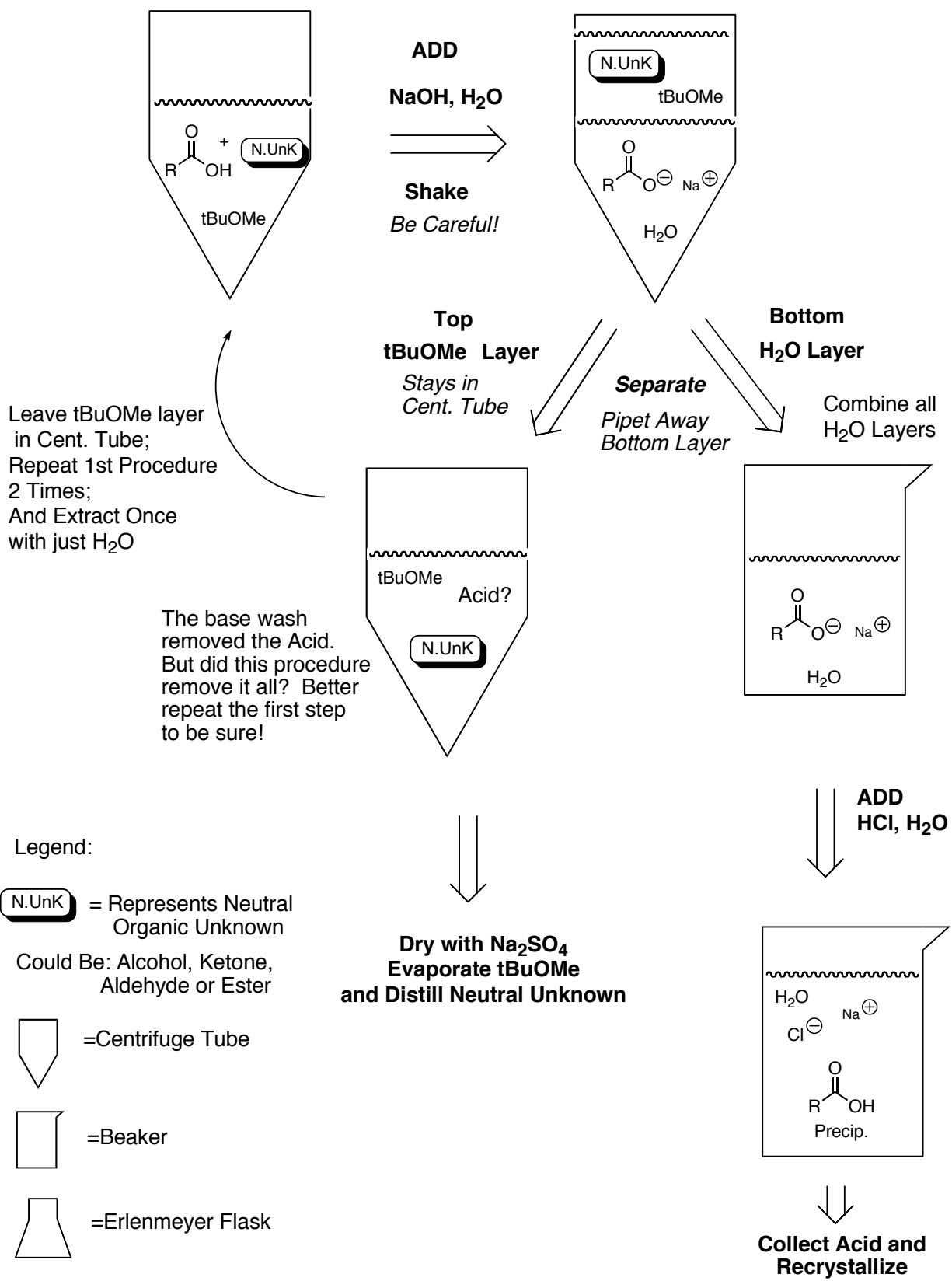


Gas-phase sample:



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Extraction Flow-Chart



Grading Template

Simple Distillation	Fractional Distillation	Acetanilide Recrystallization	Fluorene Recrystallization
Data (5)	Data (5)	% Rec (5)	% Rec (5)
Graph (5)	Graph (5)	MP: Imp (5)	MP: Imp (5)
GC (5)	GC (5)	MP: Pure (5)	MP: Pure (5)
Calc (5)	Calc (5)	TLC: Imp (5)	TLC: Imp (5)
IR (5)	IR (5)	TLC: Pure (5)	TLC: Pure (5)
General/Commentary (10)	General/Commentary (10)	General/Commentary (10)	General/Commentary (10)
Total (35)	Total (35)	Total (35)	Total (35)
TLC reaction	Alcohol Dehydration	Alkene Bromination	Liquid Unknown
TLC (10)	Equation/structures (5)	Equation/structures (5)	Boiling point (5)
General/Commentary (10)	IR (5)	Melting point (5)	GC (+ purity calc) (5)
	Yield (5)	TLC (5)	IR: Liquid (5)
	Tests (5)	IR (5)	Liquid Unk List (5)
	General/Commentary (10)	Yield (5)	Liquid Name/Struct. (5)
		General/Commentary (10)	Analysis (10)
			Procedures (5)
Total (20)	Total (30)	Total (35)	Total (40)
Solid Unknown	Exercises	Notebook	
Melting point (5)	p 135: 1bc,3; p 143: 2ab,6,7 (10)	Ink (5)	Subjective (20)
TLC: Solid Unk (5)	pp 110–111: 1cim,7,10 (10)	Table of Contents (5)	
IR: Solid (5)	Syllabus p 14: 1,2; p 188: 1,3 (10)	Signed (5)	
	pp 355–359: 3,26,28,32 (IR only) (10)	Labels (5)	
Solid Unk List (5)	Syllabus pp 15–16: 1–3 (10)	Order (5)	
Solid Name/Struct. (5)		Overall (15)	
Analysis (10)	Worksheets (5 x 10 pts each, 50)		
Procedures (5)			
Total (40)	Total (100)	Total (40)	GRAND TOTAL (465 possible)