THE UNIVERSITY OF IOWA

Organic Chemistry Laboratory

Lab Manual

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Department of Chemistry

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Welcome to the Organic Chemistry Laboratory at the University of Iowa!

From the very early stages of the development of the science of chemistry, the curious among us have reveled in the joy of discovery in the lab. Ask your chemistry professors. Most of them will tell you they are not old enough to remember labs like the one below!

Nor will they admit to getting on their knees and begging for their experiments to turn out, as the scientist in the picture appears to be doing.

But most will tell you one of the most attractive aspects of the field was getting into the lab, tinkering with the glassware, manipulating beautiful crystals or colorful liquids, and finding something new or unexpected.

This laboratory course is intended to introduce you to those simple joys, while providing a practical understanding of just how all the stuff we learn in the Organic Chemistry lecture courses became established. Not only that, it will give you tools you can apply in the future, whether you choose further study in organic chemistry or another of the many related fields of laboratory science.

Have a great semester!

GKF
January 2006

Contents

General Safety Guidelines

Safety Glasses: You must wear safety glasses at all times in the lab!

Contact Lenses: You should avoid wearing contact lenses in the laboratory. Contact lenses may trap solvents and/or vapors against the eye and result in permanent damage to the eye. Some organic vapors can also damage the contact lens itself.

Laboratory Attire: Dress appropriately in the lab to minimize the risk of injury:

- You must wear full shoes. You may not wear open-toed shoes, sandals, thongs, any canvas shoe, or shoes with perforations.
- You must cover your legs. Shorts, short skirts, and short dresses are not acceptable.
- You must wear a "non-abbreviated" shirt. You may not wear muscle shirts or tank tops.
- Do not wear loose clothing.
- Tie back long hair.

Injury: Report any injury to your TA, no matter how small. Students will be transported to Student Health Service for medical treatment during the day or to University Hospitals Emergency Room after hours. Once the situation has stabilized, you (the student) must submit an incident report form.

Supervision: Students are allowed in the laboratory only during their assigned times, and with proper supervision. Do not enter the lab if your TA is not present. If you must leave the lab for any reason, inform your TA.

Food: Eating, drinking, or use of any tobacco product is prohibited in the laboratory. This includes chewing gum, cough drops, throat lozenges, etc.

Fire: Most organic solvents are flammable and ignite readily when exposed to a source of ignition. Thus, open flames are not permitted in the laboratory, unless specifcally directed by your TA. Smoking is strictly forbidden. Know the location of all fire extinguishers and safety showers in the laboratory.

Waste Disposal: Laboratory waste (solvents, solids, sharps, etc.) must be disposed of properly. A table in this section provides general guidelines for waste disposal. If you are not sure how to dispose of something, ask your TA. Nothing goes down the sink without permission.

Pregnancy: Many organic chemicals are potential hazards to the fetus or to young children. Women who are pregnant, nursing, or who suspect they may be pregnant are strongly advised to consult with their health care provider, and may wish to take this course at a later time.

Preparation: Any chemistry laboratory can be a dangerous place if proper procedures are not followed. Most of the risks associated with laboratory work can be minimized by thorough preparation prior to arrival. Come to lab prepared.

In Case of Accident:

If an accident occurs, always inform your TA as soon as it is safe to do so.

Spills:

- any spill should be cleaned up immediately using agents found in the green spill kits mounted in each lab. Do not use these Spill Kit reagents for spills on your body.
- acids are first neutralized with Spill-X-A
- base spills are treated with Spill-X-C
- solvent spills are treated with Spill-X-S
- many solutions look like water. Please take care.
- Report the use of Spill Clean up reagents to your T.A. after use, so they can be replaced.

Chemicals:

1. If you get chemicals in your eyes

- flush immediately with lots of water at an eye wash station
- report the accident and get medical attention

2. If you get chemicals on your skin:

- wash immediately with large amounts of water
- remove contaminated clothing
- continue to wash the area with water
- report the accident and get medical attention!

Fire:

1. Chemical fires:

- small fires may often be contained by placing a watch glass or large beaker over the vessel
- large fires may require the use of a fire extinguisher
- uncontrolled fires require using the alarm to contact the fire department

2. You or Your neighbor:

- don't panic.
- shout for help.
- roll on the floor to smother flames
- WALK to the nearest safety shower

Glassware

Cuts sustained upon breaking glassware are among the most common lab injuries. Handle glassware with caution. If you break something, keep in mind what chemicals are in it, and don't try to pick up small pieces with your fingers. Brooms and other necessary clean-up materials will be made available. Take special care with mercury spills, as mercury is particularly difficult to clean up. If you cut yourself, it is best to be on the safe side and go to Student Health in case small bits of glass remain in the cut. You should keep a band-aid in your lab drawer, since regulations prohibit administration of first aid by chemistry staff except in obvious emergencies.

SAFETY IN THE CHEMISTRY LABORATORY

The University of Iowa's Department of Chemistry is concerned about your safety in laboratory courses. Therefore, all students enrolled in chemistry lab courses are required to complete a safety quiz at the beginning of each course. The quiz consists of 15 questions, which are mainly based on common sense. There are a few that you should be able to answer based on information discussed in your previous chemistry courses and a few that require some knowledge of the laboratory itself. The following clues are provided to make your laboratory experience safe and to assist you with the quiz.

1. Safety goggles are the prime protection for your eyes and state law requires that they must be worn by everyone in a lab.

2. Safety equipment, such as showers, eye baths, and fire extinguishers are found in every lab. Be sure you know how many and where they are in your lab. Have your T.A. explain how to operate them.

3. If you spill anything on your skin, it is important to wash it off immediately. Don't experiment by trying to run reactions on yourself or another student.

4. If you or another student have an accident in lab, it is important to tell your T.A. as soon as possible. Don't try to wait out the entire lab session.

5. If you break glassware, don't just throw the broken pieces into any basket. Check in your lab about a place where broken glass can be placed.

6. Eating, drinking, and chewing gum are all prohibited in all chemistry labs. We don't want anyone to become ill.

7. For your safety, shoes (not sandals or sandals and socks), long pants or skirts (not shorts or mini skirts) and shirts (not tank tops or muscle shirts) must be worn in the lab.

8. Wearing contact lenses can be hazardous because vapors might be present in the lab.

9. Keep books, backpacks, and coats out of the aisles and off of the bench tops. Ask your T.A. where they can be safely stored during lab.

10. Check the location of the closest exits from your lab and from the building so that you can exist the building quickly in case of a fire.

11. Never work alone or without supervision in the laboratory. Your T.A. will be present throughout the entire lab period. Come to lab prepared. Always be sure that you understand what you are doing before you do it. Don't be inventive. If you have questions, ASK!

The Safety Quiz is taken on computer in the labs or in Room 111C Chemistry Building. The room will be open most of the day during the first two weeks of classes. We will try to keep the hours posted. **Be sure to print out and turn in the statement that certifies that you successfully took the quiz.**

To pass the Safety Quiz, all questions must be answered correctly.

Waste Disposal

The proper disposal of chemical waste is an important part of laboratory safety. It is your responsibility to see that such waste is disposed of properly. The following guidelines should be followed to ensure the proper disposal of laboratory waste. If you are unsure as of proper disposal of any item, please consult with your TA.

Category	Examples	Disposal
Organic Waste:		
Non-Halogenated	Waste solvents, acetone, reaction intermediates, products.	"Organic Waste" bottle in hood
Halogenated		
Aqueous Waste:		
Hazardous	Dilute acids and bases, aqueous washes from extractions.	"Aqueous Waste" bottle in hood
Non-hazardous	Water baths, ice baths, etc. that have not been contaminated with chemicals	Pour down sink
Sharps:	Broken glassware, test tubes, tlc plates, nonmercury thermometers, etc. (not mercury thermometers!)	White plastic "Sharps" bucket
Solid waste:		
Hazardous	Contaminated paper towels, filter papers, insoluble organic & inorganic solids	"Solid Waste" container in hood
Non-hazardous	Paper towels, drying agents	Trash container
Mercury:	Broken thermometers	"Mercury Waste" container in hood

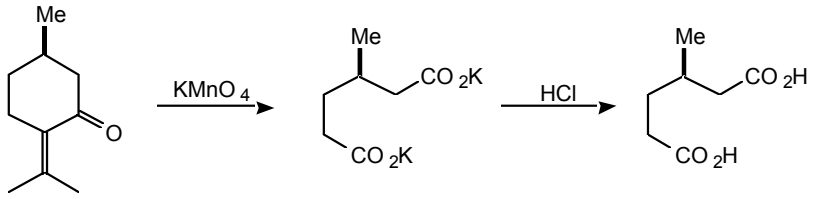
The Pre-lab Flow Sheet

You will submit a pre-lab flow sheet for each "wet" lab you do this semester (the "dry" labs are #1, #3, and #10; all others labs are wet, where you work with chemicals). The purpose of the flow sheet is to get you to think about the experiment you are doing – not only about the reaction itself, but also the processes involved. There is a reason for every step in an experimental sequence. If you are unsure about the reasons behind a specific step or action described in the laboratory handout, be sure to get help! It is always more satisfying to understand the reasoning behind a set of instructions than to follow them blindly. A sample flow sheet from an experimental procedure that was used previously, "Synthesis of (+)-(R)-3-Methyladipic Acid," is included below. Remember, though, that every experiment is different. The flow sheet you submit may not look exactly like the one in the sample.

Hints

1. Write a balanced equation for the reaction you will perform, if appropriate. Be sure to include any by-products of the reaction that will need to be separated. It is much easier to figure out what is going on if you know what you're trying to do in the first place.
2. Don't go overboard. In most cases, a single page will be sufficient to outline the experimental procedures set forth in the laboratory handout.
3. Write the flow sheet in your notebook and submit the carbon page.

Sample Procedure



pulegone | 3-methyladipic acid dipotassium salt | 3-methyladipic acid

A. Synthesis of (+)-(R)-3-Methyladipic Acid

To a 250mL Erlenmeyer flask containing 40mL of distilled water, add 5mL of pulegone. Swirl to mix the components (a two-phase mixture should result), then add 5g of $KMnO_4$. Continue swirling for 10 minutes, and then allow the mixture to stand for approximately 2 hours, swirling occasionally. After this time, heat the mixture in a boiling water bath for 10 minutes. **CAUTION! The oxidation of pulegone is exothermic**. Keep an ice bath handy as the mixture may boil over if it proceeds too quickly. After the heating period, allow the reaction to cool to room temperature, stopper the flask, and store it until the next laboratory period.

Test the reaction mixture for the presence of $KMnO_4$. This is done by withdrawing a drop of the mixture on the tip of a stirring rod and touching it to a piece of filter paper. Permanganate, if present, will appear as a purple ring around the brown MnO_2 solids. Remaining permanganate should be reduced to MnO_2 by adding a small amount of solid sodium bisulfite, and stirring vigorously (Note: an exotherm and some foaming will occur. As such, do this in the hood, and don't

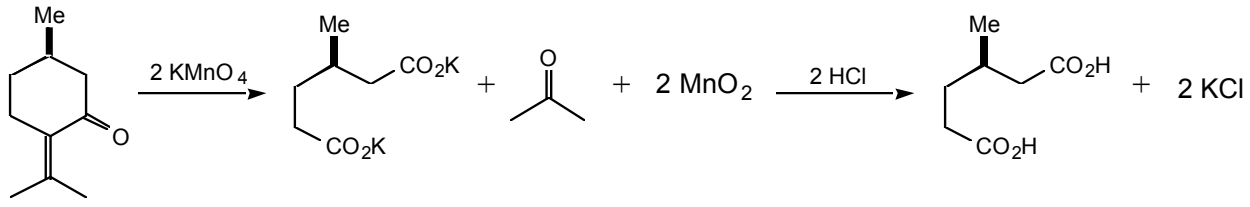
add too much bisulfite at once.). Continue adding bisulfite in small amounts until the test for permanganate is negative.

Prepare a slurry of 2-3 mL of celite in 25 mL water and vacuum filter. Continue to apply the vacuum until the celite bed is relatively dry, then discard the water. To remove the fine precipitate of MnO_2 solids, filter the reaction mixture through the celite bed in parts. The filtration will proceed much more quickly if the solids are allowed to dry out completely between additions. Wash the filtered solids with three successive 10 mL portions of water, gently stirring the MnO_2 solids above the celite while they are wet to maximize the surface area. When filtration is complete, the MnO_2 solids should be discarded in the Waste Solids bag in the hood.

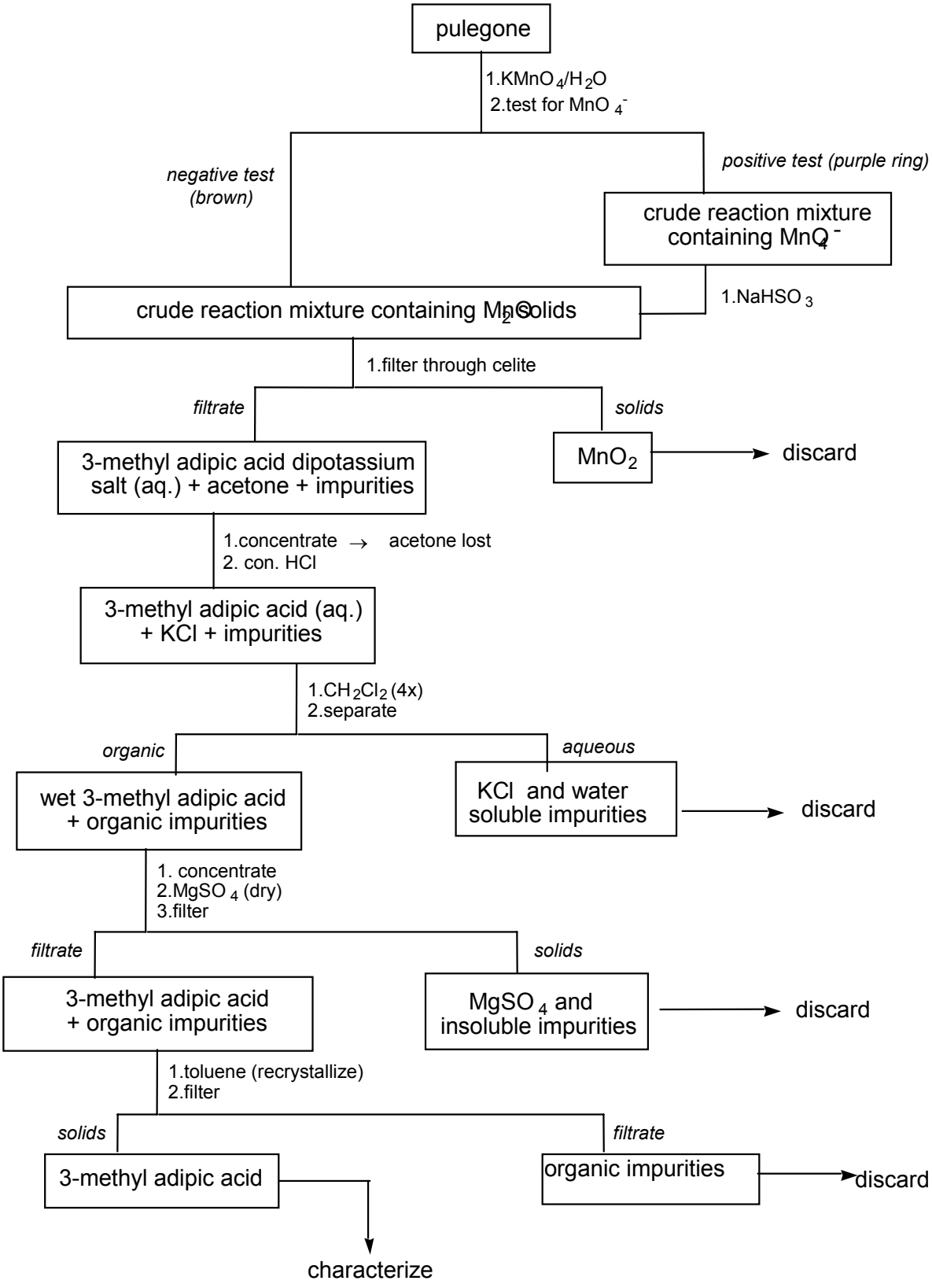
The combined filtrates should be clear and slightly yellow. Transfer them to a 250 mL beaker, add 2-3 boiling chips, and concentrate to about 15 mL on a hot plate. Cool to room temperature, and, in the hood, acidify with 10 mL of concentrated HCl. If at this point solids form, remove them by filtration. Extract the cool aqueous solution with four 15 mL portions of dichloromethane (4 x 15 mL). Be sure you are aware which layer is the aqueous, and which one is organic. Discard the remaining aqueous layer into the appropriate bottle in the hood. Residual product can later be extracted from this combined aqueous waste. Dry the combined organics over $MgSO_4$, then remove the solids by gravity filtration. Transfer the filtrates to a tared flask, and concentrate. If there is a long wait for the rotary evaporator, add 2-3 boiling chips, and remove the solvent by distillation using a water aspirator. Note that excessive heat is not required, and may cause the material to bump or boil over. Before the concentration is complete, remove the boiling stones so an accurate weight may be obtained on your crude product. Evaporate the remaining solvent on the rotovap or in the hood. **CAUTION!** There is some indication that CH_2Cl_2 may be carcinogenic.

Once concentration is complete, a thick yellow liquid should remain which may partially solidify on cooling. Recrystallize this product from toluene, using 5 mL toluene for every gram of crude product. Collect the resulting crystals of (+)-(R)-3-methyladipic acid by filtration, scraping the solids with a spatula to aid in drying them. Continue to apply the vacuum for some time as toluene is quite difficult to remove. When finished, place the toluene filtrates in the bottle marked Toluene Waste. Here too, residual product can later be isolated. Record the weight of your crystalline product, and obtain a melting point and a solution cell IR (use CH_2Cl_2 as the solvent). Calculate your % yield based on the amount of pulegone you used. Turn in the remainder of your product to your TA when you submit your laboratory report. Note that a portion of your grade will depend on the product you turn in.

Balanced Equation:



Here is a sample flowsheet <u>generated before the lab period</u> on the basis of information presented in this procedure.


pulegone
1.KMnO4/H2O
2.test for MnO4-
negative test (brown)
positive test (purple ring)
crude reaction mixture containing MnO4-
1.NaHSO3
crude reaction mixture containing MnO2 solids
1.filter through celite
filtrate
solids
3-methyl adipic acid dipotassium salt (aq.) + acetone + impurities
MnO2
discard
1.concentrate → acetone lost
2. con. HCl
3-methyl adipic acid (aq.) + KCl + impurities
1.CH2Cl2 (4x)
2.separate
organic
aqueous
wet 3-methyl adipic acid + organic impurities
KCl and water soluble impurities
discard
1. concentrate
2.MgSO4 (dry)
3.filter
filtrate
solids
3-methyl adipic acid + organic impurities
MgSO4 and insoluble impurities
discard
1.toluene (recrystallize)
2.filter
solids
filtrate
3-methyl adipic acid
organic impurities
discard
characterize

The Laboratory Notebook

I. Purpose:

Your notebook will serve as a permanent record of your experimental work over the course of the semester. It will contain the information you need to complete your work efficiently and safely. You will also use the information contained in your notebook to write laboratory reports explaining your results. Therefore, it is important that your notebook be thorough and accurate. As a general rule, a good notebook is one from which someone else can repeat your experimental work in the same way that you have done it.

II. General Guidelines:

1. Your notebook must be bound/spiral bound, the pages numbered, and have a carbonless copy.
2. Write your name, the course name, and section # on the cover or front page.
3. Always use permanent ink, not pencil.
4. Write it down NOW. Your notebook is a log of what you do as you do it.
5. Use complete sentences.
6. Write everything in your notebook. Weights, temperatures, everything. When recording experimental data, always include units.
7. Do not erase. If you make an error, draw a single line through it, and continue. The original statement should still be legible.
8. Never remove both the original and copy pages from your notebook. You may remove the original copies.
9. Date every page as you use it.

III. The Notebook:

The first several pages of your notebook should be reserved for a Table of Contents. From there, each experiment recorded in your notebook should contain the sections outlined below. Sections A - F contain preliminary information and should be entered and completed <u>prior to the laboratory period</u> in which you begin the experiment. Section G, the Experimental, is recorded <u>as you proceed each day</u>. Original pages from your notebook will be collected at the end of each laboratory period. The carbonless copys should remain in your notebook. <u>Late notebook pages will not be accepted.</u>

A. Title

Start each experimental write-up with an accurate, descriptive title.

B. Purpose

Discuss the general purpose of the experiment in at most two or three sentences. If the experiment is a synthesis (as opposed to a technique), write the chemical equation, including reagents and expected product(s). For multistep syntheses, write one equation for each transformation, including the preparation of reagents.

C. References

Cite the reference(s) upon which your experimental procedure is based. In most cases this will be your laboratory handout. While the source of information is often obvious in this course, inclusion of references in one's notebook is an important practice.

D. Chemical Properties

Make a table that lists the chemical properties of all reactants and reagents you will be using in the experiment. This table should include the name of the compound, MW, density (d), mp, and bp.

E. Safety Guidelines:

Make a table listing the safety hazards of compounds you will use. Include solvents. For each compound list the toxicity (if known), the flash point (in °C), and any other important safety information (flammable, corrosive, irritant, etc.). *Note: Sections D and E may be combined into one table.*

F. Equipment

Sketch any equipment setups or apparatus that you use for the first time this semester. Include in your drawing the positions of any clamps that are used. If you have already drawn the apparatus for an earlier experiment, you need only indicate the page in your notebook where the drawing can be found.

G. Experimental:

This section of your notebook is written during the course of a laboratory period. It is a record of what you do as you do it, and must be completed before you leave the lab for the day.

1. The Pre-lab flow sheet goes here. Note any modification to your intended procedure.
2. Keep a log of both your actions and your observations. Any reader should be able to repeat the experiment as you ran it based on what you have written. Include any thoughts you have about what may be going on, or how the experiment might be changed in the future.
3. Make sure to record any melting points, boiling points, weights, etc. before you leave the lab whether you think you need them or not. Chances are that you will. Drawings of all tlc plates should also be included here.
4. Record your progress and observations completely and accurately. The information included here may help you understand later if your experiment was successful, or what went wrong.
5. At the end of each day initial and date what you have written.
6. Submit your original notebook pages to your TA before you leave for the day. These pages will be attached by your T.A. to the rest of your lab report once you turn it in and will be graded as part of your laboratory report. Late notebook pages will not be accepted.

IV. References

The following references (and many others) are available either in the laboratory or the library. You should familiarize yourself with them as you will use them frequently throughout the semester.

A. General Chemical Properties

1. *Aldrich Handbook of Fine Chemicals and Laboratory Equipment*; Aldrich Chemical Co., 2000-2001 (or later edition).

2. R.C. Weast, Ed. *CRC Handbook of Chemistry and Physics*", 75th ed.; CRC Press: Boca Raton, FL, 1990 (or later edition).

3. M. Windholz, Ed. *The Merck Index*, 10th ed.; Merck and Co.: Rahway, NJ, 1983 (or later edition).

B. Safety

1. J.W. Zubrick, "The Organic Chem Lab Survival Manual: A Student's Guide to Techniques", 5rd ed. John Wiley and Sons: New York, 1999, pp 1-7.

2. R.J. Lewis, "Hazardous Chemicals Desk Reference", 2nd ed.; Van Nostrand Reinhold: New York, 1992

3. R.J. Lewis, Sr. "Sax's Dangerous Properties of Industrial Materials", 8th ed. Van Nostrand Reinhold: New York, 1992.

Interpretation of Experimental Data

When evaluating experimental data, it is important to recognize what the data are telling you, as well as the strengths and limitations of each method you are using. In addition, it is important to be able to communicate your interpretations clearly, since the validity of your interpretation is lost if someone else is unable to determine what you are trying to say. This semester, you will need to evaluate the results from several techniques.

I. Thin Layer Chromatography (TLC)

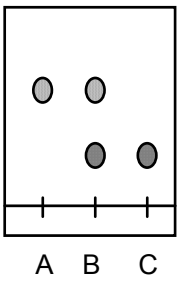
Thin layer chromatography (TLC) is a useful method for evaluating reaction mixtures and for identifying organic compounds. TLC data are often used in conjunction with other data. TLC can be used in the following ways:

1. Evaluation of a Reaction Mixture

When evaluating a reaction mixture, the disappearance of one spot (starting material) and the appearance of a different spot over time indicate that the original compound has been converted to something else. This is an indication that the reaction is proceeding or has gone to completion.

Generally speaking, the more polar a compound, the lower its R_f value, and vice versa. Thus, for a given set of conditions, the R_f values of two spots on a TLC plate may provide some evidence as the identity of a compound, and the success (or failure) of a reaction.

Example: Upon treatment with $NaBH_4$, a ketone, 2-pentanone, is reduced to give the corresponding alcohol, 2-pentanol, as shown in the following equation. The progress of the reaction is monitored by TLC. The reaction mixture is sampled before the reaction begins (Lane A), after 30 minutes (Lane B), and again after 1 hour (Lane C). The single spot in Lane A represents that of the starting ketone. Evaluation of the reaction's progress after 30 min (Lane B) suggests that the reaction is proceeding, but not complete. After 1 hour (Lane C), TLC evaluation shows that all starting material has been consumed, and the reaction is finished. Note that the relative R_f values in this case are as expected with the less polar ketone having a higher R_f value that the (more polar) alcohol.



2. As an Indicator of Purity

A pure compound should produce a single spot in TLC. Two (or more) spots in a single "lane" indicate that the compound is impure. However, while TLC can often show clearly that a substance is impure, sometimes TLC may fail to detect an impurity. Different compounds (and impurities) may exhibit very similar behavior on TLC and thus may be impossible to distinguish using this method. As such, other experimental techniques should be used to confirm the purity of a substance even if it appears to be a single compound by TLC.

Example: Analysis of a sample by TLC, shows the presence of two components, the desired compound, **b**, and a higher R_f impurity **a**. The sample is purified by column chromatography, and the collected fractions analyzed by TLC. This analysis shows a good separation of the sample components. The desired compound is contained in Fractions 3-6. Of these, Fractions 4-6 are pure by TLC.

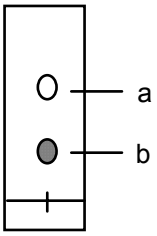


Figure 1: TLC plate showing the original laboratory sample. Compound **b** is the desired product; compound **a** an impurity

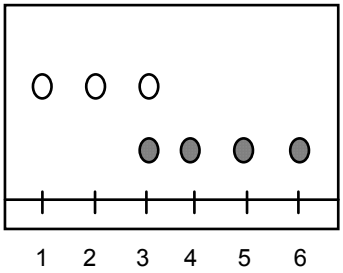
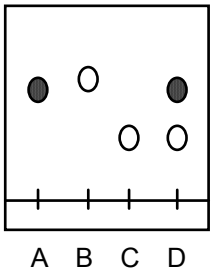


Figure 2: TLC plate showing the content of fractions collected by column chromatography. Pure **b** is contained in Fractions 4-6.

3. Identification of Compounds

For a given set of conditions, two samples having different R_f values are different compounds, while those having identical R_f values may be the same. As noted above, different compounds may have identical R_f values. However, comparison of an unknown compound or reaction mixture with an authentic sample(s) can provide some insight as to the identity of that compound, or mixture components.

Example: An unknown sample whose possible components are available in pure form is analyzed by TLC. The three known components (A - C) are spotted on a TLC plate along with the unknown mixture (D). The plate is developed and the unknown components identified as compounds A and C on the basis of their Rf values and physical characteristics (e.g. color). Compound B is not present in the unknown mixture.



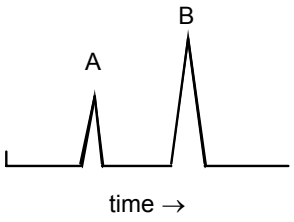
II. Gas Chromatography

Gas chromatography (GC) is a useful tool for the analysis of volatile, thermally stable organic compounds. In certain cases, we can use GC as a means of quantitative evaluation of organic mixtures. Gas chromatography is commonly used in the following ways:

1. To evaluate the components of a sample mixture

We can use GC to quantitatively evaluate a mixed sample of known components. Since the detector response is proportional to the amount of compound passing through it, the area under a peak is proportional to the total amount of compound in the sample. If the detector responds equally to two compounds, the ratio of areas in a single chromatogram is equal to the ratio of compounds in the mixture.

Example:



For the sample chromatogram at left, peak areas are calculated using the following equation:

Area = peak height x peak width at 1/2 height

By this method: Area A = 240mm^2
Area B = 600mm^2

So, the ratio of components A:B in this sample is 1.0 : 2.5, assuming equal detector response.

2. As an indicator of purity

When evaluating a compound by GC, the observation of a single, large peak under a variety of conditions (varied temperatures, columns, etc.) is a strong indication that the sample is pure.

Example: Based on GC, the sample on the left appears to be pure. The sample on the right is clearly not pure.

3. Identification of an Unknown

We can use GC to help to identify unknown compounds. One method is to compare the retention time of the unknown with those of authentic samples of known compounds. Another method involves adding a known compound to the sample. The known compound was likely a component of the sample if, upon injection a mixture of the unknown and the suspected compound (authentic sample), gc analysis provides a single, sharp peak. If there is a broadened peak, a peak with a "shoulder", or multiple peaks, the unknown and authentic components are different.

III. Melting Point

When you isolate a solid product in the laboratory, you should obtain its melting point. The melting point of a compound is the temperature range from the formation of the first drop of liquid among the crystals to the temperature at which all the crystals have melted. A pure substance will have a higher melting point and will melt over a narrower range than will the same substance that contains even a trace amount of an impurity. Measured melting points will be inaccurate, if the thermometer that is used to measure them is inaccurate (this can be as much as 1-2°C).

We may also determine melting points using differential scanning calorimetry (DSC). In DSC, a sample is heated and the amount of heat that the sample absorbs is determined as a function of temperature. At the melting point, the amount of heat absorbed is larger than the amount of heat absorbed than when the solid or liquid is becoming warmer. You will receive a supplemental hand-out on using DSC to determine melting points.

The melting point of a compound can be utilized as follows:

1. As an indicator of purity:

A pure compound should melt over a narrow range, and the value of its melting point should be close to values reported in the literature. Generally speaking, impurities lower the melting range and broaden the melting range. If no literature value is available, look at the size of the melting range. Pure substances generally melt over a 1-2°C range. Samples that have a larger melting range are probably impure.

2. To aid in the identification of an unknown solid

Melting point can help to identify an unknown sample, if it consists of a pure compound that has a known melting point. Just compare the melting point of the unknown to the literature value. In this way, it is frequently possible to narrow substantially the list of possibilities.

Mixed melting points (*i.e.* determining the melting point of a mixture of an unknown sample and known material) may help to substantiate the identity of an unknown. If the two samples consist of the same compound, the melting point of the mixture will be the same as the pure compounds. If the substances are different, the melting point of the mixture will be depressed.

IV. Boiling Point

One way to determine boiling point is to distill the sample and record the temperature in the still head. Another method is described in Lab #2. Boiling points vary with atmospheric pressure. So, it is important to specify the pressure at which a boiling point was measured.

Knowledge of boiling point can be utilized in the following ways:

1. As an indicator of purity

Boiling point is less useful an indicator of purity than melting point. Generally speaking, however, a pure substance will distill at a constant temperature (±1-2°C), while a mixture will distill over a range of temperatures.

2. To aid in the preliminary identification of unknown liquids

Boiling point can help to identify an unknown compound, if its boiling point has already been reported. One can also compare the boiling point of an unknown with those of authentic samples of possible compounds.

V. Chemical Tests

Periodically, you will utilize chemical tests to help to identify functional groups in your compound or to test for impurities. Usually, a chemical test produces a visual change (such as precipitate formation) that is due to a chemical reaction between the test reagents and a functional group in the sample. However, for any test result to be meaningful, you must:

1. Understand the purpose of the test you are running.

If you don't know why you are performing a chemical test, it will be difficult for you to interpret your results. It usually helps to understand the chemical reaction that may occur, and what functional group must be present to produce a positive result.

2. Know what to expect for both positive and negative test results.

Chemical tests can often identify compounds that have a common functional group (*e.g.* ketones) or distinguish different structural features (*e.g.* 1° vs. 3° alcohol). A good chemical test gives accurate results with most compounds. However, every compound is different. In certain cases, the compound being tested will not react in the expected way (a false positive or false negative test). Sometimes, a test result will be inconclusive. In these cases, it is important to look at all your data, and to consider possible reasons for the false result (it's often quite easily explained if you understand the chemical reaction). To avoid potential problems, you should test both known positive and known negative compounds, and compare those results to the result with the unknown.

Reporting Data from Chemical Tests

Usually, you should record the details of the observations of chemical tests in your notebook, and report only the results in your report. However, your report must indicate exactly what the result that you obtained means relative to the issue at hand (*e.g.* "The starch iodide test gave a positive result indicating the presence of peroxides in the reaction mixture.").

VI. Infrared Spectroscopy

Infrared (IR) spectroscopy is an excellent method for the identification of organic functional groups. It can often confirm the presence (or absence) of a specific functional group in a compound, and indicate a compound's purity. It may also indicate the functional groups that are present in an unknown sample.

Characterization of a Known Compound by IR

1. Know the structure of the compound you are attempting to characterize.
2. Identify the functional groups you would expect to see in the IR.
3. Determine the position (cm^{-1}) at which you would expect to find each peak for a given functional group. Remember that for some functional groups (*e.g.* carboxylic acid, nitro, etc.) you will expect to see several peaks.
4. Obtain a good, clear IR of your sample.
5. Upon considering your preliminary expectations, identify those peaks in the IR that support the identity of your compound.
6. Sometimes, unexpected peaks will be present in your IR spectrum that you will need to explain. Common impurities include unreacted starting materials, reagents, water, and solvents.

Evaluation of an Unknown Sample by IR

• Preliminary Evaluation: Identification of Major Functional Groups

1. Determine what you would expect to see (peak position, # of peaks) for each of the possible major organic functional groups. Consider also any special circumstances that could affect what you see (e.g. hydrogen bonding, amine substitution, etc.).
2. Obtain a good clear IR of your sample. If the compound is a solid, it is a good idea to obtain both nujol mull and thin film spectra.
3. By inspection of your IR, determine which functional groups are possibly present in your sample. While you will probably not be able to narrow it down to a single group, you should be able to eliminate a number of options based on peaks that are not present (*e.g.* no C=O stretch? esters, carboxylic acids, aldehydes, and ketones are eliminated from consideration).

• Subsequent Evaluation: Indications of Minor Functional Groups

1. Using the information you have obtained from functional group tests and other sources, reinspect your IR spectrum to gain additional support for your findings. Consider minor functional groups including double and triple bonds, halides, nitro groups, ethers, etc. Be very careful. IR spectra are usually very complex. Do not try to read more into the spectrum than is actually there.

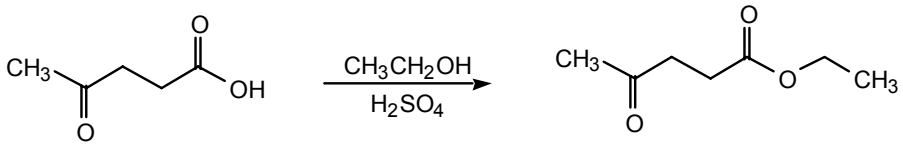
Reporting IR Data

Report all information from your IR spectrum that is relevant to the identification and purity of the compound(s) that you have prepared. IR data should be reported in table format as shown in the example below. Peak positions should be reported in cm^{-1} and their significance explained (*e.g.* OH, C=O, etc.). Also identify specifically the functional group each peak represents (*e.g.* The C=O stretch is found in esters, carboxylic acids, aldehydes and ketones. For

full credit, you must specify which group this peak represents in your spectrum.). Note that in some cases the absence of a peak may be significant. In these cases it is important to note within the body of your report that this peak is absent, and interpret what that absence implies.

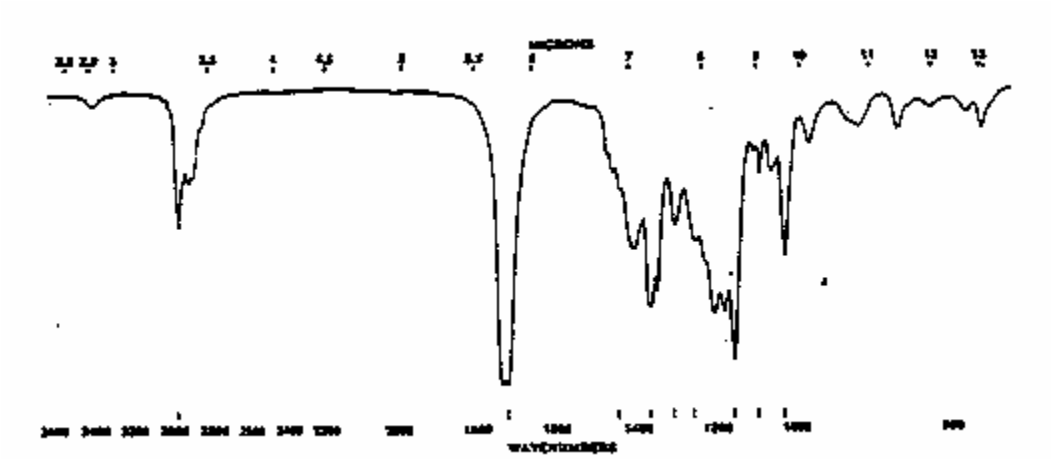
Example: Ethyl Levulinate

An esterification is performed as shown below. As part of this process, students are asked to take IR spectra of the final product, ethyl levulinate.



The IR spectrum of ethyl levulinate is shown below. You should include your spectra as Appendix B to your lab report.

You should interpret your spectrum, and report the data in the Results and Discussion



section as shown below. You should discuss the data further in the body of the report as appropriate. In this case, in addition to discussing the absorbances that are present, it is appropriate to note the absence of a broad OH stretch at about 3200cm^{-1} which would be expected from the CO_2H function in the starting material. The absence of this absorbance indicates that the reaction was successful and has gone to completion. Additional interpretation of the IR spectrum is okay, but not absolutely necessary. Don't over interpret — incorrect or unwarranted conclusions will cost points.

Table of IR Data for Ethyl Levulinate

Position (cm^{-1})	**Vibration**	**Functional Group**
1720cm^{-1}	C=O	Ketone
1740cm^{-1}	C=O	Ester
2950cm^{-1}	C-H	Alkane

VII. Nuclear Magnetic Resonance Spectrometry

Nuclear magnetic resonance (NMR) spectrometry is one of the most important diagnostic tools available to an organic chemist. This method provides information on the relative positions and numbers of spin active nuclei (*e.g.* protons; ^1H) in a compound, and can often identify structural features of a molecule. In many cases, NMR can be used to determine a complete chemical structure in a very short period of time. NMR can also define product ratios, purity, etc. *Note: Because of the number of students in the course, and the level of sophistication of high-field NMR instruments, you will not be able to able to acquire your own NMR spectra. However, in most cases, you will prepare a sample that someone else will use to acquire NMR data. So, you will usually have the spectrum of your own sample.*

Characterization of a Known Compound by Proton NMR

1. Draw the structure of the compound that you are trying to characterize. Count the total number of protons, and identify those that are equivalent.
2. Determine roughly what you would expect to see (peak position, # of peaks, multiplicity, etc.) for each set of equivalent protons. Consider also any special circumstances that could affect the spectrum (*e.g.* the vicinity of heteroatoms, proton exchange, etc.).
3. Take a look at your NMR spectrum. Identify reference solvents (*e.g.* TMS, chloroform) and omit them from consideration. Note that water is also a potential impurity (broad signal at *ca.* 1.5 – 1.6 ppm in $CDCl_3$ solution).
4. Determine peak integration.
5. Determine the chemical shift of each resonance in your spectrum.
6. Identify the multiplicity (splitting) of each resonance in the spectrum. You may also wish to determine coupling constants (*J*-values) for each set of resonances. This information can be used to determine which groups of protons are adjacent to each other in the structure.
7. Using the information obtained above, account for the resonances you see in the NMR spectrum. It may be helpful to consult a correlation table of chemical shifts.

Characterization of an Unknown Compound by Proton NMR

• *To Differentiate Between Several Known Possibilities*

1. Draw structures for each of the possible compounds. In each case, count the total number of protons, and identify those that are equivalent.
2. Determine roughly what you would expect to see (peak position, # of peaks, multiplicity, etc.) for each set of equivalent protons. Note any characteristics that may help to distinguish one structure from another.
3. Take a look at your NMR spectrum. Identify reference solvents (*e.g.* TMS, chloroform) and omit them from consideration. Note that water is also a potential impurity (broad signal at *ca.* 1.5 – 1.6 ppm in $CDCl_3$ solution).
4. Determine the peak integration.
5. Determine the chemical shift of each resonance in your spectrum.
6. Identify the multiplicity (splitting) of each resonance in the spectrum. A preliminary assessment of these patterns relative to your expectations in step 2 may allow you to eliminate one or more structures. You may also wish to determine coupling constants (*J*-values) for each set of resonances. This information can be used to determine which groups of protons are adjacent to each other.

7. Using the information obtained above, account for the resonances you see in the NMR spectrum. It may be helpful to consult a correlation table of chemical shifts.

• *Starting from Scratch*

1. Take a look at your NMR spectrum. Identify reference solvents (*e.g.* TMS, chloroform) and omit them from consideration. Note that water is also a potential impurity (broad signal at *ca.* 1.5 – 1.6 ppm in $CDCl_3$ solution).
2. Determine peak integration. If the molecular formula is known, then the absolute number of protons can be verified.
3. Determine the chemical shift of each resonance in your spectrum.
4. Identify the multiplicity (splitting) of each resonance in the spectrum. You may also wish to determine coupling constants (*J*-values) for each set of resonances. This information can be used to determine which groups of protons are adjacent to each other.
5. Using the information obtained above, account for the resonances you see in the NMR spectrum. In this situation it is generally most helpful to put together small fragments first and proceed from there. It may also be helpful to consult a correlation table of chemical shifts.

Reporting NMR Data:

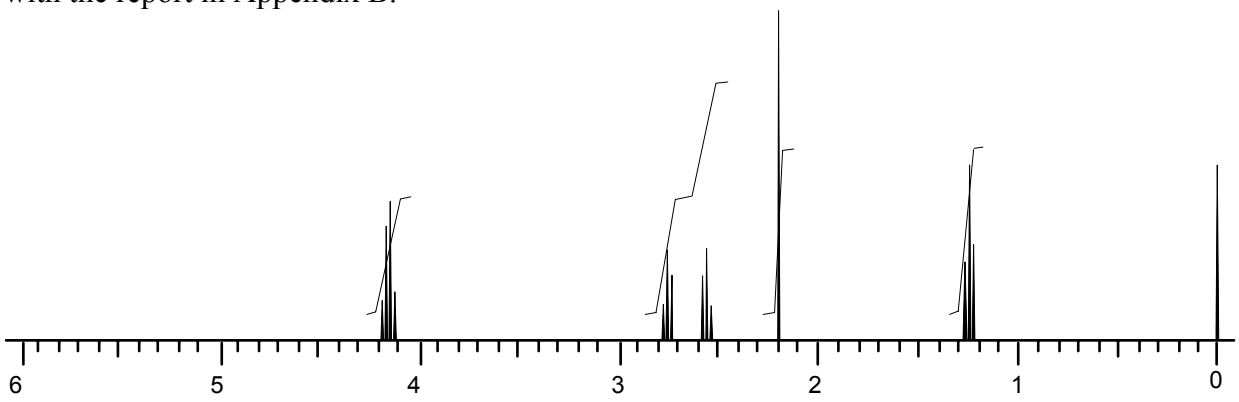
A single NMR spectrum provides a great deal of information that must be clearly interpreted and reported in an organized manner. You should report NMR data in table format. Refer back to this table as needed to clarify your explanations. Include a drawing of your compound (number the atoms as necessary) in the Results and Discussion section to facilitate identification and interpretation of specific resonances.

When reporting NMR data, you must include the position in ppm, the integration (# protons), and the peak multiplicity (splitting). In general, you must interpret every peak (excluding standards such as TMS). While you may not be able to assign every set of protons in your compound to a specific resonance (they may be grouped together or difficult to distinguish - two methyl singlets, for example) you must account for every proton. A possible exception: protons on heteroatoms are exchangeable and may not be seen.

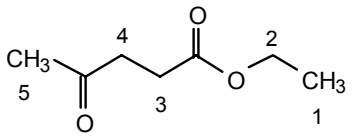
Integration must be reported in whole numbers, and should reflect the actual number of protons represented by the resonance (not the relative intensity). The total number of protons reported should agree with the number present in the compound being evaluated. If these values do not agree, you must provide an explanation.

Example: Ethyl Levulinate

The NMR spectrum of ethyl levulinate is shown below. You should include your spectra with the report in Appendix B.



You should interpret the spectrum and report the data in the Results and Discussion section. Note that a labeled structure of ethyl levulinate is included as well as the tabulated data. You should discuss the data in the body of the report as appropriate.



Ethyl Levulinate

Table of NMR Data for Ethyl Levulinate:

Position	Shift (in ppm)	Integration	Multiplicity	Assignment
1	1.25	3H	Doublet	$-CH_3$
2	4.15	2H	Quartet	$-OCH_2$
3 or 4	2.55	2H	Triplet	$-CH_2(C=O)$
3 or 4	2.74	2H	Triplet	$-CH_2(C=O)$
5	2.19	3H	Singlet	$-(C=O)CH_3$

In this case the spectrum does not provide enough detail to allow accurate measurement of *J*-values, but there is little to be gleaned from *J*-values in this particular instance anyway.

The Laboratory Report

I. Format

Reports should be typed, computer-printed (double-spaced) in 12-point font, or printed legibly in blue or black ink, and must follow the format outlined below. A typical report will be 3 to 4 pages long. It should be complete, but concise. To receive full credit, use the proper format and follow instructions carefully.

II. Parts of the Report

A. Title Page:

1. Title
2. Experiment #
3. Identifying information (at lower right): Your name, Section #, TA, and date submitted.

B. Purpose

Discuss the general purpose of the experiment in at most two or three sentences. (*e.g.* to investigate and compare various methods of distillation). This should be more than a simple restatement of the title. If you are performing a synthesis, include the balanced chemical equation. *Note that the chemical equation provided in the handout is not always balanced.*

C. Experimental

During the course of the experiment, you should have kept a clear written account of the procedures that you followed in your notebook. You do not have to reproduce those details here. However, you do need to make reference to the location of your notebook pages. You should submit the preliminary information and experimental procedure from your notebook to your TA at the end of each laboratory period. Your TA will compile these pages and attach them to your report as "Appendix D". *Note: Late experimental pages will not be accepted.*

D. Results and Discussion

This is the most important section of the report. Here that you should interpret your own experimental data, and reach conclusions as to what those data imply. You will need to explain clearly how you drew these conclusions. It usually works best to divide this section into parts which correspond to the individual components of the experiment (*e.g.* each synthetic step). In a sentence or two, tell what you did (*e.g.* reacted A with B to give C), then tell what you found. Do not include a detailed experimental account – we should already be able to find this in your notebook pages. Instead, concentrate on your results. Give all the evidence you have that a particular step was successful (or was not!). You will not always be told every piece of evidence that you should look for, but you should always include the following (when relevant):

1. Amount (in grams) and percent yield (indicate which reagent was the limiting reagent.)
2. Physical properties (color, state, etc.)
3. mp or bp (always report a range), and give the literature value for the mp or bp for comparison.
4. TLC (Draw the plates on your notebook, report the R_f value(s) and the solvent system used)
5. GC (Attach the properly labeled GC chart, report the retention time, the # of other peaks present, and/or the % purity)

6. IR; Attach the IR spectra properly labeled with experimental details (such as method of sample preparation and date acquired) on the spectrum, report key absorbances only (in cm^{-1}), and identify the functional group each absorbance represents. This information should be presented in a table. Explain the significance of the results, but do not overinterpret. Note absent absorbances in your write-up, too, where relevant. (For example, upon reduction of a ketone-containing ester to an hydroxy ester, the IR spectrum of your product should still contain an ester C=O absorption, but the ketone C=O absorption should be gone, unless your reaction did not work properly, or your product is contaminated with acetone, or ???)
7. NMR; attach the properly labeled NMR spectra, for every resonance in the spectrum, report the position in ppm, integration (# protons), and the multiplicity (e.g., 3.6 ppm, 3H, triplet), and assign each signal to a proton (or protons) in the compound. This information should be presented in a table. Explain why (or whether?) the spectral data are consistent with the structure. Explain any extraneous peaks.
8. MS; attach the properly labeled mass spectra. Indicate the position of the molecular ion, and any useful information concerning isotopes. Identify significant fragments and their formulas. Explain whether the MS is consistent with the expected results.
9. Functional group tests and formation of derivatives; interpret what the results mean.

Always present data in table format whenever possible. You should include any graphs, structures, etc. that are necessary for your discussion. Tabulated values and specific absorbances, resonances, etc. should be cited in the text as appropriate for clarity. Any spectra that you recorded should be included in Appendix B. However, you should completely discuss this information in the body of your report. Include a drawing of your compound (number the carbon atoms) in this section to facilitate identification and interpretation of specific resonances.

Draw specific conclusions based on the data that YOU obtained. Did you really make the compound or not? Did the distillation work or not? Is your product pure? If not, does the evidence suggest what might have happened? The answers to these kinds of questions MUST be consistent with YOUR data, and MUST be supported with experimental evidence FROM YOUR OWN WORK as compared to literature-based expectations. Be sure to clearly explain how you drew your conclusions. Such evidence should include a comparison of the physical and spectral properties of your product with those of the starting material, and with literature values expected for the product whenever possible. You can often find these values in the CRC handbook or Merck Index in the library. Discuss the yield of the product you obtained. Is it unreasonably low? Suggest possible explanations.

E. Conclusions

Summarize the conclusions you reached in the Results and Discussion section. Was your experiment successful? Where appropriate, apply these conclusions to more generalized areas. For example, discuss what your specific result tells you about a general theory or class of reactions. Did any of your results agree or disagree with your expectations? If a new technique was utilized, comment on its effectiveness relative to what you were trying to accomplish.

F. Appendices:

You may not always have material for each appendix, but the material you do have must be labeled and appear in the following order:

1. Appendix A: Calculations (yields, R_f values, etc.)*
2. Appendix B: Spectra (IR, NMR, MS) GC traces, etc.
3. Appendix C: Answers to any questions that may be assigned for a given experiment.
4. Appendix D: Experimental Information (notebook pages; these will be attached by your TA)

* For each chemical transformation you perform, make a Table of Reagents which lists the amounts of reactants/reagents that you used in the reaction (in mL or grams). Convert these measurements into moles, and then into equivalents based on the limiting reagent. Identify the limiting reagent for each synthetic step (Note: a catalyst is never the limiting reagent!). Include a % yield calculation for each synthetic step. For other computations, a sample calculation is sufficient. In each case, include the equation you utilized, complete with units.

II. Style

Some rules for writing are commonly accepted for scientific literature, and should be followed when generating your report:

1. Write in the past tense when describing what you did.
2. Use the passive voice. (Write "The product was recrstallized." Do not write "I recrystallized the product," or "Recrystallize the product."
3. Incorporate data into the text of the report when explaining things, even if the data are already in a table. This helps to clarify the discussion.

III. Grading of Lab Reports

This is a laboratory course. So, experimental results are significant. Therefore, a portion of your report score will reflect your experimental success, such as the quality and amount of the product(s) that you submit. On the other hand, significant effort should be evident even in cases where a poor yield or an impure product was obtained. So, product quality and/or quantity are not generally the major components of the score. Your score will also reflect such issues as how well you have adhered to the directions above, whether you have provided all of the appropriate data, and whether your discussion clearly indicates that you understand what your own results mean.

MODEL LAB REPORT, EXPERIMENT #2

Find below a 'skeleton copy' of a lab report for Experiment #2, which supplements the information given in your course pack (pp. xxix – xxxi)

You can also use this model for future lab reports. This model, for example, gives you an idea of how much space you should devote to each section (*e.g.* Purpose), and how each section of Experiment #2 should be organized.

The Purpose, Experimental, Results and Discussion, and Conclusions should take up *no more* than a total of five typed, double-spaced pages.

Remember, write your report in the past tense when describing what you did, and do not write in the first person (*e.g.* I, we).

Any questions should be directed to either your TA or the instructor.

Organic Chemistry Techniques

Experiment #2

(NOTE: You MUST follow this format for the title page; otherwise, you will lose points)

Name

Section 01

TA Name

Date Submitted

Purpose:

The 'Purpose' enables you to summarize the objective of Experiment #2, while pointing out the kinds of methods that were used in Parts I-III (*e.g.* micro boiling point).

Experimental:

Please use "See Course Pack" for the experimental.

Results and Discussion:

The 'Results and Discussion' enables you to outline your results, compare and contrast your results (*e.g.* simple vs. fractional distillation), and discuss the meaning of your results (*e.g.* this result indicates that compound X is more polar) for each Part of the experiment.

Specific information that you should include for the Results and Discussion is outlined in your course pack for each Experiment.

Part I:

Results and Discussion for Part I goes here.

Part II:

Results and Discussion for Part II goes here.

Part III:

Results and Discussion for Part III goes here.

Conclusions:

The 'Conclusions' enables you to judge whether your experiment was successful.

Accordingly, you should give a brief overview of whether your experiment was successful, particularly as it relates to your results and the Purpose.

Appendix A: Calculations

This section is for your calculations, and can be done (neatly) by hand.

For Experiment #2, your calculations will enable you to fill out the data sheet provided in the course pack.

Calculations for Experiment #2 include:

1) peak areas
2) percent recoveries (individually and overall)
3) volumes
4) retention times
5) R_f values

Appendix B: Spectra

This section is for all spectra. For Experiment #2: GC traces, IR spectra, and TLC plates.

Attach all spectra and TLC plates. Also, provide a hand-drawing of each TLC plate, clearly illustrating the position, shape, and determined identity of each spot.

Appendix C: Experimental Information

This section is for the completed data sheet provided in your course pack.

Attach the data sheet here.