Chemistry 360
Organic Chemistry II

Laboratory Manual

Athabasca University
Faculty of Science and Technology

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The following sources are also hereby respectfully acknowledged:

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The experiments described in this laboratory manual are mainly variations of similar experiments that may be found described in the laboratory manuals of other universities or in commercially produced lab texts. Each experiment has been modified and rewritten, keeping the needs of Athabasca University students in mind.

Ross Witherell, Jason Norman, Nina Vo, James Sochan, Scott McGavin, Nyron Jaleel, Klaus Thomson, Robert Carmichael, Jerry Pyrozko, Roger Klemm, and Glen Conlin, have all checked the procedures described in this manual. The continued comments and suggestions for improvement received from all the individuals mentioned above have been and always will be greatly appreciated by the course professor and course coordinator.

General Introduction

Welcome to the laboratory component of Athabasca University's Chemistry 360. The series of experiments performed in this course are a logical extension of those performed in Chemistry 350. Although the laboratory component of this course is very intensive, we hope that you will find the experience intellectually stimulating and memorable. We also hope you can take advantage of every opportunity to meet and discuss organic chemistry with your tutor and other Athabasca University students.

If you were to take a course such as Chemistry 360 in a traditional college or university, you would probably be expected to attend a three-hour laboratory session every week for 10-12 weeks. During this time, you would receive somewhere in the order of 30-36 hours of laboratory instruction. In our course, you will receive approximately 32 hours of instruction, spread over four days.

Although we feel that our method of providing the laboratory component of this course is the best that we can achieve, given the circumstances under which we operate, there are undoubtedly some disadvantages to the system. We bring these disadvantages to your attention so that you can adjust your work habits accordingly and minimize any potential problems.

a. Hours of work. At each day-long laboratory session, you will be working for approximately eight hours. Your instructor will ensure that you take a proper lunch break, but we also recommend that you take both a morning and an afternoon refreshment break. Regular breaks make it easier for you to concentrate while you are working and will decrease the likelihood of an accident. We also recommend that you take a brief walk outside during one or more of your breaks.

b. Feedback. The laboratory sessions are done in a concentrated fashion, with all experiments in the course being done in a few days during one visit. However, as you write up your laboratory reports, it is strongly suggested that you submit only a few reports at a time (especially the first experiments). This will allow your academic expert to provide you with constructive feedback that you can use in writing subsequent reports.

c. Preparation. Athabasca students must prepare several experiments for each day of laboratory work. For example, before attending the first laboratory session, you must read through Experiments 10-12, making sure that you understand exactly what you will be doing, noting possible problems, and so on. The following two sections on

"Lab Registration" and "Organization" (including a suggested schedule for completing the labs) will, we hope, help you prepare for your laboratory sessions.

Organization

The laboratory component of *Chemistry 360* comprises approximately 32 hours of supervised laboratory work. The laboratory sessions may differ from other laboratory classes that you have attended, in that not all the students will be working on the same experiment at any given time and the experiments are not necessarily exactly 3 hours in length. Your lab instructors will help guide the work schedule of the lab class, considering availability of instruments and other factors. However, **you must be prepared to do more than one experiment at a time.**

Suggested schedule for completing labs (lab instructor discretion)

	8:30am	9am	10am	11am	12noon	1pm	2pm	3pm	4pm	5pm	
Day 1	Orientation	Start Ex.10		Start 11	BREAK		Start Ex.12/13			Cleanup	**Day 1**
			Start Ex.11.....						Start Ex.15		
Day 2	Complete Ex. 12		Complete Ex.13		BREAK					Cleanup	**Day 2**
				Compl.Ex.14 and 15							
Day 3	Start Exp 16				BREAK					Cleanup	**Day 3**
								Analyses			
Day 4	Start Exp.17				BREAK					Cleanup	**Day 4**
			Complete all analyses								

Materials to be Provided by the Student

When attending a *Chemistry 360* laboratory session, each student must provide the following items:

1. **an electronic calculator**.
2. **a lab notebook**, to record observations and results.
3. **a pen**, a pencil and a ruler.
4. **a black 'Sharpie'** marking pen for making labels.
5. Optional: *Organic Chem Lab Survival Guide* from the Athabasca University library

Evaluation

All students must work individually, except where otherwise indicated in the lab manual. Pairing up and the pooling of data, solutions, etc., is not permitted.

Your lab reports must be legible and preferably typed. Although neatly handwritten and scanned to PDF documents are permitted for the Short Forms, you will need to type the Formal Reports.

Note that the penalties for plagiarizing laboratory reports are identical to those incurred for other types of plagiarism. See Athabasca University Student Academic Misconduct Policy: https://www.athabascau.ca/university-secretariat/_documents/policy/student-academic-misconduct-policy.pdf

You must attain an average of 60% for laboratory work to pass the course. The laboratory component is 20% of your final composite grade in the whole course.

Experiment Products

Products prepared in the lab are to be submitted to the lab instructor for evaluation. The product should be weighed and submitted in a labelled vial (your name, product name, weight, melting point or boiling point, and date submitted).

Marking of Laboratory Reports

Your laboratory reports should be emailed as separate PDF attachments to your academic expert within 1 month of your last supervised laboratory session. (NB: Currently there is no option to use the assignment drop box within the LMS.) Late lab reports will be penalized 10% for every month they are late. Thus, sending in your lab reports **four months late will mean that you fail** the lab component, since you need an overall average of 60% to pass the lab component and course

Laboratory Examination

Currently, there is no written lab exam for the *Chemistry 360* laboratory component.

Writing Laboratory Reports

The first key to obtaining good marks on laboratory experiment reports is to keep a neat and organized lab notebook. Prepare your notebook in advance by setting out the purpose and main reactions of the experiment, certain properties of the reagents and expected products (plus calculations), and a table to receive your results and observations. The second key is to understand the type of experiment you are being asked to perform. In this course, it will be either an investigative or preparative experiment. This knowledge should help you to prepare your lab notebook in an appropriate way and will obviously dictate the format of the report you will write and submit for marking. The final key is to always remember to be concise in your writing, no matter what the type of report.

Standard Report Formats

Investigative	Preparative
Title, date and references	Title, date and references
Purpose	Purpose and Introduction
Procedure	Procedure
-Table of Reagents	-Table of Reagents
Results	Results
-Observations	-Observations
-Table of Products/Inferences	-Table of Products
Questions	Discussion
Conclusion	Questions
	Conclusion

In *Chemistry 360*, you are expected to prepare a report on each experiment, as soon as possible after you have completed it and to submit the report to your instructor for grading. Some hints designed to assist you in writing your reports are given below, although you should also consider any specific instructions given to you by the instructor.

Some general comments on laboratory reports may be found in Chapter 4 of *The Organic Chem Lab Survival Manual* (or Chapter 2 in 3rd ed.). In addition, each experiment in the *Chemistry 360 Laboratory Manual* contains a section discussing the approach to be used when writing up that experiment. In general, each report should include the sections outlined below.

Organic Chemistry 360 Lab Report Writing Hints

1. **Title, date, name and student ID number.**

2. **Purpose/Objective of experiment**

   Example: To prepare cyclohexene from purified cyclohexanol by acid catalyzed dehydration reaction. Also the technique of … **Note**: Have a main purpose and several minor purposes.

   Try to be as specific as possible.

   e.g., The main objective of this experiment is to synthesize the alkene, cyclohexene, from cyclohexanol, using an acid catalyzed dehydration mechanism. The product formed is stabilized by 'salting out' of the water using brine, neutralizing any trace acid present with sodium carbonate, and drying using a drying agent anhydrous calcium chloride. Purified cylclohexene is obtained by distillation and the final product is characterized by bp, density, infrared spectroscopy and refractometry. A minor objective is to become familiar with infrared spectroscopy sample preparation.

3. **Introduction**

   Give a brief introduction to the purpose of the experiment and the approach to be used for this for all lab reports, whether they be investigative or synthetic style reports. Do not copy directly from the laboratory manual. Usually, one or two paragraphs will be adequate, i.e., should be kept to less than a page long and demonstrate that you understand the objective and the key concepts of the experiment. You may include relevant balanced and fully labelled chemical equations at this point. Use only the third person, present tense, passive voice when writing the introduction. For example,

   Correct: In this experiment, cyclohexanol is converted to cyclohexene using……

   Incorrect: In this experiment, I will be performing an acid catalyzed dehydration…

   do not just write the General Reaction equation, e.g., ROH (alcohol) + $H^+ \leftrightarrow$ R-C = C-R (alkene)

4. **Procedure**

   You may simply refer to the relevant pages in the lab manual (referenced properly). Whatever you do, do not regurgitate the laboratory manual. If the procedure has been modified, or changed in any way, note the changes here. Remember that the procedure section should be sufficiently detailed for another student to be able to repeat the whole experiment based on your report. Prepare a simple flow

chart of the procedure, and record any observations alongside., Finally, keep the following points in mind:

i. use the third person, the passive voice, and the past tense.
   Correct: The solution was heated on a hot plate for 30 minutes.
   Incorrect: I heated the solution on a hot plate for 30 minutes.
   Incorrect: The solution is heated on a hot plate for 30 minutes.

ii. avoid the "recipe format".
   Incorrect: Heat the solution on a hot plate for 30 minutes.

iii. incorporate your observations into the procedure.
   Example: The solution was heated on a hot plate for 30 minutes, during which time the colour of the solution changed from red to green.

iv. avoid unnecessary detail.
   Acceptable: 20 mL of hydrochloric acid (3 mol· L^{-1}) was added to the solution with constant stirring.
   Unnecessary detail: 20 mL of 22.5 °C hydrochloric acid (3 mol· L^{-1}) was poured from a graduated cylinder into a 100-mL beaker containing the solution. During this process the solution in the beaker was stirred with a 15- cm long glass rod having a diameter of 5 mm.

v. Remember to include a <u>table</u> of reagents.

Experiment X Table of Reagents

Reagent	Solid or Liquid	FW (g/mol)	Volume Used (mL)	Density (g/mL)	Weight Used (g)	moles used <u>(g/mol)</u>	MP/BP (°C)	Hazardous Properties
Cyclohexanol	L	100.16	21.0	0.963	20.22	0.202	161.1	Irritant, hygroscopic
Acetone	L	58.08	10.0	0.818	8.18	0.14	56.5	Flammable, irritant
...								

Reference: _____

Note: By filling out the amount and moles used, you will have determined your limiting reagent. The limiting reagent must be calculated in preparative type experiments to determine your % yield.

vi. It is perfectly acceptable to record your observations alongside a flow chart of the procedure.

Procedure	Observations
Equipment and Glassware Preparation	All clean and dried with acetone, then placed in 110°C oven for 30 min.
Reaction Mixt. Preparation (perform in fume-hood)	
1. Add 11.2 mL bromobenzene to 50 mL diethyl ether	-solution clear and colourless
2. Add 2.4 g of Mg (s) to 250mL round bottom flask	-...
3.	-
4.	-
5.	-
Reaction Workup	
1.	-
2.	-
3.	-
Analysis	-shiny sl. translucent needles, mass of prod=2.5 g

5. References:

Use an acceptable scientific journal sytle/format for your objectives. Be consistent. Do not use one format in one report and a different one in the next.

Author name (surname, initials.), year published. Title, publisher name, publisher location (e.g. AB for Alberta), page numbers.

6. Results

This is most important section of your report. Wherever possible, **tabulate your data**. A summary of observations is also acceptable here. Show your calculations for the % yield. The discussion portion gives you an opportunity to discuss the significance of your results, to assess the validity of the method, to indicate possible reasons for a poor yield, and so on. Do not over-comment on IR spectra, just pick out and comment on the spectral peaks of importance.

Show sample calculations. Remember there is a difference between % Recovery yield calculations and % Yield calculations where you must determine limiting reagents and a theoretical yield (Exp. 10, 12, 13, 16 and 17).

Label and title all attached flowcharts, spectra etc.

7. Discussion

First, your discussion should state what you've made (draw the structure and name it) and what it appears like (was it as expected, compared to standard or literature) e.g., white shiny crystalline solid.

Next discuss the **yield and purity** of the product(s) you recovered/synthesized. Qualitatively assess the performance (e.g., very good >80%, good 60-80%, fair 40-60%, poor <40%). [Note: This scale might not be appropriate for all experiments. You may have to adjust it accordingly.]

A discussion should **quote actual experimental values** and not talk in vague terms. e.g., "The product obtained was found to be pure." (too vague)

"The product obtained was found to be fairly pure because it had a mp of 110-112° C, a map range of only 2° C. This result was 3 degrees below the literature value of 115° C for 'compound X', and this also shows that the product was not completely pure."

or

"The infrared spectrum of the alkene product (see page xx of the report) had the absorption bands of the expected alkene, 3050 cm^{-1} sp^2 C-H stretch and 1650 cm^{-1} C=C sharp absorption. No broad alcohol band was observed at 3300 cm^{-1}, indicating no reagent alcohol remains and that the reaction resulted in the conversion of the alcohol to the alkene product."

The next section of your discussion covers sources of error and loss. Try to think of at least 2 of each for every experiment.

Sources of error -**theoretical** (assuming reaction goes to 100% completion), and **practical** (the 'instrument' used was not calibrated, or the 'glassware' used to measure my reagent was not calibrated)

Sources of loss - -**theoretical** (e.g., reaction byproduct formation if any (be specific), and **practical** (surface adhesion loss on glassware (be specific), mechanical transfer loss (spilt product when transferring to vial at the end of the experiment!).

Finally, mention at least one way to improve the experiment (should you get to do it again!).

Example Discussion of Product Formed

A clear colorless liquid with a slight alcohol odor, corrected bp 196-201° C, and refractive index of 1.5262 (at 20° C), was obtained from the reaction of...[also draw and name structure of product here]...

Example Discussion of Product Yield

The yield of 1-phenylethanol was 13.2 g of clear, colorless liquid, and the % yield was 56%. The theoretical yield for the reaction was calculated to be 23.57 g, but this assumes that all the limiting reagent (acetophenone) reacted and that no byproducts formed (styrene) Thus, this a fairly good yield for this reaction, which normally gives yields of product around 85% (ref: textbook pp#).

Example Discussion of Product Purity

The product appears to be pure. According to the CRC Handbook the product should be a clear, colorless liquid, with a bp of 203° C. The product obtained was clear and colorless with a (barometric pressure corrected) bp of 195-201° C. The boiling point of the product was 2 C below the literature value, indicating some impurity and/or error, and boiled over a range of 6° C, which definitely means some impurities are still present.

The refractive index of the product was 0.0010 below the literature value of 1.5272, indicating again that some slight impurities are present.

The infrared spectrum for the product shows good purity. All the absorbance bands for an aromatic/aliphatic alcohol were present; O-H stretch @ 3350 cm^{-1}, aromatic C-H stretch @ 3080 cm^{-1} and alkane C-H stretch @ 2850-2950 cm^{-1}, C=C stretching @ 1600, 1500 and 1450 cm^{-1}, and C-O stretch for a alcohol @ 1077 cm^{-1}. No absorbance bands due to reasonable impurities were observed in the infrared spectrum.

The HPLC chromatogram showed high purity, 99.54%, with only traces of acetophenone and styrene being present.

Example Discussion of Sources of Loss and Error

The boiling point of the product was 2° C below the literature value, however an uncalibrated thermometer was used to take this reading. This may account for why the temperature reading was low, but does not explain why the product boiled over a range of 6° C.

The refractometer used in this experiment was uncalibrated. This is a practical source of error for the experiment. And might partly account for why the RI was 0.0010 below the literature value of 1.5272.

8. Answers to post lab questions

The post lab questions are in the lab manual at the end of each experiment.

9. Conclusion

You would usually include a sentence or short paragraph that summarizes your results and puts them into some kind of context. If you have made a product, it would be wise to draw its structure again here.

Note: A good concluding statement is sometimes very hard to write. You must address the objectives you've mentioned at the start of the experiment (do not repeat your objectives word for word!!), mention your key result and say something about the success/failure of the experiment, all in one or two (max.) sentences.

Note: that in some cases the format given above may be completely inappropriate. In such situations, you will be advised as to the most suitable form in which to submit your report.

Submitting Laboratory Reports

Your lab reports are submitted to your AE for marking.

Weights, Volumes, Measurements and Calculations

SI units and the metric system are used in chemistry.

Measurement	SI Unit	Conversion Factors
Length	Meter (m)	1 m = 100 cm 1 cm = 10 mm 1000 mm = 1 m 1 cm = 0.3937 inches (in) 1 in. = 2.54 cm 1 angstrom (A) = 10^{-8} cm 1 mile = 1.6093 km
Mass	Kilogram (kg)	1 kg = 1000 g 1000 mg = 1 g 1000 mg = 1 µg 1 kg = 2.205 pounds (lbs) 1 lb = 453.6 g 1 amu* = 1.6605402 × 10^{-24} g electron rest mass = 9.10939 × 10^{-28} g proton rest mass = 1.672623 × 10^{-24} g neutron rest mass = 1.67495 × 10^{-24} g
Volume	Cubic meter (m^3)	1 cm^3 = 1 mL 1000 mL = 1 L 1 liter (L) = 10^{-3} m^3 1 in^3 = 16.4 m^3 1 liter (L) = 1.057 quarts (qt)
Density	d	Density = g/mL or kg/L
Mole	m	6.0221367 × 10^{23} atoms/mol**
Temperature	Kelvin (K)	0 °K = -273.15 °Celsius (C) 0 °K = -459.67 °Fahrenheit (F) °F = (9/5)C + 32° °C = (5/9)(°F - 32)
Molar Mass Molecular Weight Formula Weight	MM MW (Σ of atomic weights of a molecular formula) FW (Σ of atomic weights of a chemical formula)	MM = g/mole MW = g/mole FW = g/mole
Time	Second (s or sec)	1 minute (min) = 60 s 1 hour (hr) = 60 min 1 day (d) = 24 hr 1 day (d) = 86,400 s

* 1 atomic mass unit is derived by assigning the value of 12 amu to a single atom of ^{12}C isotope of carbon.

** the number of atoms in exactly 12 g of ^{12}C.

Prefixes used to indicate decimal fractions and multiples in the SI system

Prefix	Symbol	Number Unit	Example
mega-	M	10^6	1 megabyte (Mb) = 10^6 bytes
kilo-	k	10^3	1 kilogram (kg) = 10^3 g
deci-	d	10^{-1}	1 decimeter (dm) = 0.1 m
centi-	c	10^{-2}	1 centimeter (cm) = 0.01 m
milli-	m	10^{-3}	1 milligram (mg) = 10^{-3} g
micro-	µ	10^{-6}	1 microgram (µg) = 10^{-6} g
nano-	n	10^{-9}	1 nanometer (nm) = 10^{-9} m
pico-	p	10^{-12}	1 picogram (pg) = 10^{-12} g
femto-	f	10^{-15}	1 femotometer (fm) = 10^{-15} m

Other Important Concepts in Organic Chemistry Yield

The yield is the weight or quantity (in grams) of dried*, pure product that is recovered in an experiment. This number is used to calculate the percentage yield (see below).
*The product should always be air dried to a constant weight. Do not heat organic compounds to dry them as they often will decompose, melt or oxidize. Instead use vacuum drying when trying to remove moisture/solvents from an organic solid.

Theoretical Yield

The theoretical yield is the maximum weight or quantity (in grams) of product that can be expected to be formed from a reaction. This number is also used to calculate the percentage yield (see below). The theoretical yield cannot be calculated until the limiting reagent for a reaction has been determined.

Limiting Reagent

The limiting reagent in a reaction is the reactant added to the reaction vessel in the fewest number of moles, after taking into account the stoichiometry of the reaction equation. Consider the following example, where 0.01 g of 1-butyne are reacted with 3 mL of a 1% solution of bromine in carbon tetrachloride, yielding 0.35 g of tetrabromonated product.

To determine the limiting reagent, the first step is to write out the molecular/chemical formula and then calculate the molecular or formula weights for the reactants.

1-butyne	bromine	1,1,2,2-tetrabromobutane
C_4H_6	Br_2	
Mwt = 54.09 g/mol	FW = 159.81 g/mol	
Moles = ?	Moles = ?	
Molar Equiv = ?	Molar Equiv = ?	

The second step is to then calculate the # of moles of each reactant added to the reaction vessel. To calculate the number of moles of each reactant, divide the quantity of the reactant (g) by the molecular or formula weight. This procedure is made slightly more complicated for bromine, since we are not given a gram amount but rather a weight percentage. (2% solution = 2 g/100 mL) therefore 3mL will contain 0.06 g (2g /100 mL = ? g/3 mL, ? = (2 g × 3 mL)/100 mL).

The third step is to look at the stoichiometry of the reaction. Notice that 2 moles of bromine react with 1 mole of 1-butyne. To take this fact into account, the moles of reactant are converted into molar equivalents (since it takes 2 moles of bromine for every mole of 1-butyne, divide the bromine moles by 2 to get the molar equivalent).

1-butyne	bromine	1,1,2,2-tetrabromobutane
$H_3CH_2CC \equiv CH + 2\,Br_2 \xrightarrow[CCl_4]{} CH_3CH_2CBr_2CHBr_2$		
C_4H_6	Br_2	$C_4H_6Br_4$
Mwt = 54.09 g/mol	FW = 159.81 g/mol	Mwt = 213.9 g/mol
Amt. Used = 0.01 g	Amt. Used = 3 mL	Yield = 0.035 g
	%wt. = 1%	
Moles = 0.000185 mol Molar Equiv = **1.85×10^{-4}**	Moles = 0.000375 Molar Equiv = 1.88×10^{-4}	Moles =?

Therefore, **1 butyne is the limiting reagent** since there are fewer molar equivalents present of 1- butyne than of bromine.

% Yield Calculation

The percentage yield is one of the most important calculations to learn in organic chemistry. It is a measure of the efficiency of the reaction procedure, and is determined by comparing the actual yield to the theoretical yield:

$$\%\ \text{yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100\%$$

There are six steps in the calculation of the % Yield for a reaction. Note: The first four steps were illustrated in the calculation of the moles of the limiting reagent.

Step 1: Write the molecular formulas and determine molecular weights for reactants and products.

Step 2: Determine the number of moles of each of the reactants.

Step 3: Convert moles to molar equivalents, if necessary, by looking at stoichiometry of reaction.

Step 4: Determine the limiting reagent = maximum number of moles of product formed.

Step 5: Convert moles of product to grams of product = theoretical yield.

Step 6: Solve for % yield using the equation given above.

To illustrate the % yield calculation, we will carry on with the same example as above,

$$H_3CH_2CC \equiv CH + 2\,Br_2 \xrightarrow[CCl_4]{} CH_3CH_2CBr_2CHBr_2$$

1-butyne	bromine	1,1,2,2-tetrabromobutane
C_4H_6	Br_2	$C_4H_6Br_4$
Mwt = 54.09 g/mol	FW = 159.81 g/mol	Mwt = 213.9 g/mol
Amt. Used = 0.01 g	Amt Used = 3 mL	Yield = 0.035 g
	%wt. = 1% soln	
Moles = 0.000185 mol	Moles = 0.000375 mol	Moles = 0.000185 mol
Molar Equiv = **1.85×10^{-4}**	Molar Equiv = 1.88×10^{-4}	Theor. Yield = 0.04 g

Therefore the % yield for the above reaction is:

$$\%\ \text{yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100\% = \left(\frac{0.035\ \text{g}}{0.04\ \text{g}} \right) \times 100\% = 87.5\%\ \text{yield}$$

% recovery yield

The percentage recovery is used when compounds are extracted from natural sources, or when a reagent hasn't been changed during a procedural step, such as a recrystallization. The % recovery calculation is used to measure either (1) the % content of the starting material that is the compound of interest or (2) the efficiency by determining the amount of loss during a procedural step. It is often confused with % yield:

$$\%\ \text{recovery yield} = \left(\frac{\text{actual yield}}{\text{amount of starting material}} \right) \times 100\ \%$$

% Error

The percentage error calculation is used to measure the % difference between the actual experimentally derived value and the theoretical expected value. It too is often confused with % yield:

$$\%\ \text{error} = \left(\frac{|\ \text{actual value - theoretical value}\ |}{\text{theoretical value}} \right) \times 100\ \%$$

Safety

General

Some people will approach the laboratory component of their Athabasca University chemistry course with a certain amount of trepidation. In a sense, this is a good thing—no one can afford to adopt a complacent attitude towards laboratory safety. However, you should realize that you could well face a greater chance of being killed or injured as you drive to the laboratory session than you will while you are working in the laboratory. Most of the hazards that you are likely to face while performing the experiments in this laboratory are relatively minor and easily avoided. They include:

minor cuts—most cuts can be avoided if a student never uses broken or cracked glassware and is particularly careful when carrying out potentially dangerous operations, such as inserting glass tubing into a rubber stopper.

burns—burns usually occur when a student forgets that something which has just been heated on a hot-plate or in a heating mantle may be very hot.

chemical spills—spills can usually be avoided if students pay particular attention to the technique used when pouring chemicals from a container, and injury caused by spills can be minimized if students wear the appropriate protective clothing: safety glasses, gloves, and lab coat or apron.

Another possible danger is the presence of hazardous gases or vapours in the air. In this course, we have kept the use (or production) of such materials to a minimum. Where eliminating such materials is not practical, you will be advised to work in a fume hood, which will protect both you and your co-workers from exposure to undesirable concentrations of toxic or otherwise unpleasant vapours.

When designing the laboratory component of this course, we found it necessary to strike a balance between minimizing possible hazards and exposing you to a full range of techniques. By its very nature, chemistry often necessitates the handling of dangerous substances; if chemistry students are never exposed to such situations, we would never have any fully trained chemists. Having said this, perhaps we should reassure you that, provided you follow the safety rules that follow, we do not anticipate that any problems will arise.

Safety Rules

1. **Safety glasses must always be worn in the laboratory.** Wearers of prescription glasses may wear their own eyeglasses but should be aware of the possibility that chemicals or flying glass could enter the eye through the gap between the temple and the frames of the glasses. Thus, in potentially hazardous situations, wearers of spectacles are advised to wear safety goggles or a safety mask over their prescription glasses. Contact lenses must *not* be worn in the laboratory.

   Note 1: Safety glasses will be provided by Athabasca University and must always be worn—even when you are not actively using chemicals and glassware. Remember that injury could result through carelessness on the part of one of your fellow students.

   Note 2: Contact lenses are not permitted for two reasons.

   a. If a chemical is splashed into the eye of a person wearing contact lenses, neither the normal tearing mechanism nor external irrigation (with water) is effective in removing chemicals from under the contact. The contact must first be removed before

tearing and irrigation is effective; however, the contact may be difficult to remove because of the tight squeezing shut of the eye that occurs in response to the chemical in the eye. Since time is of the essence with a chemical burn, a delay caused by the necessity of removing a contact lens could have serious consequences.

b. Soft contact lenses present an additional hazard. Any chemical (including vapours) that encounters such a lens can diffuse into the interior of the lens, which then acts as a reservoir that can create additional exposure, even if the lens is removed and rinsed.

Note 3: The correct emergency treatment for chemicals that enter the eye is to wash the injured eye thoroughly with plain water for 15 minutes. Medical attention should be sought for all eye injuries. An eye-wash fountain should be available in the laboratory; make sure that you are aware of its location.

2. A lab coat should be always worn. You must purchase a lab coat to participate in the laboratory component of this course. A lab coat will not only make you look and feel like a chemist but will also protect you and your clothes if you inadvertently spill a chemical.

3. Protect your feet. Bare feet, open-toed sandals, etc., are not permitted. Spilling concentrated sulfuric acid on your big toe or cutting your foot on a piece of broken glass would result in a trip to the hospital. Avoid high-heeled shoes; remember that you will be “on your feet” for up to eight and one-half hours on any given lab day.

4. Tie back long hair. Long hair can be a fire hazard. Also, when you bend over to inspect the contents of a beaker containing a chemical, long hair can easily fall into that chemical. Not only could this damage your hair, but it could also ruin your experiment!

5. Never run in the laboratory and never be tempted to become involved in practical jokes or other horseplay.

6. On no account attempt an unauthorized experiment.

7. Never work in the laboratory when the supervisor is not in attendance. Our regulations require that at least one qualified supervisor be present in the laboratory whenever a student is working there.

8. Eating, drinking and smoking are not permitted in the laboratory. Food and drink may become contaminated by toxic substances. Smoking is a fire hazard. When you leave the laboratory, wash your hands, particularly before eating.

9. In the event of fire:
   a. do not panic; many small fires can be extinguished without the use of a fire extinguisher, simply by cutting off the air supply. For example, when a flammable liquid 'catches' fire in a beaker, the fire can quickly be put out by placing an asbestos pad or watch-glass over the beaker.
   b. if the use of a fire extinguisher is necessary, leave it to the supervisor and concentrate on getting yourself to the nearest exit.
   c. if your instructor is incapacitated (e.g., through injury), be prepared to extinguish a fire, especially if human life is in danger. To do so, you must know the location of the nearest fire extinguisher and how to use it. Most of the extinguishers that you will encounter are of the ABC type, which means they are effective on fires involving trash, wood or paper (Class A), liquids and grease (Class B), and electrical equipment (Class C). These extinguishers are not effective on Class D fires. (i.e. those involving active metals such as sodium and potassium). Fires involving the latter substances are unlikely to occur during a *Chemistry 360* lab, but you should be aware of the special problems that these materials can cause. When using a fire extinguisher, aim at the base of the fire and use a sweeping motion. Note that you should never attempt to extinguish a laboratory fire using water. (A possible exception might be to extinguish a burning paper towel by placing it in a sink and turning on the tap.)
   d. if your clothing catches fire, wrap yourself in a fire blanket (or a coat if no fire blanket is available) and roll on the ground.

10. Report all accidents. All accidents, however minor, must be reported to your supervisor and the details entered online in the *Student Incident Report Form* (QR code below). If you are involved in an accident, do not resume work until you have received the appropriate first aid or medical attention. Never work with open cuts on your hands; cover all small cuts and scratches with 'band-aids'.

11. Always dispose of chemical wastes in the correct manner. In general, you would never dispose of chemicals, particularly organic solvents, by pouring them down the drain. Throughout the *Chemistry 360* laboratory manual you will find that you are told repeatedly to "pour excess reagents into the waste container provided". Ensure that waste chemicals are placed in the correct container—putting the wrong

material into a container is potentially dangerous. Never attempt to return “used” chemicals to their original containers. Note that certain substances, such as dilute acids or solutions of “harmless” compounds (e.g., sodium chloride), etc., *may* be washed down the drain with copious amounts of water. When in doubt, check with your instructor. Be particularly careful to place any chlorinated hydrocarbons in the waste container designated for such substances.

12. **Never pour concentrated inorganic acid (e.g., H_2SO_4) or base into a bottle marked ‘Organic Waste only’.** Violent exothermic reactions can occur between potential reagents, causing a splatter of toxic and corrosive material.

13. **Never over fill a waste bottle.** Keep an eye on the volume level in the waste bottle and let the instructor know when it is ¾ full.

Some General Advice About Laboratory Work

1. People with clean and tidy benches are less likely to be involved in accidents. Communal areas, such as balance rooms and fume hoods, should also be kept tidy. Clean up all spills. Any glassware containing chemicals that is left in a communal area should be clearly labelled with the owner's name and details of the contents (e.g., L. Worker, concentrated nitric acid).

2. Do not rummage through a cupboard or communal glassware/supply drawer or box without care and attention. Sharp object may be present. Discard sharp objects (needles, razor blades, broken glass in the appropriate sharps discard receptacle.

3. Always wear your lab coat when working in the lab and wear protective latex gloves whenever handling corrosives and solvent. Do not store sharp objects (e.g., Pasteur pipettes) in your coat pocket.

4. When assembling apparatus or glassware, always check with the instructor before proceeding with the experiment.

5. Handle all organic solvents (e.g., acetone, dichloromethane) with care. Most are flammable, and many have a long-term, cumulative effect on the body.

6. If a fire starts, or the fire alarm sounds, unplug any electrical apparatus and vacate the laboratory in an orderly manner.

7. When diluting a concentrated acid, always **add the acid to the water**. Do so slowly, with stirring.

8. If you get acid on your clothing, neutralize it with **dilute** ammonia solution (1 $mol \cdot L^{-1}$) and wash well with water.

9. If you get alkali on your clothing, wash it off with large quantities of water.

10. If you get any corrosive chemical on your skin, wash it off immediately with water and consult your instructor. Pay special attention to the safety notes given in bold type in the "Procedure" sections of the lab manual. These notes will inform you of any special precautions that you might need to take and will also inform you if the "wash well with water" maxim does not apply.

11. If you spill a large quantity of acid on the bench or floor, use crude sodium bicarbonate (available from the instructor) to neutralize the acid and then wash well with water.

12. Mercury from broken thermometers presents a special kind of hazard. The vapour from the spilled mercury represents a long-term hazard and so the liquid mercury should be cleaned up very carefully. If you break the thermometer, ask your instructor for assistance in cleaning up the mercury. Do not touch the mercury globules with your hands.

13. Always check for any possible hazards associated with using a given chemical. The quickest way of doing so is to make certain that you read the label on the container from which the chemical is removed. Some chemical manufacturers use symbols or codes on the labels of their chemical containers to indicate possible hazards. When in doubt, consult your instructor.

14. As mentioned in the safety rules, all accidents that result in injury must be reported to your supervisor and the details entered online in the *Student Incident Report Form*.

WHMIS

**** You are required to complete the WHMIS (Workplace Hazardous Materials Information System) course on health and safety in the workplace before beginning the laboratory component of this course. ****

Under "WHMIS Training" of the "Laboratories" section of the online course you can access the training and/or provide a certificate of successful completion. There are three main features of WHMIS:

1. Chemical manufacturers are now obliged to label each container of hazardous material, giving details on the product's hazards and what action to take in an emergency.

2. The manufacturer must provide the consumer with a Material Safety Data Sheet (*MSDS*) for each hazardous product. These sheets give complete details on the possible health effects that exposure to the product can produce, preventive measures that should be taken, etc.

3. Employers must provide an appropriate education program for all workers whose work may bring them into contact with hazardous products.

The WHMIS regulations do not affect you as a student, although if you are involved in a chemistry-related job you should be familiar with them. Most of the chemicals that you will handle in this course are no longer in their original containers. Under the WHMIS regulations, such chemicals do not require detailed labels. However, you should read all labels carefully and pay special attention to the hazard warnings that appear throughout the laboratory manual. The hazard symbols that you may observe on certain chemical containers are reproduced on the following page. A file containing up-to-date MSDSs for all the chemicals used in *Chemistry 360* is maintained at each of the locations where laboratory sessions for these courses are held. Additional information on WHMIS may be obtained from Alberta Community and Occupational Health, Occupational Health and Safety Division.

Hazard Symbols

	**Exploding bomb** (for explosion or reactivity hazards)		**Flame** (for fire hazards)		**Flame over circle** (for oxidizing hazards)
	**Gas cylinder** (for gases under pressure)		**Corrosion** (for corrosive damage to metals, as well as skin, eyes)		**Skull and Crossbones** (can cause death or toxicity with short exposure to small amounts)
	**Health hazard** (may cause or suspected of causing serious health effects)		**Exclamation mark** (may cause less serious health effects or damage the ozone layer*)		**Environment*** (may cause damage to the aquatic environment)
	**Biohazardous Infectious Materials** (for organisms or toxins that can cause diseases in people or animals)				

* The GHS system also defines an Environmental hazards group. This group (and its classes) was not adopted in WHMIS 2015. However, you may see the environmental classes listed on labels and Safety Data Sheets (SDSs). Including information about environmental hazards is allowed by WHMIS 2015.

From the Canadian Centre for Occupational Health and Safety (https://www.ccohs.ca/images/oshanswers/pictogram_names.gif)

Some Major Does and Don'ts

1. Never leave a reagent stock bottle open and unattended. Securely close and put the bottle away immediately after obtaining your aliquot/sample.
2. Use a clean metal spatula (not a glass rod) to break up clumps of solids in bottles.
3. Think ahead as to where you are going to set aside or discard any wastes or contaminated glassware.
4. Never work hastily. Always be in control and know the next procedural step(s).
5. Label your glassware/reaction vessels. If you don't you will lose marks!
6. Some reagents require special handling, even in discarding. For instance, aluminum trichloride, sodium metal, and acetyl chloride react violently with water.
7. Never discard an organic compound or rinse out dirty

glassware in the sink. Discard (and rinse out with acetone) all organics (halogenated or non-halogenated) in the appropriate waste container in the fumehood.

8. Never discard concentrated acid or base or rinse out acid or base contaminated glassware in the sink. All concentrated acids and bases MUST FIRST BE DILUTED (note original volume and concentration of solution!) AND THEN NEUTRALIZED before discarding. Get your instructor to assist you with this!!
9. Do not assemble an apparatus over a sink.
10. Avoid skin contact with unknown compounds or reagents. Do not breathe vapours.
11. Before using flammable organic liquids, check that there are no flames in the vicinity. NEVER heat flammable liquids over a flame!
12. Never heat a closed system. A closed system will explode. Do not heat an Erlenmeyer flask that is more than 2/3rds full. Always use boiling stones.
13. Use gloves when handling heated glassware.
14. For recrystallizations, use an Erlenmeyer flask, not a beaker. Beakers tip over easy.
15. Do not hold chemicals near your face, ever!
16. Always keep your work area clean and tidy.

Chemistry 360 Technique Review

In *Chemistry 350*, Organic Chemistry I, students learned the following techniques:

	Solid Organic	Liquid Organic
Purification Method	Recrystallization	Distillation (simple or fractional)
Assessment of Purity	Melting point, TLC, Polarimetry	Boiling point, Refractive index, Polarimetry
Identification	Mixed Melting Point, *(Co-Spot TLC)*,* Qualitative Organic Analysis, IR Spectroscopy	Qualitative Organic Analysis, IR Spectroscopy, Derivative Formation
Separation of Mixtures	Liquid-Liquid Extraction Solid-Liquid Extraction	Distillation (simple or fractional)
Drying of Organic Compounds	Air Drying, Vacuum Drying	Pre-drying-'salting out' Drying Agents (e.g. anhydr. $CaCl_2$)

*not done in this course.

Please review these techniques before attending the CHEM360 Supervised Labs.

1. Melting Point Determinations

Four stages of melting may be observed:

1. First signs of change (for example, shrivelling).
2. First signs of liquid formation. -RECORD the lower limit at this point
3. Formation of a meniscus.
4. Formation of a completely clear liquid. -RECORD the upper limit.

Pure compounds have sharp melting points. Impure compounds have broad ranges.

2. Recrystallizations

Five steps of single solvent recrystallization:

1. Select the solvent (soluble in hot, insoluble in cold).
2. Dissolve in a minimum of hot solvent.
3. Decision Time? Hot gravity filtration if solid impurities (particulates) present. Add charcoal if coloured impurities present.
4. Slow cool to room temp. Allow crystals to form. Place crystals on ice.
5. Collect product by vacuum filtration. Save filtrate for possible second crop. Wash crystals with **ice cold** solvent and allow to air dry to a constant weight.

Six steps of a two solvent recrystallization:

1. Determine the solvents (one soluble at all temps. (A), one insoluble all temps.(B), both must be miscible).
2. Dissolve in a minimum of hot solvent A.
3. Decision Time? Hot gravity filtration if solid impurities (particulates) present. Add charcoal if coloured impurities present.
4. Add solvent B until the solution clouds. Heat to clear solution.
5. Slow cool to room temp. Allow crystals to form. Place crystals on ice.
6. Collect product by vacuum filtration. Save filtrate for possible second crop. Wash crystals with **ice cold** solvent and allow to air dry to a constant weight.

3. Distillation Procedure:

Six steps are required to perform a distillation

1. Select the heat source (heating mantle, Bünsen burner, steam bath, or water bath).
2. Clean, dry and assemble the distillation apparatus. Use joint grease?-No.
   - i) Start assembling the apparatus from the bottom up.
   - ii) Place heat source in position. Use lab jack to adjust height.
   - iii) Clamp distillation flask in position.
   - iv) Place three-way connector into distillation flask.
   - v) Place thermometer adapter into the top of three-way connector.
   - vi) Approximately set height of receiving flask using a utility clamp.
   - vii) Place condenser into position and secure with joint clamps.
   - viii) Attach tubing to water inlet and water outlet to the condenser.

ix) Adjust height of thermometer.
x) Inspect to ensure no joint is under stress and that the system can be safely heated (i.e. it is open to the air via the vacuum take-off adapter, and it is not a BOMB.)

3. Turn on the cold-water supply to the condenser. Check for water leaks.
4. Add the liquid to be distilled to the distillation pot. Add boiling stones.
5. Heat the liquid and collect the product in the receiving flask.
6. Allow the apparatus to cool and disassemble it. Clean all glassware parts thoroughly with acetone (discard in organic wastes) before washing with soapy water.

4. Extractions

Five steps to performing an extraction using a separatory funnel. They are:

1. Dissolve the unknown compound in a solvent. Place the mixture in the separatory funnel supported with a ring clamp on a retort stand.
2. Add the extraction solvent to the separatory funnel.
3. Stopper the funnel, invert the funnel, vent, shake gently and vent again. Continue shaking/venting until no further pressure is released and then gently shake the funnel for 30 sec.
4. Return the separatory funnel to the ring clamp and allow the layers to separate.
5. Remove the stopper, drain the lower layer through the stopcock (out the bottom). Remove the upper layer by pouring it out of the top of the separatory funnel.

CHEM360 Infrared Spectra Analysis Review:

To be done before attending the CHEM360 Supervised Labs:

1. Review the Theory on Infrared Spectroscopy
2. Review the Listing of Organic Functional Groups and their corresponding Infrared Spectra.
3. Perform the Sample Infrared Spectrum Problems.
4. Answer the Unknown Spectra (to be analyzed at home).

Table 1 Correlation Table of Infrared Absorption and Functional Group.

Type of Absorption	Wavenumber (cm^{-1})	Intensity of Absorption	Absorption of:
O-H stretch	3400-3640	strong, broad	alcohol
	2500-3300	strong, very broad	carboxylic acid
N-H stretch	3310-3350	medium ('W' shape)	amine (1º)
C-H stretch	3300	strong	sp C-H of alkyne
	3030	medium	aromatic
	3020-3100	medium	sp^2 C-H of alkene
	2850-2960	medium to strong	sp^3 C-H of alkane
	2750 & 2850	weak-medium ('W' shape)	O=C-H of aldehyde
C≡N stretch	2210-2260	medium, sharp	nitrile
C≡C stretch	2100-2260	medium, sharp	alkyne
C=O stretch	1670-1780	strong, sharp	carbonyl
	1730-1750		ester
	1720-1740		aldehyde
	1705-1725		ketone
	1700-1725		carboxylic acid
	1640-1700		amide
	ca 1800 and 1760		anhydride
C=C stretch	1650-1670	weak-medium, sharp	alkene
	1600, 1500, 1450	strong sharp	aromatic
C=N stretch	1640-1670	medium, sharp	imine
N-H bend	1500-1650	medium to strong, sharp	amine and amide
N=O stretch	1500-1600 (1540) and 1320-1390	strong, sharp	nitro-compound
C-N stretch	1030, 1230	medium	amine
C-O stretch	1050-1150	strong	alcohol
	1250-1310	strong broad	ester-conjugated
	1240	strong, broad	ester-acetates
	1175	strong, broad	ester-unconjugated
C-Cl stretch (terminal)	600-800	strong	alkyl halide
Ar-Cl stretch	1000-1175	medium-strong	aryl halide
C-Br stretch (terminal)	500-760	strong	alkyl halide
C-I (terminal)	500	strong	alkyl halide

Note: when a C=C bond is in conjugation with a carbonyl, the observed carbonyl absorption frequency will be < ~ 30 cm^{-1}.

Calculation of the # Degrees of Unsaturation in a Compound

(*See also Alkenes: 'Structure and Reactivity' in McMurry's 4th ed., pp. 180-182, 5th ed. pp. 190-192).

Number of Degrees of Unsaturation = nC +1 + 1/2N - 1/2 nH - 1/2 nX

e.g., Therefore, for Compound A, C_7H_{12} = (7) +1 + 1/2(0) - 1/2 (12) - 1/2(0)

= 7 + 1 - 6 = **2** degrees of unsaturation in Compound

Note: an aromatic ring = 4 degrees of unsaturation, 1 for the ring + 3 for the 3 double bonds = 4

Online Laboratory Resources

Organic Chemistry Resources

Find background information, unknowns, etc

Lab Registration/Booking

Lab Schedule

upcoming chemistry lab sessions

Lab Exemption

to recognize equivalent lab work done elsewhere

Student Incident Report Form

all accidents that result in injury must be reported to your supervisor and the details entered here

Athabasca University Student Academic Misconduct Policy

Student Support Centre

course-related academic and logistical inquiries
fst_success@athabascau.ca

Experiment 10
Fischer Esterification: An ester from a carboxylic acid and an alcohol

Preparation

Before beginning this experiment, you should have read through the details of this experiment and prepared a flow chart for the procedure to be followed, and:

1. studied "Carboxylic Acid Derivatives and Nucleophilic Acyl Substitutions" of the theory component of the course, and
2. completed the equivalent of Experiments 1 through 9, CHEM350

You may also wish to read, Chapter 19 of *The Organic Chem Lab Survival Manual* (Chapter 26 in 3rd ed.).

Before you come to the laboratory you should have read the background information and completed the pre-lab questions.

Procedure

Part A: Preparation of reagents and equipment.

1. The procedure is given for a 4:1 molar ratio when excess of an alcohol is used. Reverse the ratio if you synthesize an acetate ester. See Table 10.2 below.

Table 10.2 Choose one pair of carboxylic acid and alcohol.

Ester Name	Carboxylic acid	Moles used	Alcohol	Moles used
Isoamyl acetate	acetic acid	0.48	isoamyl alcohol	0.12
Methyl butanoate	butyric acid	0.12	methanol	0.48
Isoamyl butanoate	butyric acid	0.12	isoamyl alcohol	0.48
Isobutyl propionate	propionic acid	0.12	isobutyl alcohol	0.48
Propyl ethanoate	acetic acid	0.48	1-propanol	0.12
Methyl salicylate	*salicylic acid*	*0.05*	*methanol*	*0.10*

**Note: the combination of salicylic acid and methanol requires special workup procedures.*

2. Set up a reflux apparatus as shown in Figure 10.5, using a clean and dry condenser and an appropriately sized round-bottomed flask.

3. Measure out 0.12 mol of an isoamyl alcohol and add it to the round-bottomed flask.

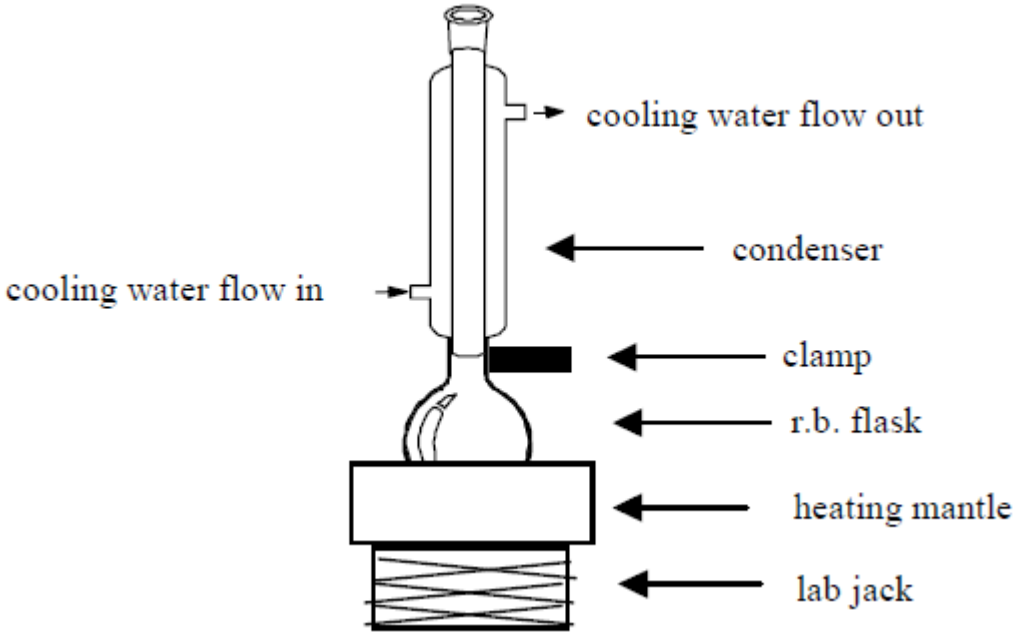


Figure 10.5 Reflux apparatus

4. Measure out 0.48 mol of acetic acid and add it to the round-bottomed flask already containing the alcohol.

Part B: Synthesis of the ester

1. Add several boiling stones to the round-bottomed flask containing the alcohol and carboxylic acid.

2. Very slowly and carefully add 0.05 moles of concentrated sulphuric acid, while swirling and cooling the flask.

3. Quickly reassemble the reflux apparatus, and heat the reaction for **45min to 1 hour**, while maintaining a steady reflux (during the 1-hour reflux period, please start your next experiment).

Part C: Reaction Workup-recovery and purification of the ester

1. Remove the heating mantle and cool the reaction mixture to room temperature. You may speed the cooling up by placing the stoppered

round-bottomed flask into a lukewarm water bath. Do not use an ice bath!

2. Pour the cooled mixture into a small separatory funnel containing 20 mL of water ice. Rinse the round-bottomed flask with a further 5 mL of cold distilled water and add this also to the separatory funnel. Stopper the separatory funnel and invert it several times.

3. Extract your ester with 25 mL of diethyl ether and separate the layers. Keep the aqueous layer. Do not discard anything yet.

4. Wash the crude ester (in the diethyl ether) with 25 mL cold distilled water. [The purpose of this step is to wash away the water-soluble impurities].

5. Wash the crude ester (in diethyl ether) with 25 mL of 5% M sodium carbonate. Be extra careful to frequently vent the separatory funnel, as you gently swirl the contents of the funnel. Do not invert the funnel at first. Carbon dioxide gas is formed during this step, and significant pressure builds up inside the funnel. When the amount of gas has declined, then invert and periodically vent the funnel.

6. Repeat the wash of the crude ester with another 25 mL of 5% sodium carbonate. Less CO_2 gas should be produced in this step than the previous.

7. Check the pH of the solution. It should be close to pH = 7.0.

8. Wash the crude ester with 25 mL of saturated sodium chloride. Draw the aqueous salt solution out the bottom of the funnel and pour the ester out the top of the separatory funnel into a small, clean, dry Erlenmeyer flask.

9. Dry the crude ester with anhydrous calcium chloride. Stopper and swirl the flask periodically for 15 min. Be sure to add enough of the anhydrous drying agent so that some of it is still freely moving in the liquid. When the ester is dry, the crude ester should be clear and transparent; cloudiness indicates that water is still present.

10. Decant the dry ester (or use a Pasteur pipette), and if time permits, set up an apparatus for a simple distillation.

11. Distil the crude ester, and collect the product in an appropriately sized, preweighed, clean, dry, round-bottom flask.

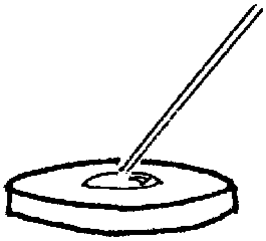
Part D: Characterization of the ester

1. Determine the yield, boiling point, refractive index, and % yield of the crude/purified ester. Store your ester in a suitably labelled glass vial, and hand it to your instructor for grading.

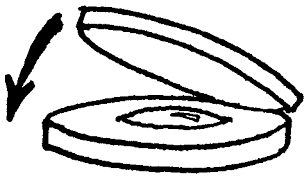
Part E: Infrared spectroscopy

1. With the assistance of your instructor, obtain an infrared spectrum of your pure product, and compare it to your starting reagents spectra. Submit these spectra with your data tables with your laboratory report.

Preparation of the sample for infrared spectroscopy is done by 'thin film' in a salt (NaCl or KBr) disk 'sandwich' (see diagram below).



Place drop of liquid sample on disk using a Pasteur pipette.



Place another salt disk on top of the liquid, and gently press into a thin film.

Remember to only handle the salt disks by their edges. Clean the disks with chloroform. Do not use water or acetone.

Safety

Methanol is poisonous if swallowed. Its vapour is harmful to the eyes, lungs and skin and other organs. Highly flammable.
Ethanol is poisonous and its toxicity is increased by the presence of the denaturing substances that are added to laboratory ethanol to reduce its illegal consumption. High concentrations of ethanol vapour can be dangerous. Highly flammable.
1-Propanol is harmful to the lungs, skin, eyes and other organs. Poisonous if swallowed. Highly flammable. Use in a fume hood.
2-Methyl-1-propanol (isobutyl alcohol) is a flammable liquid, and an irritant.
3-Methyl-1-butanol (isoamyl alcohol) is an irritant. Avoid breathing vapours.

Butyric acid is corrosive and toxic.
Propionic acid (propanoic acid) is corrosive and toxic.
Glacial acetic acid is poisonous if swallowed. Both the liquid and vapour are irritating to the skin and eyes and can cause burns and ulcers. Flammable.
Concentrated sulfuric acid is highly corrosive. Wear gloves and proper eye protection when using this substance. Avoid contact with skin or clothes. Use only in a fume hood.
Sodium carbonate is basic but does not pose any specific safety problems. Will decompose on the addition of acid to form carbon dioxide gas.
Saturated sodium chloride is an irritant and hygroscopic.
Sodium sulfate is an irritant and is hygroscopic.
Chloroform (trichloromethane) is poisonous if swallowed. Its vapour is an anaesthetic and causes nausea, headaches, vomiting and unconsciousness.
Additional information regarding the potential hazards in handling these chemicals may be obtained from the Safety Data Sheets that are available in the laboratory.

Waste disposal

The aqueous washes from the reaction workup may be washed down the drain with plenty of water.

All organic wastes should be placed into the appropriate non-halogenated waste container.

Write-up

This experiment should be written up using the standard format for "preparative type" experiments. Do not forget to report the mass of alcohol and carboxylic acid used, the mass of crude ester obtained, and the mass, percentage yield and boiling point plus refractive index data of the product. Your report should also include an assessment of the success of the experiment based on your analysis of the infrared spectra.

CHEM360 Experiment 10 Report

Date:_____

Student Name:_____ ID Number:_____

Title:

Objective(s):

Equation(s): (General and specific reaction, draw structures, and provide names)

Introduction:

Procedure:

(Reference: use proper format. Any Changes/Modifications?)

Procedure for the Fisher esterification of acetic acid with isoamyl alcohol.

Procedural Step	Observations/Comments/Inferences
Record amounts of reagents used.	

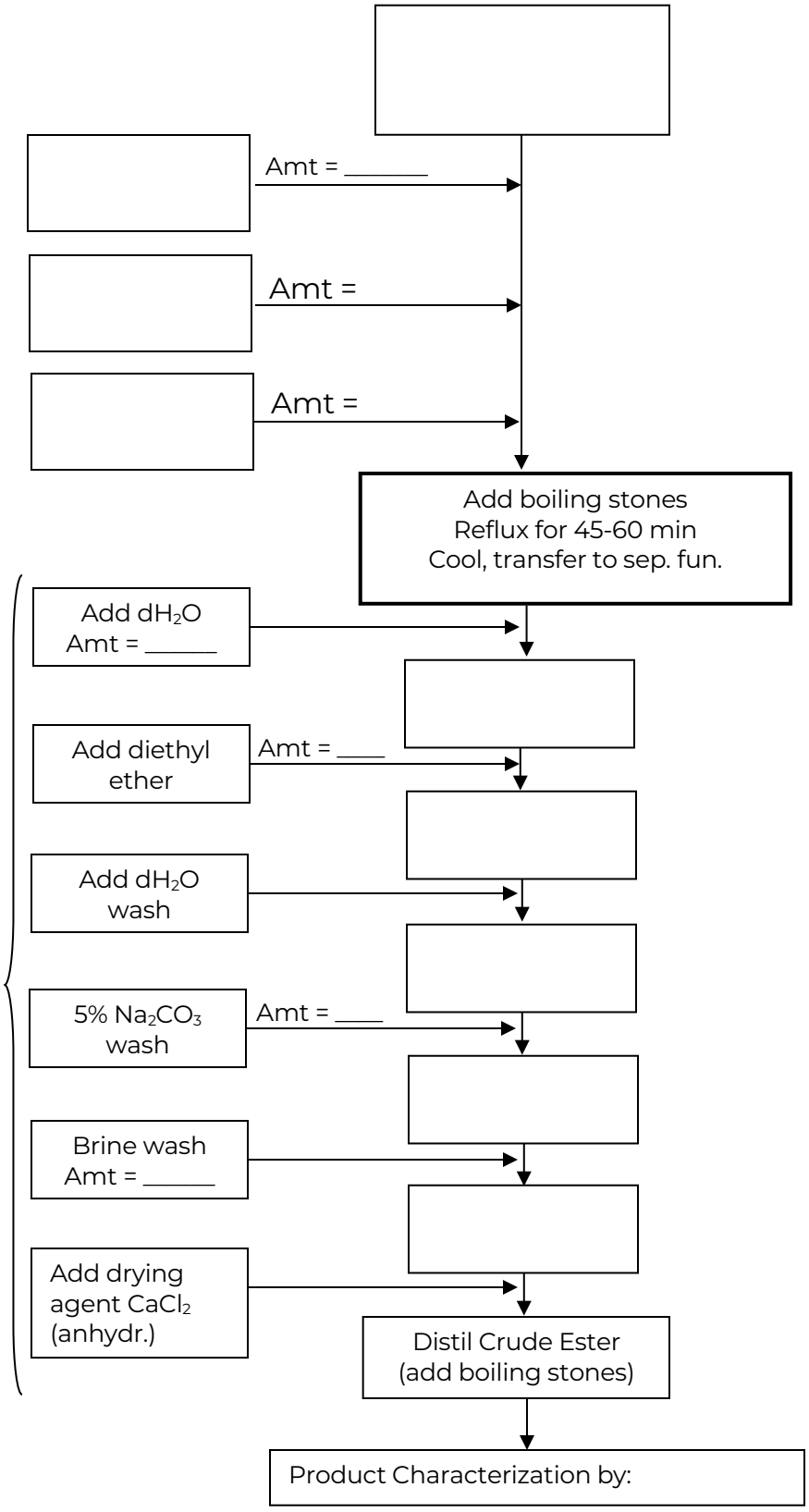
Table 10.1 Table of Reagents for Experiment 10 Fisher Esterification.

Reagent	Formula	Mwt. (g/mol)	d (g/ml)	Mp* (°C)	Bp* (°C)	Haz. Prop.
Acetic acid, glacial (conc.) 17.4 M						
Isoamyl alcohol (3-methyl -1-butanol)	$(CH_3)_2CH(CH_2)_2OH$	88.15			130	Irritant
Sulfuric acid, conc. 18 M	H_2SO_4		1.840			
Distilled water	H_2O	18.02	1.000	0	100	none
Diethyl ether						
5% sodium carbonate (aq)	$Na_2CO_{3\,(aq)}$					
Sat. sodium chloride (aq) (brine)	$NaCl_{\,(aq)}$					
Calcium chloride (anhydr)	$CaCl_2$					
acetone, wash						
Isoamyl acetate	$CH_3CO_2C_5H_{11}$	130.19			142	

*find and record either the melting point if the reagent is a solid at room temperature, or the boiling point if the reagent is a liquid at room temperature.

EXPERIMENT 10 FLOW CHART

REAGENT PROCEDURE / STEP OBSERVATION



Experiment 10 Results:

Table 10.2. Summary Table of Observations
This table is optional. Use only to tidy up observations, if necessary, from the previous pages. Otherwise just say "see previous pages 9-10."

Procedural Step	Comment or Observation and Inference

Table 10.3. Table of Product Data for Isoamyl acetate, Fisher Esterification Product.

Table 10.3. presents the summary of the results of the experiment. The calculations for limiting reagent, theoretical yield and percent yield are shown below the table. Note: _____ was found to be the limiting reagent.

	Yield Mass (g)	Appearance of Liquid	Boiling Pt.* (°C)	Refractive Index n_D obs.	Refractive Index^ (n_D^{20})	Theoretical Yield (g)	% Yield
Isoamyl acetate							

*Corrected for barometric pressure effects using the formula...
^Corrected to 20°C using the formula:

Limiting Reagent and Theoretical Yield Calculation:

Moles of acetic acid used in the reaction =

Moles of isoamyl alcohol used in the reaction =

Theoretical Yield of iosamyl acetate =

% Yield Calculation:

Table 10.4.Tabulation of Characteristic Infrared Absorptions for Starting regents and Product.

Table 10.4 contains the results of the Infrared Spectral Analyses for the isoamyl alcohol, acetic acid, and isoamyl acetate as obtained by thin film in a FTIR. See also attached spectra for peak numbering and identification.

Isoamyl alcohol	Peak Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strg, med., or weak)	Functional Group Indicated
>3000 cm-1 Region					
3000-2000 cm-1 Region					
2000-1400 cm-1 Region					
Fingerprint Region					

Functional Groups Absent:

Acetic acid	Peak Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strg, med., or weak)	Functional Group Indicated
>3000 cm-1 Region					
3000-2000 cm-1 Region					
2000-1400 cm-1 Region					
Fingerprint Region					

Functional Groups Absent:

Isoamyl acetate	Peak Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strg, med., or weak)	Functional Group Indicated
>3000 cm-1 Region					
3000-2000 cm-1 Region					
2000-1400 cm-1 Region					
Fingerprint Region					

Functional Groups Absent:

Discussion:

Comments on reasons for yield (high or low), purity (high or low), sources of error, infrared spectrum results:

Conclusion:

Structure of Product

Questions

Answers to be submitted with report.

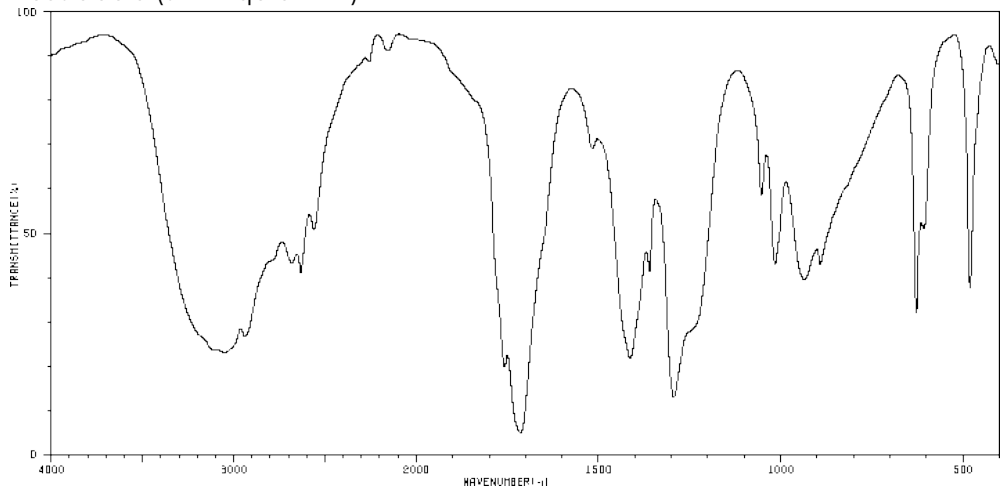
1. If the cost of **both** the alcohol and carboxylic acid were prohibitive, how would you maximize the yield of your Fischer esterification product while keeping costs down?

2. Why did you wash your product with water (3X), before washing it with the solution of sodium hydrogen carbonate? What was the purpose of washing with sodium hydrogen carbonate?

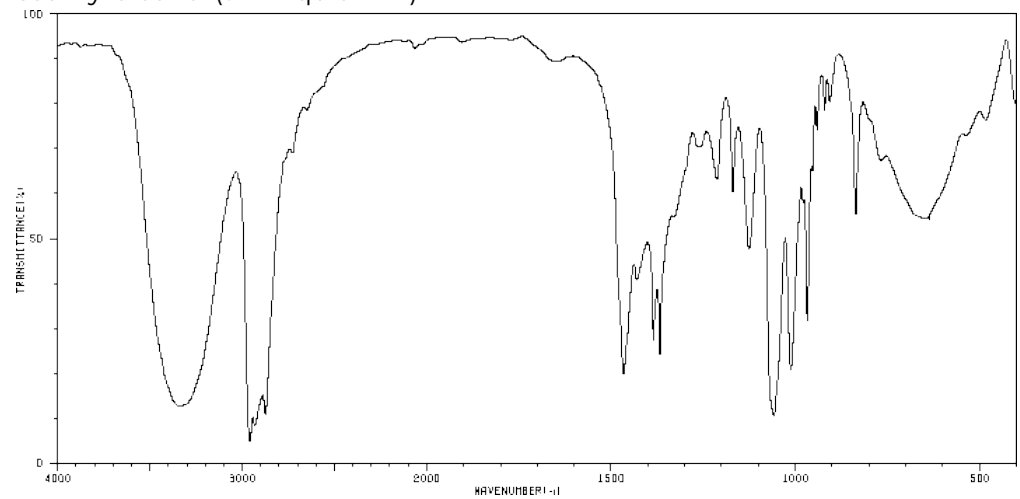
3. Explain the function of the acid catalyst in a Fisher esterification reaction.

4. What would the reactants be to produce isoamyl valerate via Fischer esterification reaction?

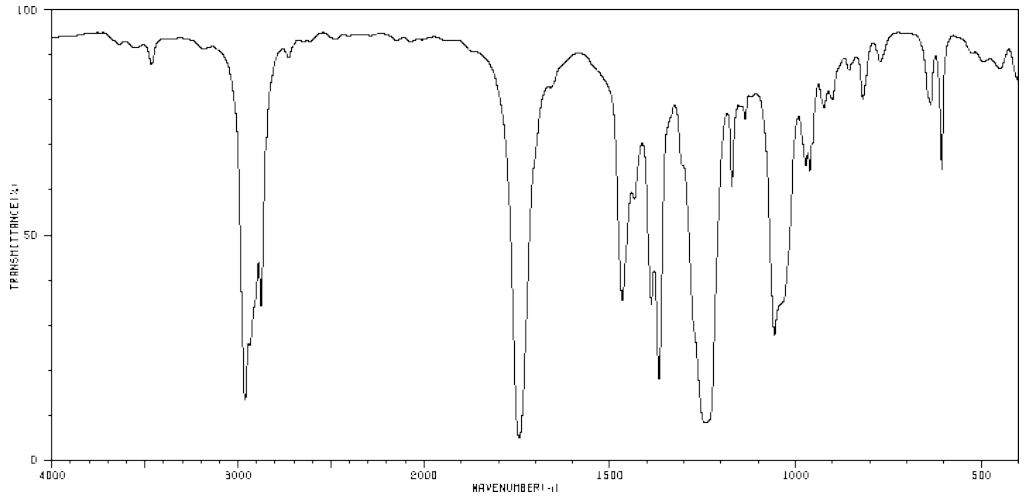
Acetic acid (thin liquid film)



Isoamyl alcohol (thin liquid film)



Isoamyl acetate (thin liquid film)



Experiment 11
Reactions of the common functional groups Part II:
Alcohols and alkyl halides

Preparation

1. 'Reactions of Alkyl Halides', in the theory component of the *Chemistry 350* course, and
2. 'Alcohols and Phenols' in the theory component of this course.

Before you come to the laboratory you should have read the background information

Procedure

Make sure that your test tubes are clean and dry. The presence of acetone in your test tubes may affect your results.

For each test carried out, record your observations, explain what the observations infer, and write an equation.

Part A: Reactions of alcohols

Perform the tests described below on each of the following alcohols: 1-butanol, 2-butanol, 2-methyl-2-propanol and cyclohexanol (use the sample obtained in Experiment 3, if you still have some).

1. **Oxidation of Alcohols**
   Place about 3 mL of the sodium dichromate solution (0.04 mol· L^{-1}) in a small test tube and add one drop of concentrated sulfuric acid. **(Caution: Concentrated sulfuric acid can cause serious skin and eye injuries. Wear gloves and proper eye protection.)** Shake the test tube and then add three drops of the alcohol being tested. Warm the test tube and its contents by placing it in a beaker of warm water for several minutes. Record your observations.

2. **Lucas Reagent Test for Stable Carbocations**
   Place 10 drops of Lucas reagent in a small test tube. **(Caution: Lucas reagent contains concentrated hydrochloric acid. Use in a fume hood, wear gloves and protect your eyes.)** Add one drop of the alcohol being tested. Mix the contents by vigorously swirling the test tube for about 3 to 5 seconds, place it in a test tube rack, and allow it to stand, without additional mixing, until a cloudiness develops. If the solution has not turned cloudy within one hour, you may assume that no reaction has occurred.

Part B: Reactions of alkyl halides

Perform the tests described below on each of the following compounds:
1-chlorobutane, 2-chlorobutane, 2-chloro-2-methylpropane, 1-bromobutane, 2-bromobutane, chlorobenzene, benzyl chloride, 3-chloro-1-butene (i.e., crotyl chloride), bromocyclohexane, bromocyclopentane, and β-bromostyrene (i.e.,C_6H_5- CH=CHBr).

1. **Ethanolic Silver Nitrate Test for S_N1 mechanism**
   Label a series of eleven clean dry test tubes from 1 to 11. Into each test tube place four (4) drops of the halide being tested (i.e., a different compound in each test tube). Add 2 mL of the 1% (~0.1 M) ethanolic silver nitrate solution to each test tube, making a careful note of the time at which each addition was made. Record the time taken for any precipitates to appear. For those solutions, which are still clear after 5 minutes, heat the test tube in a beaker of hot water and again note the time taken for any precipitates to appear.

2. **Sodium Iodide/Acetone Test for S_N2 mechanism**
   Label a series of eleven clean dry test tubes from 1 to 11. Into each test tube place four (4) drops of the halide being tested (as before, a different compound in each tube). Add 2 mL of the 15% sodium iodide in acetone solution, making a careful note of the time at which each addition was made. Record the time taken for any precipitates to appear. For those solutions, which are still clear after 5 minutes, heat the test tube in a beaker of hot (50° C) water for six minutes, taking care not to boil off the acetone. Again, make a note of the time taken for any precipitates to appear.

Safety

In addition to the dangers involved when using concentrated sulfuric acid and Lucas reagent, you should also be aware of the potential dangers presented in handling the following substances:

1-butanol is harmful to the skin and can cause internal injury through skin absorption. It is highly flammable and has a harmful vapour.

2-butanol presents the same safety hazards as 1-butanol.

2-methyl-2-propanol can cause irritation to the skin and eyes. It is flammable and its vapour can cause drowsiness.

cyclohexanol is flammable, irritating to the skin and eyes, and is harmful if inhaled or ingested.

sodium dichromate is carcinogenic. Avoid contact with skin. Harmful if swallowed.

1-chlorobutane is flammable. Use only in a fume hood. Wear gloves and eye protection.

2-chlorobutane is flammable. Use only in a fume hood. Wear gloves and eye protection.

2-chloro-2-methylpropane is flammable. Use only in a fume hood. Wear gloves and eye protection.

1-bromobutane is harmful to the eyes and lungs. Toxic if swallowed. Highly flammable. Use only in a fume hood and wear gloves and eye protection.

2-bromobutane presents the same safety hazards as 1-bromobutane.

chlorobenzene is poisonous by swallowing, inhaling and skin absorption. It is also highly flammable. Use only in a fume hood.

benzyl chloride is poisonous if swallowed. The vapour irritates the respiratory system, eyes and skin. Use only in a fume hood. Wear gloves and eye protection.

1-chloro-2-butene (i.e., crotyl chloride) may be fatal if inhaled! It is harmful if ingested, inhaled or absorbed through the skin. Exposure can cause headache, wheezing and nausea. It is very flammable and may flashback. Do not use near an ignition source or open flame. Use in fumehood.

bromocyclohexane is poisonous and inhalation can cause headache and vomiting. Flammable.

bromocyclopentane is poisonous and an irritant to eyes and skin. Flammable.

β-bromostyrene is harmful when swallowed and may cause some skin irritation. Flammable.

silver nitrate is corrosive as a solid. Avoid contact with eyes and skin.

sodium iodide does not present any specific safety hazards. However, the ingestion of large amounts of this substance could be hazardous.

acetone (2-propanone) is an irritant to the eyes, skin and lungs. It is a narcotic and is harmful to the liver and kidneys if it is swallowed. Highly flammable. Use only in a fume hood or other well-ventilated area.

ethanol is highly flammable. The toxicity of this liquid is increased by the presence of denaturing substances. Avoid ingestion.

Waste disposal

Separate containers will be available for the disposal of each of the following materials:

- alcohol/acidic dichromate mixtures
- alcohol/Lucas reagent mixtures, alkyl halide/silver nitrate mixtures, alkyl halide/sodium iodide mixtures

Write-up

Use the investigative 'short style' format for writing this laboratory report. Be very brief for the purpose and nature of the tests and present the procedure in tabular format (i.e., Table of Reagents). Present your results in the form of a four-column table (test, observation, inference, equation). You should attempt to form a conclusion as to the reaction mechanism and to its relative rate/favourability.

CHEM360 Experiment 11 Report

Date:_____

Student Name:_____ ID Number:_____

Title:

Objective(s):

General Equation(s): (structures and names)

Procedure: (Ref:)
Changes/Modifications?

Table 11.1. Table of Reagents for Experiment 11.

Reagent	Formula	Mwt.	Vol/Mass	d	mp	bp	Haz. Properties
1-butanol	C_4H_9OH	74.12	4 drops	0.810	-89.5	117-118	Flamm., Irritant
2-butanol	C_4H_9OH	74.12	4 drops	0.807		100	Flamm., Irritant
2-methyl-2-propanol	C_4H_9OH	74.12	4 drops	0.7887	25.5	82.3	Flamm., Irritant
Cyclohexanol	$C_6H_{11}OH$	100.16	4 drops	0.9624	25.1	161.1	Irritant, Hygroscopic
1-chlorobutane	C_4H_9Cl	92.57	8 drops	0.8862	-123	78.4	Flammable
2-chlorobutane	C_4H_9Cl	92.57	8 drops	0.8732	-131	68.2	Flammable
2-chloro-2-methylpropane	C_4H_9Cl	92.57	8 drops	0.8420	-25.4	52	Flammable
1-bromobutane	C_4H_9Br	136.9	8 drops	1.2758	-112	101.6	Flammable, Irritant
2-bromobutane	C_4H_9Br	136.9	8 drops	1.2585	-112	91.2	Flammable, Irritant
Chlorobenzene	C_6H_5Cl	122.4	8 drops	1.1058	-45.6	132	Flammable, Irritant
benzyl chloride	$C_6H_5CH_2Cl$	126.59	8 drops	1.1002	-39	179.3	Toxic, Cancer susp.agent
3-chloro-1-butene	C_4H_7Cl	90.55	8 drops	0.8978		64-65	Flamm., Lachrymator
Bromocylclohexane	$C_6H_{11}Br$	163.06	8 drops	1.3359	-56.5	166.2	Flammable, Irritant
Bromocyclopentane	C_5H_9Br	149.04	8 drops	1.3873		136.7	Flammable, Irritant
β-bromostyrene	$C_6H_5CHCHBr$	183.05	8 drops	1.4269	7	219	Irritant
sodium dichromate	$Na_2Cr_2O_7$	261.6	12 mL				Toxic, Cancer susp. agent
sulfuric acid	H_2SO_4	98.08					Corrosive, Toxic, Oxidizer
Lucas reagent	Solution of $ZnCl_2$ and HCl						Toxic, Irritant
zinc chloride, anhydrous	$ZnCl_2$	136.28		2.91	283	732	Corrosive, Toxic
hydrochloric acid, conc.	HCl	36.46		1.20		(110)	Corrosive, Highly toxic
sodium iodide	NaI	149.9					Mosit. Sens., Irritant
silver nitrate	$AgNO_3$	169.8					Highly toxic, Oxidizer
nitric acid	HNO_3	63.01		1.400			Corrosive, Oxidizer
acetone	CH_3COCH_3	58.09		0.818		56.5	Flammable, Irritant
ethanol	CH_3CH_2OH	46.07		0.785		78.5	Flammable, Poison

Experiment 11 Part A Results: Reactions of Alcohols (1°, 2°, and 3°)

1. Alcohol Oxidation by Sodium Dichromate			
Test Substance	Observation	Inference	Equation
1-butanol			
2-butanol			
cyclohexanol			
2-methyl-2-propanol			

2. Lucas Reagent Test			
Test Substance	Observation	Inference	Equation
1-butanol			
2-butanol			
cyclohexanol			
2-methyl-2-propanol			

Experiment 11 Part B Results: Reactions of Alkyl Halides

Silver Nitrate Test (SN1 Mechanism)			
Test Substance	Observation	Inference	Equation
1-chlorobutane			
2-chlorobutane			
2-chloro-2-methylpropane			
1-bromobutane			
2-bromobutane			
Chlorobenzene			
Benzyl chloride			
3-chloro-1-butene			
Bromocyclohexane			
Bromocyclopentane			
β-bromostyrene			
1-chlorobutane			
2-chlorobutane			
2-chloro-2-methylpropane			
1-bromobutane			
2-bromobutane			
Chlorobenzene			
Benzyl chloride			
3-chloro-1-butene			
Bromocyclohexane			
Bromocyclopentane			
β-bromostyrene			

Conclusion:

Questions:

1. There are four isomeric alcohols having the formula $C_4H_{10}O$, and in this experiment you investigated the properties of three of them. How would you expect the fourth isomer to behave when treated with (i) acidic sodium dichromate, and (ii) Lucas reagent?

2. Based on your results, arrange the eleven halogen-containing compounds in order of *decreasing* reactivity in (i) S_N1 reactions and (ii) S_N2 reactions.

3. a. What results would you expect to observe when benzyl alcohol, $C_6H_5CH_2OH$, is treated with (i) acidic sodium dichromate, and (ii) Lucas reagent?

   b. What results would you expect to obtain when 1-chloro-2,2-dimethylpropane is treated with (i) ethanolic silver nitrate, and (ii) sodium iodide in acetone?

Experiment 12
The reduction of benzophenone with sodium borohydride

"To reduce or be reduced, that is the question." –Carbon Compound, since life began.

Preparation

Before beginning this experiment, you should have read through the details of this experiment and prepared a flow chart for the procedure to be followed, and

1. studied 'A Preview of Carbonyl Compounds' of the theory component of the course,
2. read 'Alcohols from Reduction of Carbonyl Compounds', and

You may also wish to read, Chapter 19 of *The Organic Chem Lab Survival Manual* (Chapter 26 in 3rd ed.).

Objectives

The purpose of this experiment is to provide a practical example of the reduction of a carbonyl group using sodium borohydride. Thin-layer chromatography will be used to assess the purity of the product, and further practice in obtaining and interpreting infrared spectra will be provided.

Introduction

The two most common reducing agents used to reduce carbonyl compounds to alcohols are sodium borohydride ($NaBH_4$) and lithium aluminum hydride ($LiAlH_4$). Both reagents are capable of transferring hydride ions to aldehydes and ketones to form complexes, which can then be hydrolyzed to the corresponding alcohols. If an aldehyde is used in the reaction, a primary alcohol is produced; if a ketone is used, the product is a secondary alcohol.

Sodium borohydride is a weaker reducing agent than lithium aluminum hydride. Reductions using the former may be carried out in aqueous or

alcoholic solutions, while those involving the latter require the use of an inert solvent (e.g., tetrahydrofuran). However, there are certain limitations to the use of sodium borohydride and these are discussed in your textbook near the topic 'Alcohols from Reduction of Carbonyl Compounds'.

The general equation for a sodium borohydride reduction is summarized below in Fig. 12.1:

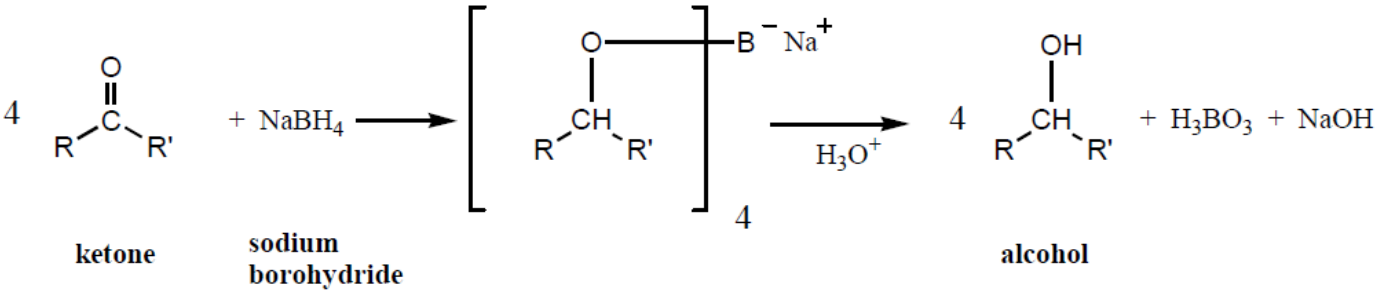


Figure 12.1 General reaction for sodium borohydride reduction of a ketone.

In the present experiment, you will reduce benzophenone to diphenylmethanol:

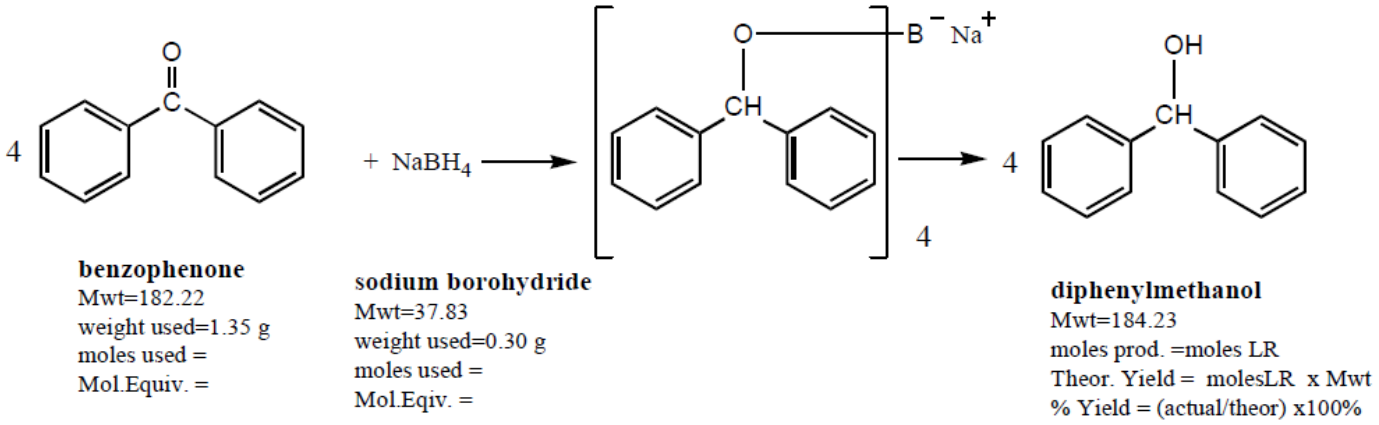


Figure 12.2 Benzophenone reaction with sodium borohydride.

In this experiment you will compare the purity of crude diphenylmethanol with that of recrystallized diphenylmethanol by spotting both samples on a single TLC plate. A sample of benzophenone will also be spotted on the same plate so that you can determine whether any of this starting material is present in either the crude or recrystallized product. Visualization will be achieved using an iodine tank as described in paragraph 2 of the "Visualization" section on page 145 of *The Organic Chem Lab Survival Manual* (p.249 in 3rd ed.).

Note: As an additional check on the purity of your product, an infrared spectrum will be run on the crude product, the recrystallized product, and the benzophenone starting material.

Thin-Layer Chromatography

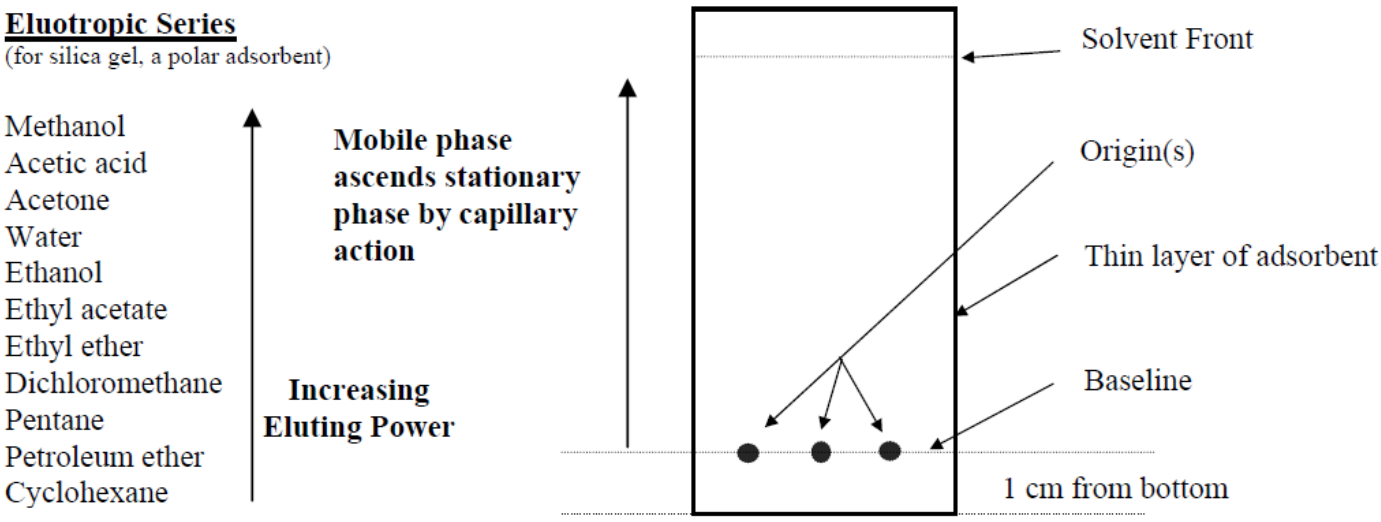
A discussion of this technique can be found in Chapter 19 The Organic *Chem Lab Survival Manual*, and in in your textbook under the topic 'Chromatography: Purifying Organic Compounds', hence the discussion here will be very brief. Please note that you will be provided with pre-prepared plates, i.e., you need not concern yourself with the details given in section titled "Preparation of TLC Plates" (pp. 140-141, or 244-245 in 3rd ed. of the *The Organic Chem Lab Survival Manual*. Similarly, you will be provided with an adequate supply of spotters.

Thin-layer chromatography is an indispensable analytical and preparative tool in organic chemistry. Chemists use it to check the purity of and identify compounds, check reaction mixtures, and follow the progress of reactions.

There are essentially **7 steps** to performing thin layer chromatography:

1. Prepare the chromatogram (draw baseline and assign origins).
2. Dissolve compound in a spotting solvent (low bp, cmpd. highly soluble, make 1% solution).
3. Place 'spot(s)' on chromatogram (use capillary tube to keep the spot to a small diameter).
4. Prepare the development chamber/tank (allow to equilibrate).
5. Develop the chromatogram (to within ~2cm of top).
6. Stop development. Visualize the chromatogram (iodine tank, UV light)
7. Analyze the chromatogram. Determine R_f's.

Thin layer chromatography uses a thin layer of solid adsorbent (usually silica gel) on either a plastic or metal backing. The mobile phase is/are solvent(s) chosen carefully to move the compound from the point of origin to about 1/2 way up the chromatogram (R_f=0.5). Note: a pure compound will only show a single 'spot' on the chromatogram after development.



Perhaps the most difficult concept in TLC is the choice of the developing solvent (mobile phase or eluent). If the compound spotted is highly polar, it will bind more tightly to the polar absorbent, thus requiring a more powerful eluting solvent to 'mobilize' it and move it up the chromatogram. If the compound spotted is non-polar, it will bind less to the polar absorbent, thus requiring a less powerful eluting solvent to 'mobilize' it and move it up the chromatogram. Sometimes a mixture of solvents (they must be miscible) is required to get the compound to move just right.

For instance, suppose a student was asked to check the purity of an unknown solid. At first she/he tried pentane:ethyl acetate (1:1) and found that the unknown barely moved from the baseline. To readjust the solvent system to get an R_f = 0.5, should the student increase the concentration of pentane (to 3:1) or increase the concentration of ethyl acetate (to 1:3)?

In this case, the student should prepare a more polar solvent to 'mobilize' the tightly bound compound on the silica gel (it stuck to the origin!). Therefore, the student should increase the concentration of the ethyl acetate, so that the solvent system is pentane:ethyl acetate (1:3).

Finally, what if you have a chromatogram of an amine (polar) and an ether (fairly non-polar). Would the **amine have a higher R_f than the ether if a polar mobile phase like ethanol→methanol was used** as the developing solvent? (Answer = Yes).

Procedure

Part A: The reduction of benzophenone

1. In a 25-mL Erlenmeyer flask, dissolve 1.35 g of benzophenone in 9 mL of methanol. If available, place a magnetic stir bar into the flask, and place the flask on a stir plate.

2. In a second 25-mL Erlenmeyer flask, dissolve 0.3 g of sodium borohydride in

3. 4.5 mL of cold distilled water.

4. Use a Pasteur pipette to add the aqueous solution of sodium borohydride **one drop at a time** to the solution of benzophenone. Swirl the reaction mixture between the addition of each drop to disperse any cloudiness. Do not add more sodium borohydride until the cloudiness caused by the previous drop has disappeared.

5. When all the sodium borohydride has been added, use a magnetic stirrer to stir the reaction mixture until a heavy slurry of diphenylmethanol crystals has formed.

6. Decompose the excess sodium borohydride by *slowly* adding the slurry of crystals and solvent to a mixture of 30 g of crushed ice and 3 mL of concentrated hydrochloric acid in a 250 mL beaker. **(CAUTION: Prepare the latter by adding the concentrated hydrochloric acid to the crushed ice, not vice versa. Do this step in a fume hood. Wear gloves and protect your eyes.)**

7. Collect the diphenylmethanol by suction filtration. Wash the crystals with two 15 mL portions of water. Leave the aspirator (or vacuum pump) running for about 30 minutes to dry the crystals as best you can.

8. Place about 0.1 g of the crude diphenylmethanol in each of two *clean, dry* test tubes (13 × 75 mm) and stopper the tubes with corks. Save these samples for thin-layer chromatography and infrared spectroscopy.

9. Recrystallize the remainder of the diphenylmethanol using hexane as the solvent. (**Hint:** About 25-30 mL of solvent will be required, use 50° C water bath to warm solvent.) After the crystals have been dried and weighed, place about 0.1 g of the diphenylmethanol in each of two **clean, dry** test tubes (13 × 75 mm) and stopper the tubes with corks. These small

samples will be used in Parts B and C.

10. Determine the yield, melting point, mixed melting point with authentic standard (if available), and %yield of the pure diphenylmethanol. Store your crystals in a suitably labelled glass vial and hand it to your instructor for grading.

Part B: Thin-Layer Chromatography (TLC)

1. Prepare solutions of benzophenone, crude diphenylmethanol and recrystallized diphenylmethanol by dissolving each solid in about 1 mL of chloroform. (For the two diphenylmethanol samples, use the first of the two test tubes set aside in each of steps 7 and 8 of Part A. In the case of benzophenone, use about 0.1 g so that all the solutions are of approximately the same concentration.) Stopper the test tubes.

2. Prepare a solution consisting of 1 mL of ethyl acetate dissolved in 5 mL of ligroin (or petroleum ether bp 60-80° C) for use as the eluent.

3. Pour the eluent into a 150-mL beaker lined with filter paper as shown below. Cover with a watch glass and allow the beaker to stand undisturbed until it is needed.

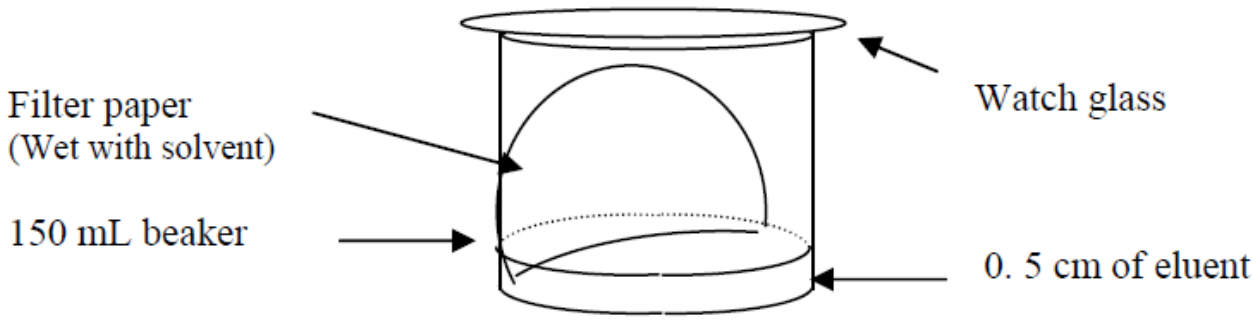


Figure 12.3 Development chamber.

4. Use the supplied capillary tube to spot the pre-prepared TLC plate with each of three solutions prepared in step 1, above, as shown Figure 12.2).

(See "Spotting the Plates" on pages 142-143 of *The Organic Chem Lab Survival Manual,* pp.246-247 in 3rd ed)

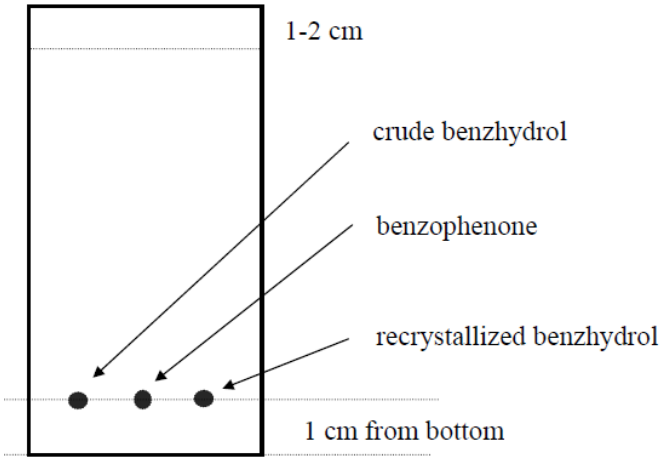


Figure 12.4 Appearance of the freshly spotted TLC plate

5. Place the TLC plate in the developing chamber. Make sure that the solvent level is **not** higher that the baseline on the TLC. Cover the beaker with a watch glass and wait for the solvent to travel up the plate until it reaches the line that you have marked about 1 cm from the top of the plate.

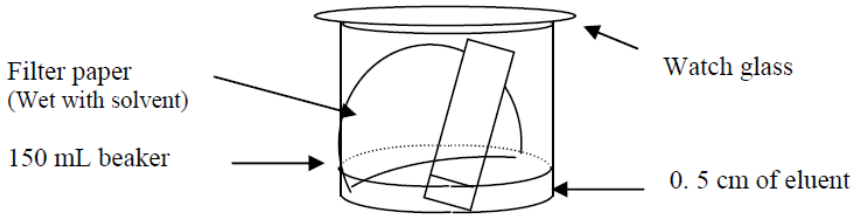


Figure 12.5 Developing the chromatogram

6. Allow the plate to dry.

7. Use tweezers to place the plate in the iodine tank (or UV light box) that will be provided. Allow the plate to remain in the tank until the spots on the plate are clearly visible. Use tweezers to remove the plate from the iodine tank and mark the spots with a pencil. Calculate the value for benzophenone and diphenylmethanol.

8. Keep the plate in a safe place so that you can submit it to your instructor when you have completed the experiment.

Part C: Infrared spectroscopy

1. With the assistance of your instructor, obtain an infrared spectrum of benzophenone, your crude diphenylmethanol and your recrystallized diphenylmethanol. Submit these spectra with your laboratory report.

Safety

Benzophenone is harmful if swallowed, inhaled or absorbed through the skin. Flammable.
Methanol is harmful to the lungs, skin, eyes and other organs. Poisonous if swallowed. Highly flammable. Use in a fume hood.
Sodium borohydride is toxic if ingested. Avoid contact with skin and take precautions against inhaling its dust.
Diphenylmethanol is an irritant and is poisonous when ingested.
Concentrated hydrochloric acid is extremely corrosive to the skin and eyes. Its vapour is irritating to the eyes, lungs and skin. Wear gloves and eye protection. Use only in a fume hood.
Hexane is highly flammable. Its vapour is irritating and can have a narcotic effect.
Chloroform (trichloromethane) is poisonous if swallowed. Its vapour is an anaesthetic and causes nausea, headaches, vomiting and unconsciousness.
Ethyl acetate is harmful if swallowed. Prolonged exposure to its vapour can cause corneal cloudiness and anaemia. Highly flammable.
Ligroin (or petroleum ether bp. 60-80° C) is harmful if inhaled or swallowed. Can cause skin irritation and exposure may produce a burning sensation, headache and vomiting. Very flammable!
Iodine causes internal irritation if swallowed. Its vapour is harmful to the respiratory system. Contact with the skin or eyes is dangerous.

Additional information regarding the potential hazards in handling these chemicals may be obtained from the Material Safety Data Sheets that are available in the laboratory.

Waste disposal

The aqueous filtrate obtained when the crude product is isolated by suction filtration may be washed down the drain with plenty of water.

The filtrate from the recrystallization (hexane) should be placed in the container provided for non-halogenated organic wastes, as should the TLC eluent (ethyl acetate/ligroin).

The solutions of benzophenone and diphenylmethanol that were prepared for TLC should be placed in the container for halogenated organic wastes as the solvent used was chloroform, $CHCl_3$.

Write-up

This experiment should be written up using the standard format for "preparative type" experiments. Do not forget to report the mass of benzophenone used, the mass of crude diphenylmethanol obtained, and the mass, percentage yield and melting point plus mixed melting point data of the recrystallized product. Your report should also include an assessment of the purity of both the crude and recrystallized product based on your analysis of the thin-layer chromatogram and the infrared spectra.

CHEM360 Experiment 12 Report

Date:_____

Student Name:_____ ID Number:_____

Title:

Objective(s):

Reaction Equation(s): (structures and names)

Introduction:

Procedure:
Reference format: author surname, initials, date. Title of text, publisher, pages)
Any Changes/Modifications?

Part A: Reduction of Benzophenone

Procedural Step	Observations/Comments/Inferences
Preparation of organic reagent Preparation of reducing agent	

Part B: Thin Layer Chromatography of Reagent and Product.

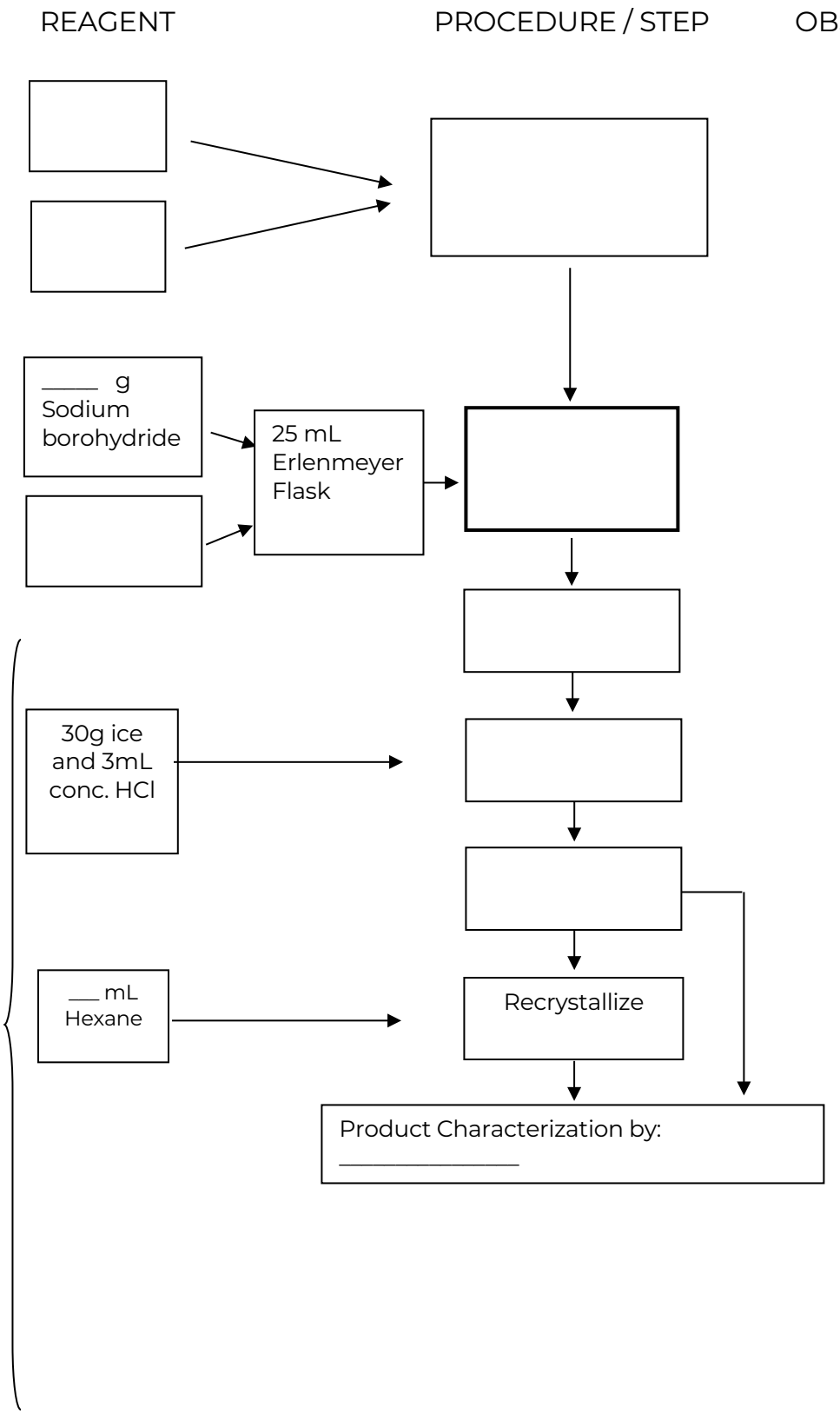
Procedural Step	Observations/Comments/Inferences
1. Preparation of eluent 2. Preparation of spotting solutions 3. Number of spots per lane: 4. Appearance of developed TLC	

Table 12.1. Table of Reagents for Exp. 12

Reagent	Formula	Mwt.	Vol/ Mass	d	moles	mp	bp	Haz. Properties
Benzophenone (or diphenylketone)	$C_6H_5COC_6H_5$	182.22		NA			NA	
Sodium borohydride	$NaBH_4$	37.83		NA		400	NA	
Methanol	CH_3OH	32.04		1.3288		-93.9	65	
Hydrochloric acid (conc. = 12M)	HCl	36.46		1.20		NA		
Hexane	C_6H_{14}	86.18		0.659		NA	69	
Ethyl acetate	$C_2H_5CO_2\ C_2H_5$	88.11	2 mL	0.902		NA	77	
Ligroin	Mineral spiritis		10 mL	0.656		NA	60-80	
Chloroform	$CHCl_3$	119.39	3 mL	1.500		NA	61.3	
Iodine	I_2	253.81	trace	NA		133	NA	
Diphenylmethanol (or benzhydrol)			?				NA	

NA = not applicable

SAMPLE EXPERIMENT 12 FLOW CHART



Experiment 12 Results:

Table 12.2. Summary Table of Observations
(this table is optional. Use only to tidy up your observations from the previous page if necessary.)

Procedural Step	Comment or Observation

Table 12.3. Table of Product Data for Diphenylmethanol, the Carbonyl Reduction Product.

Table 12.3. presents the summary of the results of the experiment. The calculations for limiting reagent, theoretical yield and percent yield are shown below the table. Note: _____ was found to be the limiting reagent.

Product Name	Yield (Mass in g)	Appearance of Solid	Observed Melting Pt.* (°C)	Lit. Melting Pt. (°C)	Theoretical Yield (g)	% Yield

*uncalibrated thermometer used.

Limiting Reagent and Theoretical Yield Calculation:

Moles of benzophenone used in the reaction =

Moles of sodium borohydride used in the reaction =

Theoretical Yield of diphenylmethanol =

% Yield Calculation:

Table 12.4. Infrared Spectrum Data Analysis (see attached spectra)

	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

Fig 12.1. TLC Analysis of Benzophenone, Crude and Recrystallized Diphenylmethanol

Discussion:

Comments on and reasons for yield (high/med/low), purity (high/med/low), sources of error (uncalibrated thermometer?, side reactions?):

Conclusion:

Structure of Product

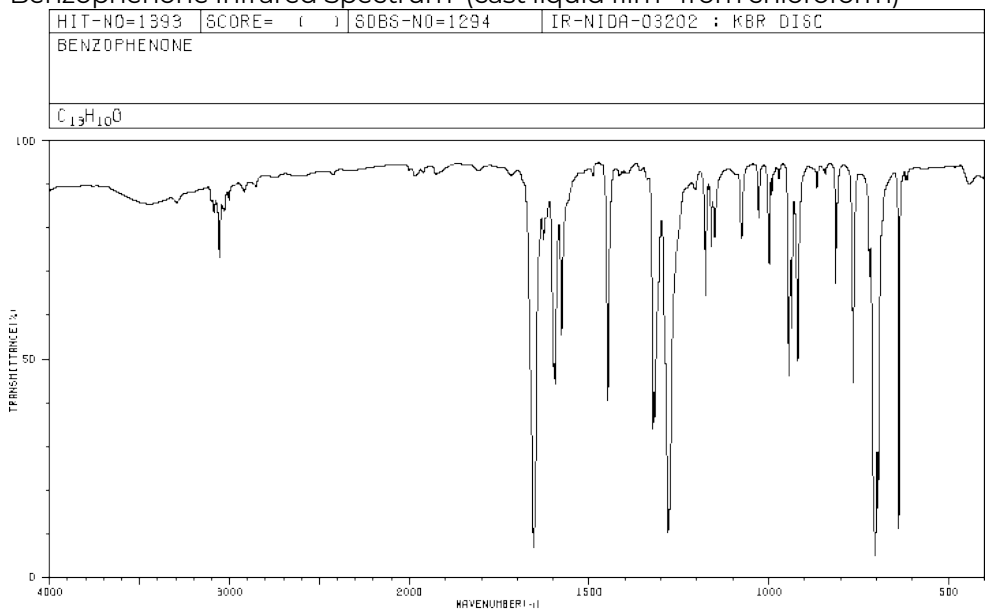
Questions

Answers to be submitted with report.

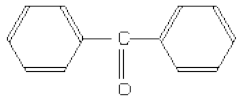
1. Aldehydes and ketones can be reduced to alcohols using hydrogen gas and a metal catalyst. Suggest two reasons why the use of sodium borohydride is preferred over the catalytic hydrogenation to prepare diphenylmethanol from benzophenone.

2. In this experiment, you destroyed the excess sodium borohydride by reacting it with hydrochloric acid (Part A, Step 5). What gas evolved during the process? Write a balanced equation for the reaction that occurred. (**Hint:** one of the products was boric acid).

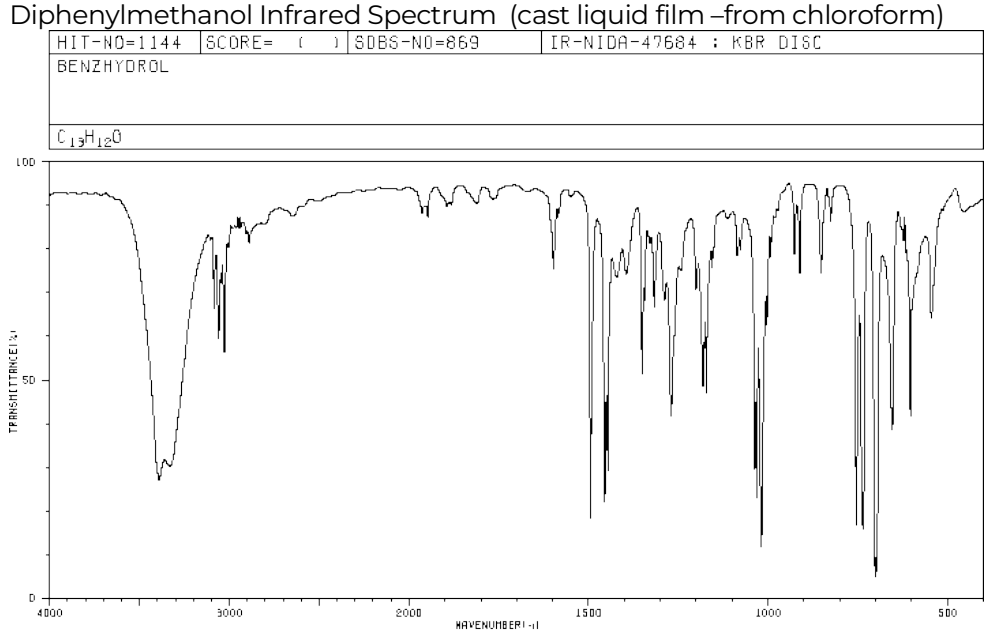
Benzophenone Infrared Spectrum (cast liquid film –from chloroform)



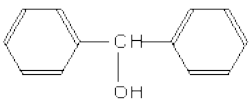
3291	81	1665	6	1205	86	992	84	720	66
3088	81	1627	74	1176	62	945	44	705	4
3067	79	1595	42	1162	72	936	55	697	15
3057	70	1577	69	1151	74	919	47	639	10
3030	81	1449	38	1076	74	867	86		
3003	84	1323	32	1028	79	814	64		
2919	84	1281	10	999	68	766	42		



Diphenylmethanol Infrared Spectrum (cast liquid film –from chloroform)



3392	26	1598	72	1345	66	1172	44	863	72
3359	30	1495	17	1317	64	1156	72	754	16
3351	29	1458	21	1269	86	1037	28	735	15
3086	64	1446	27	1271	39	1032	22	702	4
3059	57	1422	70	1244	72	1019	11	654	37
3049	70	1595	72	1201	86	1003	60	604	39
3027	53	1361	49	1182	46	912	72	646	62



Experiment 13
An aldol condensation

Preparation

Before beginning this experiment, you should have read through the details of this experiment, prepared a flow chart for the procedure to be followed, and:

1. studied 'Carbonyl Condensation Reactions' of the theory component of the course,
2. read 'Mixed Aldol Reactions', and
3. completed Experiments 10 through 12.

Read the background information

Introduction

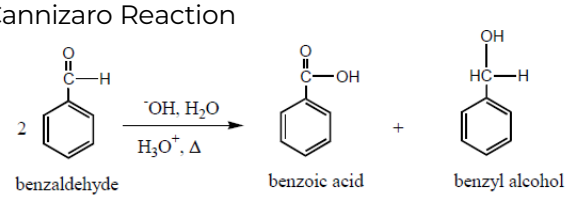
You will be assigned one of four aromatic aldehydes and one of four ketones, thus the instructions given in the "Procedure" section are general in nature and may need to be modified depending on which combination you are given.

The four aldehydes that will be available are benzaldehyde, 4-methylbenzaldehyde, 4- methoxybenzaldehyde and cinnamaldehyde (3-phenylpropenal).

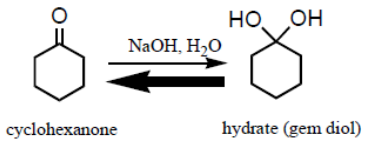
The four ketones that will be available are acetone, cyclopentanone, cyclohexanone and 4- methylcyclohexanone. Your instructor may add other aldehydes or ketones to this list at their discretion.

Other base initiated reactions to be aware of

1. Cannizaro Reaction



2. Formation of Hydrates



cyclohexanone hydrate (gem diol)

Before coming to the laboratory

1. You may contact your laboratory instructor to find out which aldehyde and ketone have been assigned to you. Otherwise, be prepared to perform your calculations for the amount of ketone and aldehyde required in the lab (see below).

2. Determine the mass of the aldehyde and ketone that you will need. If either substance is a liquid, determine the volume that you should use as it is easier to measure out a given volume of liquid than a given mass. The necessary densities are given in the table below.

Compound	Density ($g \cdot mL^{-1}$)
benzaldehyde	1.0415
4-methylbenzaldehyde	1.0194
4-methoxybenzaldehyde	1.1191
cinnamaldehyde [(E)–3-phenylpropenal]	1.0497
acetone	0.7899
cyclopentanone	0.9487
cyclohexanone	0.9478
4-methylcyclohexanone	0.9138

3. Draw a flow chart of the procedure to be followed.

Procedure

1. Into a 125-mL Erlenmeyer flask, place **0.020 mol of the ketone, plus 0.040 mol of the aldehyde**, 25 mL of 95% ethanol, and 30 mL of 1 $mol \cdot L^{-1}$ sodium hydroxide solution. A precipitate may begin to form immediately. Add a magnetic stir-bar to the reaction mixture and stir on a stirrer/hot-plate until no more precipitate forms. (If no precipitate forms during this time, warm the reaction mixture on the hot-plate for an additional 15–30 minutes.)

2. Cool the Erlenmeyer flask in ice and then collect the condensation product by suction filtration.

3. Wash the crude product (must be kept ice-cold at all times!) with:

(a) 10 mL of ice-cold 95% ethanol,
(b) 10 mL of ice-cold 95% ethanol containing 4% acetic acid, and
(c) 10 mL of ice-cold 95% ethanol.

4. In the hood, recrystallize the product from 95% ethanol or toluene. (You may have to determine for yourself which of these two solvents is the more appropriate. See Chapter 10 in *The Organic Chem Lab Survival Manual* pp. 48-50, and 59-61 or Chapter 13 pp. 118-120 and 129-131 in 3rd ed.). Please see your instructor before trying to recrystallize all your product. This might take several litres of solvent!

5. Determine the yield, melting point, and percent yield of your recrystallized product.

6. Obtain an infrared spectrum of your starting aldehyde, your starting ketone and your recrystallized product. **Note:** Spectra of solids should be obtained using Nujol mulls; liquids should be run "neat." Consult your instructor if you require assistance.

Safety

Benzaldehyde is harmful to the eyes, lungs and skin. Poisonous by swallowing and skin absorption. Contact may cause dermatitis. Flammable.

4-Methylbenzaldehyde handle the same as benzaldehyde.

4-Methoxybenzaldehyde is harmful if swallowed, inhaled or absorbed through the skin. It is an irritant to both skin and eyes. Flammable.

3-Phenylpropenal (cinnamaldehyde) may be harmful by inhalation, ingestion or skin absorption. Vapor or mist irritating to the eyes and upper respiratory tract. Flammable.

Acetone (2-propanone) is an irritant to the eyes, skin and lungs. Harmful to the liver and kidneys if swallowed. Highly flammable. Use only in a well-ventilated area.

Cyclopentanone is poisonous by inhalation, ingestion or skin absorption. Causes **severe** eye irritation! Flammable.

Cyclohexanone may be **fatal** if inhaled. Mild exposure may cause wheezing, headache, nausea and vomiting. Target organs: liver, kidneys, central nervous system and lungs.

4-Methylcyclohexanone is harmful when swallowed and causes eye and skin irritation. Flammable.

Ethanol (95%) may contain denaturing substances that enhance its toxicity.

Sodium hydroxide solution is corrosive to the skin, harmful if swallowed, and extremely dangerous to the eyes.

Acetic acid (ethanoic acid) can be irritating to the skin and eyes, particularly if concentrated. Dilute solutions of ethanoic acid are relatively harmless.

Toluene is poisonous by skin absorption. Its vapour irritates the eyes and respiratory system and can cause dizziness, headaches and nausea.

Additional information regarding the potential hazards in handling these chemicals may be obtained from the Material Safety Data Sheets that are available in the laboratory.

Waste disposal

The filtrate from the suction filtration and washings should be placed in the container provided. If 95% ethanol was used in the recrystallization, the filtrate from this process may be placed in the same bottle.

If toluene was used in the recrystallization, the filtrate should be placed in the container provided for non-halogenated hydrocarbons.

Write-up

This experiment should be written up using the standard format for "preparative type" experiments.

CHEM360 Experiment 13 Report

Date:_____

Student Name:_____ ID Number:_____

Title:

Objective(s):

Reaction Equation(s): (structures and names)

Introduction:

Procedure:

(Reference: author surname, initials, date. Title of text, publisher, pages)
Any Changes/Modifications?

Mixed Aldol Condensation Reaction Observations

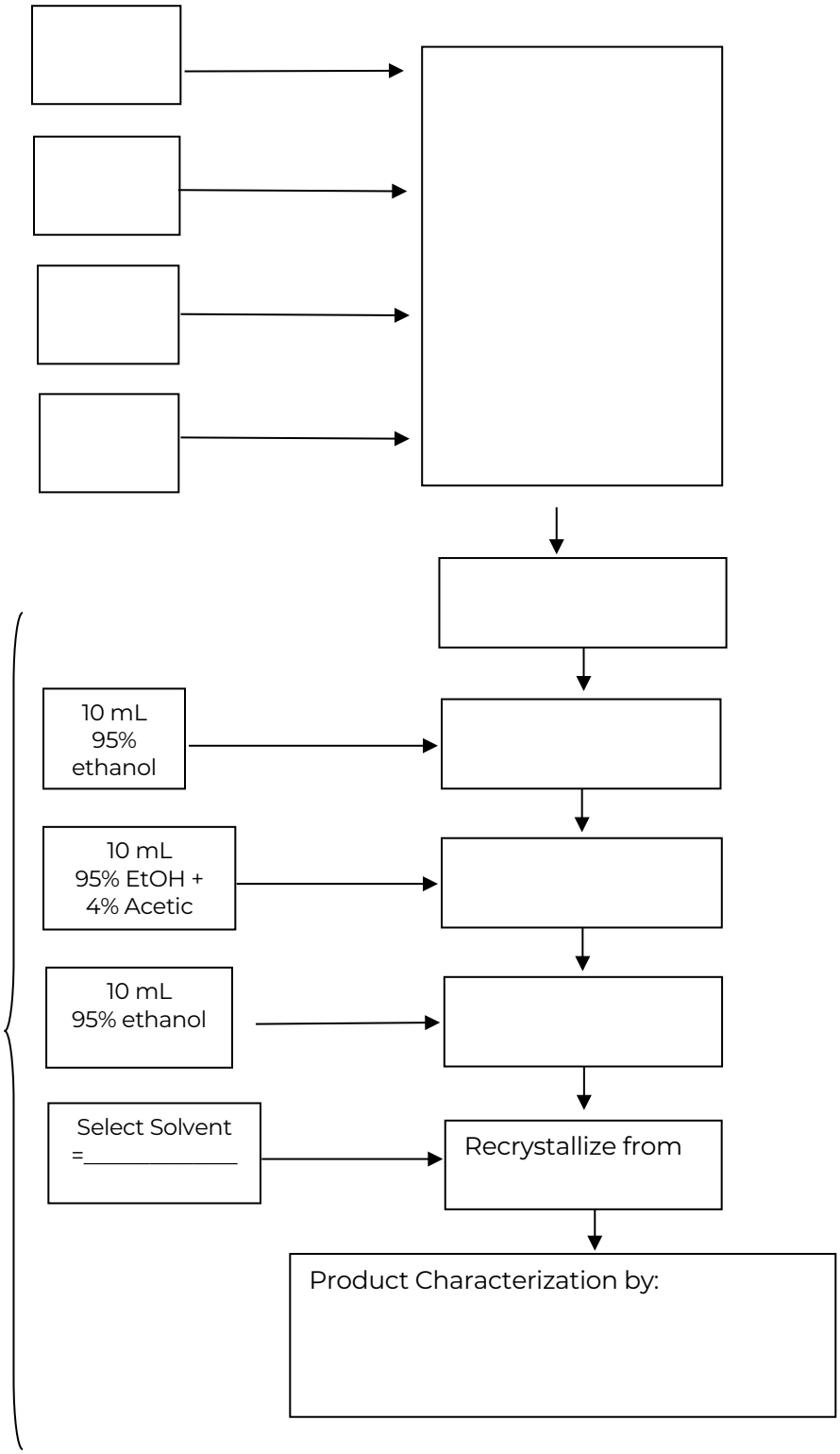
Procedural Step	Observations/Comments/Inferences

Table 13.1. Table of Reagents for Exp. 13

Reagent	Formula	Mwt.	d	mp	bp	Haz. Prop.
Benzaldehyde			1.044		179.5	
4-methylbenzaldehyde	$CH_3C_6H_4CHO$		1.019		204-205	
4-methoxybenzaldehyde	$CH_3OC_6H_4CHO$		1.119		248	
Cinnamaldehyde	$C_6H_5CH{=}CHCHO$		1.048		248	
Acetone	CH_3COCH_3		0.818		56.5	
Cyclopentanone	C_5H_8O		0.951		130.6	
Cyclohexanone	$C_6H_{10}O$		0.947		155	
4-methylcyclohexanone	$CH_3C_6H_9O$		0.914		169-171	
Ethanol	CH_3CH_2OH		0.785		78.5	
Sodium hydroxide	NaOH (1M)		~1.00			
Acetic acid	CH_3COOH		1.049		118.1	
Toluene	$C_6H_5CH_3$		0.865		110.6	
Benzalacetone	$C_6H_5CHCHCOCH_3$					
Dibenzalacetone						
Dibenzalcyclohexanone						
Dibenzalcyclopentanone						
Chloroform	$CHCl_3$					
Carbon tetrachloride	CCl_4					

SAMPLE EXPERIMENT 13 FLOW CHART

REAGENT PROCEDURE / STEP OBSERVATION



Experiment 13 Results:

Table 13.2. Summary Table of Observations
(this table is optional. Use only to tidy up your observations from the previous page if necessary.)

Procedural Step	Comment/Observation/Inferences

Table 13.3. Table of Data for Aldol Condensation Product.

Table 13.3 presents the summary of the results of the experiment. The calculations for limiting reagent, theoretical yield and percent yield are shown below the table. Note: Both reagents are added in equal stoichiometric amounts. The _____ was used as the limiting reagent as it is a 1:1 ratio with the product.

Product Name	Yield (Mass in g)	Appearance of Solid	Observed Melting Pt.* (°C)	Lit. Melting Pt. (°C)	Theoretical Yield (g)	% Yield

*Uncorrected for temperature calibration

Limiting Reagent and Theoretical Yield Calculation:

Moles of ketone actually used in the reaction =

Moles of aldehyde actually used in the reaction =

Theoretical Yield of Aldol product =

% Yield Calculation:

Table 4. Infrared Spectrum Data Analysis (see attached spectra)

Aldehyde =	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

Ketone =	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

Aldol Product =	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group absent:

Discussion:

Comments on and give reasons for high or low yield and purity, and sources of error (practical and theoretical), etc.:

Conclusion:

Structure of Product

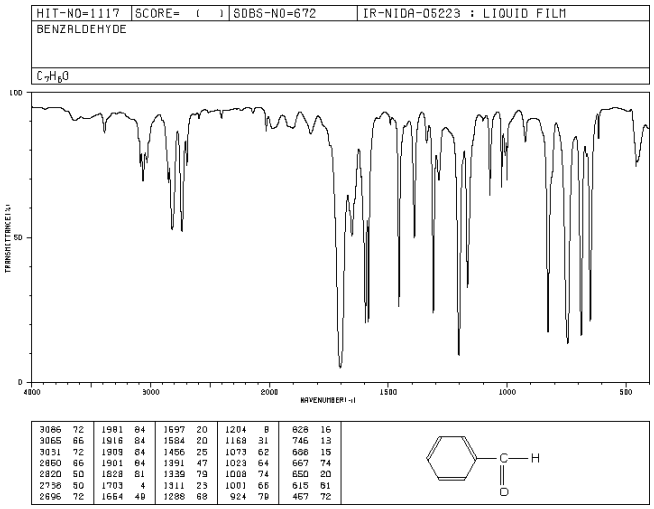
Questions

Answer to be submitted with report.

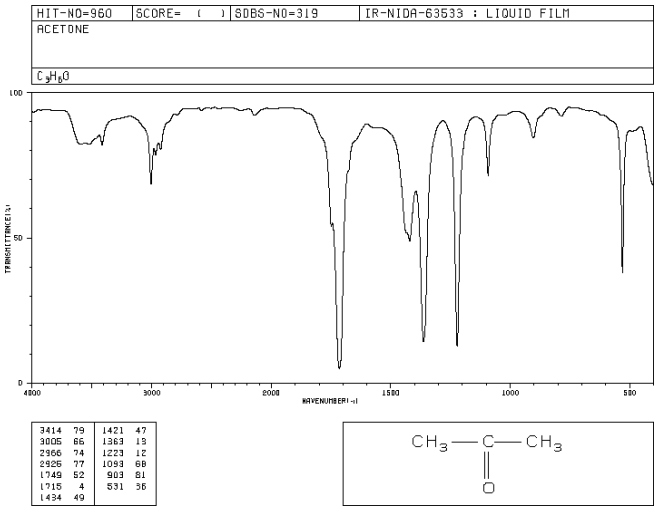
1. The product obtained in this experiment results from a crossed condensation between an aldehyde and a ketone. Identify two other base-initiated reactions that could conceivably occur involving either or both reactants. Suggest reasons why these reactions do not result in the formation of large quantities of by-products

2. What is the purpose of adding sodium hydroxide to the reaction mixture? (use equations if necessary to explain your answer).

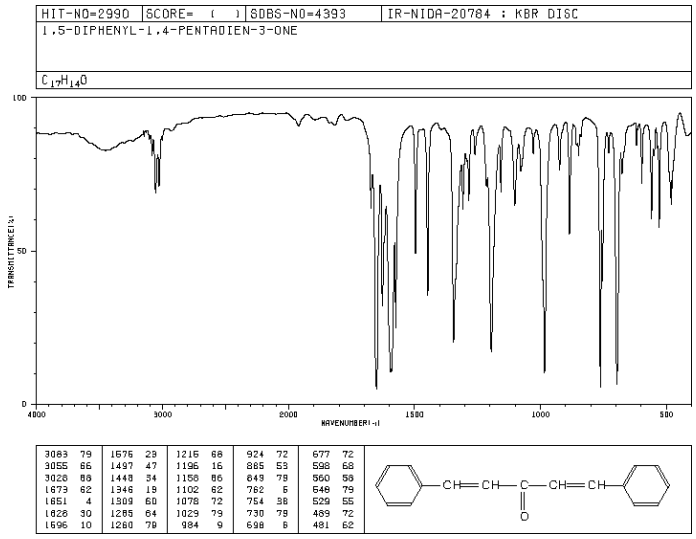
Literature Infrared Spectrum of Benzaldehyde



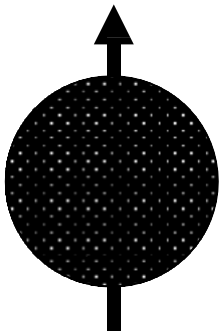
Literature Infrared Spectrum of Acetone



Literature Infrared Spectrum of Dibenzalacetone (cast thin film on KBr)



Experiment 14
IR-NMR Exercise



Preparation

Before beginning this experiment, you should have

1. studied ‘Structure Determination: Mass and Infrared Spectroscopy’ and
2. studied ‘Structure Determination: Nuclear Magnetic Resonance’.

You may also wish to read Chapter 29 in J.W. Zubrick’s ‘The Organic Chem Lab Survival Manual: A Students Guide to Techniques’ pp.201-222, and Chapter 30 in J.W. Zubrick’s ‘The Organic Chem Lab Survival Manual: A Students Guide to Techniques’ pp.223-233.

The tutorial can be found in our online resources

CHEM360 Experiment 14 Report

Date:_____

Student Name:_____ ID Number:_____

Title:

Objective(s):

Procedure:

(Ref:)

Changes/Modification:

ATTACH YOUR 4 UNKNOWN IR/NMR SPECTRA PROBLEMS TO THIS TITLE PAGE.

The unknown spectra problems can be found online

Experiment 15
Reactions of the common functional groups Part III: Aldehydes and ketones

Preparation

You should read in your textbook:

1. 'Functional Groups,
2. 'A Preview of Carbonyl Compounds' and 'Aldehydes and Ketones', and
3. 'Oxidation and Reduction in Organic Chemistry'.

Read the background information

Procedure

Part A: Reaction with 2,4-dinitrophenylhydrazine

This test should be carried out on the aldehyde and ketone used in Experiment 13.

1. In a small test tube, dissolve one drop of the carbonyl compound in about 0.5 mL of methanol and add approximately an equal volume of Brady's reagent. Also prepare a positive and negative control tube. Shake all the solutions in for several minutes.

2. If no precipitate forms, warm the test tube in a beaker of hot water for 5 - 10 minutes and then allow the solution to cool. Record your observations.

Part B: Silver mirror test

As in Part A, this test should also be carried out on the aldehyde and ketone used in Experiment 13.

1. Add one drop of sodium hydroxide solution (3 $mol \cdot L^{-1}$) to 2 mL of silver

nitrate solution (0.3 mol· L^{-1}) in a small test tube.

2. To the solution prepared in Step 1, add ammonium hydroxide solution (1 mol·· L^{-1}) until the precipitate that first forms just redissolves.

3. Place 2 or 3 mL of the freshly prepared ammoniacal silver nitrate solution (from Step 2) in a **clean** test tube. To this solution add one or two drops of the carbonyl compound being investigated and allow the solution to stand at room temperature for several minutes. Also prepare a positive and negative control tube. Record your observations. Note: A dirty test tube often causes a finely divided black precipitate of silver to form instead of the expected silver mirror. Either result may be regarded as being positive.

CAUTION: Tollens' reagent decomposes on standing to form sodium fulminate, a very explosive substance. Decompose any excess of this reagent by adding concentrated nitric acid to your stock solution and your test solutions before washing them down the sink with plenty of water. Do not attempt to store Tollens' reagent and do not be tempted to give any excess reagent to a fellow student for use "later".

Part C: Schiff's test

1. Add 1 mL of Schiff's reagent to a few drops of each of the following:

   a. solution of formaldehyde
   b. the aldehyde that you used in Experiment 13
   c. the ketone that you used in Experiment 13

2. If no immediate reaction occurs, allow the solution to stand for 30 minutes. Record your observations.

Part D: Iodoform test

This test should be carried out on each of the following compounds: acetone, cyclohexanone, acetophenone, 1-butanol, and 2-butanol.

1. To one drop of the liquid being tested, add 3 mL of iodine in potassium iodide solution followed by enough sodium hydroxide solution (3 mol· L^{-1}) to make the iodine colour disappear. The formation of a yellow precipitate indicates that iodoform has been produced.

2. If no precipitate forms immediately, allow the reaction mixture to cool in

an ice- water bath and add further iodine in potassium iodide solution until a permanent yellow colour persists. If a yellow precipitate still does not form, you can assume that no iodoform has been produced.

Safety

Sodium hydroxide solution is corrosive to the skin, harmful if swallowed, and extremely dangerous to the eyes.

Silver nitrate solution should not be allowed to contact the skin or eyes.

Ammonium hydroxide (or **ammonia solution**) is basic, therefore care should be taken to prevent contact with skin or eyes. Inhalation of ammonia fumes should also be avoided. Use only in a fume hood.

Aldehydes and ketones used in Experiment 13 should be handled with care. See Experiment 13 for details of specific hazards.

Methanol is harmful to the eyes, lungs, skin, and other organs. Avoid inhaling the vapour or ingesting the liquid. Highly flammable.

Brady's reagent is a solution of 2,4-dinitrophenylhydrazine in methanol and sulfuric acid and should be handled accordingly. Protect your eyes and avoid contact with skin. Solid 2,4-dinitrophenylhydrazine is explosive and is harmful by inhalation of its dust and by skin absorption.

Tollens' reagent forms an explosive mixture on standing. See "Procedure" section for details of how to dispose of excess Tollens' reagent.

Formaldehyde solution is a skin irritant and is poisonous if swallowed. Its vapour is very irritating to the eyes and lungs.

Schiff's reagent contains sulfur dioxide in solution. Avoid contact with the skin or eyes. Vapour escaping from this solution may irritate the respiratory system, especially in individuals suffering from bronchitis and asthma.

Acetone (propanone) is an irritant to the eyes, skin and lungs. Harmful to the liver and kidneys if swallowed. Highly flammable. Use only in a fume hood or other well-ventilated area.

Acetophenone is harmful if swallowed, inhaled or absorbed through the skin. It causes **severe** eye irritation! Flammable.

Cyclohexanone: see Experiment 13 for specific hazards.

1-Butanol and 2-butanol: see Experiment 11 for specific hazards.

Iodine in potassium iodide solution may cause internal irritation if ingested. Avoid contact with skin.

Iodoform is harmful by inhaling, ingesting or skin contact.

Additional information regarding the potential hazards in handling these chemicals may be obtained from the Material Safety Data Sheets that are available in the laboratory.

Waste disposal

The test solutions from Parts A and C should be placed in the container marked "non-halogenated organic wastes".

Instructions for dealing with excess Tollens' reagent and the test solutions from Part B are given in the "Procedure" section.

The test solutions from Part D should be placed in the container marked "halogenated organic wastes".

Write-up

See Experiment 11 for a suggested way of writing up this type of experiment. Keep the introduction brief. Do not regurgitate all the theory. Simply define the tests used. You should not attempt to write equations for the Schiff's test.

CHEM360 Experiment 15 Report

Date:_____

Student Name:_____ ID Number:_____

Title:

Objective(s):

Reaction Equations:

Introduction:

Procedure:

(Ref:)

Changes/Modification:

Table 15.1. Table of Reagents for Experiment 15.

Reagent	Formula	Mwt.	d	mp	bp	Haz. Properties
Benzaldehyde	C_6H_5CHO	106.12	1.044	-26	179.5	
4-methylbenzaldehyde	$CH_3C_6H_4CHO$	120.15	1.019		204-205	
4-methoxybenzaldehyde	$CH_3OC_6H_4CHO$	136.15	1.119	-1	248	
trans-cinnamaldehyde	$C_6H_5CHCHCHO$	132.16	1.048		248	
Acetone	CH_3COCH_3	58.08	0.791	-94	56	
Cyclopentanone	C_5H_8 (=O)	84.12	0.951	-51	130-131	
Cyclohexanone	C_6H_{10} (=O)	98.15	0.947	-47	155	
4-methylcyclohexanone	$CH_3C_6H_9$ (=O)	112.17	0.914		169-171	
Formaldehyde	HCHO	30.03	1.083			
Acetophenone	$C_6H_5COCH_3$	120.15	1.030	19-20	202	
1-butanol	$CH_3(CH_2)_3OH$	74.12	0.810	-90	117.7	
2-butanol	$C_2H_5CH(OH)CH_3$	74.12	0.807		99-100	
Methanol	CH_3OH	32.04	0.791	-98	64.7	
Brady's Reagent	Solution			See hydrazine, 2,4-dinitrophenyl		
2,4-dinitrophenyl hydrazine	$(O_2N)_2C_6H_3NHNH_2$	198.14				
Sulfuric acid, conc. (18 M)	H_2SO_4	98.08	1.840			
Ethanol, 95%	CH_3CH_2OH	46.07	0.785		78.5	
Tollen's Reagent	Solution		See ammonia + silver nitrate			
Schiff's Reagent	Solution		mixture of roseaniline hydrochloride and sulfur dioxide, Toxic			
Ammonium hydroxide	NH_4OH	35.05	0.90			
Silver nitrate	$AgNO_3$, 0.3 M	169.87	4.352	212		
Nitric acid	HNO_3	63.01				
Sodium hydroxide	NaOH, 3 M	40.00	~1.00			
Iodine in potassium iodide	I_2 in KI					

Experiment 15 Part A Results:

Brady's Test 2,4-dinitrophenylhydrazine			
Test Substance	Observation	Inference	Equation
Aldehyde =			
Ketone =			
Positive control			
Negative control			

Part B Results:

Tollen's Test - Silver Mirror			
Test Substance	Observation	Inference	Equation
Aldehyde =			
Ketone =			
Positive control			
Negative control			

Part C Results:

Schiff's Test			
Test Substance	Observation	Inference	Equation
Formaldehyde			
Aldehyde =			
Ketone =			

Iodoform Test			
Test Substance	Observation	Inference	Equation
Acetone			
Cyclohexanone			
Acetophenone			
1 butanol			
2-butanol			

Conclusion:

Comments on tests, sources of error, and false positives/negatives:

Questions

Answers to be submitted with your report.

1. Write a balanced equation for the reaction of acetaldehyde (i.e. ethanal) with ammoniacal silver nitrate. Remember that this is a redox reaction.

2. Outline a systematic functional group test procedure that would enable you to distinguish among hexanal, 2-hexanone, 3-hexanone, 2-hexanol, and cyclohexanol.

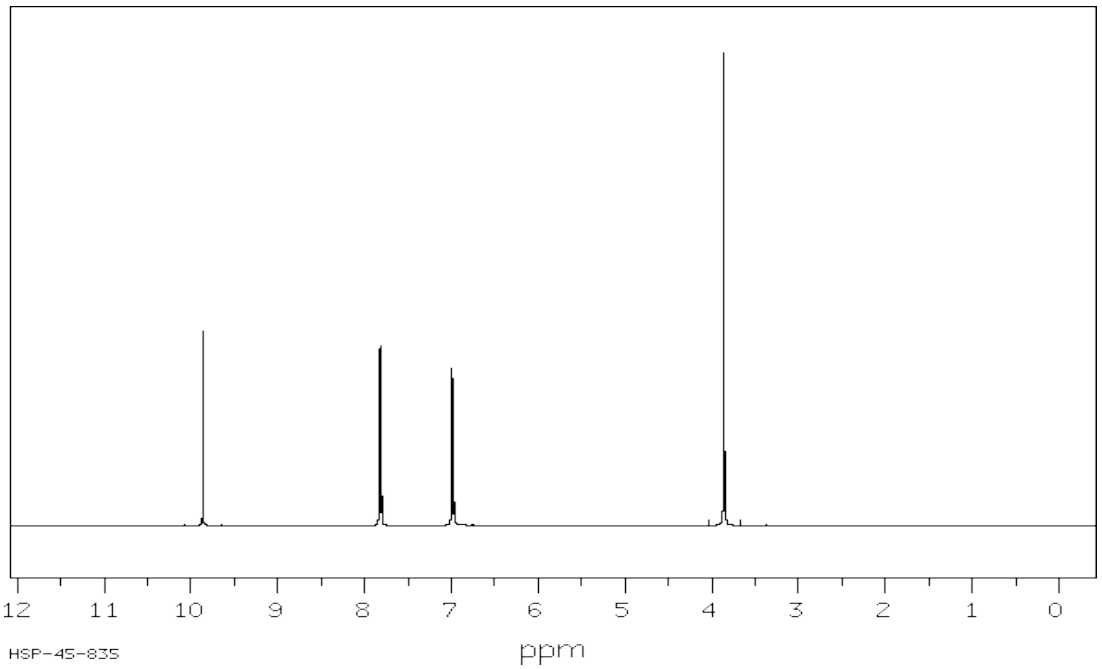
3. Aldehydes and ketones can also be easily distinguished by their infrared spectra and their identity deduced from their ^{1}H-NMR spectra. Explain why this is.

4. From the following results, identify the unknown compounds.

    a) Compound A: 2,4-DNPH positive, Tollens Test positive, Schiff's test positive, Iodoform negative (see Spectrum (A) next page).

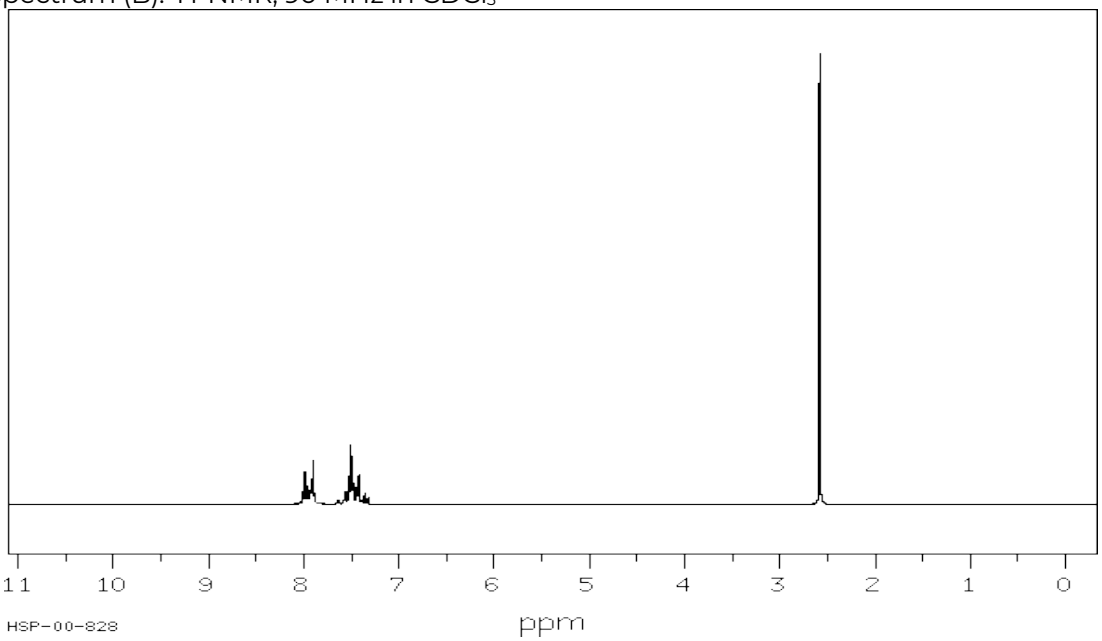
    b) Compound B: 2,4-DNPH positive, Tollens Test negative, Schiff's test negative, Iodoform positive (see Spectrum (B) next page).

Spectrum (A): ^{1}H-NMR, 400 MHz in $CDCl_3$



Molecular Formula $C_8H_8O_2$, δ 9.9 = 1H, δ 7.8 = 2H, δ 7.0 = 2H, δ 3.9 = 3H.

Spectrum (B): ^{1}H-NMR, 90 MHz in $CDCl_3$



Molecular Formula C_8H_8O, δ 7.9 = 2H, δ 7.3-7.7 = 3H, δ 2.6 = 3H.

Experiment 16
Triphenylmethanol by a Grignard reaction

"One never notices what has been done; one can only see what remains to be done". Marie Curie

Preparation

To begin this experiment, you should have read through the details of this experiment, and prepared a flow chart for the procedure to be followed, and

1. read 'Alcohols from reaction of Carbonyl Compounds with Grignard Reagents' in the chapter titled 'Alcohols from Reaction of Carbonyl Compounds' in the theory component of the course,
2. read 'Alcohols Nucleophilic addition of Grignard Reagents and Hydride Reagents: Alcohol Formation' in the chapter titled 'Aldehydes and Ketones: Neuclophilic Addition in the theory component of the course,
3. calculated the volume of bromobenzene (density = 1.4950 g· mL^{-1}), and ethyl benzoate (listed in CRC Handbook under 'benzoic acid, ethyl ester'; density = 1.0468 g· mL^{-1}) required for the reaction,
4. completed Experiment 12 (TLC), and
5. you may also wish to optional read pages 124-129 of *The Organic Chem Lab Survival Manual* (pp.221-226 in 3rd ed.).

Read the background information

Procedure

Part A: The preparation of phenylmagnesium bromide

CAUTION: Diethyl ether is highly flammable!!! There must be no flames in the laboratory while this experiment is in progress.

1. In this experiment, all glassware must be dry. Drain any water out of

your condenser, wash it with acetone, and place it in the oven to dry (15 minutes at 110– 120° C). Similarly, carefully clean a 200–mL round-bottom flask (and if necessary, a Claisen adapter and a 125 mL separatory funnel minus stopcock) and place it/them in the oven to dry.

2. Place 2.4 g of magnesium turnings in the clean, dry, 200-mL round-bottom flask. (Make sure that the magnesium turnings used are those supplied specifically for use in Grignard reactions.) Attach the condenser to the flask (do not forget the grease!) and then attach a (granular calcium chloride) drying tube (see Figure 16.5) to the top of the condenser.

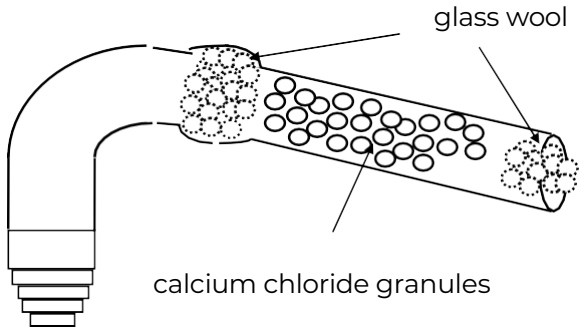


Figure 16.5. A calcium chloride (granular) drying tube

3. Clamp the round-bottom flask to a retort stand. Place a hot plate/stirrer beneath the flask. Clamp condenser and begin to circulate water through the condenser. Use a Claisen adapter to attach the separatory funnel and condenser to the round bottom flask.

4. Dissolve 0.10 mol of bromobenzene in 50 mL of anhydrous diethyl ether and transfer the solution to an equalizing funnel. [An equalizing funnel, also called a pressure-equalizing addition funnel, enables you to add reactant to a reaction mixture without opening the system to air and atmospheric moisture (see Figure 60(c) on page 126 of *The Organic Chem Lab Survival Manual* or Fig.110(c) on p.227 of 3rd ed.).
If no equalizing funnels are available, you can achieve the same result by using a separatory funnel with a drying tube instead of a stopper. [If necessary, please consult your instructor.]

5. Add 10 mL of anhydrous ether to the round-bottom flask containing the magnesium and a magnetic stir-bar. Attach a Claisen adapter to the flask. Insert the condenser (with drying tube attached) into the mouth of the adapter and insert the equalizing funnel into the arm of the

adapter (see also Figure 61, p. 128 of *The Organic Chem Lab Survival Manual*; Fig. 111 on p.228 in 3rd ed.).

6. Allow about 10 mL of the bromobenzene solution to run out of the equalizing funnel into the round-bottom flask. Stir the reaction mixture slowly and watch for signs that the reaction has begun. These signs include:
   a. the evolution of heat, i.e., the flask gets warm
   b. bubbles begin to appear from the magnesium metal
   c. a white precipitate begins to appear, i.e., the solution becomes cloudy
   d. the brown colour of the iodine disappears

Do not proceed with the next step until your instructor has confirmed that the reaction is under way.

(a single crystal of iodine maybe added to help initiate the reaction)

7. When the reaction has begun, add the bromobenzene solution at such a rate that a steady reflux is maintained. (This usually means that the bromobenzene solution is added dropwise.) If the reaction becomes too vigorous, slow the rate at which the bromobenzene is being added and cool the round-bottom flask in an ice-water bath (i.e. remove the hot-plate/stirrer and replace with an ice-water bath supported by a lab jack).

8. After all the bromobenzene solution has been added and the reaction appears to have ceased, use a bath of warm (40–50° C) water to heat the round-bottom flask for about 20–30 minutes. During this period, a steady reflux should be maintained, and virtually all of the magnesium should dissolve. *Do not* attempt to accelerate this process by using a heating mantle or a Bunsen burner.

Part B: The reaction of phenylmagnesium bromide with ethyl benzoate

1. In a small, dry Erlenmeyer flask, dissolve 0.047 mol of ethyl benzoate in 15 mL of anhydrous diethyl ether. Transfer this solution to the equalizing funnel that previously contained the solution of bromobenzene.

2. Cool the round-bottom flask containing the Grignard reagent in an ice-water bath.

3. Slowly, and with constant stirring, allow the solution of ethyl benzoate to

run into the flask containing the Grignard reagent. The formation of a coloured precipitate indicates that the intermediate magnesium salt is being formed. If the reaction appears to be too vigorous, continue to cool the flask in the ice-water bath.

4. When addition of the ethyl benzoate solution is complete, heat the reaction mixture to 40-50° C for 30 minutes using a bath of warm water (as before). Again, a heating mantle or Bunsen burner must not be used.

Part C: The isolation of triphenylmethanol

Note: A precipitate may have formed. If so, it will have to be redissolve by adding more diethyl ether than 5 mL indicated in Step C.2 below. Caution: the total volume of all the washes etc. must be kept < 250 mL (maximum size of separatory funnel available.

1. Place 50 g of ice and 50 mL of sulfuric acid (2 mol· L^{-1}) in a 400-mL beaker and decant the reaction mixture into the beaker leaving any solid, unreacted magnesium in the round-bottom flask. **CAUTION: An exothermic reaction will occur in the beaker!**

2. Rinse the round-bottom flask, first with 5 mL of diethyl ether and then *cautiously* with 5 mL of sulfuric acid (2 mol· L^{-1}). Add each of the washings to the 400-mL beaker containing the hydrolyzed reaction mixture and try to leave any unreacted magnesium in the round-bottom flask.

3. Pour all the hydrolyzed mixture into a separatory funnel (250 mL) and add 75 mL of diethyl ether. Shake the funnel (carefully) and separate the layers.

4. Wash the organic layer with an equal volume of water. Separate the layers.

5. Wash the organic layer with an equal volume of sodium hydrogen carbonate solution (0.6 mol· L^{-1}). Separate the layers. Note: If a yellow solid develops, remove it, dissolve in ether, and then 're-separate'.

6. Wash the organic layer with an equal volume of water. Wash the organic layer with an equal volume of brine (saturated sodium chloride solution). Separate the layers and transfer the organic phase to an Erlenmeyer flask. Add about 1 g of anhydrous sodium sulfate, stopper

the flask and allow the solution to dry for 10–15 minutes during which time the flask should be swirled frequently.

7. Filter the dried solution through a fluted filter paper, collecting the filtrate in a 200– mL round-bottom flask. Add about 25 mL of ligroin (high boiling point petroleum ether) to the filtrate.

8. Add a boiling chip to the solution in the flask and set up the apparatus for a simple distillation using a hot-water bath as the heat source.

9. Distil the diethyl ether into a receiver that is being cooled in an ice-water bath. When most of the diethyl ether has been removed, cool the flask in an ice-water bath and crystals of triphenylmethanol should begin to appear.

10. Collect the solid triphenylmethanol by suction filtration. If the yield appears to be very low, you may not have removed enough diethyl ether from the mother liquor. If this is the case, return the filtrate to the round-bottom flask and distil off some more diethyl ether and hence obtain a second crop of crystals.

11. Save samples of the filtrate and the crude triphenylmethanol for testing by thin-layer chromatography.

12. Recrystallize the bulk of your triphenylmethanol from absolute (100%) ethanol.

13. Determine the yield, melting point, mixed melting point with authentic standard (if available), and %yield of your recrystallized product. Transfer the product to a suitably labelled vial.

Part D: Observation of the triphenylmethyl carbocation

1. Dissolve a small amount (~0.05 g) of triphenylmethanol in a few drops of reagent grade methanol in a 'large test tube'. Place the test tube plus sample in a **small beaker of ice** in a fume hood. With the test tube point away from you, carefully add 1 mL of concentrated sulfuric acid using a Pasteur pipette, mixing frequently throughout the addition, and note any colour change.

   CAUTION: Concentrated sulfuric acid is extremely hazardous and causes serious chemical burns. **Wear latex gloves** and protect your

eyes. The heat generated during this test can cause the liquid in the test tube to splatter out.

2. *Carefully* pour the solution obtained in step 1 into 10 mL of cold water. Note any changes that occur.

3. Repeat steps 1 & 2, using the diphenylmethanol that you prepared in Experiment#12.

	Observations	
After Procedure Step	Triphenylmethanol (Exp.16)	Diphenylmethanol (Exp. 12)
Appearance of dry crystals		
Addition of methanol		
Addition of 1 mL sulphuric acid		
Dilution into 10 mL water		

Part E: Analysis by Thin-Layer Chromatography

IMPORTANT: If you did not complete Experiment 12, you should review the sections pertaining to thin-layer chromatography provided in the instructions for that experiment. Also, you should read Chapter 19 of *The Organic Chem Lab Survival Manual* (Chapter 26 in 3rd ed.), omitting the sections on "Preparation of TLC Plates" and "Preparative TLC".

1. Prepare solutions of each of the following substances by dissolving about 50 mg of substance in 2 mL of dichloromethane (methylene chloride) in small test tubes: crude triphenylmethanol, recrystallized triphenylmethanol, and biphenyl. You will also need the small sample of the mother liquor obtained in step 11 of Part C.

2. Prepare a development chamber using a 9:1 mixture of ligroin and dichloromethane as the eluent. (See Experiment 12 and p. 144 of *The Organic Chem Lab Survival Manual*; p. 247 in 3rd ed.)

3. Spot the TLC plate with samples of the four solutions as shown in Figure 16.6.

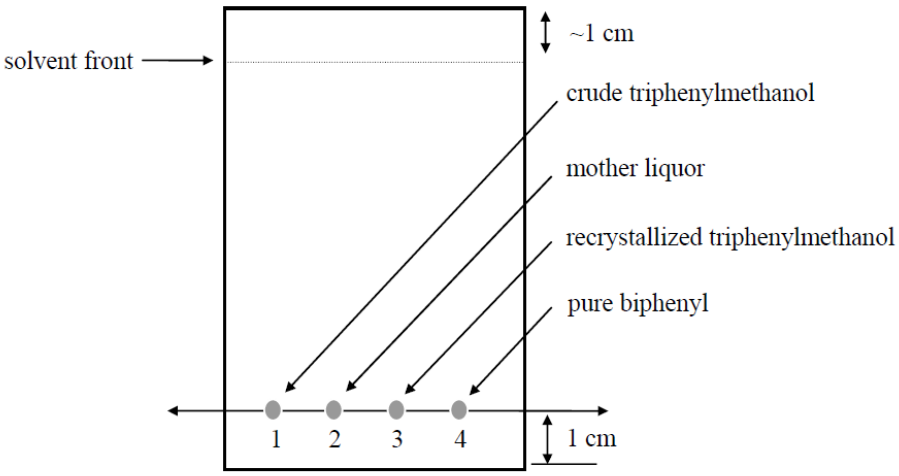


Figure 16.6. Thin-layer chromatography plate

4. As in Experiment 12, dip the lower end of the TLC place in the eluent contained in the development chamber. Observe the progress of the solvent up the plate. Remove the plate from the chamber when the solvent front reaches the line down at the top of the plate.

5. Dry the plate by shaking it in air and examine the dried plate under an ultraviolet lamp. Circle any spots with a pencil.

6. Calculate the R_f values of triphenylmethanol and biphenyl.

7. Submit your pure triphenylmethanol and your report, with a **sketch** of the TLC plate attached to your AE for marking.

Safety

Diethyl ether (ethoxyethane) is highly flammable. Inhalation of the vapour may result in intoxication, drowsiness and unconsciousness. Never attempt to evaporate an ether solution to dryness as this could result in the formation of highly explosive peroxides.

Ethyl benzoate is an irritant and is harmful when swallowed. Flammable.

Bromobenzene is poisonous if swallowed and is also poisonous by skin absorption. The vapours from this compound may be narcotic in high concentrations. In low concentrations it irritates the eyes. Flammable.

Concentrated sulfuric acid is highly corrosive. Wear gloves and proper eye protection when using this substance. Avoid contact with skin or clothes. Use only in a fume hood.

Petroleum ether (or ligroin bp. 60-80o C) is harmful if inhaled or swallowed. Can cause skin irritation and exposure may produce a burning sensation, headache and vomiting. Very flammable!

Dichloromethane is harmful if inhaled, swallowed or absorbed through the skin. It is dangerous to the eyes and has strong narcotic powers.

Iodine can burn the skin. Causes internal irritation if swallowed. Its vapour is harmful to the respiratory system.

Magnesium metal is flammable. Magnesium fires should be extinguished only with sand or a Class D fire extinguisher. Do not attempt to extinguish a magnesium fire using water or ABC-type fire extinguishers.

Biphenyl is harmful if swallowed, inhaled or absorbed through the skin.

Methanol is poisonous if swallowed. Its vapour is harmful to the eyes, lungs and skin. Highly flammable.

Ethanol is poisonous and its toxicity is increased by the presence of the denaturing substances that are added to laboratory ethanol in order to reduce its illegal consumption. High concentrations of ethanol vapour can be dangerous. Highly flammable.

Additional information regarding the potential hazards in handling these chemicals may be obtained from the Material Safety Data Sheets that are available in the laboratory.

Waste disposal

Small quantities of unreacted magnesium (from Part C, step 1) should be dissolved in dilute hydrochloric acid and washed down the drain with plenty of water.

The aqueous layer from step 3 of Part C may be washed down the drain, as may the aqueous washings from subsequent steps in the procedure.

The sodium sulfate used to dry the ethereal solution of triphenylmethanol should be placed in a garbage can.

The diethyl ether that is removed from the triphenylmethanol by distillation should be placed in the container for "Non-halogenated Organic Wastes."

The diethyl ether/ligroin mixture from the suction filtration in step 10 of Part C should be placed in the container for "Non-halogenated Organic Wastes."

The (ethanol) filtrate from the recrystallization of triphenylmethanol should be placed in the container for container for "Non-halogenated Organic Wastes."

The solutions obtained in Part D may be washed down the drain with plenty of water.

The solutions used in the thin-layer chromatography section of the experiment, and the 9:1 mixture of ligroin and dichloromethane used as the eluent in this part of the experiment, should be placed in the container for "Halogenated Organic Wastes."

Write-up

This experiment may be written up using the standard approach for preparative-type experiments. Do not forget to include details such as the melting point and yield of the product. In addition, be sure to include a discussion of the results of your thin-layer chromatography analysis.

CHEM360 Experiment 16 Report

Date:_____

Student Name:_____ ID Number:_____

Title:

Objective(s):

Reaction Equation(s):

Introduction:

Procedure:
(Ref:)
Changes/Modification:

A. Procedure for formation of Grignard Reagent.

Procedural Step	Observations/Comments/Inferences

B. Procedure for the reaction of the Grignard Reagent with ethyl benzoate to form Tiphenylmethanol.

Procedural Step	Observations/Comments/Inferences

C. Procedure for isolation of Triphenylmethanol.

Procedural Step	Observations/Comments/Inferences

D. Procedure for the observation of the carbocation.

Procedural Step	Observations/Comments/Inferences

E. Procedure for assessment of product purity by Thin Layer Chromatography.

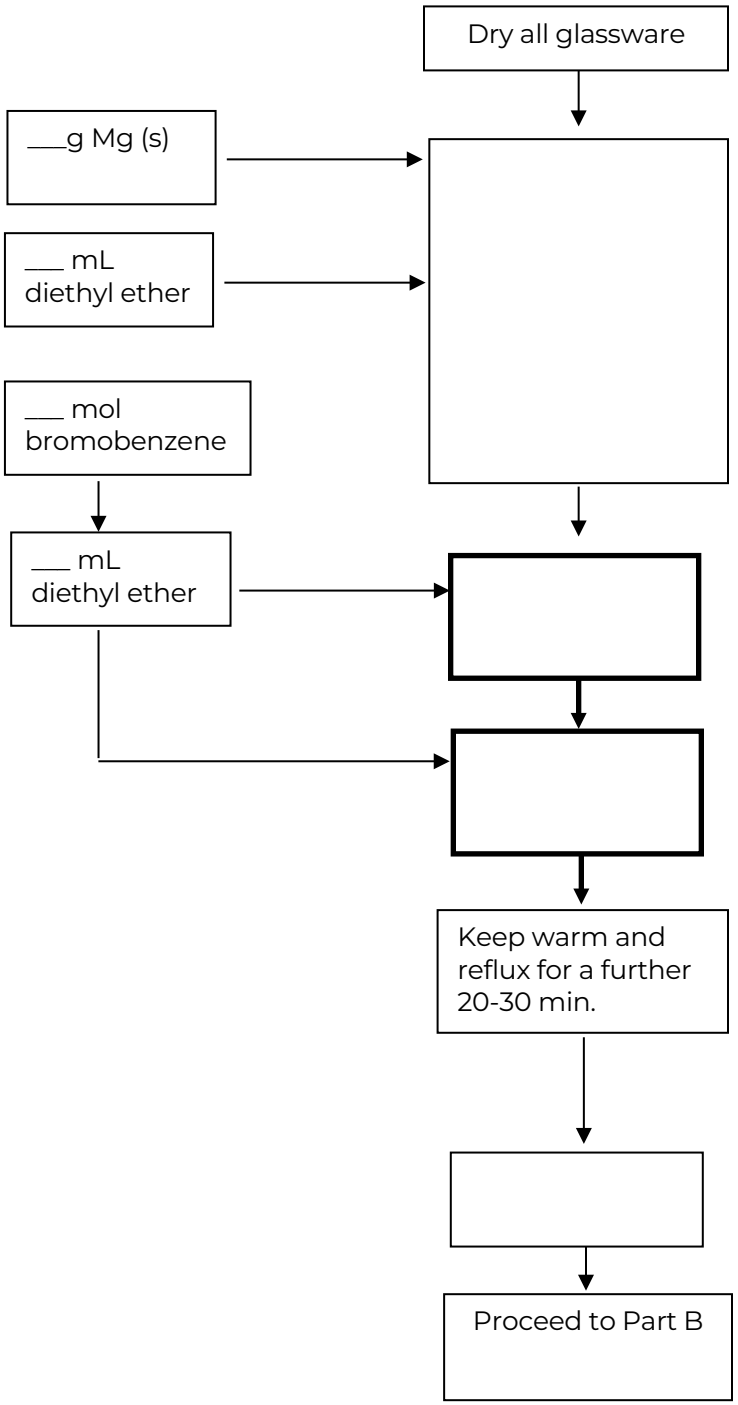
Procedural Step	Observations/Comments/Inferences

Table 16.1. Table of Reagents for Experiment 16.

Reagent	Formula	Mwt.	d	mp	bp	Haz. Properties
Bromobenzene	C_6H_5Br					
Magnesium		24.31	1.75	649	1090	
Ethyl benzoate	$C_6H_5CO_2C_2H_5$					
Diethyl ether	$C_2H_5OC_2H_5$	74.12	0.7138	-116	34.5	
Sulfuric acid, 2M		98.07				
Sodium H carbonate		84.01	2.159	270		
Sodium sulfate, anhyd		142.04	2.68			
Dichloromethane		84.93	1.325	-95.1	40.1	
Biphenyl	$(C_6H_5)_2$	154.21	0.992	71	255.9	
Ligroin	(high bp pet. ether) alkane mixt.		0.656		60-80	
Iodine		253.8	4.930	133		
Methanol	CH_3OH	32.04	0.7914	-94	65	
Ethanol	C_2H_5OH	46.07	0.7893	-117	78.5	
Triphenylmethanol	$(C_6H_5)_3COH$					

SAMPLE EXPERIMENT 16 FLOW CHART Part A

REAGENT | PROCEDURE / STEP | OBSERVATION



SAMPLE EXPERIMENT 16 FLOW CHART Part B and C

REAGENT	PROCEDURE / STEP	OBSERVATION

Experiment 16 Results:

Table 16.2. Summary Table of Observations
(this table is optional. Use only to tidy up your observations from the previous page if necessary.)

Procedural Step	Comment or Observation

Table 16.3. Table of Product Data for Triphenylmethanol, the Grignard Reaction Product.

Table 16.3. presents the summary of the results of the experiment. The calculations for limiting reagent, theoretical yield and percent yield are shown below the table. Note: _____ was found to be the limiting reagent.

Product Name	Yield (Mass in g)	Appearance of Solid	Observed Melting Pt.* (°C)	Lit. Melting Pt. (°C)	Theoretical Yield (g)	% Yield

*uncalibrated thermometer used.

Limiting Reagent and Theoretical Yield Calculation:

Moles of magnesium used in the reaction =

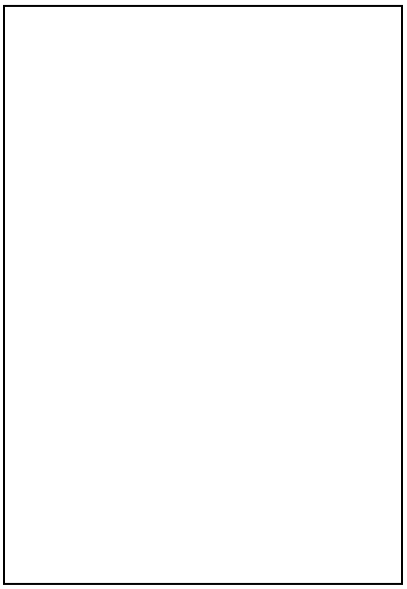
Moles of bromobenzene used in the reaction =

Moles of ethyl benzoate used in the reaction =

Theoretical Yield of triphenylmethanol =

% Yield Calculation:

Fig 16.1. TLC Analysis of Biphenyl, Mother Liquor, Crude and Recrystallized Triphenylmethanol



Lane#	Dist to Center Spot ( )	Dist to Solvent Front ( )	Rf

Discussion:

Comments on and reasons for yield (high/med/low), purity (high/med/low), sources of error, etc.:

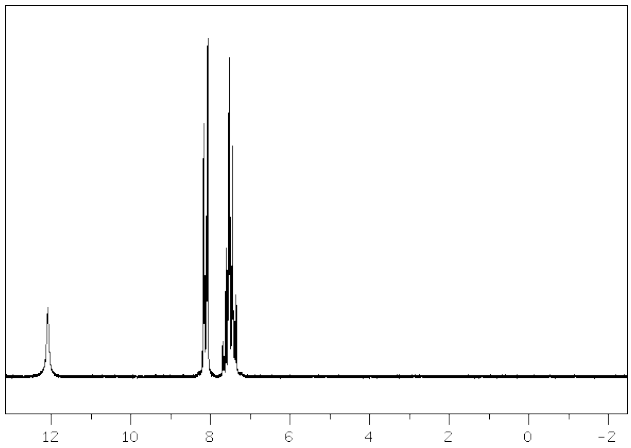
Conclusion:

Structure of Product

Questions

Answers to be submitted with your report.

1. How do you account for the fact that biphenyl is formed as a by-product in this reaction?
2. Why do you think that reactions involving Grignard reagents are sometimes carried out in an atmosphere of nitrogen or argon?
3. A Grignard reaction was performed, and the following ^{1}H-NMR (90 MHz in $CDCl_3$) was obtained of the purified product. Deduce the product's structure (Molecular Formula = $C_7H_6O_2$). Also write the overall reaction for its formation from <u>any</u> organohalide and carbonyl compound.



^{1}H-NMR Spectral Data:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment
1	δ 7.5	3H				
2	δ 8.1	2H				
3	δ 12.1	1H		Xchngs with D_2O		

Experiment 17
multi-step synthesis: Benzocaine

Preparation

Before beginning this experiment, you should have read through the details of this experiment, and prepared a flow chart for the procedure to be followed, and

1. read 'An Introduction to Organic Synthesis', and
2. studied the 'Oxidation of Aromatic Compounds'.
3. studied the 'Nucleophilic Acyl Substitution Reactions of Carboxylic acids' and 'Chemistry of Amides'.
4. studied the 'Synthesis of Amines'.
5. completed at least three "preparative type" experiments (e.g., Experiments 10, 12, 13, and 16)

You may also wish to read the section on "Steam Distillation" on pp. 117-119 of *The Organic Chem Lab Survival Manual* (Chapter 20 pp. 208-212 in 3rd ed.).

Read the background information

Introduction

By comparing our starting material, 4-nitrotoluene, with our penultimate product, 4- aminobenzoic acid, we see that our goal will be to convert a methyl group into a carboxyl group and to reduce a nitro group to an amino group. The final step in the synthesis will then be a simple esterification. However, it is important that the first four steps are carried out in the correct order. For example, if the methyl group is oxidized to a carboxyl group in the first step, the subsequent reduction of the nitro group to an amine would result in the formation of a product containing both an acidic and basic group (-CO_2H and -NH_2, respectively). Such a product would be soluble in the acidic reducing mixture (tin and hydrochloric acid) and would also be soluble in base. Thus, isolation of the product from the reaction mixture would be difficult to achieve. The problem cannot be solved by esterifying the carboxyl group before reducing the nitro group because the ester would simply hydrolyze back to a carboxylic acid under the conditions employed in the reduction.

The approach that you will use involves the reduction of the nitro group before the methyl group is oxidized. The reagent used to bring about the reduction is a mixture of tin and hydrochloric acid. After the reduction is complete, the reaction mixture is made basic and the product, 4-methylaniline, is extracted using a process called *steam distillation*. Because 4-methylaniline contains two activating groups, CH_3 and NH_2, it is very susceptible to oxidation. To prevent oxidation from occurring, the amine is immediately converted to a salt by dissolving it in aqueous acid.

Once 4-nitrotoluene has been converted to 4-methylaniline (in fact 4-methylanilinium chloride), the next step is to oxidize the methyl group. This cannot be done directly, however, as the highly activated aromatic ring would be destroyed under the conditions employed. Instead, the highly activating amino group is acetylated to give an acetamido group, CH_3-(C=O)-NH-, which is much less activating. The product of this reaction, 4'- methylacetanilide, is then oxidized to 4-acetamidobenzoic acid under approximately neutral conditions. The acetamido group is then hydrolyzed back to an amino group and the resulting 4-aminobenzoic acid is esterified to give the desired product.

(i) The reduction of 4-nitrotoluene

The reduction of nitro compounds is the principal [3] method of preparing primary aromatic amines. This reduction can be achieved through the use of hydrogen and a suitable catalyst, or by using a metal/acid combination such as tin and hydrochloric acid. A variety of nitrogen compounds is formed as the reduction proceeds, but under the conditions used in this experiment none of the intermediates can be isolated. The actual product of the reduction is the double salt, $(C_6H_5NH_3)_2SnCl_6$, and the free amine is liberated by treating this double salt with base. This treatment also has the added advantage that it renders any tin salts soluble through the formation of stannate ions (SnO^{2-}). The amine is extracted from the reaction mixture by steam distillation. (See “Steam Distillation” on pp. 117-119 of *The Organic Chem Lab Survival Manual* or pp.208-212 in 3rd ed.). You will employ a set-up similar to the one shown in Figure 57 (Fig.106 in 3rd ed.), except that, instead of a three- necked flask, you will use a single-necked flask and a Claisen adapter. As we have previously explained, 4-methylaniline is very susceptible to air-oxidation, thus it is immediately converted to a salt through the addition of hydrochloric acid.

(ii) The acetylation of 4-methylaniline

This step is relatively straightforward and requires no detailed explanation.

(iii) The oxidation of 4'-methylacetanilide

Although alkanes and aromatic hydrocarbons are generally very resistant to oxidation, the carbon attached to the aromatic ring of an alkylaromatic hydrocarbon is sufficiently activated to be quite easily oxidized. While it is occasionally possible to obtain other oxidation products, an alkyl group is normally cleaved between the α- and β-carbons to give the corresponding aromatic carboxylic acid. In the oxidation of a methyl group, the partially oxidized intermediates, the alcohol and the aldehyde, are more easily oxidized than the methyl group, so that only under rather special conditions is it possible to stop the oxidation and isolate these intermediates. Thus, benzoic acid or some other aromatic acid is the usual product.

The use of chromium (VI) as an agent for oxidizing the side chain of an aromatic hydrocarbon requires elevated temperatures and acidic conditions. However, the permanganate ion can bring about such oxidations at about 80-90° C in an almost neutral solution. The permanganate ion is reduced to manganese(IV) oxide and, as we see from the half-equation,

$$3e^- + MnO^-_{4\,(aq)} + 2H_2O_{(l)} \longrightarrow MnO_{2\,(s)} + 4OH^-_{(aq)}$$

the reaction mixture becomes increasingly basic as the oxidation proceeds. In order to prevent the base-promoted hydrolysis of the acetamido group, magnesium sulfate is added to the reaction mixture so that the hydroxide ion is removed as the sparingly soluble magnesium hydroxide.

$$Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \rightleftharpoons Mg(OH)_{2\,(s)}$$

The oxidation is slow; in part because the starting material is not very soluble, when the reaction is complete, a large amount of solid manganese (IV) oxide and some unreacted permanganate ions are present. These substances may be reduced to water-soluble manganese (II) ions through the addition of an acidic solution of sodium hydrogen sulfite.

The acidification also serves to convert the product from the soluble potassium salt to the less soluble carboxylic acid and the latter then crystallizes out of solution.

(iv) The hydrolysis of 4-acetamidobenzoic acid

The hydrolysis of an amide group is generally performed under acidic conditions. At elevated temperatures it is possible that, with the presence of the electron-withdrawing carboxyl group in the para position, some nucleophilic displacement could occur. Once produced, the free amine could also undergo some air oxidation.

The product of this reaction is an amino acid. In basic solutions, the amino acid will be converted to the water-soluble carboxylate salt, while in acidic solutions it will be present as the water-soluble amine salt (see Figure 17.2). Thus, care must be taken in adjusting the pH of the final solution so that 4-aminobenzoic acid itself is precipitated.

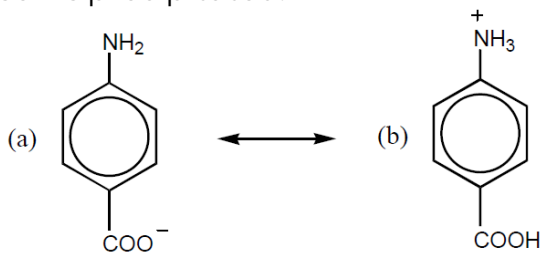
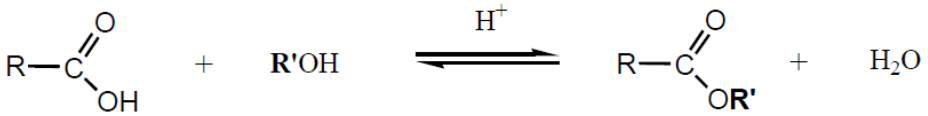


Figure 17.2 4-Aminobenzoic acid in its anionic form (a) and in its protonated form (b).

(v) The esterification of 4-aminobenzoic acid

The acid catalyzed esterification of a carboxylic acid is an equilibrium reaction that usually requires either a large excess of one of the reactants (usually the alcohol) or the removal of one of the products (usually water) for a good yield of ester to be obtained.



carboxylic acid alcohol ester

As the product of our reaction is quite soluble in ethanol, some of the latter must be removed from the reaction mixture before the product can be isolated.

Procedure

This experiment involves approximately twelve hours of work. We suggest that the various steps be spread over three days as outlined below.

DAY 1: Reduction of 4-nitrotoluene and the acetylation of 4-methylaniline. [OPTIONAL]
DAY 2: Oxidation of 4'-methylacetanilide.

DAY 3: Hydrolysis of 4-acetamidobenzoic acid and esterification of 4-aminobenzoic acid.

Part A: The reduction of 4-nitrotoluene to 4-methylaniline

Note: It is desirable to have dry starting material in Part C of this experiment, thus it is advantageous to complete Parts A and B during the same laboratory period.

1. Place 24.0 g of tin and 13.0 g of 4-nitrotoluene in a 500-mL round-bottom flask and attach a condenser and an acid-vapour trap (see Figure 17.3). Prepare about 100 mL of sodium hydroxide solution containing 10% more sodium hydroxide than the mass you calculated would be required to neutralize all the hydrogen chloride that will be liberated during this step.
   CAUTION: Sodium hydroxide will burn your skin and is particularly dangerous to the eyes. Wear gloves and safety glasses while preparing and working with this solution. Much heat is generated when dissolved in water.

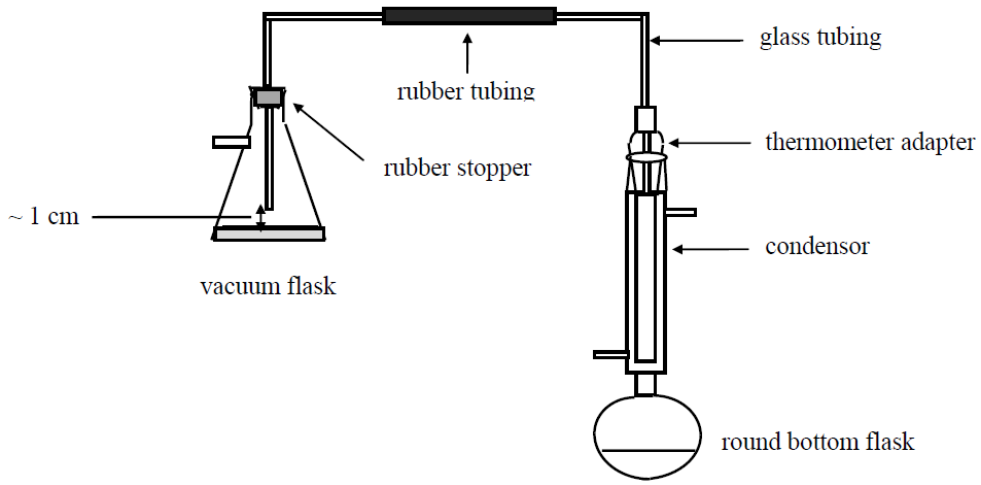


Figure 17.3 Acid-vapour trap

2. Briefly remove the acid-vapour trap and, through the top of the condenser, add 60mL of concentrated hydrochloric acid in six 10-mL portions. After each portion of hydrochloric acid is added, re-connect the acid-vapour trap and shake the flask gently to ensure that the reactants are thoroughly mixed. **CAUTION: Concentrated hydrochloric acid is highly corrosive and its fumes are harmful. Wear gloves, protect your eyes and work in a fume hood.**

An exothermic reaction will begin to occur, and the reaction mixture may begin to boil. Keep the mixture close to boiling but cool the flask in a cold-water bath if the reaction becomes too vigorous. CAUTION: Do not over-cool the mixture at the start of the reaction or else it may become too violent later.

3. When about half of the hydrochloric acid has been added, the rate of addition may be increased. The addition should be completed in about 30 minutes.

4. After all the acid has been added, heat the mixture for a further 30 minutes using a beaker of water on a hot plate as a heat source. Warm gently at first, and be prepared to quench the reaction by cooling the reaction vessel in cold water if the reaction becomes too violent. (Use heating mantle on setting 2).

5. In a 250-mL beaker, dissolve 38 g of sodium hydroxide in 60 mL of water. CAUTION: Sodium hydroxide is highly corrosive. Wear gloves and protect your eyes. Much heat is generated when sodium hydroxide dissolves in water. Be careful!

6. Remove the acid trap, raise the round-bottomed flask out of the heating mantle and cool the reaction mixture to room temperature and cautiously add the solution of sodium hydroxide that was prepared in step 5. Cool the reaction vessel during the addition and ensure that the contents of the flask are mixed thoroughly. When all the sodium hydroxide has been added, the reaction mixture should be strongly alkaline. Use red litmus paper to ensure that this is so.

7. Assemble the apparatus for steam distillation--the exact procedure may depend on the location at which the laboratory session is being conducted (see "Introduction" and pp. 117-119 of *The Organic Chem Lab Survival Manual* or pp. 208-212 in 3rd ed.). Remember to add fresh boiling stones.

8. Steam distil the product. Very cold water may cause the 4-methylaniline to solidify in the condenser. If this occurs, turn off the water supply to the condenser for a short while or, if necessary, briefly drain the water from the condenser jacket.

9. Cool the steam distillate and carefully add 8 mL of concentrated hydrochloric acid in order to dissolve all the 4-methylaniline. CAUTION: Hydrochloric acid is extremely corrosive. Wear gloves and protect your eyes.

10. If necessary, add water to the solution from step 9 so that the total volume of he solution is about 200 mL.

Part B: The acetylation of 4-methylaniline

1. In a 50-mL beaker, dissolve 13 g of sodium acetate trihydrate in 18 mL of water.

2. If you have not already done so, transfer the solution of 4-methylaniline (from Part A) to a 400-mL beaker and warm it to 50° C on a hot plate.

3. **In a fume hood**, add 11 mL of acetic anhydride to the warm solution of 4-methylaniline and stir quickly. Immediately add the sodium acetate solution from step 1. Mix thoroughly and cool in an ice-water bath.

4. Isolate the crystals from the reaction mixture by suction filtration and wash three times with small quantities of cold water.

5. Allow the crystals to dry thoroughly and record their yield and melting point. Calculate the overall yield obtained from Parts A and B of this experiment.

6. Measure out 10.0 g of dry product for use in Part C of the experiment. Transfer the remainder to a sample vial and submit it to your instructor for grading.

Part C: The oxidation of 4'-methylacetanilide

1. Transfer 5.0 g of 4'-methylacetanilide and 51 g of magnesium sulfate heptahydrate to a 600mL beaker and add 350 mL of water. (**Note:** if you did not obtain 5.0 g of 4'methylacetanilide in Part B of the experiment, please ask your instructor to provide you with some of this material. Ensure that you retain a small sample of the 4'- methylacetanilide that you prepared so that you can hand it in to your instructor for grading. NO SAMPLE means NO GRADE!)

2. Heat the reaction mixture to 80—90° C on a hot plate/stirrer.

3. Obtain 15.0 g of potassium permanganate and divide the sample into ten approximately equal portions.

4. Add the first portion of potassium permanganate to the hot solution of 4'-methylacetanilide, with constant stirring. When the purple colour

fades, add the second portion, and so on until all the potassium permanganate has been added. The addition should take about one hour. It is OK to occasionally rinse down sides of beaker with distilled water.

5. Keep stirring and heating for 10—15 minutes after the purple colour due to the final portion of potassium permanganate has faded.

6. Cool the solution and add 18.0 g of solid sodium hydrogen sulfite (sodium bisulfite). In a fume hood, cautiously acidify the reaction mixture with concentrated hydrochloric acid (~8 - 20 mL). **CAUTION:** Concentrated hydrochloric acid is highly corrosive; wear gloves and protect your eyes. Avoid inhaling the vapour.

7. Check that the reaction mixture is acidic by using congo red indicator paper. (NOTE: Congo red indicator paper turn blue in acid solutions--the exact opposite of litmus paper.) If all of the brown precipitate of manganese (IV) oxide has not dissolved and the solution is acidic, more sodium hydrogen sulfite should be added. An off-white precipitate of 4-acetamidobenzoic acid should remain.

8. Cool the reaction mixture thoroughly in an ice-water bath. Isolate the 4-acetamidobenzoic acid by suction filtration, wash the product with a small quantity of water, and dry thoroughly.

9. Determine the yield of 4-acetamidobenzoic acid obtained, but do not attempt to determine its melting point.

10. Measure out 4.0 g of dry 4-acetamidobenzoic acid for use in Part D of the experiment. Transfer the remainder to a sample vial and submit it to your instructor for grading.

Part D: The hydrolysis of 4-acetamidobenzoic acid

1. Transfer 4.0 g of 4-acetamidobenzoic acid and 25 mL of hydrochloric acid (HCl- 6 mol L^{-1}) to a 250-mL round-bottom flask with boiling stones and equipped with a reflux condenser.
(**Note**: If you did not obtain 4.0 g of 4-acetamidobenzoic acid in Part C of the experiment, please ask your instructor to provide you with some of this material. Ensure that you retain a small sample of the 4-acetamidobenzoic acid that you prepared so that you can pass it to your instructor for grading. NO SAMPLE means NO GRADE!)

2. **In a fume hood**, using a heating mantle as your heat source, reflux the reaction mixture gently for 30-40 minutes, cool in an ice-water bath, and add an equal volume of water.

3. Transfer the reaction mixture to a 400-mL beaker and, in a fume hood, use a Pasteur pipette to add concentrated ammonia solution until the mixture is just alkaline to litmus. **CAUTION: Concentrated ammonia is highly corrosive; wear gloves and protect your eyes. Avoid inhaling the vapour.**

4. Estimate the volume of the reaction mixture and add 1 mL of glacial acetic acid for each 30 mL of reaction mixture (see step D.3). **CAUTION: Glacial acetic acid is highly corrosive; wear gloves and protect your eyes. Avoid inhaling the vapour.**

5. Cool the reaction mixture in an ice-water bath and watch for crystals to begin to form. If necessary, scratch the inside wall of the beaker with a glass stirring rod to initiate the crystallization process.

6. Isolate the 4-aminobenzoic acid by suction filtration and allow it to dry thoroughly. Record the yield and melting point of the dry crystals.

7. Measure out 2.5 g of **dry** 4-aminobenzoic acid for use in Part E of the experiment. Transfer the remainder to a sample vial and submit it to your instructor for grading.

Part E: The esterification of 4-aminobenzoic acid

1. Transfer 2.5 g of dry 4-aminobenzoic acid to a 250-mL round-bottom flask. (Note: If you did not obtain 2.5 g of 4-aminobenzoic acid in Part D of the experiment, please ask your instructor to provide you with some of this material. Ensure that you retain a small sample of the 4-aminobenzoic acid that you prepared so that you can pass it to your instructor for grading. NO SAMPLE means NO GRADE!)

2. Obtain 40 mL of absolute (100%) ethanol in a 250-mL beaker and to it add, carefully with stirring, 2.5 mL of concentrated sulfuric acid. **CAUTION: Concentrated sulfuric acid is highly corrosive; wear gloves and protect your eyes.**

3. Add the ethanol/sulfuric acid mixture to the 4-aminobenzoic acid in the 250-mL round-bottom flask. Attach a reflux condenser and, using a heating mantle (setting 4-5) as a heat source, reflux the mixture for

~one hour (or for 10 minutes after the last of the solid has dissolved; this may occur in as little as 20 min).

4. Rearrange the apparatus for a simple distillation and distil off 25 mL of ethanol. This ethanol should be stored in a stoppered flask and used for the recrystallization in step 9.

5. Cool the residue that remains in the distilling flask and then pour the residue into a 600mL beaker.

6. Rinse the distilling flask with 85 mL of distilled water and add this rinse-water to the 600mL beaker containing the reaction mixture.

7. Add sodium carbonate solution (2 mol· L^{-1}) to the reaction mixture until the mixture is neutral to litmus. This addition should be carried out with care, because much foaming will occur. Stir the reaction mixture throughout the addition. Do not add excess sodium carbonate solution.

8. Cool the reaction mixture on ice and isolate the ethyl 4-aminobenzoate by suction filtration.

9. Recrystallize the product using a two solvent recrystallization method. Crush the solid thoroughly in a 125 or 250-mL Erlenmeyer flask and add the 'preheated' ethanol (recovered in step 4) until all the ethyl 4-aminobenzoate has dissolved. (Remember that any inorganic impurities that are present will not dissolve.)

10. Add a pinch of charcoal and heat the mixture to boiling on a hot plate.

11. Add an equal volume of water (pptte. should dissolve) and boil for two minutes. Filter through a fluted filter paper into a pre-heated Erlenmeyer flask.

12. Bring the filtrate to the boil once more and add small portions of water until the boiling solution appears to be slightly cloudy.

13. Allow the solution to cool to room temperature. Scratch the inside of the flask with a glass rod if no crystals have appeared after 30 minutes. When crystals have begun to form, cool the flask in an ice-water bath and then isolate the product by suction filtration.

14. Dry the crystals thoroughly and record the yield and melting point. Store your product in a suitably labelled vial and submit it to the

instructor for grading.

Safety

Tin is harmful if inhaled, swallowed or absorbed through the skin.

4-Nitrotoluene is highly toxic! DANGER! May be fatal if swallowed or absorbed through the skin. It is readily absorbed through the skin. Chronic effects include cancer and genetic mutation. Use gloves!

Concentrated hydrochloric acid is extremely corrosive to the skin and eyes. Its vapour is irritating to the eyes, skin and lungs. Wear gloves and eye protection. Use in a fume hood.

Sodium hydroxide is highly corrosive, both as a solid and in solution. Very harmful if swallowed. Extremely dangerous to the eyes.

4-Methylaniline (p-toluidine) may be fatal if inhaled, swallowed or absorbed through the skin. Wear gloves and use in fumehood. Flammable.

Sodium acetate trihydrate is an irritant and may be harmful if swallowed or absorbed in the body.

Acetic anhydride is poisonous if swallowed, causing immediate irritation, pain and vomiting. The liquid irritates and may severely burn the skin and eyes. The vapour irritates the respiratory system and the eyes. Flammable.

4'-methylacetanilide (p-acetoluidide)

Magnesium sulfate heptahydrate is an irritant and may be harmful if swallowed or inhaled. It can cause central nervous system depression.

Potassium permangante is a skin irritant. Its' dust is harmful to the lungs. Can explode on sudden heating.

Sodium hydrogen sulfite (sodium bisulfite) causes severe irritation! It is harmful if swallowed or absorbed through the skin. It is also very destructive to the upper respiratory system.

4-Acetamidobenzoic acid is an irritant and may be harmful if ingested, inhaled or absorbed through the skin.

Concentrated ammonia solution has a pungent odour and is poisonous if inhaled or swallowed. Both the solution and vapour are irritating to the eyes. The solution burns the skin.

Glacial acetic acid is poisonous if swallowed. Both the liquid and vapour are irritating to the skin and eyes and can cause burns and ulcers. Flammable.

4-Aminobenzoic acid is used in preparations that are intended to prevent sunburn, thus it is not normally considered to be a safety hazard.

Ethanol is highly flammable. The toxicity of this liquid is increased by the presence of denaturing substances. Avoid ingestion.

Concentrated sulfuric acid is very corrosive to eyes, skin and other materials. Violent reaction possible when mixed with water. Wear gloves and eye protection when using this substance.

Sodium carbonate solution is slightly basic but does not pose any specific safety problems.

Additional information regarding the potential hazards associated with handling the above chemicals may be obtained by consulting the Material Safety Data Sheets that are available in the laboratory.

Waste disposal

Please consult the laboratory instructor regarding the disposal of the various wastes produced in this experiment.

Write-up

This experiment may be written up using the standard format for “preparative type” experiments. Do not forget to calculate the individual step yields for each Part of the experiment and the overall percentage yield obtained for the complete 5-step sequence.

CHEM360 Experiment 17 Report

Date:_____

Student Name:_____ ID Number:_____

Title:

Objective(s):

Reaction equation(s):

Introduction:

Procedure:

(Ref:)

Changes/Modification:

Part C. Procedure for the synthesis of 4-acetamidobenzoic acid.

Procedural Step	Observations/Comments/Inferences
Record amount/appearance of pure 4-methylacetanilide used Reaction/Equipment Setup Reaction Reaction Work-up	

Part D. Procedure for the synthesis of 4-aminobenzoic acid.

Procedural Step	Observations/Comments/Inferences
Record amount of pure 4-acetamidobenzoic acid used Reaction/Equipment Setup Reaction Reaction Work-up	

Part E. Procedure for the synthesis of benzocaine.

Procedural Step	Observations/Comments/Inferences
Record amount/appearance of pure *p*-aminobenzoic acid used Reaction/Equipment Setup Reaction Reaction Work-up	

Table 17.1. Table of Reagents for Experiment 17

Reagent	Formula	Mwt.	d	mp	bp	Haz. Properties
4-methylacetanilide						
magnesium sulfate -7H_2O	$MgSO_4$ -7H_2O					
potassium permanganate	$KMnO_4$					
sodium hydrogen sulfite	$NaHSO_3$					
4-acetamidobenzoic acid						
hydrochloric acid	HCl					
Ammonia (conc.)	NH_3					
acetic acid, glacial						
4-aminobenzoic acid						
Ethanol						
sulfuric acid	H_2SO_4					
sodium carbonate	Na_2CO_3					
ethyl-4-aminobenzoate						

SAMPLE EXPERIMENT 17 FLOW CHART Part C

REAGENT	PROCEDURE / STEP	OBSERVATION

SAMPLE EXPERIMENT 17 FLOW CHART Part D

REAGENT	PROCEDURE / STEP	OBSERVATION

SAMPLE EXPERIMENT 17 FLOW CHART Part E

REAGENT	PROCEDURE / STEP	OBSERVATION

Experiment 17 Results:

Table 17.2. Table Summarizing Observations
This table is optional. Use only to tidy up your observations from the previous page if necessary.

Procedural Step	Observations/Comments/Inferences

Table 17.3.1 Properties of the 4-methylacetanilide Oxidation Product, 4-acetamidobenzoic acid

Table 17.3.1 shows a summary of the results of the 4-acetamidobenzoic acid synthesis. The calculations for theoretical yield and percent yield are shown below the table. Note: _____ was the limiting reagent, since the only other reagent involved in the reaction, potassium permanganate was added in excess.

Name of Product	Mass (g)	Appearance of Solid	Melting Pt. (°C)	Theoretical Yield (g)	% Yield

Theoretical Yield Calculation:

% Yield Calculation:

Table 17.3.2 Properties of the 4-methylacetanilide Oxidation Product, 4-aminobenzoic acid

Table 17.3.2 shows a summary of the results of the 4-aminobenzoic acid synthesis. The calculations for theoretical yield and percent yield are shown below the table. Note: _____ was the limiting reagent, since the only other reagent involved in the reaction, phosphoric acid, served as a catalyst.

Name of Product	Mass (g)	Appearance of Solid	Melting Pt. (°C)	Theoretical Yield (g)	% Yield

Theoretical Yield Calculation:

% Yield Calculation:

Table 17.3.3 Properties of Fisher Esterification Product, benzocaine

Table 17.3.3 shows a summary of the results of the benzocaine synthesis. The calculations for theoretical yield and percent yield are shown below the table. Note: _____ was the limiting reagent, since the only other reagent involved in the reaction, phosphoric acid, served as a catalyst.

	Mass (g)	Appearance of Solid	Melting Pt. (°C)	Theoretical Yield (g)	% Yield

Theoretical Yield Calculation:

% Yield Calculation:

(Theoretical) Overall % Yield Calculation

In addition, analyze the following Infrared and ^{1}H-NMR spectra and place the data in your results section. Use the following table formats for recording your analyses:

Infrared data 4-acetamidobenzoic acid:

	Absorption Band#	Frequency (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, med. or weak)	Functional Group Indicated
> 3000 cm^{-1}					
Between 3000 and 2000 cm^{-1}					
Between 2000 and 1400 cm^{-1}					
< 1400 cm^{-1}					

Functional Group(s) absent:

^{1}H-NMR data 4-acetamidobenzoic acid:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

Infrared data 4-aminobenzoic acid:

	Absorption Band#	Frequency (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, med. or weak)	Functional Group Indicated
> 3000 cm^{-1}					
Between 3000 and 2000 cm^{-1}					
Between 2000 and 1400 cm^{-1}					
< 1400 cm^{-1}					

Functional Group(s) absent:

^{1}H-NMR data 4-aminobenzoic acid:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

Infrared data benzocaine:

	Absorption Band#	Frequency (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, med. or weak)	Functional Group Indicated
> 3000 cm^{-1}					
Between 3000 and 2000 cm^{-1}					
Between 2000 and 1400 cm^{-1}					
< 1400 cm^{-1}					

Functional Group(s) absent:

^{1}H-NMR data benzocaine:

Signal #	Shift	Integrat'n	Splitting	Comment	#Neighbour H	Signal Assignment

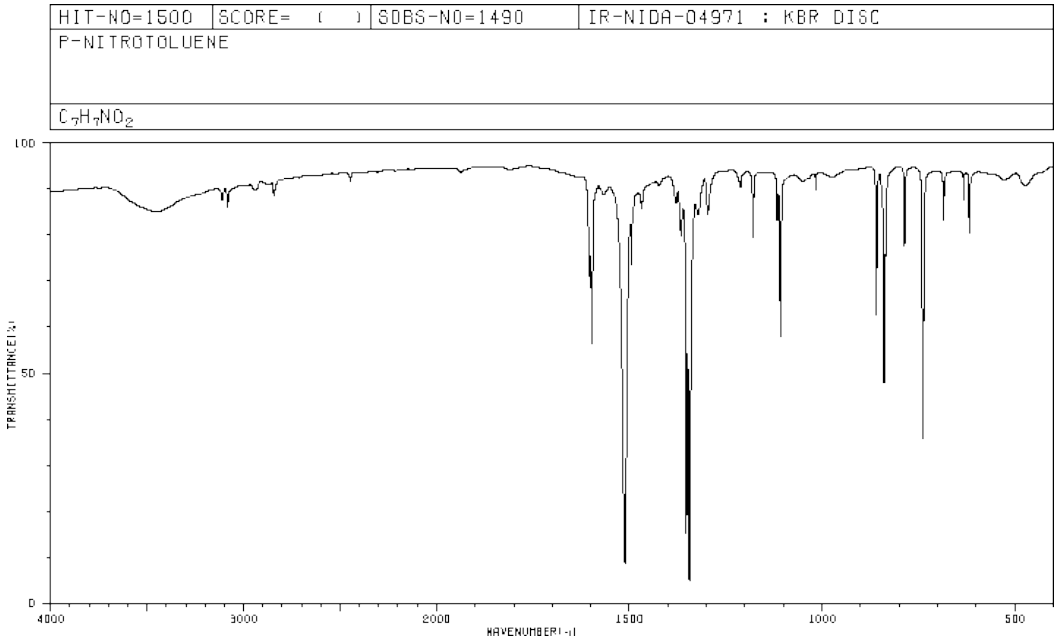
Discussion:

Comments on and reasons for yield (high or low), purity (high/med/low), sources of error, overall synthesis effectiveness, etc.

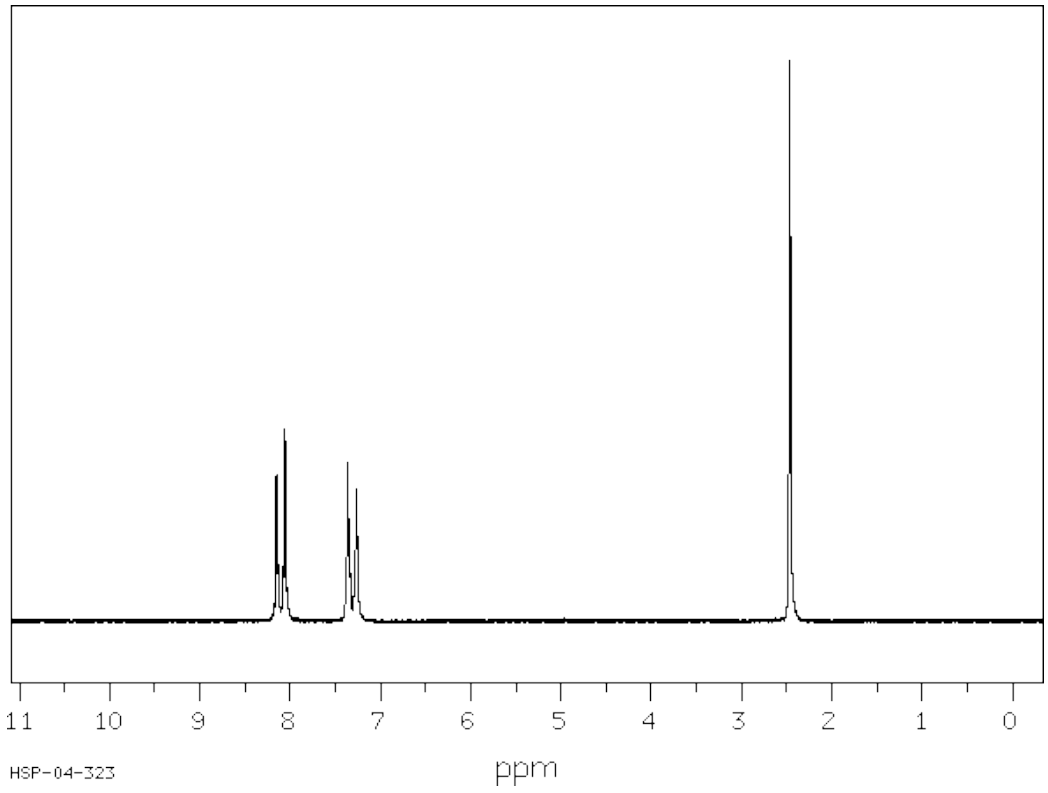
Conclusion:

Structure of Product

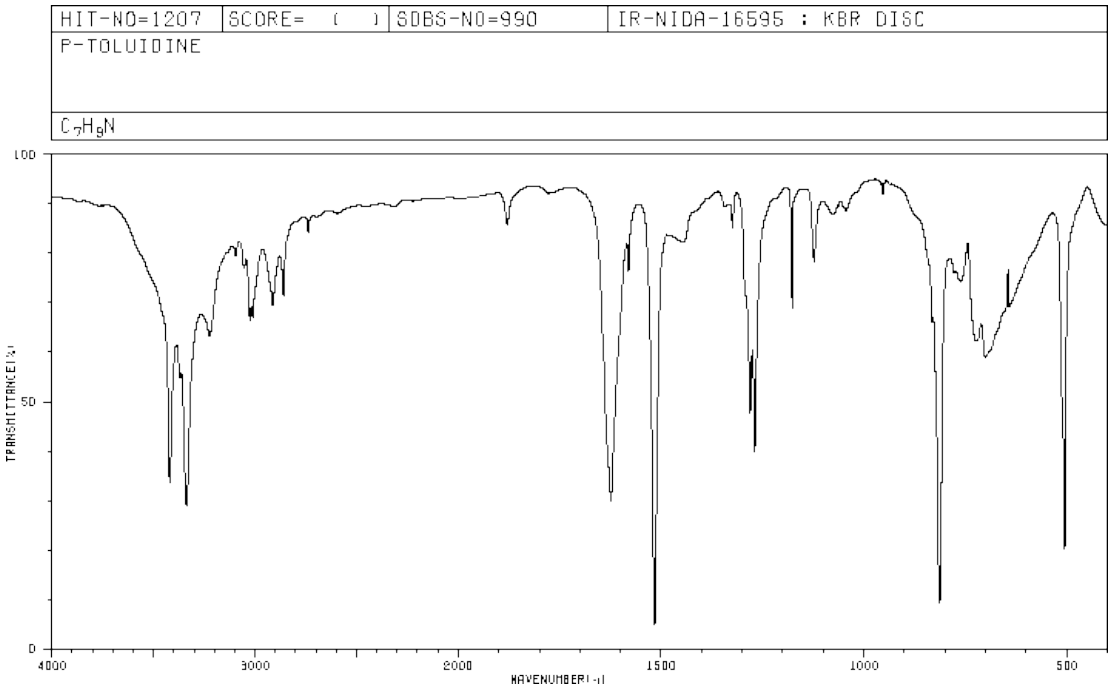
Infrared Spectrum of *p*-nitrotoluene



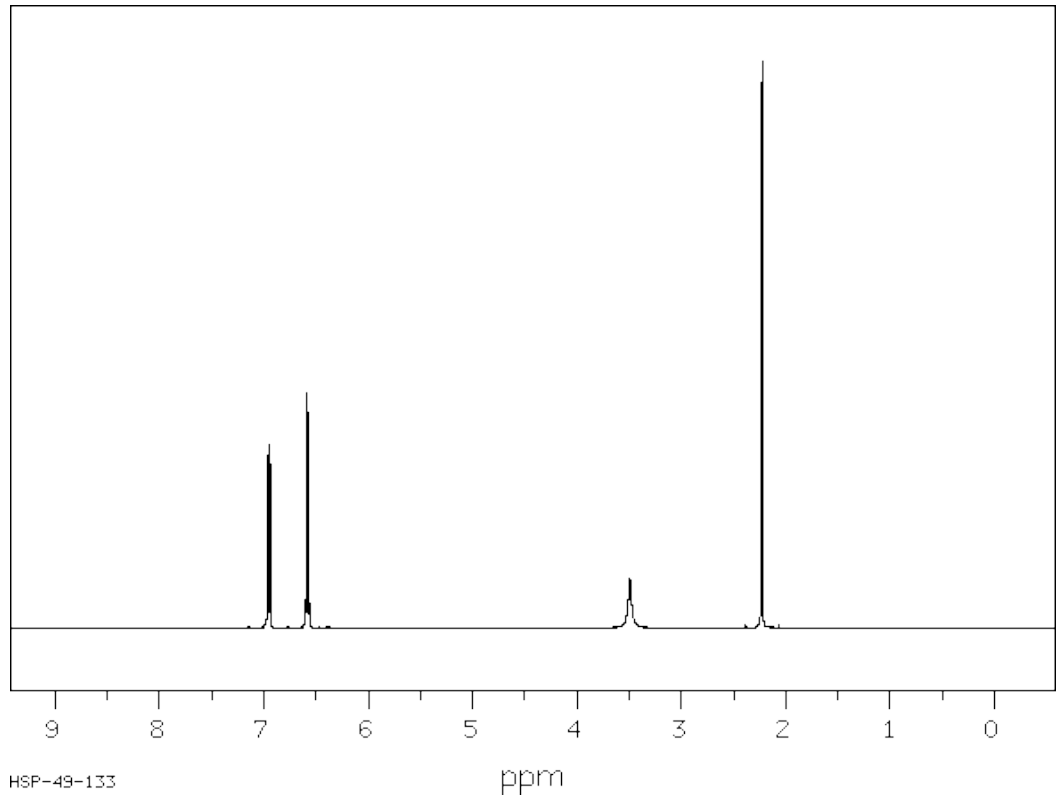
^{1}H-NMR Spectrum of *p*-nitrotoluene (90 MHz in $CDCl_3$)



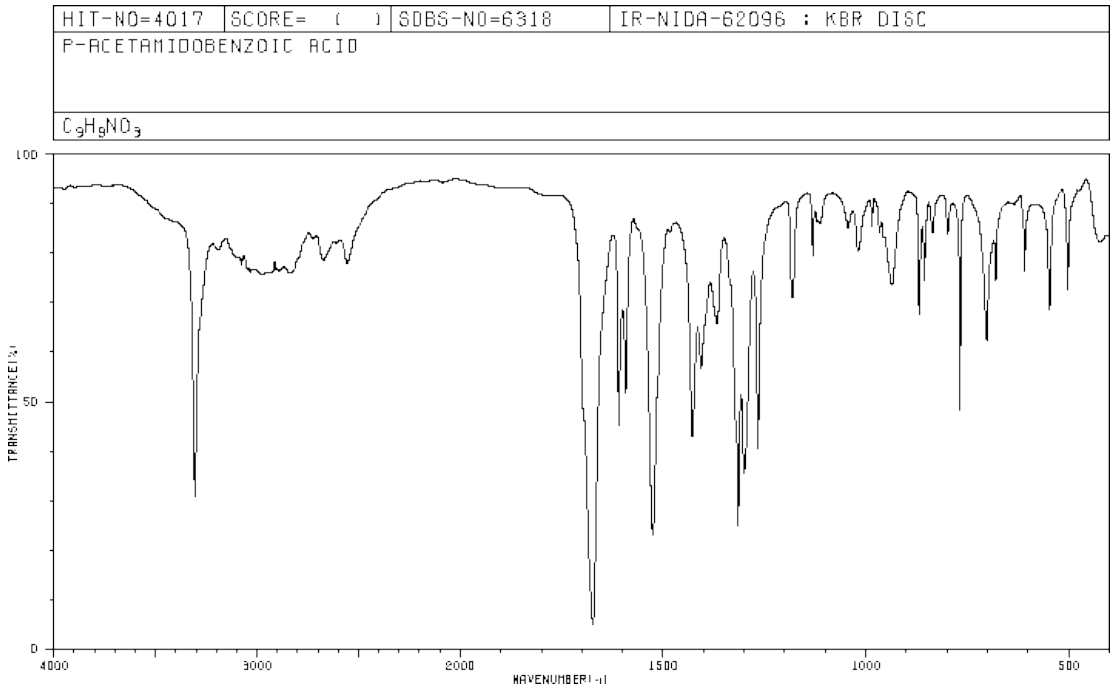
Infrared Spectrum of *p*-methylaniline (*p*-toluidine)



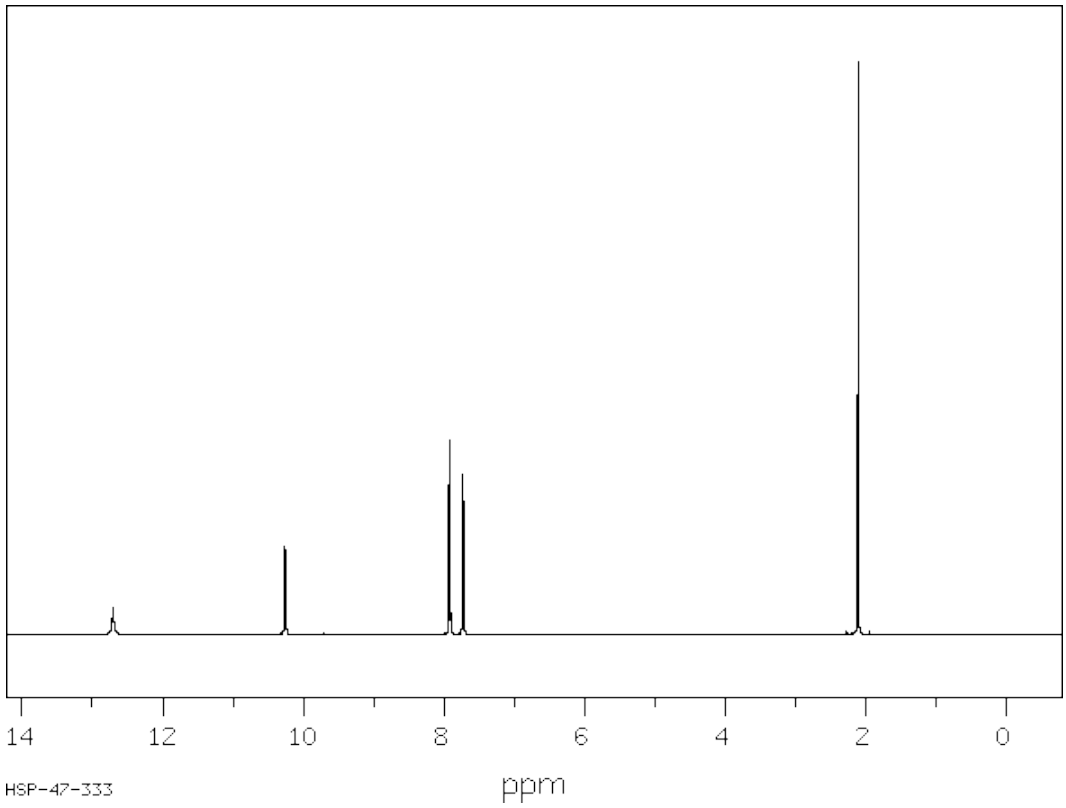
^{1}H-NMR Spectrum of *p*-methylaniline (400 MHz in $CDCl_3$)



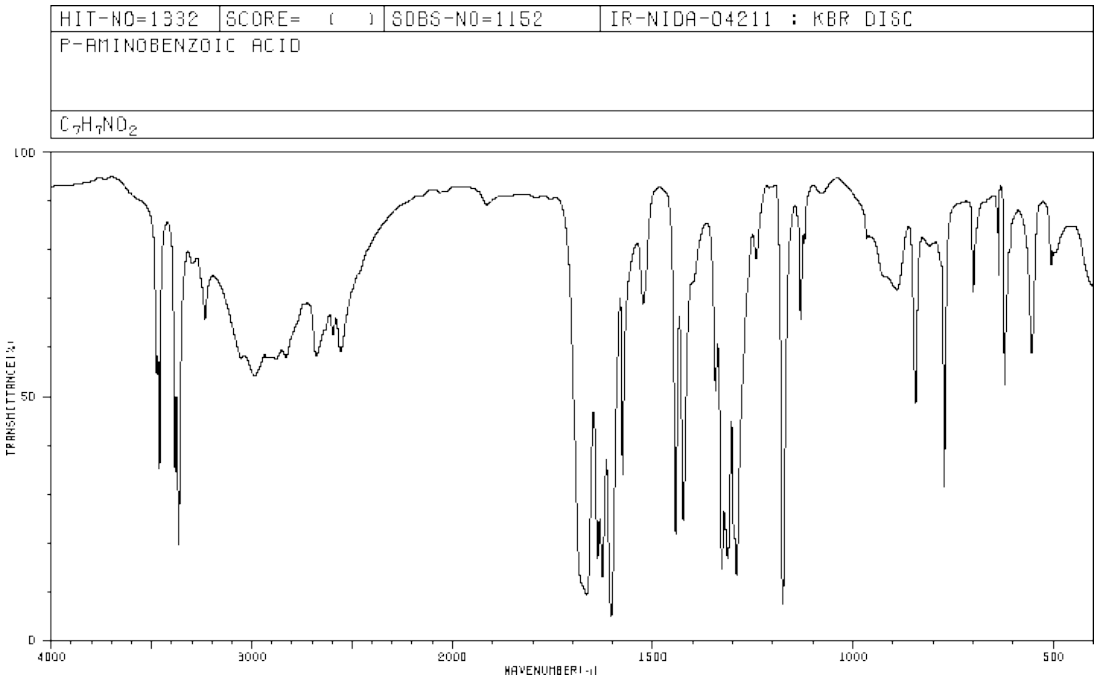
Infrared Spectrum of *p*-acetamidobenzoic acid



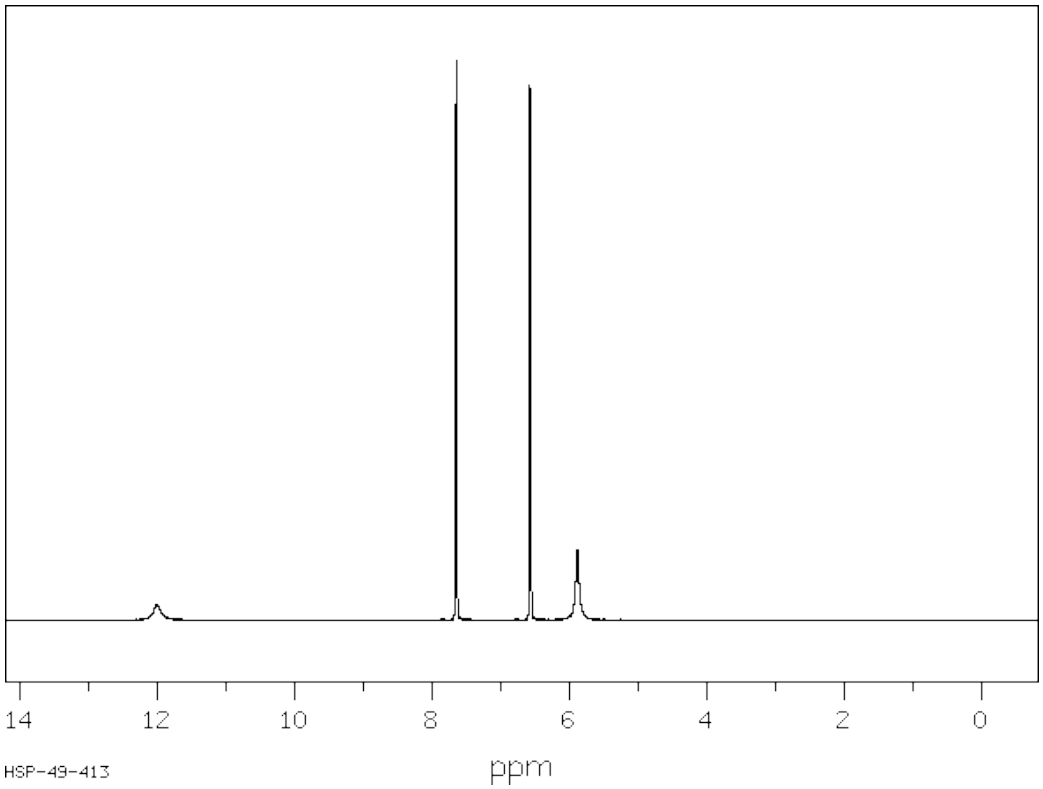
^{1}H-NMR Spectrum of *p*-acetamidobenzoic acid (400 MHz in DMSO-d_6)



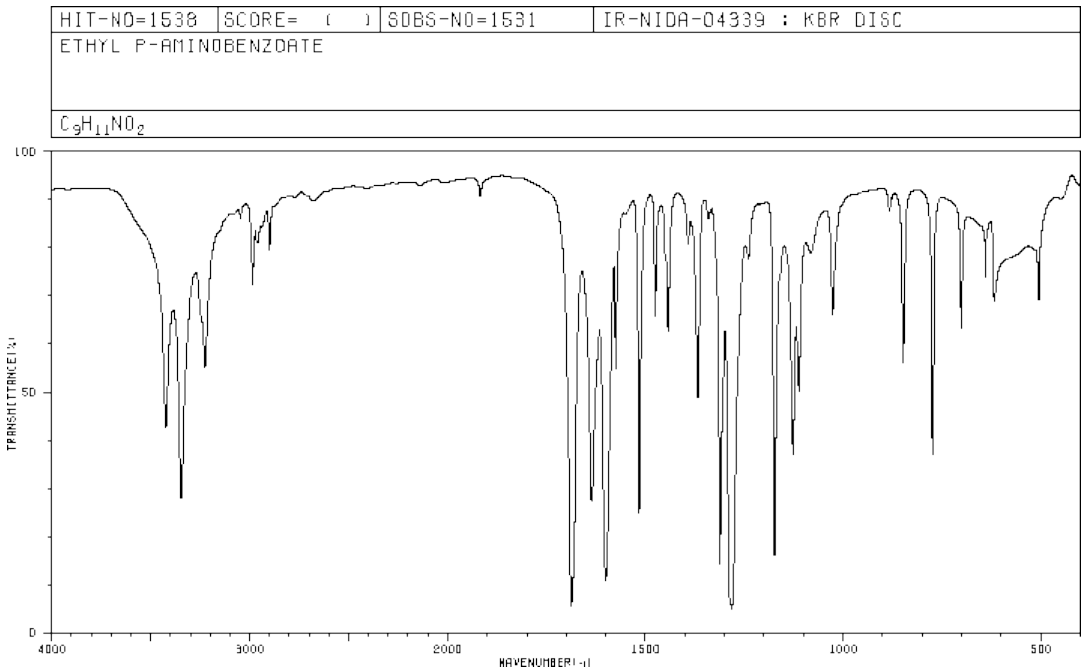
Infrared Spectrum of *p*-aminobenzoic acid



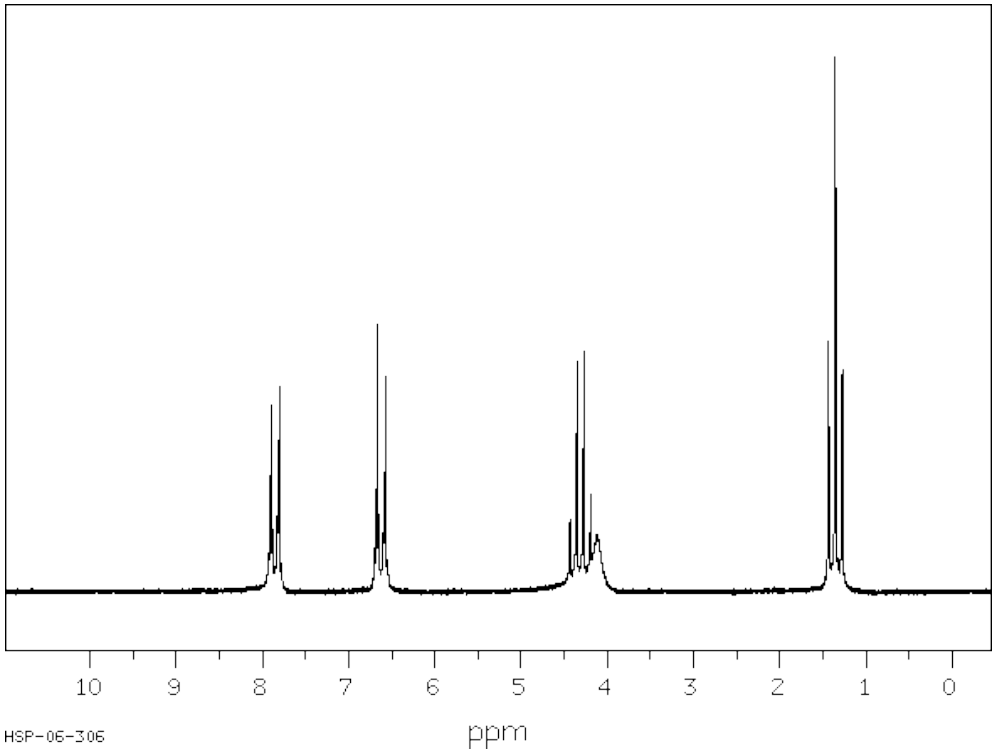
^{1}H-NMR Spectrum of *p*-aminobenzoic acid (400 MHz in DMSO-d_6)



Infrared Spectrum of Ethyl *p*-aminobenzoate (benzocaine)



^{1}H-NMR Spectrum of Ethyl *p*-aminobenzoate (90 MHz in $CDCl_3$)



Questions

Answers to be submitted with your report.

1. In Step 6 Part A, what is the purpose of adding sodium hydroxide to the reaction mixture?

2. In the discussion pertaining to the hydrolysis of 4-acetamidobenzoic acid, it was argued that the presence of the electron-withdrawing carboxyl group in the para position could result in the occurrence of some nucleophilic displacement if the hydrolysis was carried out under acidic conditions and an elevated temperature. What would the product of such a nucleophilic displacement reaction?

3. Write the balanced equation for the oxidation of 4'-methylacetanilide to 4- acetamidobenzoic acid as carried out in Part C of the synthesis.

4. Write the mechanism for the reaction of 4-methylaniline with acetic anhydride. What was the purpose of adding sodium acetate to the reaction mixture when you performed this acetylation in Part B of the synthesis?

CHEM 360 ORGANIC CHEMISTRY II

PREPARATION, PERFORMANCE, AND PRODUCT EVALUATION FORM

NAME_____ ID_____ DATE_____

exp#	PRODUCT SUBMITTED	DATE SUBMITTED**	QUANTITY (units?)	PRODUCT CHARACTERISTICS						EXPERIMENT GRADE	INSTR. INIT.
				APPEARANCE	M.P./B.P.	IR (Y/N)	TLC	OTHER	B.PRESS.		
10 (5 marks)	ESTER=						N/A				
	carboxylic acid=						N/A		N/A		
	alcohol=						N/A		N/A		
11 (0 marks)	FUNCTIONAL GROUPS	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
	ALCOHOLS AND ALKYL HALIDES								N/A		
12 (5 marks)	DIPHENYLMETHANOL						Rf=		N/A		
	DIPHENYLMETHANOL(crude)						Rf=		N/A		
	BENZOPHENONE						Rf=	N/A	N/A		
13 (10 marks)	ALDOL CONDENSATION*						N/A		N/A		
	aldehyde=						N/A		N/A		
	ketone=						N/A		N/A		
14 (0 marks)	IR/NMR TUTORIAL	N/A	N/A	N/A	N/A	N/A	N/A	Submit 4	N/A	N/A	
	Unknowns^^=										
15 (0 marks)	FUNCTIONAL GROUPS	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
	ALDEHYDES AND KEYTONES										
16 (10 marks)	TRIPHENYLMETHANOL					N/A	Rf=				
	TRIPHENOLMETHANOL (crude)	N/A	N/A		N/A	N/A	Rf=	N/A	N/A		
	MOTHER LIQUOR	N/A	N/A		N/A	N/A	Rf=	N/A	N/A		
	BIPHENYL	N/A	N/A		N/A	N/A	Rf=	N/A	N/A		
	Amt.Bromobenzene= , Amt.Ethyl benzoate=				N/A	N/A	N/A	N/A	N/A		
17 (~7 ea.) (20 marks)	4'-METHYLACETANILIDE	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A		
	4'-ACETOAMIDOBENZOIC ACID^				N/D	N/A	N/A		N/A		
	4-AMINOBENZIOC ACID^^					N/A	N/A		N/A		
	BENZOCAINE^^^					N/A	N/A				
	^Part C Amt. 4'-methylacetanilide used= ^^ Part D Amt. 4'-acetamidobenzioc acid used=			^^^Part E Amt. 4-aminobenzioc acid used=					Total= (/50)		

N/A= not applicable, N/D= not determined

*This form is the official results form for Chem360. To get credit for the lab it must be fully completed and then initialled by the instructor. Keep safe at all times.

**Lab reports are due 1 month after completion of each experiment. Late lab reports typically lose 10% per month late.

***This form will not be signed until the student has done a complete cleanup of their bench area.