Chemistry 350

Organic Chemistry I

Laboratory Manual 2019-21

Course team

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CHEM 350 Lab Manual Contents

CHEM 350 Lab Manual Contents (cont.)

Acknowledgements

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 particular needs of Athabasca University students in mind.

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The procedures described in this manual have been checked in our Athabasca laboratories by Jerry Pyrozko, Roger Klemm, Glen Conlin, and Robert Carmichael. Special thanks to Ms. Aimee Caouette for her help on the Infrared Spectrospcopy Tutorial (Summer 1999). The comments and suggestions received from the individuals mentioned above were greatly appreciated by the course co-ordinator.

The following sources are also hereby acknowledged:

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General Introduction

Welcome to the laboratory component of Athabasca University's *Chemistry 350 Organic Chemistry I*. This course, together with *Chemistry 360*, constitutes the equivalent of a second year university introductory organic chemistry course. Although the laboratory component of this course will involve a lot of work, we hope that you will find the experience both intellectually stimulating and enjoyable. One of the benefits of having a compulsory laboratory component in a course such as ours is that it gives students an opportunity to meet the course professor and other Athabasca University students. Such opportunities are rarely provided for the majority of AU students.

If you were to take a course such as *Chemistry 350* in a traditional college or university, you would probably be expected to attend a three-hour laboratory session every week for 10-13 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 24 hours of instruction, spread over three days. The special *CHEM350* Lab Session has 20 hours of supervised lab instruction, along with 20 hours of homework as outlined in the *CHEM350 Laboratory Report Book*. Students attending lab session in Athabasca can expect the following:

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 morning and an afternoon refreshment breaks. Regular breaks make it easier for you to concentrate while you are working, and will decrease the chances of an accident. We also recommend that you take a brief walk outside during a break to get some fresh air.

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. If you choose to mail in hard copies of your reports, remember to make backup copies.

Remember, if you have difficulty in writing your laboratory report, contact your academic expert through the Student Success Centre [fst_success@athabascau.ca] or the Science Lab Co-ordinator at (sciencelab@athabascau.ca or 780-675-6729).

Also remember to keep a duplicate copy of all your experimental results; as suggested in the "Writing Laboratory Reports" section.

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 1-4, making sure that you understand exactly what you will be doing, noting possible problems, and so on. The sections "Lab Registration" and "Organization" (which includes a suggested schedule for completing the labs) will, we hope, help you prepare for the lab sessions.

Lab Registration

To arrange to attend a laboratory session, please use our online booking form at: https://secure3.athabascau.ca/Labs/booking.php/

To use the online booking form, you will need to first check on the dates and locations of available sessions: For an up to date listing of the laboratory schedule, consult our web site at: http://science.athabascau.ca/Labs/schedules/organic-chemistry.php
(and select the appropriate year)

If you have any difficulties in using the form, please contact the Science Lab at: sciencelab@athabascau.ca

Students may change the dates they have selected right up to the day of the lab session. We only ask that you notify us of any change of plans, so that we do not worry unnecessarily over your whereabouts.

Note: the organic chemistry lab instructor has the right to refuse any walk-ins (i.e., students who have not registered).

Lab Exemptions

You may be eligible to receive an organic chemistry I lab exemption
http://science.athabascau.ca/Labs/exemptions/chemistry.php from this course.

Organization

The laboratory component of *Chemistry 350* comprises approximately 24 hours of supervised laboratory work. During this time, you will be expected to complete all of the following experiments listed below. You will notice a number in parentheses following the title of each experiment. This number indicates the maximum number of marks that can be obtained for each experiment. In addition, the instructors' continuous assessment will be worth a further 15 marks, giving a total of 100 marks.

1. Melting-point determinations (5)

2. Recrystallization (5)

3. Distillation (5)

4. Refractive index (5)

5. Extraction, separation and the use of drying agents (10)

6. Reactions of the common function group (Part 1: Hydrocarbons) and infrared spectroscopy tutorial (15)

7. Extraction of (+ or -) usnic acid (10)

8. Preparation of cyclohexene from cyclohexanol, or Methylpentenes synthesis (15)

9. Aromatic substitution: The nitration of acetanilide (15)
   (Total Marks = 85)

As you can see, a total of nine experiments are listed, and we may add others as we find it necessary to modify the course.

The *Chemistry 350* laboratory sessions may differ from other laboratory classes that you have attended, in that not all of the students present will be working on the same experiment at any given time. The main reason is that some experiments require the use of an expensive instrument, and it is not feasible for Athabasca University to provide every individual student with such an instrument. Thus, at any given time during the first laboratory session, you may observe three students working on Experiment 1 and six working on Exp. 2, while the rest of the class is working on Exp.3. The course is organized in such a way that many of the experiments can be completed in any order.

One notable exception to this generalization is that all students must complete Experiments 1 through 5 before proceeding to any other experiment.

The CHEM350 labs are available in several different formats: over 3 days straight, or in a 2.5 day special lab format.

Suggested Schedule for Completing the Labs (3 days)

Schedule 1

	8:30am	9am	10am	11am	12noon	1pm	2pm	3pm	4pm	5pm	
Day 1	Orient'n	Start Ex.3A and 3B		Start Ex.2..... ..	BREAK		Start Ex8			Cleanup	**Day 1**
									Start Ex.4		
Day 2	Complete Ex. 2		Start Ex.5.....		BREAK					Cleanup	**Day 2**
				Start Ex6A							
Day 3	...Start Ex. 9				BREAK					Cleanup	**Day 3**
		Start Ex.7					Ex 1	Compl. all analyses			

Schedule 2
(Special Labs)

Fri eve	**6 pm**	**7pm**	**8pm**	**9pm**	**10pm**						
Day 1	Orient'n	Start Ex.3A 3B			Ex4						**Day 1**
				Start Ex.2.....							
	8:30am	**9am**	**10am**	**11am**	**12noon**	**1pm**	**2pm**	**3pm**	**4pm**	**5pm**	
Day 2	Start Ex 8		.....		BREAK	Start Ex.5			Ex 6	Cleanup	**Day 2**
Day 3	.Complete Ex. 9				BREAK					Cleanup	**Day 3**
			Start Ex.7				Ex.1	Compl all analyses			

Note: The schedule requires the student to be prepared to do more than one experiment at a time. For instance, on Day 1 (Schedule 1), once Experiment 3 is in progress, the student may find the time to begin Experiment 2.

Materials to be Provided by the Student

When attending a *Chemistry 350* laboratory session, each student must provide himself or herself with the following items:

1. **a lab coat**. Lab coats can usually be purchased at college or university bookstores, at army surplus stores, and similar establishments. In case of difficulty, see "Uniforms—Retail" in the "yellow pages" of your telephone directory.

2. **safety glasses**. Safety glasses can usually be purchased at college or university bookstores, or at safety supply stores.

3. **an electronic calculator**.

4. **CHEM350 Report Book** (available online as a .pdf download via web page): http://science.athabascau.ca/Labs/resources/organic_chemistry.php or **a lab notebook**. A lab notebook should be bound. The preferred size is approx. 23.5 cm × 18.4 cm.

5. **a pen**, a pencil and a ruler.

Optional Materials to be Obtained by the Student

1. students may request a set of important reference pages from the *Organic Chem Lab Survival Guide* from the Athabasca University library. The survival guide you obtain may be the first or third edition. The relevant pages in the first or third edition of the survival guide worth reading are noted in each of the experiments. Please note a copy of the guide will be available in the lab.

2. a black 'Sharpie' marking pen for making labels.

Evaluation

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

Your lab reports must be legible and preferably typed.

Note that the penalties for plagiarizing laboratory reports are identical to those incurred for other types of plagiarism.

You must attain an average of 60% for laboratory work in order to pass the course. The grade for laboratory work, which is worth 20% of the overall *Chemistry 350* mark, is determined as follows:

Performance on assigned experiments	85 marks
Instructors' continuous assessment*	15 marks
Total	100 marks

*The lab instructors will assess each student for such things as preparedness, ability to solve unexpected problems, efficiency, competence in handling glassware and chemicals, etc.

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 mailed to your academic expert within 1 month of your last supervised laboratory session. Twenty years of statistics show that late lab reports show a drop of 10% for every month they are late. Thus student who send in their lab reports **four months late typically 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 350* laboratory component.

Laboratory Academic Conduct

Acknowledging Others' Work (see also in Moodle)

In the definitions, most short-answer questions, and the examination for this course, you are expected to summarize or paraphrase the material that you have learned in your own words. You are not expected to provide formal references to the textbook **or Lab Manual**. However, for some short-answer questions, you may wish to quote from the textbook, following the quoted material with an in-text citation; for example, "(Smith, 1996, p. x)." **If you use more than three consecutive words from the textbook** or any other source, you must use quotation marks and provide a citation.

If you use any other source (e.g., another textbook, a dictionary, encyclopedia, journal article, or Internet source) for any of your TMA **or Lab Report** answers, you must acknowledge the source following the paraphrase or quote. Appendix B of the Study Guide provides examples of a suitable bibliographic style. Note that for Internet sources, you must also indicate the authors (even if you must use "Anonymous"), the date on which the item was posted to the Internet (if given), the title, the URL (**http://www**, etc.), and the date on which you retrieved the material. See also Chapter 10 of A Handbook of Biological Investigation . Quotations should amount to less than 10% of any answer.

Remember that using old assignments **or lab reports**, your own or those of other students, and plagiarism (presenting others' work as your own) are forms of intellectual dishonesty. Such behaviour will not be tolerated at Athabasca University. In this course, students who engage in such actions will receive a grade of zero for an entire lab report or the whole course. Cheaters will get no "second chances"; plagiarism in an assignment will result in a grade of zero, and no supplemental will be allowed. Review the sections of the Student Manual and the Athabasca University Calendar that deal with intellectual indebtedness, plagiarism, and academic misconduct. The policies that govern students at Athabasca University are presented under the "Student Services" tab of your my AU portal.

The following are the regulations as quoted from Section 10 of our Athabasca University Student Academic Misconduct Policy (**SAMP**). Please note the bolded sections.
http://calendar.athabascau.ca/undergrad/page11_02_new.php#plagiarism

10.1.2.2 Plagiarism

Plagiarism involves submitting or presenting work in a course as if that work were the student's own, when, in fact, it was not. Often plagiarism exists when:

1. the work submitted was done in whole or in part, by an individual other than the person submitting the work
2. the whole or parts of a work are taken from another source without reference to the original author, publication, journal or Internet source
3. the whole or parts of the coursework submitted lacks citations even though a list of sources is provided
4. the coursework has been copied in whole or in part from an individual, a textbook, a solution manual, the Internet or any other source
5. when paid or professional editors are used inappropriately.

Students are encouraged to contact the individual to whom their coursework is being submitted to discuss their plan on the use of an editor prior to submission of their coursework.

Anyone found guilty of plagiarism under this policy may be subject to Section 5 Penalties within this policy.

10.1.2.3 Cheating

Cheating includes:

1. submitting a proposed invigilator for approval under false pretences. This includes, but is not limited to:
   - naming one's friend, relative, fellow student or co-worker for approval
   - submitting false credentials, names, occupations, and addresses
   - the misrepresentation of other information related to a proposed invigilator
2. writing an invigilated examination or any part of an invigilated examination outside of an approved invigilation centre
3. removing, by any means, an examination or any part of an examination from an approved invigilation centre
4. communicating substantive content of any examination to course mates or others
5. in the course of writing an examination, obtaining or attempting to obtain information from another student or other unauthorized source, or giving or attempting to give information to another student, or knowingly possessing, using, or attempting to use any unauthorized material and/or electronic devices
6. leaving answer papers exposed to view, or attempting to read other students' examination papers
7. representing or attempting to represent oneself as another or having or attempting to have oneself represented by another in the taking of an examination, preparation of coursework, or other similar activity
8. submitting in any course or program of study without prior approval, all or a substantial portion of any coursework for which credit has been received or is being submitted in another course or program at AU or elsewhere
9. submitting in any course or program of study (including those courses in a clinical or laboratory setting) any coursework (including laboratory results) containing a false statement(s) intended to be perceived as fact(s), or a reference that has been fabricated
10. accessing course materials or notes pertaining to the subject matter of the course or accessing internet sites during a scheduled examination when the exam prohibits access to such materials

Anyone found guilty of cheating under this policy may be subject to Section 5 Penalties within this policy.

10.1.2.4 Collusion
Collusion involves two or more persons who, by agreement between them, prepare and submit the substantially same or identical piece of coursework, claiming that it is the work of only the person submitting it, without the prior permission of the person to whom the coursework is being submitted.
Anyone found guilty of collusion under this policy may be subject to Section 5 Penalties within this policy.

10.1.2.5 Unauthorized Use of AU Materials
It is an offence to knowingly procure, sell, distribute, duplicate, transpose or receive any course material such as examinations, tests, quizzes, assignments, or laboratory results from any source without the proper written consent of Athabasca University except where licensing agreements permit otherwise.
Anyone found guilty of unauthorized use of Athabasca University materials under this policy may be subject to Section 5 Penalties within this policy.

AU Policy Regarding Laboratory Academic Conduct

All laboratory reports (both present and past) are unauthorized aids and making use of them in any way constitutes an academic offense (ref: SAMP Section 10.1.2.2.1 and 10.1.2.2.4, 10.1.2.3.7 and 10.1.2.3.10, 10.1.2.4 and 10.1.2.5)."

Undergraduate students are allowed and encouraged to discuss experimental data with one another, but students must be ever cognizant of the AU SAMP policy and realize the fact that every student is required to write an individual report. NO CONSULTATION OR COLLABORATION BETWEEN STUDENTS IS ALLOWED IN THE WRITING OF LAB REPORTS. This policy also applies to any required pre-laboratory preparation.

A mark of zero for the entire lab component of the course will be the penalty for any student found to have committed and academic offense as set out in the SAMP, if the offense was pertaining to plagiarism.
For more information please consult the following website:
http://calendar.athabascau.ca/undergrad/page11_02_new.php#plagiarism

Refer any questions concerning the Laboratory Academic Conduct policy to your laboratory instructor."

Writing Laboratory Reports

The first key to obtaining good marks on laboratory experiment reports is to keep a neat and organized Lab Report Book. Prepare your Report Book 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 and Introduction	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 350*, 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 take into account 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 350 Laboratory Manual* contains a section discussing the approach to be used when writing-up that particular experiment. In general, each report should include the sections outlined below.

Note: You are using the **CHEM350 Report Book**, but still read the following pages and follow the suggestions for filling in your preformatted lab reports.

Organic Chemistry 350 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 table 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 (g/mol)	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 in order to determine your % yield.

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

Procedure	Observations
Equipment and Glassware Preparation	All clean and dried with acetone
Recrystallize Impure Solid	-6.35 g, beige with yellow coloured flecks
1. Select the solvent	-sol in hot n-hexane, insoluble in cold n-hexane
2. Dissolve in a minimum of hot solvent	-50 mL of solvent required solution, sl. yellow
3. Decision time? Hot gravity filter or not?	- charcoal added, and hot gravity filtered. Filtrate clear and very faintly yellow, vol aft.= 55 mL
4. Slow cool and place in ice-water bath	- white crystals formed before placed in bath
5. Collect the crystals and air dry to a constant weight	- shiny white flakes mass of product = 3.22 g
Recrystallized Product	

5. References:

Use an acceptable scientific journal style/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.

If you are using the CHEM350 Report Book, fill in all the boxes in the tables provided! Show sample calculations. Remember there is a difference between % recovery yield calculations (Exp. 2,3,5,7), and % Yield calculations where you must determine limiting reagents and a theoretical yield (Exp. 8 and 9).

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.

Discussion (cont.)

Next discuss the **yield and purity** of the product(s) you recovery/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 have to 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 academic expert for marking. If you do not know who is your academic expert, then scan to .pdf and submit your lab reports to fst_success@athabascau.ca]

Finally, in most laboratory courses, a student is expected to submit her or his laboratory reports in a bound notebook. With the Athabasca University system this is not practical. Mailing costs would be too high, and there might be a problem with getting notebooks returned. Thus, you should adopt the procedure outlined below.

1. All your results, observations, etc. should be recorded directly in your bound laboratory Report Book. This takes the place of a notebook and is your permanent record of work carried out in the laboratory. (**Note:** your results will also be recorded and initialled on a Product Evaluation Form kept by the lab instructor.) How you choose to finish this Report Book is up to you, as it will not be submitted to or graded by your lab instructor. However, in the event of some future discrepancy, you may be asked to produce the original Report book or other notebook for inspection.

2. Print off the Report Book and write your reports on loose-leaf paper (21.5 cm × 28 cm) and submit by mail or e-mail (scan to .pdf) or in the Moodle dropbox for marking by your academic expert. Be sure to number the pages and write your name and the number of the experiment on each page. Should your reports get lost in the mail, you will still have your results recorded in your notebook and the report can be re-submitted. Please include your address and telephone number with your reports. **Hint:** Remember to photocopy your lab report(s) before mailing them to your tutor.

Weights, Volumes, Measurements and Calculations

SI units and the metric system are used in chemistry.

Measurement	SI Unit	Conversion Factors
Length	Metre (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* = $1.6605402 \times 10^{-24}$ 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 metre (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 actually recovered in an experiment. This number is used to calculate the percentage yield (see below).

***Note:** 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.

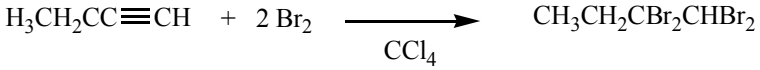
Theoretical Yield

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 is reacted with 3 mL of a 2% solution of bromine in carbon tetrachloride, yielding 0.35 g of tetrabromonated product.

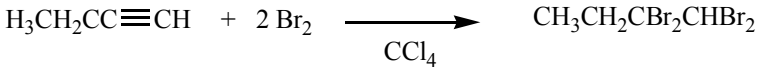
To determine the limiting reagent, the first step is to write out the molecular/chemical formula and then calculate the molecular or formula weights for the reactants.



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**	
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. = 2 %		
Moles = 0.000185 mol		Moles = 0.000375	Moles =?
Molar Equiv = **1.85×10^{-4}**		Molar Equiv = 1.88×10^{-4}	

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

% Yield Calculation

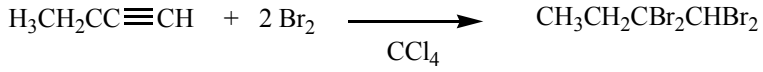
The percentage yield is one of the most important calculations to learn in organic chemistry. It is a measure of the efficiency of the reaction procedure, and is determined by comparing the actual yield to the theoretical yield:

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

There are six steps in the calculation of the % yield for a reaction. 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 our example.



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	%wt. = 2 % soln	Amt Used = 3 mL	Yield = 0.035 g
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:

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

% 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 the % content of the starting material that is the compound of interest or 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

In 1975, a survey carried out by Her Majesty's Inspectors of Schools showed that of the 70,000 accidents reported in British schools, only two per cent occurred in a science laboratory. Although Athabasca University students are not attending laboratory sessions in Britain, and are more mature than most school-children, this statistic is relevant to the laboratory component of *Chemistry 350*. The figures suggest that, although a laboratory is a potentially dangerous place to work, the chances of an injury-causing accident are relatively low. This situation exists because of the strict safety rules that are applied to students working in laboratories, and because of a willingness of both students and instructors to look out for unsafe practices and possible hazards at all times.

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 be worn in the laboratory at all times.** Wearers of prescription glasses may wear their own spectacles, 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 be worn at all times—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 comes into contact with 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 worn at all times.** You must purchase a lab coat in order 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 in the event that you inadvertently spill a chemical.

   While we are on the subject of clothes, dress sensibly. It can become very hot in the laboratory and you will not be comfortable working all day with a three-piece suit worn underneath your lab coat. Similarly, clothes worn in the laboratory tend to acquire a "chemical odour", and it may be advisable to leave your more expensive shirts and sweaters at home.

3. **Protect your feet by wearing "sensible" shoes.** 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. in the event that 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 350* 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 in the accident book. 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 350* 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. Wear your lab coat at all times 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. In the event of a real emergency, it could be important for medical personnel to know certain facts about you, facts that they could not obtain if you were unconscious or in a severe state of shock. On the next page is a copy of a *Medical Information Form* that you should have received either with this laboratory manual, or separately in the mail. We advise you to fill out the form that you received, and paste it inside the front cover of your lab notebook. You might regard some of this information as being rather personal. However, keep in mind that normally we do not expect you to show us your lab notebook (see "Writing Laboratory Reports") so confidentiality of your medical history should be maintained. If you still have doubts, keep in mind that, in the event of an accident, your instructor has been asked to put your lab notebook on your stretcher as they carry you off to the hospital.

15. As mentioned in the safety rules, all accidents that result in injury must be reported and recorded in the accident book. In addition, an "Accident Report Form" must be completed and returned to the course co-ordinator. A sample form is shown on the page after next.

Note: The *Medical Information Form* on the next page is adapted from one suggested by Ben Ruekberg and David W. Ball, *Journal of Chemical Education*, 63, **A247** (1986).

CHEMISTRY LAB SAFETY DO's and DON'TS

Before You Attend a Chemistry Lab	
DO's	**DON'T's**
Read your lab manual 'Safety' section.	Think that ignorance is bliss.
Know the procedures.	Forget your lab manual and rely on your memory.
Know the dangers.	Have a casual attitude.
Bring a lab coat.	Wear your best clothes.
Be well rested and alert.	Sleep-in and arrive late.
Fill out the Medical Information Form in your lab manual or inform the instructor of any personal medical condition.	Hide a medical condition that might jeopardize your safety or the safety of others.
Some people will approach the laboratory component of their AU chemistry course with a certain amount of trepidation. In a sense, this is a good thing because: **NO ONE SHOULD EVER ADOPT A COMPLACENT ATTITUDE TOWARDS LAB SAFETY**	

During a Chemistry Lab	
SAFETY DO's:	**SAFETY DON'T's:**
Keep your workbench neat and organized.	Place full reagent flasks near the edge of the bench.
Label all reagents/containers.	Mix unknown chemicals.
Read the MSDS for a hazardous chemical.	Forget WHMIS stands for Workplace Hazardous Materials Information System.
Ask how to discard used reagents.	Pollute the environment.
Wear your safety glasses at all times.	Take off your safety glasses or touch your face with soiled latex gloves.
Report accidents to the instructor immediately.	Attempt to clean up a spill by yourself or leave the lab to treat an injury by yourself.
Take a rest break now and then.	Be in a rush to finish.
AN EXPERIMENT DONE WELL IS... AN EXPERIMENT DONE SAFELY.	

Sample Medical Information Form: *Chemistry 350*

Name: A. Student

Social Insurance Number: 123 456 789

Address: 4812, 43rd Street, Small Town, Alberta

Phone: 675-6111

Alberta Health Care Number: 987.65.432.123

Age: 35

Sex: M

Height: 173 cm

Weight: 68 kg

Chronic medical problems: Epilepsy

Current medical problems: None

Do you normally wear contact lenses? No

Physical disabilities: Partially deaf

Allergies to medication: Allergic to penicillin

Current medication being used: None

Personal physician: Dr. V. Rich

In case of emergency, please contact: Susan Student (wife) 675-6111

Special information: My religious beliefs prevent me from accepting a blood transfusion.

Chemistry Laboratory Accident Form (Student Labs)

Name of injured student: Alan Student

Date of incident: April 1, 2006

Time of incident: 2:06 p.m.

Course: *Chemistry 350*

Instructor: A. Tutor

Nature of injury: Glass tubing penetrated palm of right hand.

How injury incurred: Student was attempting to insert glass tubing into rubber stopper without using recommended lubricant.

First aid rendered: Wound was washed thoroughly, a piece of glass appeared to be embedded in the hand. Pressure applied around the wound using a ring pad. Covered with built-up dressing.

First aid rendered by: A. Tutor (instructor), G. Help (student)

Further medical treatment sought? (if yes give details). Patient was driven to outpatients at the nearest hospital where the wound was examined and the embedded glass removed.

Instructor's comments: Student returned to lab at 4 p.m. to collect belongings. His wife had been contacted and she came to drive him home.

Was instructor in the room when the incident occured? Yes

Student's signature: A. Student

Follow up (course co-ordinator): Contacted student by phone (April 3), his condition is now being monitored by his family physician.

WHMIS

On October 31, 1988, the Workplace Hazardous Materials Information System (*WHMIS*) went into effect. This is a national system intended to provide laboratory personnel with uniform information on chemicals used in the workplace. 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.

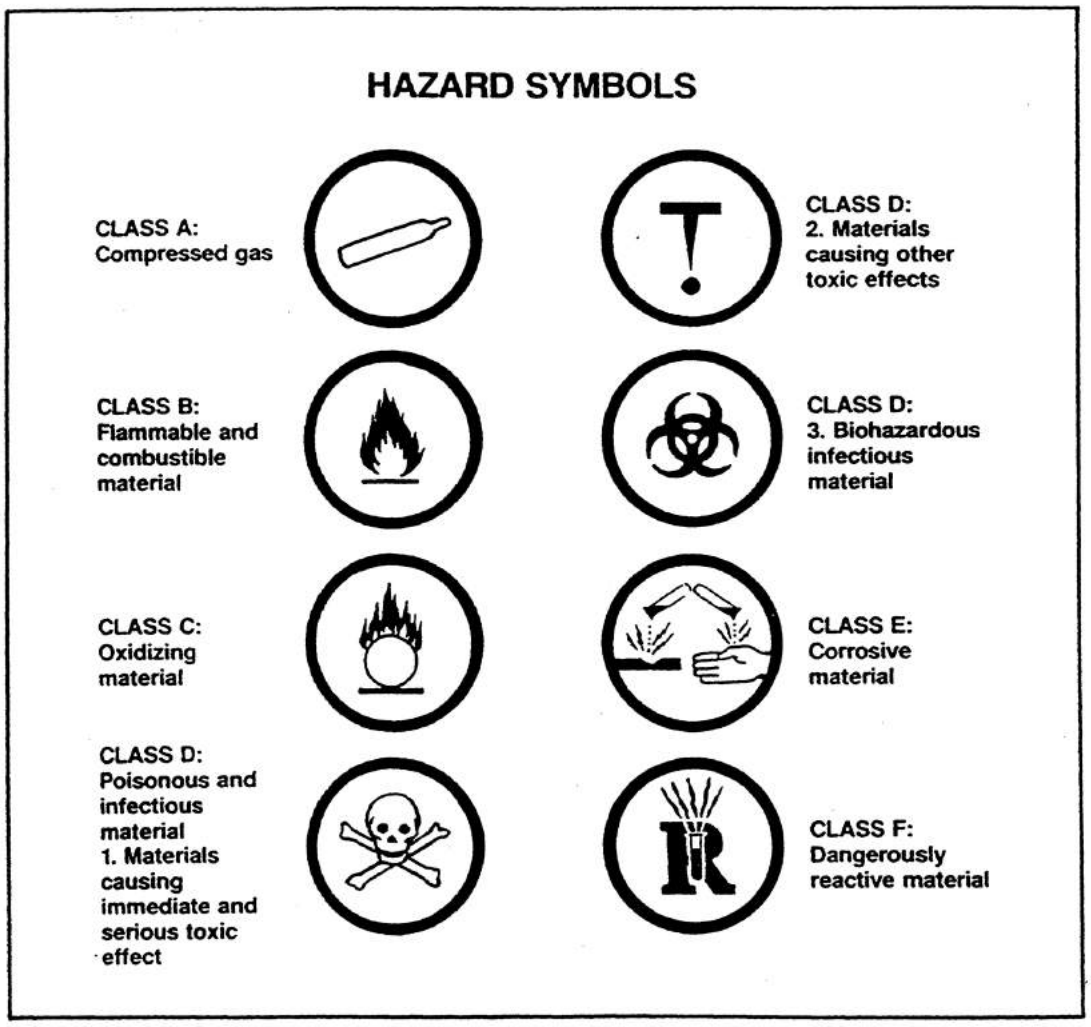
2. The manufacturer must provide the consumer with a Material Safety Data Sheet (*MSDS*) for each hazardous product. These sheets give complete details on the possible health effects that exposure to the product can produce, preventive measures that should be taken, etc.

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 350* 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.

Note: Athabasca University is now requiring all lab students take a certified WHMIS Training course (either with us or show proof that you have take one elsewhere).

Hazard Symbols

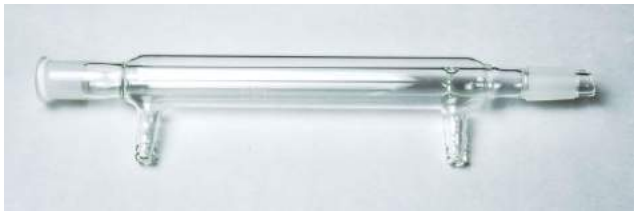


Common Apparatus

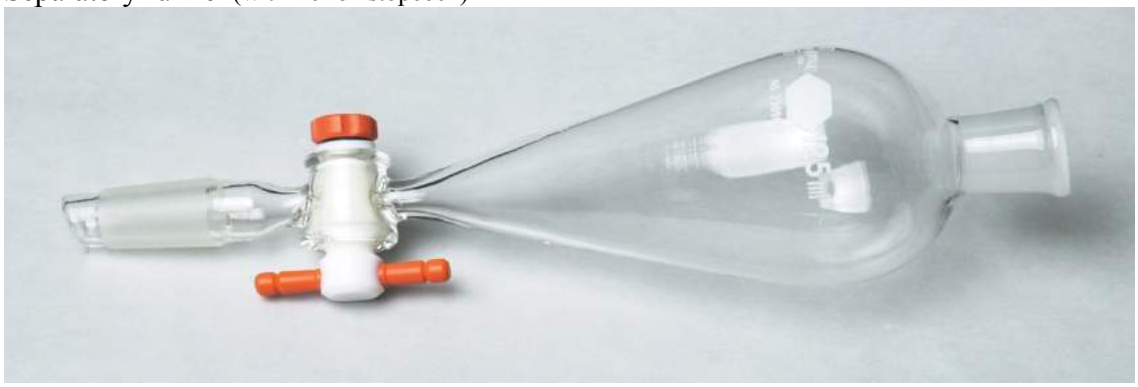
We assume that you are already familiar with the common apparatus found in a general-chemistry laboratory; however, you may not recognize some of the items of glassware that are used in organic chemistry. The following pages illustrate the glassware that is included in the kit that you will be given. Please endeavour to familiarize yourself with the name of each item **before** you attend your first laboratory session.

Condensor (West)

Distilling Column (Fractionation Column – without and with fractionating material, glass beads, inside)



Separatory funnel (with Teflon stopcock)



Connecting Adapter (three way adapter, still head)

Claisen Adapter

Pennyhead Stoppers

Vacuum Adapter

Flat bottom dish

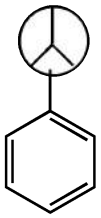
Round bottom flasks

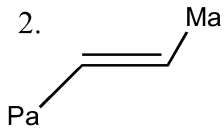
Lab jack

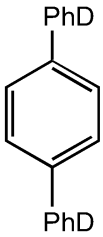
Thermometer Outlet Adapter

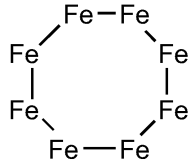
☞◆■CHEMISTRY350 ☞◆■ FunPage

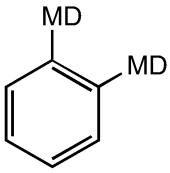
Name these most unusual compounds:

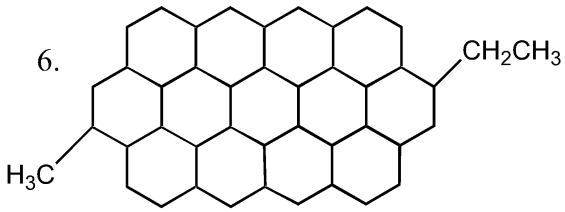
1. 

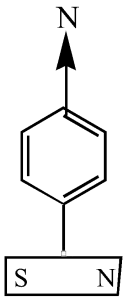
2. 

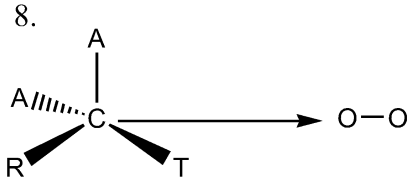
3. 

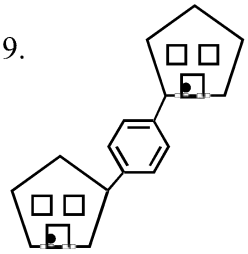
4. 

5. 

6. 

7. 

8. 

9. 

Answers:
1. Mercedes Benzene
2. Trans Parents
3. Paradocs
4. Ferrous wheel
5. Orthodocs
6. Ethylmethyl chicken wire
7. Paramagnetic benzene
8. Two Oxygen pulling A CART
9. Para Pentahouses

Experiment 1
Melting-point Determinations

Preparation

Before you come to the laboratory you should have read the whole of this experiment.

You may also wish to read, Chapter 9, "The Melting-point Experiment", in *The Organic Chem Lab Survival Manual* (Chapter 12 in the third edition).

Objectives

1. This experiment is designed to introduce you to the use of a typical "melting-point apparatus". Which of the numerous types of "melting-point apparatus" you will use may depend on the location at which you carry out the laboratory component of this course. You will use the "melting-point apparatus" repeatedly throughout this course.

2. To demonstrate that pure compounds have "sharp" melting points; that is that pure compounds melt over a small temperature range.

3. To demonstrate how an impurity lowers the melting point of a substance and broadens its melting range.

4. To illustrate the use of the "mixed melting-point" procedure.

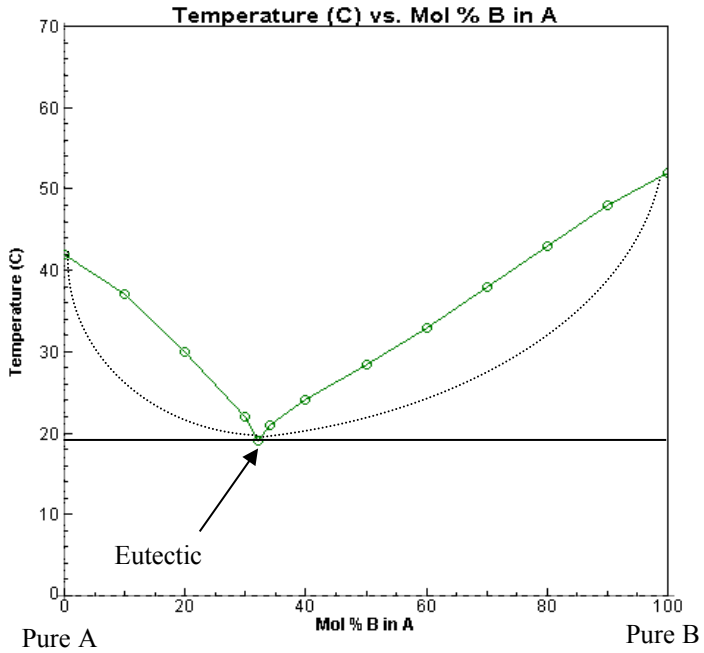
Introduction to Melting Points

Despite the increased use of spectrophotometers over the last 30 years or so, the determination of a compound's melting point is still one of the most common techniques used to assist in the identification of unknown compounds and assessing the purity of a given sample. The melting point of a compound is a unique property of that compound. Most organic compounds melt below 300° C. Contrast this with the very high melting points of inorganic compounds; e.g., the melting point of sodium chloride is 801° C).

The melting point occurs when a compound is at the temperature at which the solid and liquid phases are in equilibrium at a pressure of 1 atmosphere. Most pure organic compounds melt over a 'sharp and narrow' range of one or two degrees Celsius, hence, the term **"melting range"** is more appropriate than "melting point". **Note**: The small temperature difference observed between the temperature at which a compound starts to melt and that at which the compound is liquid is caused by 'heat transfer'. It takes a little time for the heat to transfer from the heating block, through the glass of the tube, and into the organic sample.

When an organic compound is impure, its melting point is lowered and broadened (>3° C range). Determining the melting point of a product at the end of an experiment gives us an approximate idea of its purity, because the melting point decreases ''almost' linearly as the amount of impurity increases (see Figure 1.1 below). **Note**: in Fig. 1.1, the distance between the dashed and solid lines indicates the melting range.

Figure 1.1 Melting Point Phase Diagram



Eutectic Points and Mixtures

Note the low point in the melting point phase diagram (Fig. 1.1). It shows that there is a minimum melting point for a mixture of these two compounds, and it occurs at a very specific ratio of mixtures of compound A and B. This point is called the **eutectic point** or eutectic temperature. The **eutectic mixture** is the composition of the mixture of A and B at the eutectic point (in this case, 68% A, 32% B). At the eutectic point, both compounds are melting simultaneously, resulting in a sharp melting point rather than the broad melting point typically seen for impure compounds. **Note:** Expect all mixtures of two different compounds in this lab course to exhibit a broad melting range. We have not given you any eutectic mixtures, only impure compounds!

Mixed Melting Points

We can use a procedure known as a "**mixed melting-point**" to help find the identity of an unknown compound. Suppose we suspect that a given "unknown" compound is benzoic acid (m.p. 120–121°C). First, we determine the compound's melting point, and let us suppose that we find it to be 118–119°C. This is quite close to the expected value, so the compound could well be benzoic acid. However, there are probably hundreds of organic compounds that melt in the range 118–121°C. (See "Melting Point Index of Organic Compounds" in *The Handbook of Physics and Chemistry* to verify this fact.)

How can we determine whether or not our compound is benzoic acid? What we do is to obtain a genuine sample of benzoic acid from the stockroom and mix a small amount of this pure substance with our "unknown" compound. If the melting point of the mixture so formed is still 118-119°C, we know that the unknown compound was benzoic acid—all we have done is to mix benzoic acid with benzoic acid, so that the melting point remains unchanged. If the "unknown" was not benzoic acid, then the benzoic acid that we have added acts as an impurity, and the melting point of our unknown will be lowered. It should also melt over a much broader range.

Finally Some Melting Point Hints

- Use a small amount of sample in the melting point tube. Over-filling the tube will cause it to heat unevenly and result in broader ranges (and a false indication of impurity).
- Pack your sample well. Loose sample will heat unevenly with the results described above.
- Be prepared to make multiple melting point determination of a sample.
- Once a sample has been melted, discard it. The sample may have decomposed, oxidized or rearranged ('polymorphed') during heating and cooling.

Using the Electrothermal Melting-point Apparatus

As we have indicated earlier, there are several types of "melting point apparatus" on the market. Here we will describe the Electrothermal melting-point apparatus, Model IA6304. *The Organic Chem Lab Survival Manual* describes two other commonly used types of melting point apparatus, as well as the more primitive Thiele tube. Assume that you will be using the Electrothermal apparatus, unless you are informed otherwise.

A diagram of the Electrothermal melting-point apparatus is shown in Figure 1.2. The apparatus consists of the following components:

1. A base which houses the main controls and a transformer. The base also contains two receptacles which can be used to store new and used melting point tubes. We ask that you use these receptacles only for new melting point tubes. Used tubes should be placed in the garbage bin reserved for broken glass.

2. An upper panel which houses the "fine temperature control" and the optical system for illuminating and viewing samples.

3. A block to accommodate the thermometer and up to three samples. Note that if only one sample is being investigated, the other two positions in the block must be occupied by empty tubes.

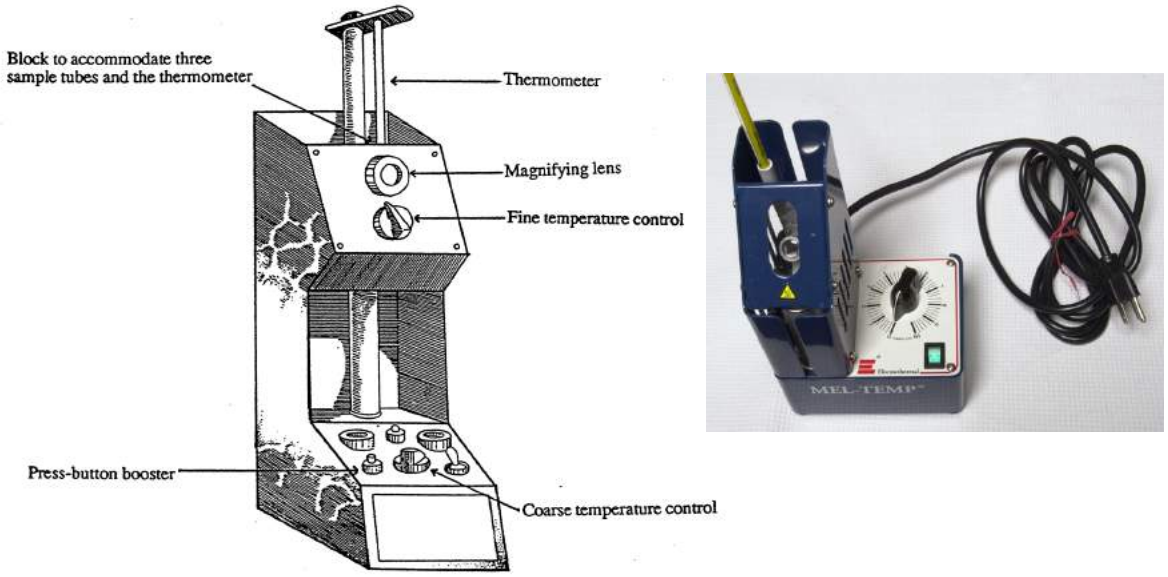


Figure 1.2. Electrothermal and Mel-Temp melting point apparatus

If the approximate melting point of the sample is known, the apparatus may be heated rapidly to within 40°C of the anticipated melting point. Rapid heating can be achieved by setting the fine control to its maximum setting, and adjusting the course temperature control to the appropriate position, using Table 1.1 as a guide. The figures given in this table are the times taken (in minutes) for the block to reach a given temperature at the various switch positions.

Table 1.1: Heating rates for Electrothermal melting-point apparatus, IA6304

	Course Switch Position (Fine Switch at Max Setting)							
Temperature Reached, °C	1	2	3	4	5	6	7	8
50	5	3	2	1.5	1	0.8	-	-
100	-	9	6	4	3	2.5	2	-
150	-	-	-	7	5	4	3	2.5
200	-	-	-	-	8	5.5	4	3.5
250	-	-	-	-	-	8	5.5	4.4
300	-	-	-	-	-	-	9	5.5
350	-	-	-	-	-	-	-	10

Once the temperature of the block is within 40° C of the anticipated melting point, the heating rate is adjusted using the "Fine Temperature Control" so that the temperature increases at a rate of *not* more than one to two degrees centigrade per minute. **Do not be impatient!** A higher rate of temperature increase will result in a melting point that is too high. The sample tubes should be inserted in the heating block when the temperature of the block is about 5° C below the anticipated melting point.

Observe the sample through the illuminated magnifying lens. You may be able to observe **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.

Not all samples will behave in this ideal manner. The range that you should record is that for steps 2-4; i.e., from the first sign of liquid formation to the formation of a completely clear liquid.

If the melting point of the sample is unknown, you will need to employ a slightly different procedure from that described above. Your first step will be to determine the approximate melting point by carrying out a "preliminary run," employing a rapid rate of heating throughout. Once the approximate melting point has been determined, you may proceed as described above.

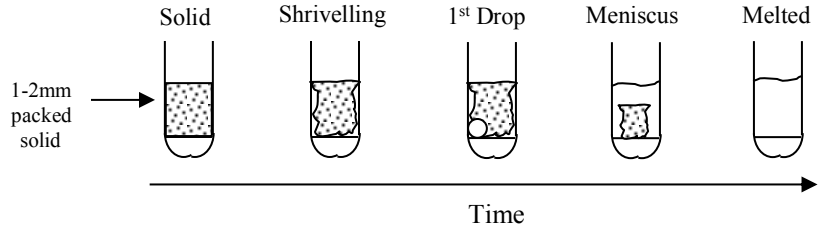
If you have a series of melting points to determine, it is advisable to do the sample with the lowest melting point first, the second lowest melting point next, and so on. This strategy will eliminate the necessity of having to allow the apparatus to cool down between determinations. The approximate times required for the apparatus to cool down between certain temperatures are given in Table 1.2. **Note: cooling times can be lessened by blowing air gently into the heating block area of the mp apparatus, using a piece of rubber tubing and some compressed air.**

Table 1.2: Cooling Times for the Electrothermal Melting Point Apparatus

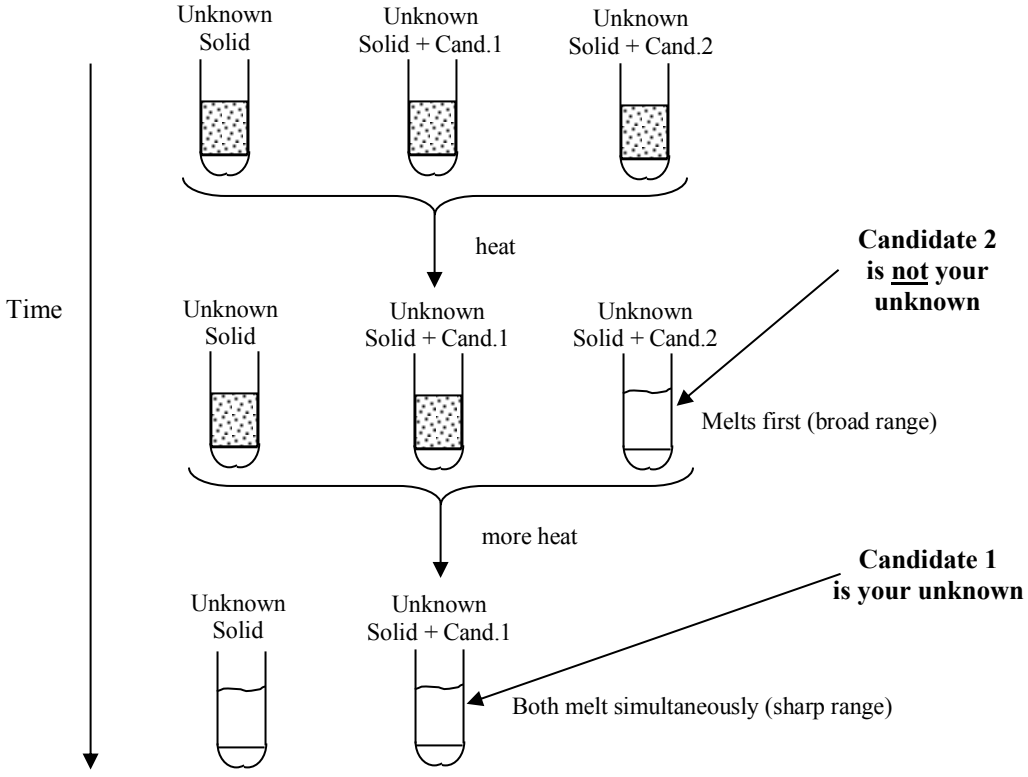
To cool	from	to	requires
	360°C	300°C	1.5 minutes
	300°C	200°C	3.0 minutes
	200°C	100°C	4.5 minutes
	100°C	40°C	7.0 minutes

Experiment 1 Background Information

This experiment contains two parts. In the first part, you will determine the melting point of an unknown, then check with your instructor on the accuracy of your reading. In the process you will learn how to fill a melting point tube, how much sample to place into the tube, how to operate the melting point apparatus. Finally, you will observe the four stages of a melting point.



In the second part, you will determine the identity of an unknown compound using the mixed melting point procedure. Note that you have been provided with two candidate identities for your unknown compound. The quickest way to determine the identity of your unknown is to prepare three melting point tubes, the first containing your unknown, the second your unknown mixed with candidate 1, and the third, your unknown mixed with candidate 2. Read all three tubes simultaneously in the melting point apparatus. Eventually one of the mixed tubes will begin to melt. This is the candidate that your sample is **not**. Finally, two of the tubes will melt simultaneously. This candidate, which you've mixed your sample, is the identity of your unknown.



Chemicals, Equipment, Utilities Required:

All equipment used for melting points must be clean and free of any organic contamination.

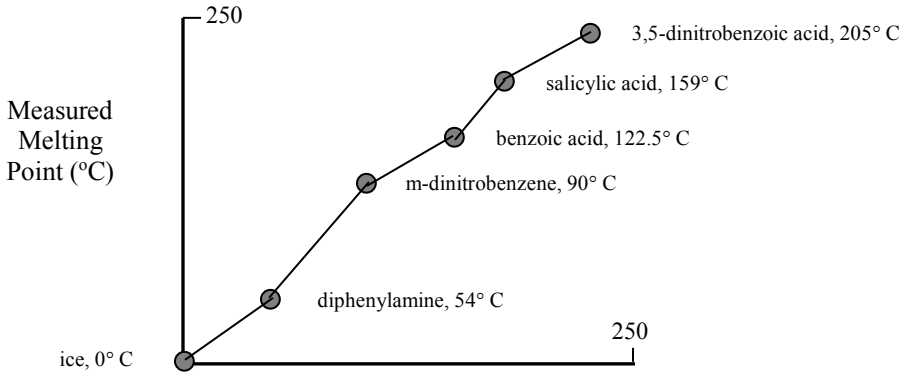
Chemicals	Equipment	Utilities
benzoic acid, biphenyl, 4-nitrobenzoic acid, 4-nitrobenzaldehyde, 2-methylbenzoic acid, urea, trans-cinnamic acid, 3-chlorbenzoic acid, salicylic acid, wash acetone.	-melting-point apparatus (Gallenkamp or Electrothermal), -thermometer, melting point tubes, porous plate, spatula, beaker, buret drop tube, mortar and pestle -hazardous waste disposal containers (in fume hood)	115V electrical

About Laboratory Melting Point Thermometers

You have been provided with a mercury-filled melting point thermometer. Be careful! They are fragile. Before using it, inspect it for any defects and check to make sure that the thermometer is reading room temperature. Broken or damaged thermometers must not be used and should be given to the laboratory instructor for proper disposal.

All thermometers are slightly different, and some may differ widely in accuracy (by 3°-5° C at higher temperatures). Inaccurate readings might be caused by defects in the thermometer glass, 'emergent stem error' and 'parallax' when reading the thermometer. To account for defects and emergent stem error*, the thermometer should be calibrated.

Note: The thermometer you have been provided with has <u>not</u> been calibrated. To calibrate your thermometer you would have to compare the thermometer reading and literature values of at least 5-7 known standard's melting points. Then you would plot a 'Thermometer Calibration Graph', similar to the one shown below:



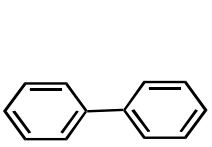
*emergent stem error occurs when the thermometer is not immersed to its recommended depth (see engraved line on stem, 76 mm from the bottom of the bulb).

Part A: List of Compound Codes Used as Simple Melting Point Unknowns

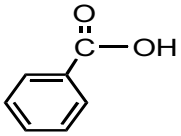
Unknown Code	Melting Point is within the range of:
1-A-1	60-80° C
1-A-2	110-130° C
1-A-3	230-250° C

Part B: List of Compound Used as Mixed Melting Point Unknowns

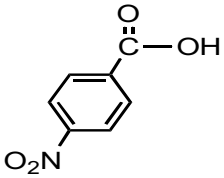
Unknown Code	Candidate 1	Candidate 2
1-B-1	4-nitrobenzaldehyde	2-methylbenzoic acid
1-B-2	4-nitrobenzaldehyde	2-methylbenzoic acid
1-B-3	urea	*trans*-cinnamic acid
1-B-4	urea	*trans*-cinnamic acid
1-B-5	3-chlorobenzoic acid	salicylic acid
1-B-6	3-chlorobenzoic acid	salicylic acid



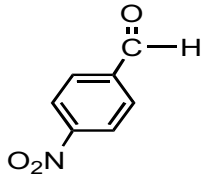
biphenyl



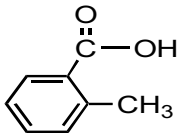
benzoic acid



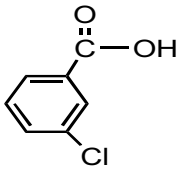
4-nitrobenzoic acid



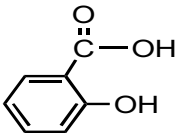
4-nitrobenzaldehyde



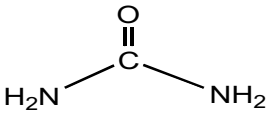
2-methylbenzoic acid



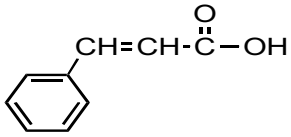
3-chlorobenzoic acid



salicylic acid



urea



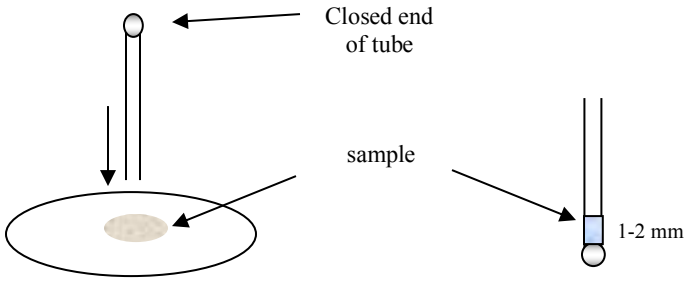
trans-cinnamic acid

Procedure

To Prepare a Melting Point Sample

1. Place about 0.1 g (a small amount) of the compound onto a porous plate, watch glass or in a mortar. Crush the solid to a fine powder by gently rubbing it with the flat end of a spatula or pestle.
2. Transfer a small quantity of the fine powder to the capillary tube by pushing it in the open end.
3. Pack the sample by using a 'drop tube'. The packed sample should be 1-2 mm in height.

Use just enough of the material so you can see it melt.



If you need more information, ask your instructor, or read the sections on "Sample Preparation" and "Loading the Melting Point Tube", page 33 in J.W. Zubrick's *The Organic Chem Lab Survival Manual*.

Part A: Single Melting-point Determination

Determine the melting point of the sample provided. You will be told the approximate melting point of the sample so that you can decide on the most appropriate setting for the melting point apparatus. Note that it may be necessary to crush the sample using a mortar and pestle before loading the melting-point tube. Record your experimentally determined melting point, and the code number of the sample.

Part B: Mixed Melting Point

You will be assigned an unknown sample and will be given a number of suggestions about its possible identity. Look up the melting point of each of these compounds in one of the reference books provided (see Appendix 1 for help if necessary) to get an approximate idea of the melting point of your compound. Determine the melting point of your assigned compound using the "melting-point apparatus". Crush a sample of your compound with each of the compounds that you believe it could be (50:50 mixture), load both into melting point tubes, and then determine the melting point of each of these mixtures. From your results, deduce the identity of the unknown compound.

Write-up

Follow the format for a standard investigative report. Be brief. An outline of what you did, the results obtained, a note of any observations made, and an answer to the assigned question is all that is required. Please make sure that your results are presented clearly. An example of how this could be done is shown below.

Part A

Melting point of sample # _____ = _____

Part B

Possible identity of unknown compound # _____ :

1. _____ ; m.p. (Reference)

2. _____ ; m.p. (Reference)

Melting point of unknown compound # _____ = _____

Melting point obtained when unknown compound # _____ is mixed with

1. _____ = _____

2. _____ = _____

Conclusion: The above results indicate that unknown compound # _____ is

probably _____.

Questions

1. In the introduction to this experiment you were warned that heating the sample too quickly in the region of the melting point will result in the experimentally determined melting point being higher than the true value. Explain why this is so.

2. What is a "eutectic mixture"? How would you decide whether a given sample was a pure compound or an eutectic mixture of two compounds?

3. You are working in the lab, and you find an unlabelled vial with a white crystalline solid inside. To determine the identity of the compound, what would you do?

4. i. Give two reasons why you should calibrate your thermometer before using it for a melting point determination.
   ii. How do you properly 'cool off' a melting point thermometer?

Remember to photocopy you lab report before mailing it to your academic expert for marking.

For additional information

If you have any questions regarding the operation of the melting point apparatus, please talk to your laboratory instructor. The instruction booklet for the apparatus, *A Guide to Melting Point Determination*, 2nd ed., published by Electrothermal Engineering Ltd., 1978, should be available for consultation in the laboratory.

Experiment 2
Recrystallization

Preparation

Before you come to the laboratory you should have read the whole of this experiment.

You may also wish to read Section 10, "Recrystallization," in *The Organic Chem Lab Survival Manual*, pp. 47-63 (Chapter13 in the third edition, pp.117-139).

Objectives

The purpose of this experiment is to show how organic compounds can be purified through the process of recrystallization. Techniques used in the experiment include hot gravity filtration and vacuum filtration. You will also learn more about the solubility of organic compounds, the use of activated charcoal, and how to fold a fluted filter paper. You will use the compound that you purify, acetanilide, in a subsequent experiment.

Introduction

When we prepare an organic compound, particularly one which may be destined for use in medicine, we obviously want that compound to be as pure as possible. Organic solids are usually purified by recrystallization (single- or two-solvent* method). Single-solvent recrystallization involves dissolving the solid in the *minimum amount of a selected hot solvent*, rapidly filtering this hot solution to remove any insoluble impurities, and then allowing the filtrate to *cool slowly* so that the desired compound comes out of solution in the form of large crystals. After cooling slowly to room temperature, the suspension of crystals in the mother liquor is chilled in ice water in order to maximize the amount of crystals formed. The crystals are collected in a Büchner funnel by suction filtration, and then dried. If desired, the filtrate can be concentrated by boiling off some of the solvent to give a second crop of crystals. (*The two solvent method is only used if a suitable single solvent cannot be found. You will learn about the two-solvent method in Experiment 7.)

Thus single solvent recrystallizations require the following 5 steps:

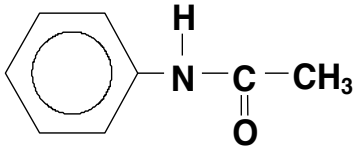
1. Select the solvent (soluble in hot, insoluble in cold).
2. Dissolve in a minimum of hot solvent.
3. Decision time? Hot gravity filtration if solid impurities (particulates) present. Add charcoal if coloured impurities present.
4. Slow cool to room temperature. Allow crystals to form. Place crystals 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.

Decision time. In addition to removing impurities which are less soluble than our compound (during the hot gravity filtration), we can also remove some of the impurities which impart colour to an otherwise colourless substance. These impurities often have a high molar mass, and they are removed by adding activated charcoal to the solution just prior to the hot gravity filtration. The coloured, high molar mass compounds absorb onto the surface of the insoluble activated charcoal, and are thus removed during the gravity filtration.

Note: impurities which are more soluble than our compound remain in the filtrate during the suction filtration, and are rinsed away with ice cold solvent in step 5 above.

In this experiment you will recrystallize acetanilide using water as the solvent. Acetanilide is an aromatic amide, and its structure is shown below (Fig.2.1).

Figure 2.1 Structure of acetanilide



Introduction to Recrystallization

There are many reasons why we may need to recrystallize an organic solid compound. For instance, the compound may need a higher level of purity for use in an organic synthesis or for final characterization, especially if the compound is new or unknown. In medicine, an organic compound must be of very high purity before it can be administered to the body.

As we learned in the previous experiment, one way we can determine if a compound is pure is to measure the melting point. A pure compound has a sharp and narrow melting point range, while an impure compound has a broad and depressed melting point. Another way to determine purity of a compound is by performing thin-layer chromatography (TLC).
Note: This technique (and co-spot TLC) are not done in *Chemistry 350*, but will be learned in *Chemistry 360*.

	Solid Organic
Purification Method	**Recrystallization**
Assessment of Purity	Melting point, *TLC**
Identification	Mixed Melting Point, *Co-spot TLC**

*not done in this course

Remember the 5 steps of a recrystallization. They are:

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

***More on Selecting a Suitable Solvent:**

A suitable solvent should also meet as many as possible of the following criteria:

1- Have a boiling point in the 60-100° C range, and this temperature should be lower than the melting point of the solid (to avoid 'oiling out').
2- Have a freezing point well below room temperature, preferably below 4° C.
3- The solvent must not react with the solid compound being purified.
4- Impurities should be highly soluble, or totally insoluble in the solvent.
5- The solvent must not be excessively hazardous.
6- 100 mL of the solvent should dissolve about 5 to 25 g of the solid when boiling and less than 2 g when cold, with at least a 5:1 ratio between the two values.

Important: You should consider a two-solvent recrystallization only when a single suitable solvent cannot be found.

Common Recrystallization Solvent Properties

Solvent	bp (°C, 760 torr)	fp (°C)	Polarity* (ε 20°C)	Comment
Water	100	0	80.37	Solvent of choice for many 'polar' compounds, Disadvantage-crystals dry slowly.
Methanol	64	-94	33.6	Good for relatively polar compounds, Advantage-easily removed.
95% Ethanol	78	-116	$24.3^{(25)}$	Excellent general solvent. Advantage-preferred over methanol i.e. higher bp. Disadvantage-contains 5% water.
Acetone	56	-95	20.7	General purpose solvent for relatively polar cmpds. Disadvantage-low bp makes if difficult to work with.
2-butanone	80	-86	18.5	Good general solvent. Advantage-higher bp than acetone.
Dichloromethane	40	-95	9.08	General solvent for intermediate polarity compounds. Disadvantage-low bp, fairly hazardous
Ethyl acetate	77	-84	$6.02^{(25)}$	Good general solvent for intermediate polarity compounds.
Toluene	111	-95	2.44	Good general solvent for aromatic compounds. Disadvantage-high bp makes it difficult to remove.
Petroleum ether	60-80	Low		Mixture of hydrocarbons, good for nonpolar cmpds.
Cyclohexane	81	6.5	2.02	Good general solvent for nonpolar compounds. Disadvantage-may freeze in ice bath.
Hexane	69	-94	1.89	Good for nonpolar compounds, Advantage-easily removed.
Methylcyclohexane	101	-127	NA	Good general solvent for nonpolar compounds. Disadvantage-high bp, volatile.

POLAR

NON POLAR

bp = boiling point, fp = freezing point, NA = not available. * As indicated by the Dielectric Constant.

Solubility* and Forces that hold Molecules Together:

*Note: solubility is a 'relative' term. Degrees of solubility are: miscible (∝), very soluble (v), soluble (s), sparingly soluble (δ), and insoluble (i).

"What solvent will dissolve a solid"? and "How much will dissolve"? are two very difficult and complex questions. A compound will generally dissolve in a given solvent if the forces that hold its own molecules together are similar to the forces holding the molecules of the solvent together. The 'rule of thumb' for predicting solubilities is **"LIKE DISSOLVES LIKE"**.

A further answer to the above questions begins with the following list of intermolecular forces and solubility factors. They are fundamental to explaining the solubility of organic compound because they account for why an orderly crystalline structure will come apart to form a disorderly array of molecules in solution.

van der Waals forces -weak attractive force holding non-polar compounds together.

dipole-dipole interaction -weak attractive force holding slightly polar compounds together and caused by permanent dipoles present in molecules.

hydrogen bonding -strong attractive force (5 kcal/mol), needs polar solvent to dissolve.

salt bridge formation -very strong attractive force, needs very polar solvent to dissolve.

heat -the hotter the solvent, the more solute will dissolve in the solvent.

Experiment 2 Background Information

In this experiment you will be given an impure sample of acetanilide (contaminated with sucrose (soluble impurity), calcium carbonate (insoluble impurity), and possibly silica. You will recrystallize acetanilide, using water as the solvent.

Chemicals, Equipment, Utilities Required:

All equipment used must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
acetanilide (impure), sucrose calcium carbonate silica (optional) distilled water ice wash acetone	-Hot plate, drying oven melting-point apparatus (Gallenkamp or Electrothermal), -250 mL Erlenmeyer flask, boiling stones, short stemmed funnel, filter paper -thermometer, melting point tubes, porous plate, spatula, buret drop tube, mortar and pestle -hazardous waste disposal containers (in fume hood)	-115V electrical, -vacuum or water aspirator line

About Handling Hot Glassware and Hotplates

- At all times use hand protection (finger cots, 'hot-hands', or insulated gloves) when holding heated glassware.
- Do not place a dry empty flask on the hot plate. It will crack.
- The surface of the hot plate is like a clothes iron. You cannot see if it is hot!! Hot plates are the most frequent source of burns to the skin in the laboratory.
- Never fill and heat a flask more than 2/3 full (even with boiling stones). The solvent will boil over.

Erlenmeyer Flasks vs. Beakers

Beakers are never used for a recrystallization. Erlenmeyer flasks are used instead. Why?

- Erlenmeyer flasks have a narrow neck that allows some refluxing of the solvent, and thus slows the rate of solvent evaporation.
- The narrow neck of an Erlenmeyer flask also allows you to swirl the liquid, thereby aiding in dissolving the solid.
- A flask can be stoppered to prevent evaporation during the cool down. You cannot easily stopper a beaker.
- It is only slightly more difficult to remove crystals from an Erlenmeyer flask than a beaker.

Procedure — Single Solvent Recrystallization

1. In this experiment, Step 1 of recrystallization, **'selecting the solvent'**, has already been done for you. Water dissolves acetanilide when hot, and acetanilide is highly insoluble in cold water.

2. **Dissolving the acetanilide.**

   a. Obtain about 100 mL of distilled water in a 250-mL Erlenmeyer flask, add one or two boiling stones, and heat the flask on a hot plate until the water boils.

   b. While you are waiting for the water to boil, place a short-stemmed funnel and a second 250-mL Erlenmeyer flask in an oven set at about 120°C, and measure out about 5 g of impure acetanilide into a third 250 mL Erlenmeyer flask. Also fill a melting point tube with a small amount of the impure acetanilide.

   c. Add one or two boiling stones to the flask containing the acetanilide, and then add about 10-15 mL of boiling water from the first flask.

   d. Place the flask containing the suspension of acetanilide on the hot plate, and bring the water to the boil. Continue to add hot water from the first flask to the acetanilide until all the latter appears to have dissolved. (Remember, the sample that you were given contains impurities, so not all of the solid will disappear.) When all the acetanilide appears to have dissolved, add a further 5-10 mL of hot water to the solution to help keep the acetanilide in solution during the hot gravity filtration.

   e. Allow the boiling solution to cool for a moment (to prevent 'bumping' of the liquid), then add a pinch of activated charcoal (see pp. 55-56 in *The Organic Chem Lab Survival Manual* or pp.127-128 in the third edition). Carefully bring the solution back to the boil in preparation for the hot gravity filtration.

3. **Hot gravity filtration.**

   a. Prepare a fluted filter paper as described in *The Organic Chem Lab Survival Manual*, pp. 61-63 (pp.132-133 in third edition).

   b. Remove the **short-stemmed funnel** and 250-mL Erlenmeyer flask from the oven. Place the funnel into an iron ring attached to a ringstand and put the fluted filter paper into the funnel. Place the clean, warm Erlenmeyer flask beneath the funnel. (See Figure 26 on p. 51 of *The Organic Chem Lab Survival Manual* or Fig.59 on p. 122 in third edition).

c. Pour a small quantity (about 5-10 mL) of solvent (hot distilled water) through the filter, and then begin to filter your acetanilide solution. **Try to keep your unfiltered acetanilide solution close to boiling all the time.**

d. When the filtration is complete, pour 5-10 mL of boiling water through the filter paper, particularly if it appears that some of the acetanilide has crystallized onto the paper. If major crystallization has occurred, consult your instructor.

Cautionary note: It is very tempting to turn the hot-plate control to its highest setting during the above steps, but you should try to resist this temptation as it is likely to result in the solution "boiling over". In this experiment we have used water as a solvent, and so there is no risk of fire. In later experiments the solvents that you use to recrystallize your products are likely to be flammable. When a flammable solvent comes into contact with an overheated hot plate, fire can result. Use an appropriate setting on your hot plate at all times, never leave a flask or beaker heating on a hot plate unattended, and do not forget to use a new boiling stone each time you heat or reheat a liquid or solution.

4. Crystal Formation

Loosely stopper the mouth of the Erlenmeyer flask that contains the hot filtrate, and allow the solution to cool while you proceed with another experiment. If crystals started to form in this flask during the filtration (step 3d above), redissolve them by warming the flask before you stopper it. In extreme cases, for example, if the entire contents of the flask seems to have solidified, consult your instructor.

5. Vacuum or Suction filtration.

a. After the filtrate has been cooling for 25-30 minutes, a good crop of crystals should have formed and the Erlenmeyer flask containing these crystals should be placed in an ice-bath for a further 10-15 minutes. During this time, the apparatus for performing a vacuum filtration should be set up. (See *The Organic Chem Lab Survival Manual*, pp. 53-55 and 56-58 or pp.123-129 in the third edition).

b. Filter off the acetanilide crystals (from the surrounding liquid; called the 'mother liquor'), washing the crystals with a small quantity of cold distilled water, as described in *The Organic Chem Lab Survival Manual*. Allow the crystals to dry overnight, or until your next laboratory session.

Note: Do not discard your filtrate until after your instructor has determined whether you need to obtain a "second crop" of crystals.

Final Analysis: Melting-point determination.

1. Determine the mass of pure, dry acetanilide obtained, and calculate your percentage yield.

2. If you have already completed Experiment 1, determine the melting point of your starting material and product. If you have not yet completed Experiment 1, please do so before you attempt to determine the melting point of your recrystallized acetanilide.

3. Submit your sample to your instructor in a suitably labelled vial. (See Section 22, "On Products," in *The Organic Chem Lab Survival Manual*, Chapter 11 in the third edition).

Optional: The "second crop."

If your yield is particularly low, for example, if you used an excessive amount of solvent, your instructor may advise you to obtain a "second crop" of crystals. Transfer the filtrate obtained from the vacuum filtration to a 250-mL Erlenmeyer flask, add a boiling stone and a pinch of activated charcoal, and then boil this solution until its volume has been reduced to about 25% of its original volume. Carry out a hot gravity filtration as before, allow the filtrate to cool, and separate the crystals from the mother liquor by vacuum filtration. After the crystals are dry, determine the yield and melting point of this second crop, and submit them to the instructor in a suitably labelled vial. Note that second-crop crystals are often not as pure as those obtained in the first crop.

Write-up

Use an investigative style report for this write-up. Be brief, and be sure to record the mass of impure acetanilide used, the mass of pure acetanilide recovered, the percentage recovery yielded, the melting point of starting material and product, and finally, the structure of the product.

Remember to photocopy you lab report before mailing it to your academic expert for marking.

Questions

Answers to these questions should be submitted with your report.

1. The table below shows the solubility of a certain organic compound in water at five different temperatures.

Temperature (^oC)	Solubility of compound (in 100 mL of water)
0	1.5 g
20	3.0 g
40	6.5 g
60	11.0 g
80	17.0 g

   a. Plot a graph of the solubility of the compound versus temperature. Draw a smooth curve through the data points.
   b. If a student attempts to recrystallize a 0.5 g sample of this compound by heating it to 80^o C with 5.0 mL of water, would all of the sample dissolve? Briefly justify your answer.
   c. Assuming that the answer to part b is "Yes", at what temperature will the crystals begin to appear when the student's solution begins to cool?
   d. If the student cooled the solution to 0^o C and filtered off the crystals, what is the maximum possible percentage recovery? What mass of the sample will remain in the filtrate?

2. Explain why you should slowly cool the filtered saturated solution obtained in step 3 of the recrystallization procedure?

3. During the last step of the recrystallization procedure, you collect the crystals by vacuum filtration. Why do you use ice cold recrystallization solvent to help transfer all the crystals to the Büchner funnel and wash the crystals?

4. Briefly explain the circumstances under which a mixed solvent recrystallization method would be used to recrystallize a given compound.

Experiment 3
Distillation

Preparation

Before you come to the laboratory you should have read the whole of this experiment.

You may also wish to read Chapter 15, "Distillation", in *The Organic Chem Lab Survival Manual* (Chapters 19-20 in the third edition). Note: You may omit the section on vacuum distillation.

Objectives

This experiment is designed to

1. demonstrate how a liquid may be purified by simple distillation and its boiling point determined during the process.

2. illustrate how two liquids can be separated by fractional distillation.

Introduction to Distillation

Just as recrystallization is used to purify an organic solid, distillation is used to purify an organic liquid compound. There are three major reasons why we might have to distil an organic liquid compound:

1. the compound may need to be purified prior to use in an organic synthesis,
2. to assist in characterization if the compound is new or unknown,
3. the organic compound must be highly pure before it can be administered medically.

In the previous two experiments, we learned that we can increase the purity of a solid compound by recrystallization, and we can check its purity by measuring the melting point and performing TLC.

An impure liquid can be purified by distillation. A pure liquid compound will have a sharp and narrow boiling point range, while an impure liquid compound has a broad and depressed boiling point. Also, a pure liquid will have a very specific refractive index (see Exp. 4). A comparison of the refractive index (*n*) with literature values gives an indication of the liquid's purity.

	Solid Organic	**Liquid Organic**
Purification Method	Recrystallization	**Distillation (simple or fractional)**
Assessment of Purity	Melting point, *TLC**	**Boiling point,** Refractive index
Identification	Mixed Melting point, *Co-spot TLC**	

*not done in this course

Distillation Procedure:

Remember there are six steps required to perform a distillation. They are:

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) Set approximate 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.

Distillation is probably the most important purification technique for organic liquids. It involves heating a liquid to its boiling point at atmospheric or reduced pressure to convert it to its vapour, and then condensing the vapour back to the liquid by cooling.

The boiling point of a liquid is that temperature at which the vapour pressure (escaping tendency) of the liquid equals the atmospheric or applied pressure; that is, when liquid and vapour are in equilibrium. Thus if you decrease the applied pressure by evacuating the system, you decrease the boiling point of the liquid. Similarly, pressurizing the system increases the boiling point. In *Chemistry 350* you will carry out all your distillations at atmospheric pressure and will not be concerned with **vacuum distillation**. However, you will be able to observe the effect that reducing the pressure has on the boiling point of a liquid when you use the rotary evaporator later in the course.

A homogenous mixture (i.e., a solution) of two liquids boils when the vapour pressure of the mixture is equal to the applied pressure, that is, when the sum of the partial pressures of the components (P_A, P_B, P_C ...) equals the applied pressure, P. Thus, at the boiling point

$$P = P_A + P_B + P_C \ \ldots$$

For those solutions which are "ideal", the partial pressure of each of the components present in the solution is given by Raoult's Law*. This law states that the partial pressure of component A, P_A, at any given temperature, is equal to the vapour pressure of the pure substance at that temperature, P^o_A, multiplied by the mole fraction of that substance present in the solution, X_A. Thus,

$$P_A = P^o_A X_A$$

$$P_B = P^o_B X_B$$

and so on.

* Francois Raoult in 1886 said "ideal solutions are characterized by the weighted averages of the properties of the components".

By combining the mathematical relationships expressed to this point, we see that

$$P = P^o_A X_A + P^o_B X_B \ \ldots$$

When a homogenous mixture of two liquids begins to boil, the composition of the vapour depends on the ratio of the partial pressures of the components present. Because the vapour

pressure of the lower boiling component is higher than that of a higher boiling component, the vapour will be "enriched" in the lower boiling point component when compared with the liquid mixture. As the distillation proceeds, the mixture becomes depleted of the lower boiling component. Thus, the boiling point rises and a greater mole fraction of the higher boiling component appears in the distillate.

A temperature-composition diagram for an ideal two-component system is given in Figure 3.1.

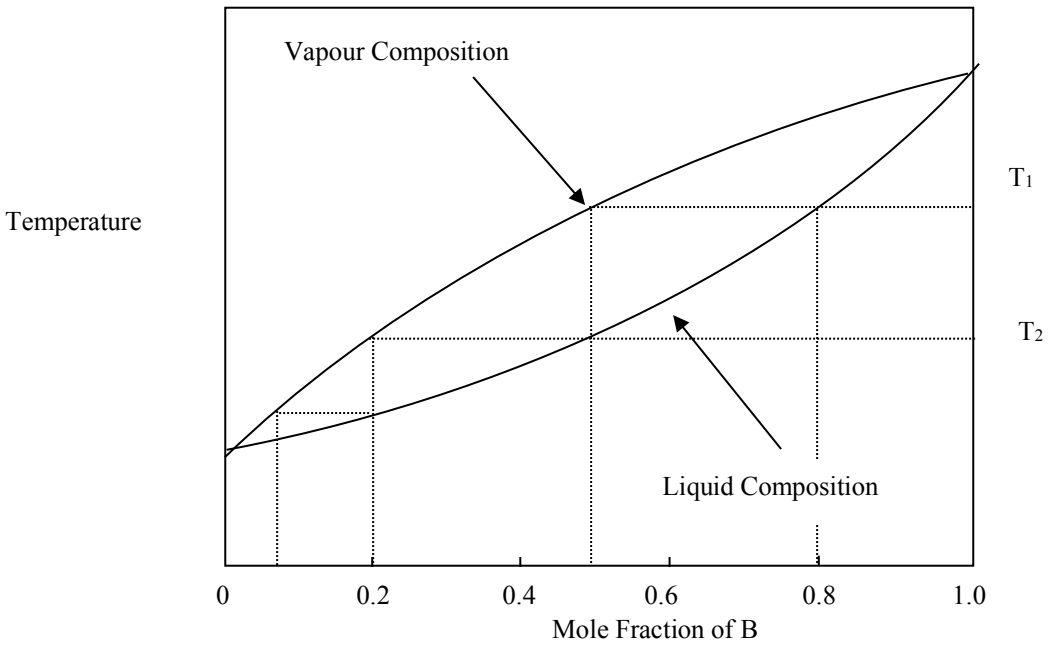


Figure 3.1. Temperature-composition diagram for an ideal two-component mixture

Figure 3.1 shows that a mixture consisting of 80 mol % B and 20 mol % A (i.e., a mixture in which the mole fraction of B is 0.80 and the mole fraction of A is 0.20) will boil at temperature T_1. The vapour composition curve shows that the composition of the vapour obtained at this temperature is 50% A and 50% B. If this vapour is condensed and redistilled, its boiling point would be T_2 and the vapour obtained would consist of 80% A and 20% B. Of course, this analysis is highly theoretical: in practice we have a dynamic situation that is constantly changing. For example, as soon as the first few drops of distillate are collected from boiling the original mixture, the mixture becomes depleted of the lower-boiling component (A) and its boiling point rises. However, in theory at least, one should be able to separate a mixture of two liquids into its components by carrying out a series of simple distillations as described above. In practice, the same result can be achieved using a process called **fractional distillation**.

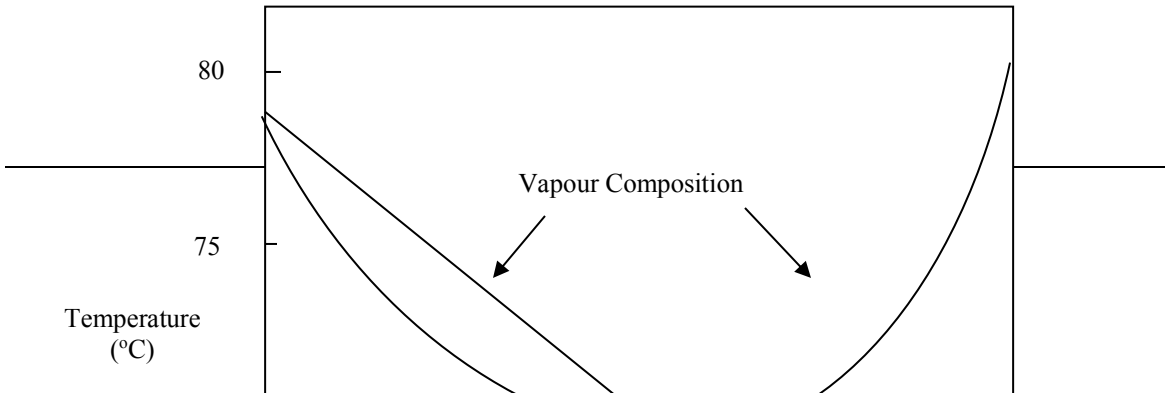
A comparison of the setups used in simple and fractional distillations (*The Organic Chem Lab Survival Manual*, Figures 51 and 56, respectively or Figs. 96 and 104 in the 3rd ed.) reveals that the only difference between the two is the inclusion of a **fractionating** column in the latter. The purpose of this column is to enable the vapour to condense and evaporate a number of times as it rises up from the distillation flask to the still head. Thus, performing a fractional distillation is equivalent to carrying out a series of simple distillations along the lines suggested above. A good fractionating column can often produce a distillate that is comparable to the product that would be obtained from 25-100 successive simple distillations. Thus, the efficiency of a column is sometimes expressed in terms of its number of **theoretical plates**, where each plate corresponds to one simple distillation. Although it might appear that the more theoretical plates a column has the more efficient it would be, it has to be remembered that the more plates there are, the greater the volume of liquid that is retained on the column and cannot be distilled; that is, the greater the **column holdup**. It is impossible to distill a sample whose volume is less than the volume of the column holdup.

Some other terms that are encountered in discussions of fractional distillation include: **height equivalent to one theoretical plate** (HETP), which is the length of column that corresponds to one simple distillation; **throughput**, the maximum volume of distillate that can be obtained per unit time while still maintaining equilibrium throughout the column; and the **reflux ratio**, the ratio of the volume of condensate formed at the top of the column and returned to the system to the volume removed as distillate, that is

$$\text{Reflux ratio, R,} = \frac{\text{volume of condensate returned to the column}}{\text{volume of condensate removed as distillate}}$$

An ideal column has a high number of theoretical plates, a low holdup, and a high throughput, and maintains its efficiency even at low reflux ratios. A glass tube packed with stainless steel sponge, which is the type of column you will be using, typically has a throughput of 2-5 mL· min^{-1}, an HETP of about 4 cm, and a holdup of 1-5 mL· $plate^{-1}$.

To this point, our discussion has been concerned with "ideal" solutions. "Real" solutions often have a particular composition for which the vapour and the liquid have an identical composition. Such a mixture is called an **azeotrope** (or **azeotropic mixture**), and the separation of such a mixture into its components cannot be achieved by means of a distillation, simple or fractional. A phase diagram for the ethanol-benzene system is shown in Figure 3.2. Notice that a low-boiling azeotrope (b.p. 68.2°) is formed by a solution containing 45.1 mol % ethanol and 54.9 mol % benzene.



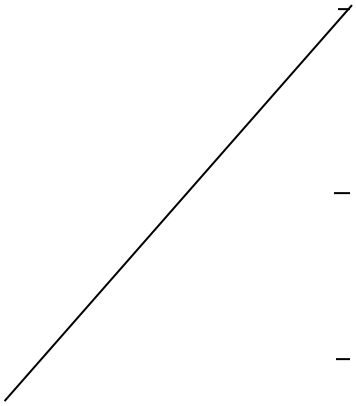
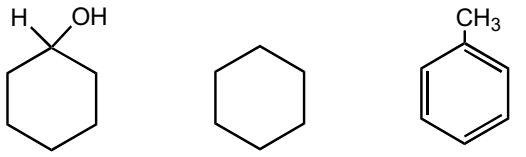


Figure 3.2. Temperature-composition diagram for a mixture of ethanol and benzene.

Experiment 3 Background Information

In Part A of this experiment, you will be given an impure sample of cyclohexanol (contaminated with toluene (soluble impurity)). You will remove the contaminating toluene first (called the 'forerun'), then collect a second fraction containing 'purified' cyclohexanol.



cyclohexanol cyclohexane toluene

In Part B of this experiment, you will be given a 1:1 mixture of cyclohexane and toluene. You will fractionally distil the mixture, collecting first mainly the cyclohexane (fraction 1), then you will collect an intermediate second fraction containing the both cyclohexane and toluene, and finally a third fraction containing mainly toluene.

Important: The boiling point of a liquid is defined as the temperature at which the atmospheric pressure and the vapour pressure of the liquid are equal. Thus the boiling point of a liquid is pressure dependent. (e.g. the lower the atmospheric pressure the lower the boiling point or the higher the elevation the lower the boiling point**). Approximate correction is 0.5° C per 10 torr difference from 760 torr (1 atm).**

Chemicals, Equipment, Utilities Required:

All equipment used must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
cyclohexanol (impure), toluene vacuum (glass joint) grease distilled water ice wash acetone	-heating mantle, lab jack, retort stands, utility clamps -distillation apparatus (distillation flask, three-way connector, thermometer adapter, condenser, vacuum adapter, receiving flask, fractionation column, boiling stones) -hazardous waste disposal containers (in fume hood)	-115V electrical, -cold water supply

About Assembling Distillation Glassware, and Using Boiling Stones and Heating Mantles

Distillation Glassware

- Remember to inspect all glassware for **star-cracks** (especially the distillation round bottom flask).

Boiling Stones

- Boiling stones must be used to promote smooth boiling and prevent 'bumping' of the liquid. Boiling stones contain many air filled pores. Air is slowly forced from the stone's pores as the vapour of the liquid being distilled penetrates the pores. The steady escape of air from the boiling stone results in a smooth boil.

- Never add a boiling stone to a solution that is already hot! A violent degassing of the liquid might result, which will cause the hot liquid to splatter out of the vessel. Also, when 're-boiling' a liquid, use a fresh boiling stone.

Heating Mantles

- Do not use a heating mantle with a damaged electrical cord.

The heating mantle which you will use will probably not be identical to the one described in Chapter 13 of *The Organic Chem Lab Survival Manual* (Chapter 18 in 3rd ed.), although both types operate on a similar principle. The heating mantles supplied by Athabasca University do not require the use of a variable voltage transformer. Instead, the voltage is regulated by a switch on the heating mantle itself. If you have any doubts about how to use the heating mantle provided, please consult the instructor *before* you begin the experiment. When using a heating mantle keep the following points in mind:

1. a heating mantle is a good general purpose heating device suitable for flammable solvents with boiling points from ~40 to 160° C.

2. heating mantles are available in various sizes. Always choose the correct size of heating mantle for the round-bottom flask you are using. (**Note:** If the correct size is not available, use glass wool to pack around the sides and bottom of the round-bottom flask to ensure a snug fit).

3. heating mantles tend to warm up slowly. Be patient, and do not use too high a setting.

4. A heating mantle is generally at a higher temperature than the round-bottom flask that it is heating. Also, heating mantles cool down very slowly. If the reaction (or distillation) being carried out gets out of control, it serves no purpose to simply unplug the heating mantle. In such situations, the heating mantle must be removed, thus, the apparatus should always be assembled with the heating mantle supported above the bench by an iron ring or, better still, on a laboratory jack (a lab jack).

5. Heating mantles are designed for heating round-bottom flasks. Never try to heat an Erlenmeyer flask or a beaker with a heating mantle.

6. Never add reagents to a flask while it is sitting in a heating mantle.

More on Heat Sources

Remember: No matter the heat source, you must use boiling stones.

Hot plates are primarily designed for heating flat-bottomed glassware (flasks, beakers). However they may be used in conjunction with a water bath to heat low boiling flammable liquids 'safely'. The water bath is normally pre-adjusted to the boiling point of the solvent to be distilled. Still, great care is necessary to ensure that none of the low-boiling flammable liquid falls directly on the hot plate surface and ignites.

Steam baths are very safe and effective heat sources. There are no electrical or flame concerns. There re very useful for heating recrystallization solvents and refluxing low boiling point liquids. A steam bath is not quite hot enough to be used to boil water or aqueous solutions.

Bünsen burners should only be used with aqueous solvents. A Bünsen burner will provide rapid heating of the non-flammable solvent. Never heat the bottom of the round-bottom flask directly. Instead, place a ring clamp and 5"× 5" wire gauze heating pad beneath the flask to diffuse the heat.

Heat Source	Suitable for	Effective Temperature (°C)
Water Bath on Hot Plate	Non-Flammable and Flammable solvents	40-80
Steam Bath	Non-Flammable and Flammable solvents	95-100
Heating Mantle	Non-Flammable and Flammable solvents	40-160
Bünsen Burner	**Non-Flammable solvents only**	40-160

Note: For liquids with bp above 160° C, vacuum distillation is recommended.

Procedure

In the first part of this experiment you will purify a sample of cyclohexanol (b.p. 161°C) by simple distillation. The reason that we have chosen to use cyclohexanol is because you will use this compound in a later experiment, and the purified sample that you obtain today can be saved for use in the later experiment. The second part of today's experiment involves the separation of a mixture of cyclohexane and toluene by fractional distillation. In Experiment 4 you will determine how successful this separation has been by measuring the refractive index of a number of fractions of the distillate.

Part A: Simple Distillation

Place 20 mL of impure cyclohexanol in a clean 100-mL round-bottom flask* and **add one or two boiling stones** to the liquid. Set up the apparatus for simple distillation as shown in Figure 51 on page 104 of *The Organic Chem Lab Survival Manual* (Fig. 96, p.190 in 3rd ed.) with a 25-mL round-bottom flask as the receiver and supporting the heating mantle (i.e., the 'heat source') using a lab jack. Pay particular attention to the positioning of the thermometer **(range: -10 ° to 260 °C):** the top of the bulb should be level with the bottom of the side arm (see Figure 3.3, below).

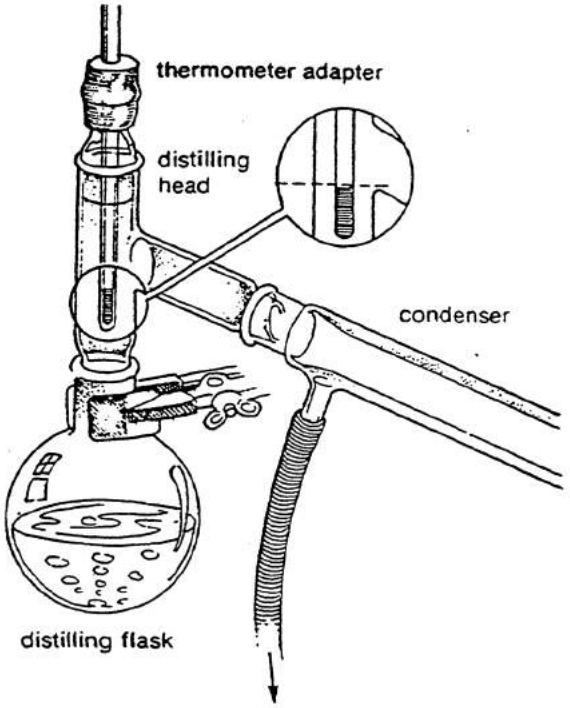


Figure 3.3. Thermometer placement during a simple distillation

Begin to heat the cyclohexanol by turning on the heating mantle to a setting of 6 or 6.5. After 10-15 minutes the liquid will begin to boil and the reading on the thermometer will increase. Allow about 4-6 mL of liquid to distil over and then replace the receiver with a clean 25-mL round-bottom flask*. The cyclohexanol should distil at a rate of about 10-20 drops per minute (monitor chilled water supply to condensor, as cyclohexanol may solidify in the condensor). Record the temperature range over which this fraction distils. This is the boiling range (i.e., the boiling point) of cyclohexanol and it should be in the order of 160°C. Collect about 14-15 mL of cyclohexanol in this way; that is continue until only a few millilitres of liquid remain in the distillation flask, or until the temperature recorded on the thermometer begins to increase. **Remember: Never distil to dryness.** Use a graduated cylinder to measure the volume of distillate collected, transfer the distilled cyclohexanol to a suitable labelled container, and hand it to your instructor for grading. Your sample will be returned to you for use in Experiments 4 and 8. Place the first few millilitres of distillate that you collected, called the **fore-run**, and the cyclohexanol that remained in the distillation flask should be placed in the container provided.

***Note:** If there are no 100-mL heating mantles available, use a 250-mL mantle and flask, and 75 mL of cyclohexanol.

Part B: Fractional Distillation

Place 25 mL of the cyclohexane-toluene mixture in a 100-mL round-bottom flask^ and add one or two boiling stones to the mixture. **Loosely** pack a fractionating column with steel sponge. Assemble the apparatus for fractional distillation as shown in Figure 56 on page 114 of *The Organic Chem Lab Survival Manual* (Fig.104, p.206 in 3rd ed.). Use a heating mantle (supported by a lab jack) as the 'heat source'. Slowly heat the contents of the flask (a setting of 3-4 on the heating mantle is about right to begin with) and watch the vapours rise in the column. When the vapours begin to reach the bulb of the thermometer, reduce the rate of heating so that for several minutes the ring of condensing vapours is kept between the top of the column packing and the sidearm. This procedure allows the vapour composition to stabilize before any distillate is collected. Now, turn up the heat slightly so that the mixture begins to distil. Collect the first few millilitres of fore-run in a small round-bottom flask and discard this material in the container provided. Collect three fractions of distillate in three different clean, dry, round-bottom flasks. The first fraction will consist of material that distils below 85°C, the second fraction will consist of material that distils between 85°C and 100°C, and the third fraction will consist of material that distils between 100° and 105°C. Use a graduate cylinder to measure the volume of each fraction, transfer the three fractions to three suitably labelled containers, and hand them in to the instructor for grading. The samples will be returned to you for use in Experiment 4.

^**Note:** As in Part A, if a 100-mL heating mantle is not available, use a 250-mL flask and mantle. If this is necessary, the volume of cyclohexane-toluene mixture used should be increased to 75 mL.

Safety

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

Cyclohexane is flammable and may irritate the skin, eyes and respiratory tract. Avoid contact with the liquid or its vapour, and keep it away from hot surfaces and open flames.

Toluene is flammable. Prolonged inhalation, ingestion or skin absorption may result in nausea, headaches, vomiting and dermatitis. Avoid contact with the liquid, do not breathe its vapours, and keep it away from hot surfaces and flames.

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

Write-up

Only a 'brief' standard investigative report of what you did is necessary. However, be sure to record the volume of each of the fractions collected, and ensure that you report the boiling point (or range) of each fraction.

Questions

Answers to these questions should be submitted with your report.

1. A student who was performing a distillation for the first time failed to position the thermometer correctly. The bulb was set too high. What effect would this have on the observed boiling point of the liquid being distilled?

2. Under perfect conditions, the number of theoretical plates required to separate and ideal mixture of two components of boiling points T_A and T_B is given by the relationship:

$$= \frac{120}{T_A - T_B}$$

   On this basis, how many theoretical plates are needed to separate a mixture of cyclohexane and toluene? **Note:** In practice, the actual number of theoretical plates required may be as high as double the number predicted by this equation!

3. You suddenly notice you have forgotten to add boiling stones to your round bottom distillation flask, but the distillation is now in progress. What should you do?

4. What is the purpose of the condenser during a distillation?

Experiment 4
Refractive Index

Preparation

Before coming to the laboratory you should have read through the whole of this experiment.

Objectives

This experiment is designed to

1. illustrate the use of refractive index as a criterion of purity.

2. demonstrate the use of refractive index in estimating the composition of a mixture of two liquids.

Introduction to Refractive Index

As we learned in the previous three experiments, we can increase the purity of a solid or liquid compound by recrystallization or distillation respectively, and assess the purity of the compound by melting point or boiling point and thin layer chromatography (TLC). In addition a pure liquid will have a characteristic refractive index. The purity can be assessed by comparing the observed refractive index with the published literature value for that compound.

	Solid Organic	**Liquid Organic**
Purification Method	Recrystallization	Distillation (simple or fractional)
Assessment of Purity	Melting point, *TLC**	Boiling point, **Refractive index**
Identification	Mixed Melting point, *Co-spot TLC**	

*not done in this course

Theory

The refractive index of a liquid is a physical property that can often be used to assist in the identification of an unknown liquid. The property arises from the fact that light travels at a different velocity in a liquid than it does in air. We can define the refractive index, *n*, of a substance as the velocity of light in air, V_{air}, divided by the velocity of light in the liquid in question, V_{liq}. However, what we actually measure is not the velocity of light in the two media, but the ratio of the sine of the angle of incidence, sin *i*, to the sine of the same angle of refraction, sin *r*. The angle of incidence corresponds to the angle at which the light strikes the surface of the liquid, and the angle of refraction is the angle to which the light is refracted within the liquid (see Figure 4.1).

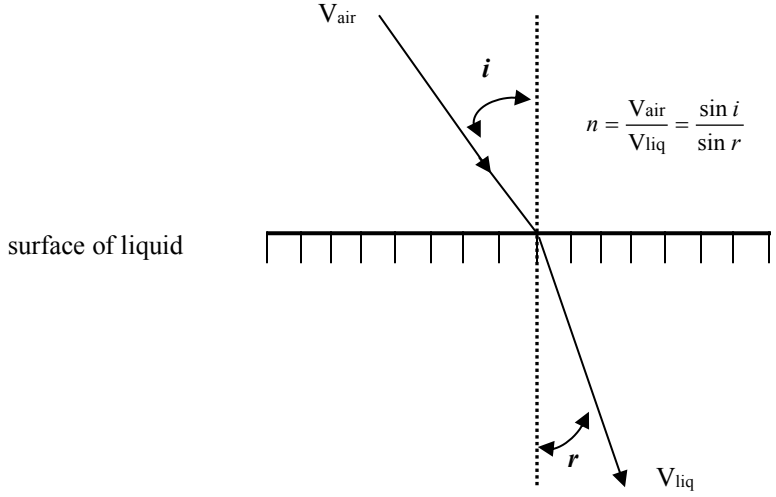


Figure 4.1. Light is refracted as it passes from air into a liquid

That is,

$$n = \frac{\text{Vair}}{\text{Vliq}} = \frac{\sin i}{\sin r}$$

Refractive index is dependent on two factors: temperature and the wavelength of the incident light. Normal practice is to report refractive indices measured at 20°C using the so-called "sodium D line," i.e., the yellow light of wavelength 589 nm given off by sodium lamps. The symbol used to represent such a refractive index is n_D^{20}. If a refractive index is measured at a temperature other than 20°C, the value obtained can be corrected to 20°C using a correction factor of 0.00045°C^{-1}. Note that the refractive index decreases with increasing temperature. Thus, if a certain compound has a n_D of 1.5506 at 25°C, the value of n_D^{20} would be

$$1.5506 + ((25^{o}\,C - 20^{o}\,C) \times 0.00045^{o}\,C^{-1}) = 1.5506 + 0.0022 = 1.5528 = n_D^{20}$$

(Equation forTemperature Correction of Refractive Index Readings)

To this point, we have only been concerned with the refractive indices of pure liquids. Most literature values of refractive index are quoted to four decimal places, and n_D is considered to be a very precise physical constant for a given substance. However, small amounts of impurity present in a substance can have a major effect on the measured refractive index. We can take advantage of this sensitivity to the presence of impurities by using refractive index as a means of determining the approximate composition of a two-component mixture of liquids. In a mixture of two liquids, A and B, having refractive indices of n_A and n_B, respectively, the observed refractive index of the mixture, n_{mix}, is related to the molar composition of the 'fraction mixture' by the following relationship: (mole fraction)

$$\text{mol\% B} = \frac{n_{\text{mix}} - n_A}{n_B - n_A} \times 100\%$$

The Abbé Refractometer

Refractive indices are measured using a **refractometer**. The particular instrument that you will be using in this experiment is an Abbé-3L refractometer, manufactured by Bausch and Lomb. A diagram of the refractometer is shown in Figure 4.2.

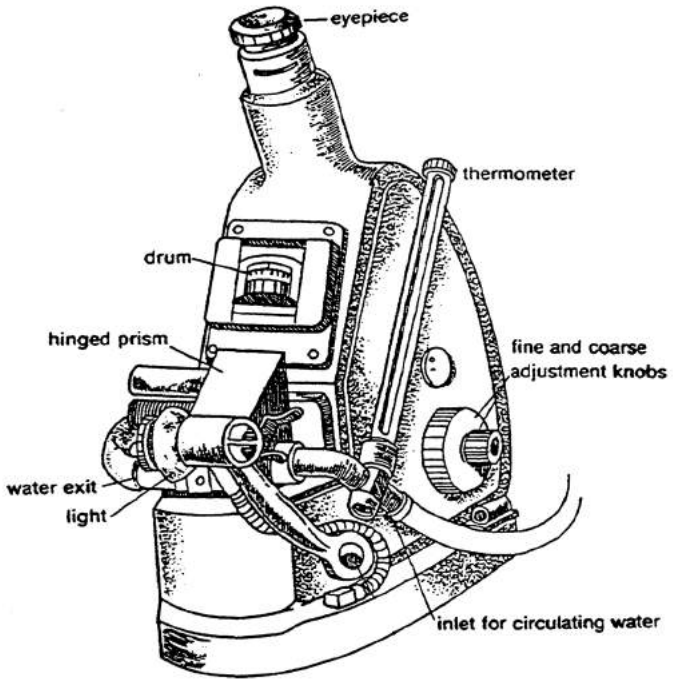


Figure 4.2. The Bausch and Lomb Abbé-3L refractometer

Some important features of this instrument are listed below.

1. it uses white light instead of a sodium lamp, but compensates internally, so that the n_D is actually obtained.
2. The sample can be temperature controlled (although we will not use this feature).
3. Only a few drops of liquid are required.

You need not be concerned with the details of how the optical system of the refractometer works. A thin film of sample is introduced between two prisms using an eyedropper, the sample is illuminated, and the experimenter looks into an eyepiece. The illuminating lamp is adjusted until the best contrast between the light and dark halves of the visual field is obtained. The hand-wheel on the side of the instrument is then rotated until the dividing line between the light and dark halves of the visual field coincides with the centre of the crosshairs (see Figure 4.3). A switch is then depressed, the scale becomes visible through the eyepiece, and the required refractive index can be read from the scale.

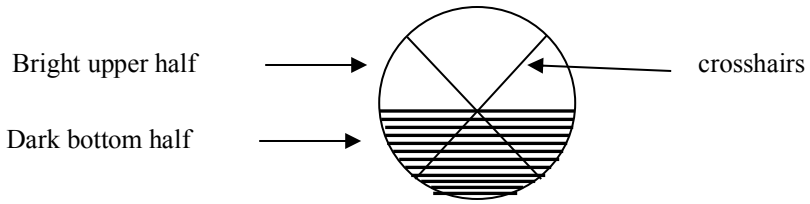


Figure 4.3. View through the eyepiece of a correctly adjusted refractometer

Summary of Refractive Index Procedure

1. Turn on refractometer, and clean the sample application area.
2. Apply sample carefully using a Pasteur pipette.
3. Adjust side hand wheel to bring the light and dark halves to the center of the X.
4. Adjust thumb wheel for chromatic abberation and sharpen the interface between the light and dark halves.
5. Readjust side hand wheel to recenter the light and dark halves in the X.
6. Read meter by holding down the on/off switch and reading the upper scale.

Experiment 4 Background Information

In Part A of this experiment you will use the product obtained in Experiment 3A.

In Part B of this experiment you will use the products obtained in Experiment 3B.

Chemicals, Equipment, Utilities Required

All equipment used must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
cyclohexanol (impure and pure), toluene, cyclohexane Exp. #B fractions 1-3 wash acetone	-Refractometer, Pasteur pipettes -hazardous waste disposal containers (in fume hood)	-115V electrical,

Final Warning about Using the Abbé Refractometer

Please be careful. Do not scratch the surface of the glass on the refractometer.

Procedure

Part A: Refractive Index of Cyclohexanol

For this part of the experiment, use the impure and purified cyclohexanol that you obtained from the simple distillation in Experiment 3. See the instructor if your sample has not yet been returned to you.

1. Ensure that the refractometer is plugged into a main outlet.

2. Open the hinged prism and use a Pasteur pipette to apply a small drop of sample (i.e., cyclohexanol) to the lower (fixed) prism.

   Caution: Do not touch the prism with your Pasteur pipette. The prism is easily scratched by any hard object, and scratching will wreck the instrument.

3. Close the prisms. A thin film of liquid will form between the surfaces of the two prisms. Turn on the instrument. The switch is on the left-hand side of the instrument as you look at it.

4. Look through the eyepiece and adjust the illuminator so that you obtain the best possible contrast between the light and dark halves of the visible field. The illuminator is adjusted by simply moving it up or down. This process requires patience and practice. Consult your instructor if necessary. Remember that certain organic liquids evaporate very quickly, although this should not be a problem with cyclohexanol.

5. Set the borderline between the light and dark halves on the intersection of the two crosshairs. This is achieved by rotating the hand-wheel located on the right hand side of the instrument as you look at it (see Figure 4.2).

6. If the borderline between the light and dark areas of the visible field appears as a coloured band (see Figure 4.4), **chromatic abberation** (colour dispersion) is said to have occurred, and you must **achromatize** the borderline. Achromatization can be achieved by rotating the compensator dial located just below the eyepiece.

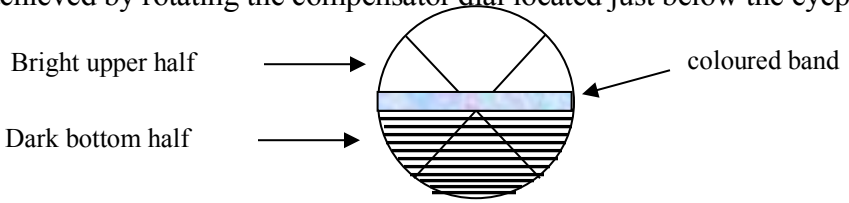


Figure 4.4. Chromatic abberation

7. Depress the contact switch (the same switch that you used to turn on the instrument) and read the refractive index of the sample from the top scale that will become visible through the eyepiece (see Figure 4.5).

   Note: The bottom scale is used for determining "total dissolved solids" and should be ignored.

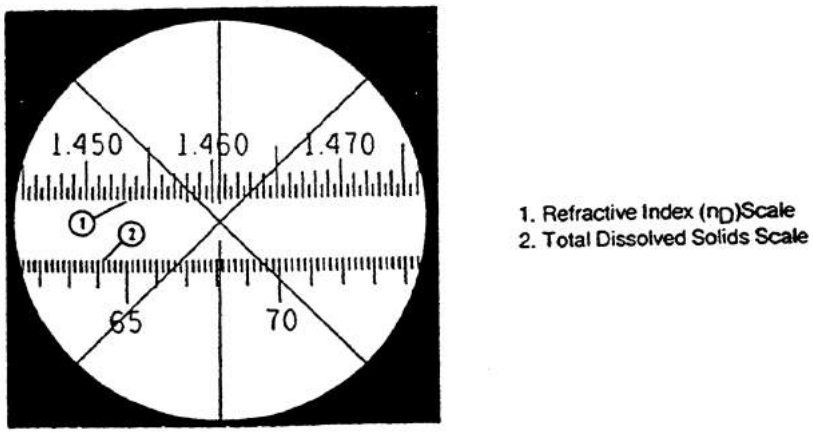


Figure 4.5. Reading the refractive index scale of an Abbé refractometer

8. Open the hinged prism and gently clean the two surfaces with a soft tissue made damp with acetone, ethanol or petroleum ether. When the solvent has evaporated from the prism surfaces, they should be locked together. **Remember:** do not touch the surfaces of the prisms with any hard or abrasive substance.

9. Proceed to Part B, or if you have completed the experiment, turn off the instrument.

Part B: The Composition of a Toluene-Cyclohexane Mixture

1. Using the instructions given in Part A as a guide, determine the refractive index of each of the following mixtures:

    a. the toluene-cyclohexane mixture used in Experiment 3.

    b. the three fractions retained from the fractional distillation carried out in Experiment 3. (**Note:** work quickly as sample will evaporate.)

2. Look up and record the literature values for the refractive indices of toluene and cyclohexane.

Safety

Cyclohexane is flammable and may irritate the skin, eyes and respiratory tract. Avoid contact with the liquid or its vapour, and keep it away from hot surfaces and open flames.

Toluene is flammable. Prolonged inhalation, ingestion or skin absorption may result in nausea, headaches, vomiting and dermatitis. Avoid contact with the liquid, do not breathe its vapours, and keep it away from hot surfaces and flames.

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

Write-up

Only a brief standard investigative report is required. Provide an outline of what you did, the results you obtained, a note of any pertinent observations, and the literature values of the refractive indices of cyclohexanol, cyclohexane and toluene. Calculate the percentage error in the value of n_D that you observed for cyclohexanol. Determine the (mole) percentage composition of the three mixtures that you examined, and use these results to assess the efficiency of the separation achieved in your fractional distillation.

Questions

Answers are to be included with your report.

1. Look up the boiling points of cyclohexanol, cyclohexane and toluene in a suitable reference book and report your findings. Don't forget that when you quote a boiling point, melting point, or similar physical property you should always cite the source. Example:

   1,3-Butadiene; b.p. = -4.4° C (*Handbook of Chemistry and Physics*, 47th ed. Cleveland, Ohio: The Chemical Rubber Co., 1966)

2. Suggest a reason why the boiling point of cyclohexanol is so much higher than those of cyclohexane and toluene.

3. Suggest a reason why the refractive index of cyclohexanol is higher than that of water.

4. To reduce the percentage error in the n_D reading of your purified cyclohexanol (compared to the literature value), what should you do?

For Additional Information

If you have any questions about the operation of the Abbé refractometer, please talk to your laboratory instructor. The instruction booklet for the refractometer, *The Bausch and Lomb Abbé-3L Refractometer Operator's Manual*, published by Bausch and Lomb, Inc., 1983, should be available for consultation in the laboratory.

Experiment 5
Extraction, separation and the use of drying agents

Preparation

Before you come to the laboratory you should have read the whole of this experiment.

In addition

1. read "Bonding and Molecular Properties" the McMurry *Organic Chemistry* textbook.

2. you may also wish to read Chapter 11, "Extraction", in *The Organic Chem Lab Survivial Manual* (Chapter 15 in 3rd ed.).

Objectives

This experiment is designed to

1. demonstrate how a solute can be extracted from one solvent to another.

2. show how a mixture of organic compounds can be separated into its components on the basis of differences in acidity and basicity.

3. illustrate the use of a drying agent to remove traces of water from non-aqueous solutions.

4. introduce the concept of using a flow-chart to summarize laboratory procedures.

Introduction to Extractions

A method often employed to begin purification of an organic solid is a process called extraction. **Liquid-liquid extractions** takes advantage of the difference in solubility of a substance in two immiscible liquids. The two immiscible liquids used in an extraction process are (1) the solvent in which the solids are dissolved, and (2) the extracting solvent. The two immiscible liquids are then easily separated using a separatory funnel.

	Solid Organic	**Liquid Organic**
Purification Method	Recrystallization	Distillation (simple or fractional)
Assessment of Purity	Melting point, *TLC**	Boiling point, Refractive index
Identification	Mixed Melting Point, *Co-spot TLC**	
Separation of Mixtures	**Liquid-Liquid Extraction**	Distillation (simple or fractional)
Drying of Organic Compounds	Vacuum Drying	**Drying Agents**

*not done in this course

For example, to separate a mixture of an ionic compound, such as sodium chloride, and an organic, non-polar solid, such as anthracene, $C_{14}H_{10}$, extraction would be the method of choice. Ionic or polar materials are often quite soluble in water, while non-polar organic materials are normally more soluble in organic solvents than in water. Thus, in order to separate a mixture of sodium chloride and anthracene, the mixture is first dissolved in a mixture of water and an immiscible organic solvent, such as hexane. Two layers form, with the polar sodium chloride contained in the aqueous layer and the non-polar anthracene dissolved in the non-polar hexane. The mixture is then transferred to a separatory funnel and is shaken to ensure complete extraction of the two compounds into the appropriate layers. The layers are allowed to separate—in this instance, the organic layer will be on top, because the density of hexane is 0.66 g· mL^{-1} and that of H_2O is 0.99 g·mL^{-1}. The lower layer is drained out through the stopcock, and the upper layer is poured out through the top of the funnel. In principle, we have only to boil off the water to get the sodium chloride and evaporate the hexane to get the anthracene, and we have successfully separated the mixture. However, to remove the last traces of impurities, the hexane layer would be washed by adding a little fresh water, shaking and draining off the aqueous layer. Similarly, the combined aqueous layers would be re-extracted with a little fresh hexane to remove the last of the anthracene.

Your task in this experiment is to isolate, purify and identify the compounds present in a three-component mixture. The mixture will consist of an organic acid* (benzoic acid, 2-methylbenzoic acid, 4-methylbenzoic acid, 4-chlorobenzoic acid, or salicylic acid), an organic base (3-nitroaniline or 4-chloroaniline) and a neutral hydrocarbon (naphthalene) as shown on page 85.

***Note:** An acid is a proton donor while a base is a proton acceptor. When an acid and a base react together a salt is formed. Salts are composed of cations and anions and are usually highly soluble in water. (Salt formation is used to separate compounds from a mixture).

An example as to when separations are used is during the Canizzaro reaction where you are required to separate an organic acid from a neutral alcohol. In fact, most organic syntheses

involve performing an extraction/separation at some point, if only to extract the desired organic compound from the reaction mixture. The organic acid and base will be purified by recrystallization, thereby providing you further practice in this important technique. The naphthalene will be purified by sublimation. The unknown compounds will be identified through use of the mixed melting point technique that was introduced in Experiment 1.

Separation of the Organic Acid

The three compounds in your mixture are all virtually insoluble in water. However, they are soluble in dichloromethane (also called methylene chloride), an organic solvent which is immiscible in water. You will begin the experiment by dissolving the mixture in dichloromethane and adding aqueous sodium hydroxide to the solution. As water and dichloromethane are immiscible, two layers will form. The dilute inorganic base, sodium hydroxide, reacts with the organic acid, HA, to produce a water-soluble salt, $RCO_2^-Na^+$:

$$RCO_2H_{(solv)} + NaOH_{(aq)} \text{----------} > RCO_2^-Na^+_{(aq)} + H_2O_{(l)}$$

Recovery and Isolation of the Organic Acid

Thus, the organic acid (in the form of its sodium salt) is extracted from the dichloromethane layer into the aqueous layer. The neutral hydrocarbon and the organic base are unaffected and remain dissolved in the dichloromethane. The two layers are separated, and each layer is washed: the aqueous layer with dichloromethane, the organic layer with aqueous base. The washings are then combined with the appropriate layers. To recover the organic acid or base, strong acid or base is added respectively. When strong acid is added to an aqueous solution containing the salt of an organic acid, the organic acid precipitates from solution (which then can be isolated by suction filtration):

$$RCO_2^-Na^+_{(aq)} + HCl_{(aq)} \text{----------} > \mathbf{RCO_2H_{(s)}} + NaCl_{(aq)}$$

Separation of the Organic Base

To this point, only one of the three components has been isolated and we still have a mixture of a neutral hydrocarbon and an organic base dissolved in dichloromethane. If dilute inorganic hydrochloric acid is added, it reacts with an organic base, RNH_2, to produce a water-soluble salt, $RNH_3^+Cl^-$, two layers again form and the organic base is extracted into the aqueous layer as its conjugate acid:

$$RNH_{2(solv)} + HCl_{(aq)} \text{----------} > RNH_3^+{}_{(aq)} + Cl^-_{(aq)}$$

Recovery and Isolation of the Organic Base

When strong base is added an aqueous solution containing the salt of an organic base, the organic base precipitates from solution (which then can be isolated by suction filtration):

$$RNH_3^+Cl^-_{(aq)} + NaOH_{(aq)} \text{ ----------> } \mathbf{RNH_{2(s)}} + NaCl_{(aq)} + H_2O_{(l)}$$

The two layers are then separated and washed as described above. The organic base can now be isolated by filtration, purified and identified.

The final task is to obtain the neutral hydrocarbon from the dichloromethane solution. Although one might think that simply evaporating the solvent would yield the desired product, the solution needs to be dried before this operation is performed. Despite the assumptions made previously, dichloromethane and water are not totally immiscible, and the small amount of water that is dissolved in the dichloromethane needs to be removed before an attempt is made to isolate the neutral hydrocarbon.

Small amounts of water can be removed from an organic solvent by allowing the solvent to stand over a drying agent in a closed vessel. The drying agent is then usually removed by filtration. Some commonly used drying agents are described below. Once the organic solution has been dried and the drying agent removed, the dichloromethane can be removed, using a rotary evaporator (see page 89), and the neutral hydrocarbon can be purified, in this experiment by sublimation.

Drying agents

There are two main types of drying agents: (1) those used to dry wet solvents (solvents saturated with water), #'s 1-6 below, and (2) those used for solvents containing very little water, #'s 7-9 below.

	Drying Agent (anhydrous)	Capacity/Efficiency:	Drying Compatibility
1	calcium chloride	large/low	not good for alcohols, amines, phenols
2	potassium carbonate	fair/fair	not good for acidic materials
3	disodium sulfate	large/ slow and low	good with organic solvents
4	magnesium sulfate	large/good and rapid	good with organic solvents
5	calcium sulfate	large/good	good with organic solvents
6	potassium hydroxide	large/v.g. and rapid	good for amines
7	sodium metal	small/v.g and v.fast	not good with acidic protons, halocarbons (violent reactions).
8	phosphorous pentoxide	small/v.g and v.fast	good only for relatively dry solvents, not good with alcohols, ketones, amines or acids
9	metal hydrides (CaH_2)	small/v.g and v.fast	good only for relatively dry solvents, not good for cmpds. with acidic H, C- hetero-atom, double bonds, or chlorocarbons (violent reactions)

Type 1 drying agents are anhydrous salts, and act by combining with water in the organic solvent to form a hydrated salt which is insoluble in the solvent and can be removed by filtration.

Example of Type 1 Drying Agent Reaction with water:

$$MgSO_4\,(s) + 7H_2O\,(l) \rightarrow MgSO_4.7H_2O\,(s)$$

Type 2 drying agents work because they react with any water present in the organic solvent. For example,

$$2Na\,(s) + 2H_2O \rightarrow H_2 + 2NaOH$$

Often such reactions are violent, and consequently these drying agents are only used on solvents which are known to contain only a very small amount of water.

It is poor technique to use an unnecessarily large quantity of drying agent when drying a liquid, as the desiccant may adsorb or absorb the organic liquid along with water. Also, mechanical losses on filtration of the dried solution may become significant. The amount of drying agent required will depend on the quantity of water present and on the drying capacity of the desiccant. In general, a portion of drying agent that covers the bottom of the vessel containing the liquid should suffice. If additional desiccant is needed, more can be added.

As many hydrates lose their water when heated, it is important that the drying agent be removed by gravity filtration (or by decantation) before any distillation is attempted.

Note: To dry an organic solid, vacuum drying is used to remove unwanted moisture. This is because most organic solids will oxidize or decompose if heated.

Summary of Liquid-Liquid Extraction Procedure

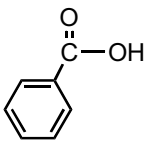
Remember there are essentially five steps to performing a extraction using a separatory funnel.

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.

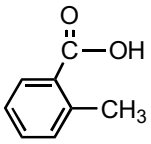
Experiment 5 Background Information

In this experiment, you will be given an unknown solid containing three organic compounds, one acidic, one basic and one neutral. You will separate the mixture using the extraction procedure, isolate the separated compounds, and then identify the individual compounds using mixed melting points. The compounds you will be working with are shown below.

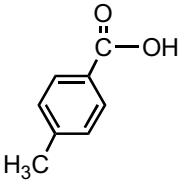
Acidic



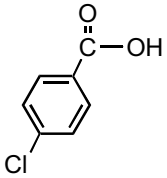
benzoic acid



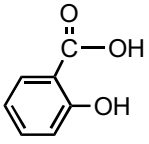
2-methylbenzoic acid



4-methylbenzoic acid

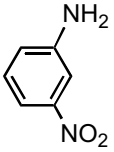


4-chlorobenzoic acid

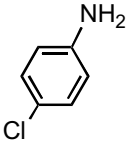


salicylic acid

Basic

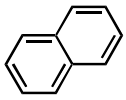


3-nitroaniline



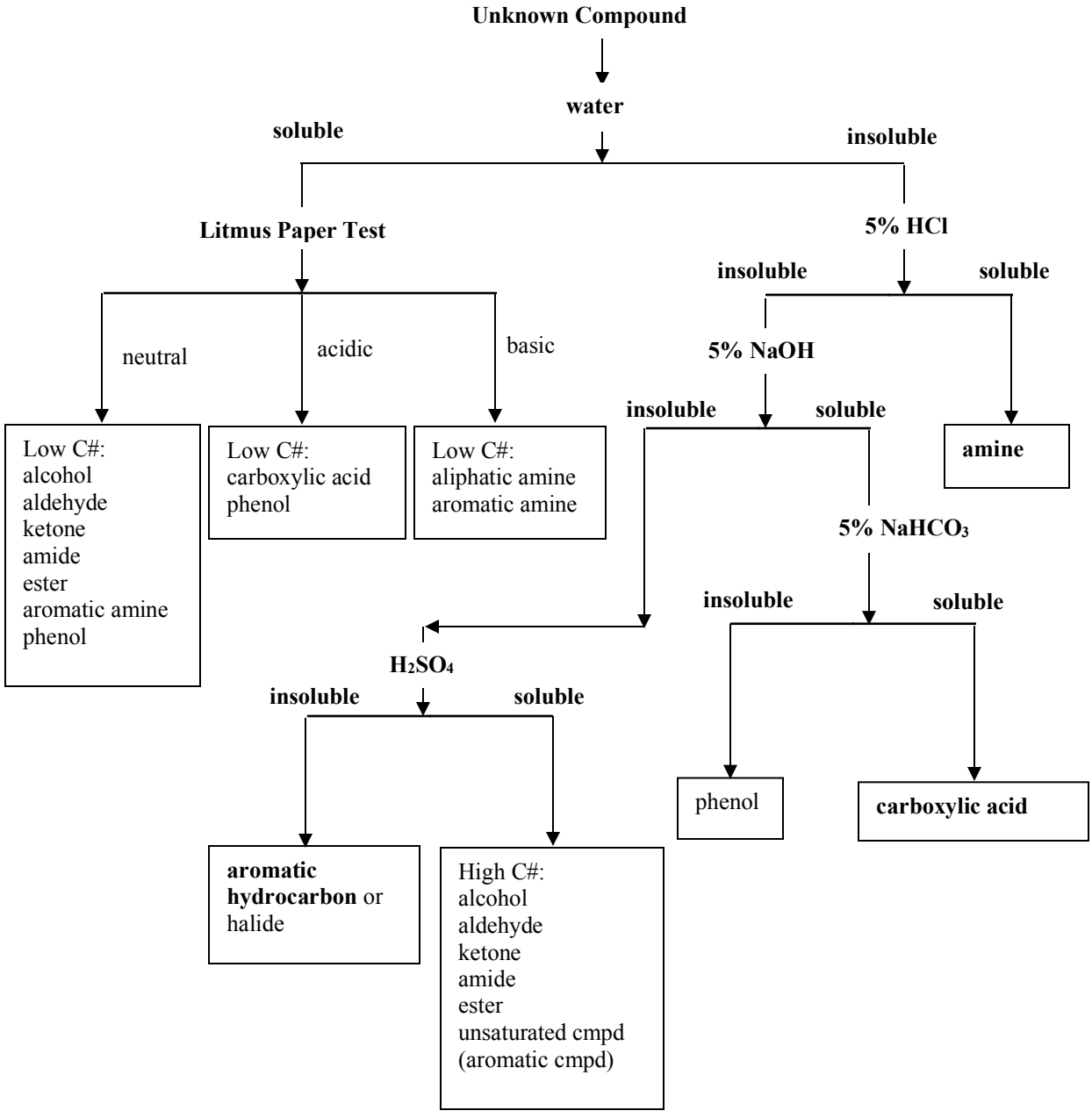
4-chloroaniline

Neutral



naphthalene

Solubility Flow Diagram for Classification of Organic Compounds



Redrawn from Lehman, J.W. 1999. Operational Organic Chemistry 3rd ed., Prentice Hall, p.534.

Chemicals, Equipment, Utilities Required

All equipment used must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
unknown organic solid mixture, dichloromethane, 5% NaOH, 1.5 M HCl, 12 M conc. HCl, 6M NaOH, distilled water, ice, methanol, ethanol, ethyl acetate, hexanes, wash acetone.	-separatory funnel and stopper, ring clamp, powder funnel -125 ml Erlenmeyer flasks (3-4) -10 mL graduated cylinder (2), Pasteur pipettes (2), stirring rod, pH indicator paper, water-ice bath -filter flask, Büchner funnel plus adapter, vacuum tubing, Whatman #1 filter paper circle -flat bottomed recrystallization dish, hot plate, Erlenmeyer flasks (2), sample vials plus labels -melting-point apparatus -rotary evaporator apparatus -halogenated and non-halogenated organic waste disposal containers (in fume hood)	-water aspirator , 115V electrical outlet

About Handling Separatory Funnels and Dichloromethane

- Inspect your separatory funnel for 'star-cracks'. Ensure that the stopper is the correct size for the separatory funnel. Pre-test your separatory funnel with acetone to check for leaks from the stopper or stopcock region.
- Very lightly grease the stopper and stopcock to prevent leaking, sticking or freezing of the ground glass joints. If the separatory funnel has Teflon® stoppers and stopcocks, greasing is not necessary, since Telfon® is self-lubricating.
- Also, choose the size of the separatory funnel so that the total volume of liquid in the funnel is less than 75% of the total capacity of the funnel. (Ref: Mayo et al, 1989. Microscale Organic Laboratory, John Wiley & Sons, New York, p.77).
- Latex gloves provide little protection against dichloromethane. Use the **Viton® rubber gloves** provided when handling this solvent. Use the **halogenated** organic waste container to dispose of unused / used dichloromethane.

The Use of the Büchi Rotavapor

The organic chemist is frequently faced with the problem of having to evaporate a relatively large volume of solvent from a solution. Although distillation is often employed to remove the solvent from such solutions, this can be a long and tedious process during which it is possible that the solvent, the product, or both may start to decompose. One method of overcoming such problems is to distil off the solvent under reduced pressure. You will recall that lowering the applied pressure will lower the boiling point of a liquid.

Rotary evaporators are commonly employed to reduce the volume of solutions by evaporating off the solvent at a reduced pressure, the model that you are most likely to use in this course is the Büchi Rotavapor-R110 (see Figure 5.1).

The solution to be evaporated is placed in flask A (note that this flask should never be more than half full) which is then attached to the vapor duct, B, using the clip provided. The joint should, of course, be greased in the normal manner. Sometimes a splash head is used between the evaporating flask and the vapor duct. The receiving flask, C, is then attached to the condenser using the clamp provided, and if it is not already in position, the introduction stopcock, D, should be inserted. Connect the cooling water (if not already connected) and carefully turn on the tap. Thick-walled rubber tubing should now be used to connect the outlet E to the aspirator. The aspirator is turned on and the evaporating flask is partially immersed in the water bath by raising the water bath to a suitable height on a lab jack (not shown in Figure 5.1). With the model R110 rotavapor it is possible to lower the evaporating flask into the water bath, eliminating the need for a lab jack. The evaporating flask is then made to rotate at a suitable speed by adjusting the control F, and the water in the water bath is heated if necessary. It is possible to refill the evaporator flask without interrupting the evaporation process, but you are unlikely to need to do this.

When the volume of the solution has been reduced to the desired amount, stop the flask from rotating, turn off the aspirator, either lower the water bath or raise the evaporating flask (depending on the model used) and remove the evaporating flask from the apparatus.

Your instructor will assist you when you first use the rotary evaporator. However, by the end of the course you should be comfortable using this useful piece of equipment.

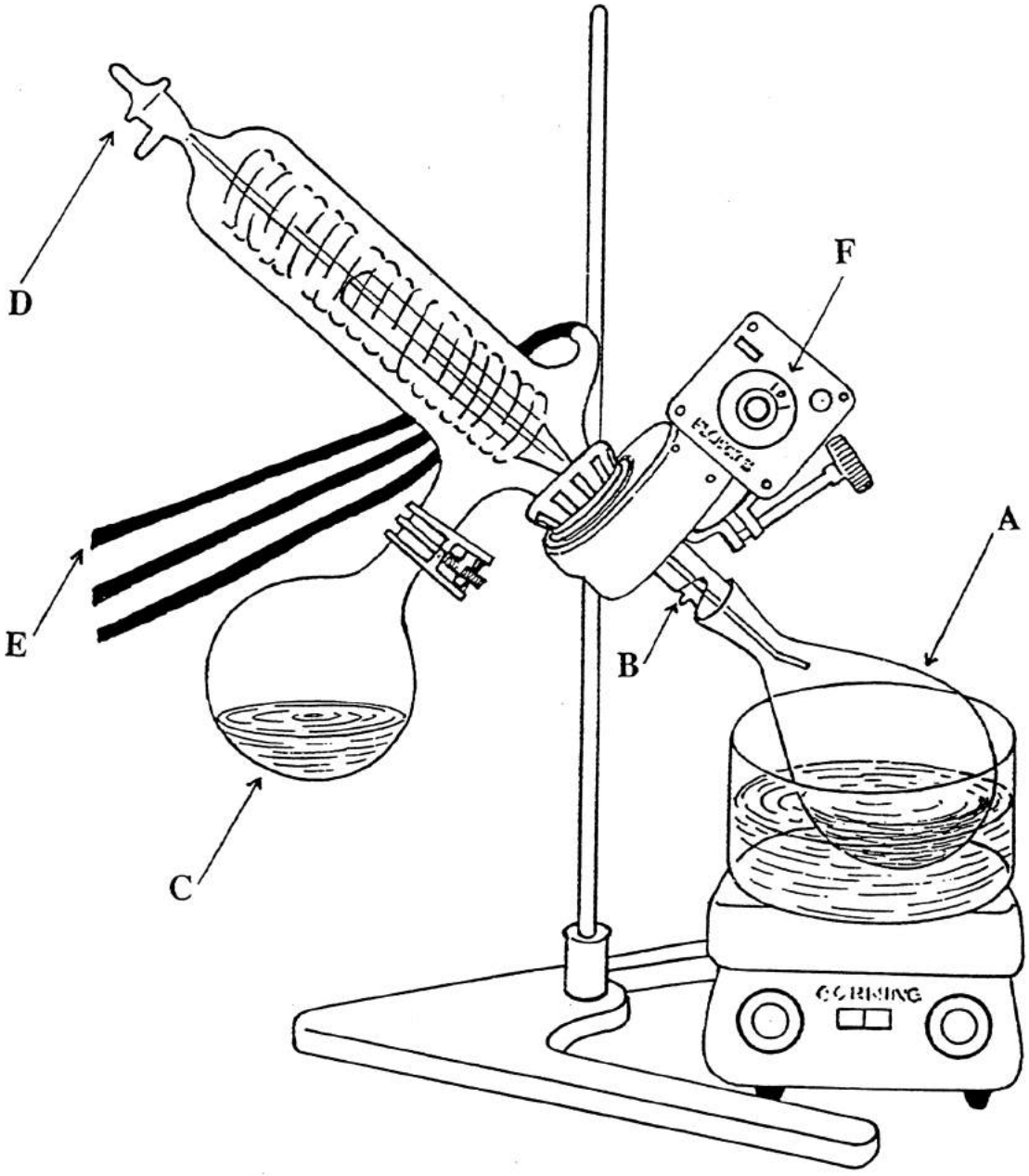


Figure 5.1. A Büchi Rotavapor
(Model used may not be exactly as illustrated.)

Calculation of Amt. of conc. HCl needed to neutralize a given amt. of base.

Given: # of mol of acid to add = # of mol of base used
NaOH conc. = 5%
Tot.Vol. NaOH used = 50 mL
conc. HCl = **12 M**

1. Convert Weight Percentage (%) of Base to Molarity (M)

Need: M = mol/L and Mwt. = g/mol or mol = g/Mwt.
substitute for mol
Therefore: M = g/Mwt/L

Since: 5% NaOH means 5 g/100mL NaOH (or 50 g/1000 mL)

Calculate: M= (5 g)/(40.00 g/mol)/0.1 L or ((50 g)/(40.00 g/mol)/1 L)
M= 1.25 mol/L

2. Determine the Number of moles of Base Used

Using: M= mol/L or mol = M x L

Calculate: mol = 1.25 M x 0.05 L
mol = 0.0625 mol (must use the same # of mol of acid to neutralize)

3. Determine the Number of mL of Acid Required to Neutralize the Base

Using: M= mol/L or L = mol/M

Calculate: L = 0.0625 mol/12 M
L = 0.0052 L
or Vol. = **5.2 mL** of conc.HCl req. to neutralize 50 mL of 5% NaOH.

Summary Equation: mol Acid = mol Base (using M = mol/L)
or M Acid × L Acid = M Base × L Base
Thus: **L Acid = (M base) × (vol Base)/(M Acid)**
L Acid = **(**(5 g)/(40.00 g/mol)/0.1 L) × 0.05 L Base)/12 M Acid
L Acid = 0.0052 L

Procedure

Part A: Extraction of the Organic Acid and Organic Base

You will be provided with about 3 g of a mixture containing an unknown organic acid, an unknown organic base and naphthalene.

1. Determine the mass of your sample and dissolve the mixture in 25 mL of dichloromethane.

2. Transfer the solution to a separatory funnel that is supported by an iron ring attached to a retort stand (see Figure 5.2) and add 20 mL of 5% sodium hydroxide solution. Stopper the funnel and shake it vigorously several times, cautiously releasing the pressure by opening the stopcock (see *The Organic Chem Lab Survival Manual*, Chapter 11 or Chapter 15 in 3rd ed.).

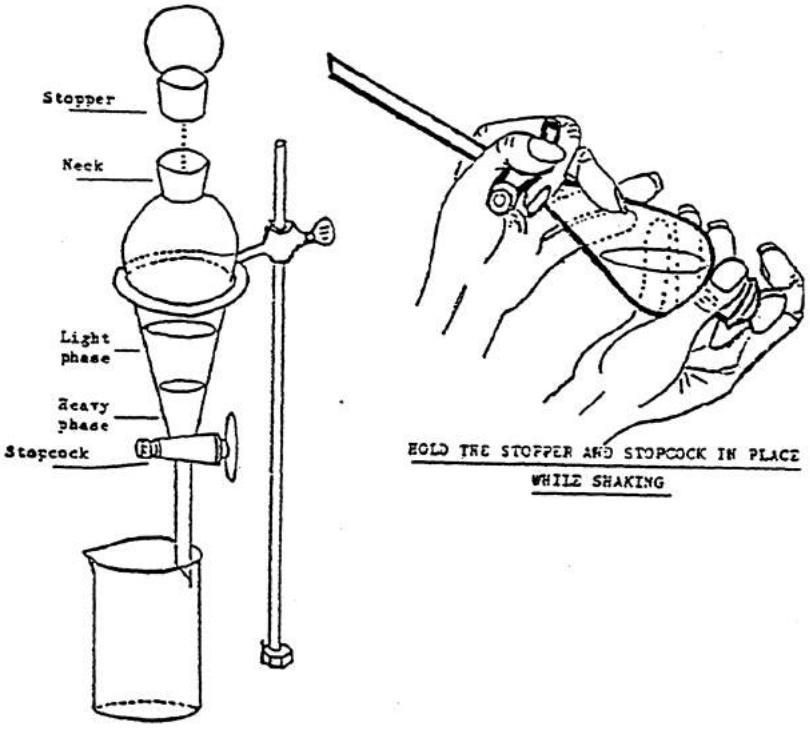


Figure 5.2. Use of a separatory funnel

3. Return the funnel to the iron ring, remove the stopper, and allow the layers to separate. Draw off the bottom layer (dichloromethane) through the stopcock into a 125-mL Erlenmeyer flask. Pour the aqueous layer out through the top of the funnel into another 125-mL flask and set it to one side for the time being.

4. Return the dichloromethane layer to the separatory funnel and add a second 20-mL portion of 5% sodium hydroxide solution. Shake, vent and allow the layers to separate as before. Draw off the lower (dichloromethane) layer into a 125-mL Erlenmeyer flask and pour the aqueous layer out through the top of the funnel into the Erlenmeyer flask containing the aqueous layer from the first separation.

5. Wash the aqueous layer by returning it to the separatory funnel, adding 15 mL of dichloromethane, shaking, venting, allowing the layers to separate, drawing off the organic layer into the 125-mL Erlenmeyer that already contains the dichloromethane from before, and pouring the aqueous layer through the top of the funnel into the 125-mL Erlenmeyer that has previously been used from storing this solution.

Confused? Take a moment to review what you have done so far. You should now have two 125-mL Erlenmeyer flasks. One of these flasks contains approximately 40 mL of dichloromethane in which the naphthalene and organic base are still dissolved. The second flask contains an aqueous solution of the sodium salt of the organic acid, plus any excess sodium hydroxide. Let us now separate the organic base from the naphthalene.

6. Pour the dichloromethane solution of naphthalene and the organic base into the separatory funnel and add 15 mL of 1.5 mol· L^{-1} hydrochloric acid. Shake, vent and separate as described previously.

7. Return the dichloromethane solution to the separatory funnel and extract with a further 15 mL of 1.5 mol· L^{-1} hydrochloric acid.

8. Combine the two hydrochloric acid extracts and wash the combined solution with 15 mL of dichloromethane. Combine the dichloromethane washings with the dichloromethane solution that you should have saved from the acid extraction.

Let us review the situation again. You should now have three 125-mL Erlenmeyer flasks, each containing a solution. The first flask contains an aqueous solution of the sodium salt of the organic acid; the second flask contains an aqueous solution of the hydrochloride salt of the organic base; and the third flask contains a solution of naphthalene in dichloromethane. The next phase of the experiment is to isolate the organic acid, the organic base, and the naphthalene.

Part B: Isolation of the Organic Acid

1. Place the Erlenmeyer flask that contains the sodium hydroxide extract into an ice bath and *carefully* add cold concentrated hydrochloric acid. (**Note:** You should calculate the volume of hydrochloric acid required before you came to the laboratory.) A precipitate of the organic acid should form. Use litmus paper (or universal indicator paper) to test the pH of the mixture and to ensure that a slight excess of hydrochloric acid has been added so that all of the organic acid will be precipitated. Filter off the precipitate by suction filtration, and wash the solid obtained several times with 10-mL aliquots of ice-cold distilled water. Allow the solid to dry (preferably overnight), and then recrystallize from an appropriate solvent. (The latter should be determined in consultation with your instructor.)

2. When the recrystallized product has dried, determine its yield (mass) and melting point. From the given list of possible organic acids, identify the one that was most likely present in your mixture. Confirm your deduction by the mixed melting point technique. If you have not done so already, transfer your product to a suitable sample vial. Hand the vial to your instructor for grading.

Part C: Isolation of the Organic Base

1. Place the Erlenmeyer flask that contains the hydrochloric acid extract into an ice bath and *carefully* add cold sodium hydroxide solution (6 mol· L^{-1}). (**Note:** You should calculate the approximate volume of sodium hydroxide required before you come to the laboratory.) Continue the dropwise addition of the sodium hydroxide solution until the pH of the solution in the Erlenmeyer flask is about 10. (Use universal indicator paper to verify the pH.) A precipitate of the organic base should appear.

   Note: If your organic base appears as an oil rather than as a precipitate, follow the procedure given at the end of this section.

2. Filter off the precipitated organic base by suction filtration, and wash the solid several times with 10-mL aliquots of ice-cold distilled water. Allow the solid to dry (preferably overnight), and then recrystallize from a solvent determined in consultation with your instructor.

3. When the recrystallized product has dried, determine its melting point. From the given list of possible organic bases, identify the one that was most likely present in your mixture. Confirm your deduction by the mixed melting point technique.
   Determine the yield (mass) of product obtained. Transfer your product to a suitable vial, and hand it to your instructor for grading.

   If your organic base appeared as an oil instead of a solid, transfer the contents of the Erlenmeyer flask to a separatory funnel. Wash the Erlenmeyer flask with three 15-

mL aliquots of dichloromethane and transfer these washings to the separatory funnel. Shake and vent the funnel, and allow the layers to separate. Run the (lower) dichloromethane layer into a clean 125-mL Erlenmeyer flask. Wash the aqueous solution remaining in the funnel with an additional 15 mL of dichloromethane and combine the washing with the dichloromethane solution in the Erlenmeyer flask. Dry the dichloromethane solution by adding anhydrous magnesium sulfate to the solution, placing a cork in the mouth of the Erlenmeyer flask, and allowing it to stand for about 10 minutes. (See Section 23 of *The Organic Chem Lab Survival Manual* or Chap.10 in 3rd ed. in order to find out how to determine the quantity of anhydrous magnesium sulfate to use.) Filter off the drying agent (gravity filtration) and evaporate off the dichloromethane using the rotary evaporator (if necessary, see your instructor for assistance). A solid organic base should be obtained. Purify the base by the method described in 3, above.

Part D: Isolation of the Neutral Hydrocarbon (optional)

1. Transfer the dichloromethane solution that contains the neutral hydrocarbon (naphthalene) from its Erlenmeyer flask to a separatory funnel. Wash the dichloromethane layer with two 20-mL aliquots of distilled water.

2. Run the dichloromethane into a 125-mL Erlenmeyer flask and dry this solution by adding anhydrous magnesium sulfate, placing a cork in the mouth of the flask, and allowing it to stand for about 10 minutes. (See Section 23 of *The Organic Chem Lab Survival Manual* in order to find out how to determine the quantity of anhydrous magnesium sulfate to use.)

3. Filter off the drying agent (gravity filtration) and evaporate off the dichloromethane using the rotary evaporator (if necessary, see your instructor for assistance).

4. Naphthalene can be readily purified by the process of sublimation. **Note:** If your instructor has substituted some other hydrocarbon for naphthalene, please consult her or him before you proceed with this stage of the experiment.

5. Transfer the crude naphthalene into a clean, dry 100-mL beaker and stand the beaker on a hot plate. Clamp a 50-mL round-bottomed flask filled with ice-cold water in such a way that the bottom of the flask is in the mouth of the beaker. (**Note:** The outside of the flask *must* be dry.)

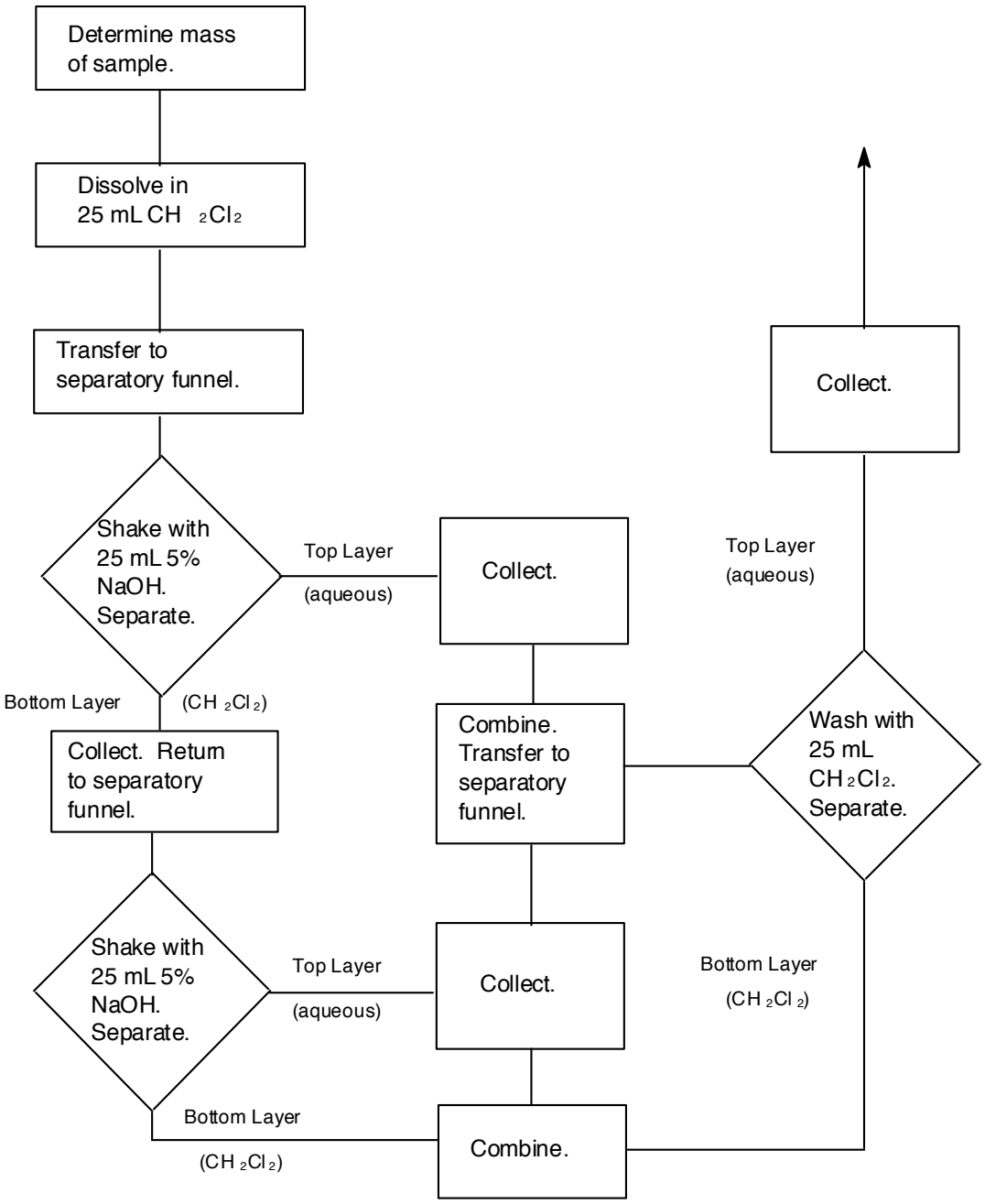
6. **Gently warm** (alternate between low and off) the beaker by turning on the hot plate to a low setting. If the naphthalene melts, you are heating too strongly. After a short while, crystals of naphthalene will appear on the bottom of the flask. When the crystals are large, scrape them off into a vial and collect a second crop. Continue with this procedure until most of the naphthalene has sublimated.

7. Determine the melting point and yield of your product. Hand the vial containing the product to your instructor for grading.

Flow-charts

The procedure described above may seem long and complicated. The student who carries out the experiment with one finger on the instructions is quite likely to make a mistake (e.g., by skipping a line) and rarely understands the significance of each step in the procedure. It is often a good idea to prepare a flow-sheet for any given experiment *before* you come to the laboratory. The flow-sheet can be used during the experiment to guide you through all the necessary steps, *in the correct order*. In addition, the very act of trying to condense several pages of instructions into a **one-page** flow-sheet can assist you in obtaining a better understanding of how each step in the procedure fits into the overall experiment. Before you come to the laboratory you should complete the flow-sheet and hand it in to your instructor. (**Note:** For this experiment, a series of short flow-charts might be more appropriate than one large one.) The flow-chart shown in Figure 5.3 summarizes steps 1-5 in Part A of this experiment.

Figure 5.3. Example of a flow-chart



Safety

Dichloromethane (methylene chloride) is harmful if inhaled, swallowed or absorbed through the skin. Wear gloves and eye protection. Use in well-ventilated area or fume hood. Potential carcinogen.

Sodium hydroxide is corrosive. Skin contact is harmful. Can cause severe burns and is dangerous to the eyes. Wear gloves and eye protection.

Hydrochloric acid is harmful to eyes, lungs and skin. If concentrated, use only in a fume hood. Wear gloves and eye protection.

Benzoic acid, 4-methylbenzoic acid, 2-methylbenzoic acid, 4-chlorobenzoic acid and salicylic acid do not present any specific hazards, but all the usual precautions should be taken, e.g., avoid ingestion, skin contact, etc.

3-Nitroaniline is toxic. It can be absorbed through the skin, so wear gloves. Avoid breathing dust. In case of contact, wash exposed area with water for at least 15 minutes.

4-Chloroaniline does not present any specified hazards, but avoid ingestion and contact with skin.

Naphthalene is harmful by ingestion, inhalation and by skin contact.

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

Waste Disposal

Solutions of sodium hydroxide and hydrochloric acid should be diluted with water and washed down the sink.

Dichloromethane should be placed in the bottle labelled "waste halogenated solvents."

Special containers will be provided for all other waste materials.

Write-up

A standard investigative report is required. In this report, you should list any significant observations, report any problems or difficulties, etc. Do not write out a detailed account of the procedure, as these details will have been included in a flow-chart, which should be re-submitted with your report. Your grade will be largely determined by your having correctly identified the unknown compounds in the given mixture, and by the quality and quantity of the samples that you submit. **Remember** to photocopy you lab report before mailing it to your academic expert for marking.

Questions

Answers to be submitted with report.

1. When extracting an organic compound from an aqueous solution into an organic solvent (e.g., diethyl ether), a chemist will sometimes add sodium chloride to the aqueous solution. What is the purpose of such an addition? What is the procedure called?

2. Why is the procedure used in this experiment called liquid-liquid extraction?

3. A CHEM350 student was working on her yield determination of her recrystallized *p*-aminobenzoic acid, when some naphthalene was inadvertently spilt into her crystals. You happen along the scene, and offer the following advice to the distraught student:
   a) Redissolve all the solid in dichloromethane, extract with dilute aqueous acid, , re-isolate the organic compound by precipitating the salt of the base with strong base, and recrystallize your *p*-aminobenzoic acid again.
   b) Redissolve all the solid in dichloromethane, extract with dilute aqueous base, re-isolate the organic compound by precipitating the salt of the acid with strong acid and recrystallize *p*-aminobenzoic acid again.
   c) Do either a or b.
   d) Discard everything into the hazardous waste container. Nothing can be done.

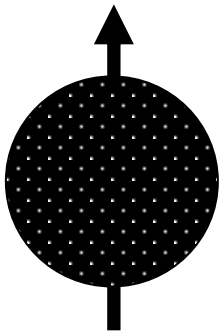
4. When an aqueous solution of an organic compound is shaken with an immiscible organic solvent, such as diethyl ether, the solute distributes itself between the two phases. When the two phases separate into two distinct layers, an equilibrium will have been established such that the ratio of the concentrations of the solute in each solvent defines a constant, K, called the distribution coefficient (or partition coefficient).

   $$K = \frac{\text{concentration of solute in solvent A, e.g., diethyl ether } (g \cdot L^{-1})}{\text{concentration of solute in solvent B, e.g., water } (g \cdot L^{-1})}$$

   The distribution coefficient for compound X in the diethyl ether/water system is 3.0. If you were given a solution containing 8.0 g of X in 500 mL of water and wanted to extract compound X into diethyl ether, show that it would be more effective to extract X using three 50 mL aliquots of diethyl ether rather than a single 150 mL aliquot. (**Hint:** Determine how much of X would remain in the aqueous solution in each case.)

Experiment 6

Reactions of the Common Functional Groups
Part 1: Hydrocarbons
Part 2: Infrared Spectroscopy Tutorial



Preparation

Before beginning this experiment, you should have read through the entire experiment and

1. studied "Structure Determination: Mass Spectrometry and Infrared Spectroscopy", in McMurry's *Organic Chemistry*.

2. you may wish to read Chapter 29 in J.W. Zubrick's "The Organic Chem Lab Survival Manual: A Students Guide to Techniques" pp.201-222.

Objectives

The purpose of this experiment is to

1. introduce the student to a number of chemical reactions that can be used to distinguish between **alkanes, alkenes, alkynes** and aromatic hydrocarbons. In this experiment, a variety of tests will be performed on a selection of known compounds. In a later experiment, the student will be expected to use the same tests in order to identify an assigned unknown compound.
2. gain a firm understanding of the various functional groups (C=O, OH, NH, etc.) present in an organic molecule, because the functionality of an organic molecule determines its reactivity. Therefore, in order to begin to understand why different organic molecules behave the way they do, you must be able to first identify the type of functional group present.
3. perform the qualitative organic analysis to determine if a molecule is an alkane, alkene or alkyne, learn to identify all the major functional groups found in organic molecules. Finally you will use infrared spectroscopy to determine the type of functional group in an organic compound.

Introduction to Qualitative Organic Analysis and Infrared Spectroscopy

Although spectroscopic techniques are now the preferred method of determining the identity of unknown organic compounds, it is still instructive to study the techniques formerly used for this purpose.

This experiment, the first of a series, will illustrate a number of relatively simple "test-tube reactions" called qualitative organic analyses* that can be used to distinguish between certain types of hydrocarbons. Subsequent experiments (in *Chemistry 360*) will explore similar methods of distinguishing among other groups of structurally similar compounds; e.g., primary, secondary, and tertiary alcohols; aldehydes and ketones; etc. The series will conclude with an experiment in which the student will be given an unknown compound. The student will be expected to determine which family or class it belongs by performing a number of "wet" tests, and will attempt to identify the compound through the preparation of appropriate derivatives. Finally the student will confirm his or her conclusion by interpreting the spectral data that will be provided by the instructor.

	Solid Organic	**Liquid Organic**
Purification Method	Recrystallization	Distillation (simple or fractional)
Assessment of Purity	Melting point, *TLC**	Boiling point, Refractive index
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	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.

*The phrase "qualitative organic analyses" is a fancy way of saying 'classical wet-chemical methods used to determine the nature/functionality of an organic molecule'. Prior to 1950, these methods were the sole means available to chemists who were interested in identifying the functional groups in compounds. Today, with the use of infrared and NMR spectroscopy, chemists have much more reliable ways of determining functionality and identifying an unknown organic compound.

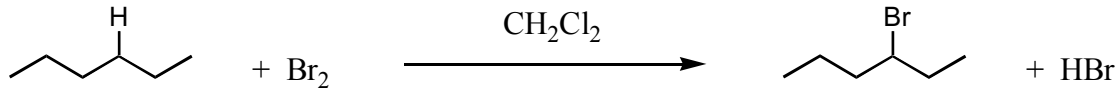
Many chemical diagnostic tests have been developed and just a few of them are listed in the table below:

Chemical Family	Solubility Class	Function Group Tests	Comment
Alkane	Neutral	**Bromine Test, Sulfuric acid Test**	Slow reaction, unreactive to Baeyer and sulfuric acid tests
Alkene	Neutral	**Baeyer Test** **Bromine Test**	Fast reaction. Color of reagent fades. No HBr formed in Bromine Test.
Alkyne	Neutral	**Ammoniacal Silver Test**	Terminal triple bond detected. Pptte formed
Alcohol	Neutral	Acetyl chloride treatment to form ester, then Ferric Hydroxamate Test 2. Lucas's test ($ZnCl_2$ in HCl)	-Forms the hydroxamate ester, then a Fe^{3+} colored complex -Test for 2° or 3° alcohols. Solution turns cloudy.
Ester	Neutral	1. Hydrolysis to carboxylic acid 2. Ferric hydroxamate Test	-Saponification with 30% NaOH then acidification. -Deep red-purple complexes formed with Fe^{3+}
Aldehyde	Neutral	1. 2,4-dinitrophenylhydrazine (2,4-DNP) 2. Tollen's Test	-Forms the 2,4-DNP derivative, a highly coloured precipitate. -Silver mirror formed in Tollen's Test
Ketone	Neutral	1. 2,4-dinitrophenylhydrazine 2. Tollen's Test 3. Iodoform Test	-Forms the 2,4-DNP derivative, a highly coloured precipitate. -No silver mirror formed in Tollen's Test -detects methyl ketones. Yellow pptte & medicinal odor
Amide	Neutral	1. Amide Hydrolysis, 2. Ferric hydroxamate Test	-Saponification with 30% NaOH and detection of NH_3 in vapors. -See esters. Required more drastic reaction (>150º C)
Carbohydrate	Neutral	1. Benedict's Reagent 2. Tollen's Test	-Detects reducing sugars. Brick red pptte of Cu_2O formed. -Silver mirror formed by reducing sugars (aldehydes and α-hydroxy ketones)
Phenol	Weak Acid	1. Ferric Chloride Test, 2. Pauly Test	-Blue or purple complex for simple phenols. Red or green complexes with polysubstituted phenols -Red, orange, yellow-green or blue azo compounds formed when treated with diazonium salt of sulfanilic acid
Carboxylic acid	'Strong' Acid	Solubility	Soluble in 5% NaOH and sat. $KHCO_3$
Amine	'Strong' Base	1. Hinsberg Test, 2. Pauly Test for aromatic amines	-Forms the sulfonamide of 1º and 2º amines -Red, orange, yellow-green or blue azo compounds formed when treated with diazonium salt of sulfanilic acid

Part 1: Experimental Theory on Functional Group Tests

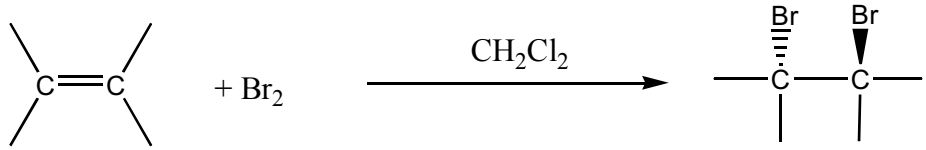
Bromine Test

Alkanes are relatively unreactive, they are insoluble in water, aqueous acids and aqueous bases. In daylight, alkanes will react *slowly* with bromine in dichloromethane:



When such a reaction occurs, the red-orange colour of the bromine solution *slowly* fades and the presence of the acid hydrogen bromide gas can be detected using moist litmus paper.

In contrast, alkenes decolourize solutions of bromine in dichloromethane very quickly:



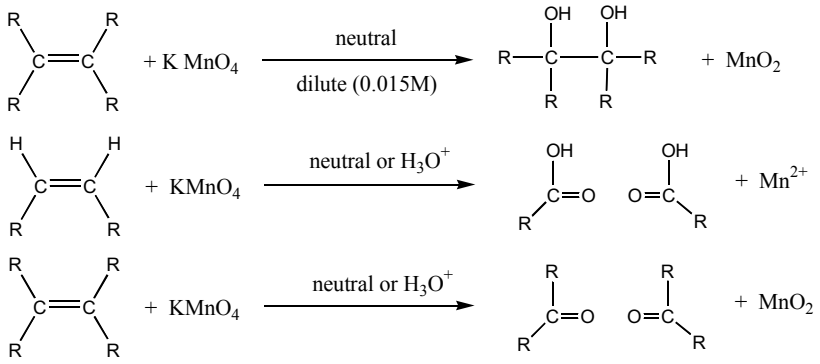
Alkynes undergo a similar reaction.

Cyclohexene is recommended as a control compound. In this test, phenols, amines, aldehydes and ketones and other compounds (e.g., alkanes) react by substitution to evolve HBr. Decolorization of more than 1 drop of bromine (1% in dichloromethane), without the evolution of HBr, indicates unsaturation (C=C or C≡C).

Benzene itself only reacts with bromine in the presence of a suitable catalyst, although other aromatic compounds may react with bromine, depending on the nature of any substituents that may be present.

Baeyer Test (0.015 M Potassium Permanganate Test)**:**

Another test for unsaturation, i.e., for the presence of a carbon-carbon double or triple bond, is the Baeyer test. In the Baeyer test, acidified, dilute potassium permanganate is added to the compound being tested. Alkenes and alkynes (and certain other compounds) cause the purple colour of the permanganate solution to disappear. For example:

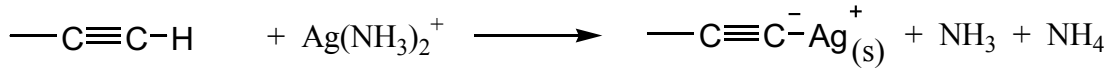


It is difficult to stop this reaction at the diol stage. $KMnO_4$ will also react further with vicinal diols, resulting in cleavage and formation of carboxylic acids or ketones, depending on whether H are present on the double bond, alkanes and aromatics do not react.

If more than 1 drop of the purple permanganate solution decolorizes, with the formation of a brown precipitate (MnO_2), it suggests the molecule being tested is unsaturated. However, be aware that easily oxidizable compounds, such as aldehydes, aromatic amines, phenols, formic acid, and formate esters, also give positive results. Most pure alcohols will not react in less than five minutes. Decolourization of only 1 drop of the permanganate solution must not be considered a positive test because of the potential presence of oxidizable impurities.

Ammoniacal Silver NitrateTest

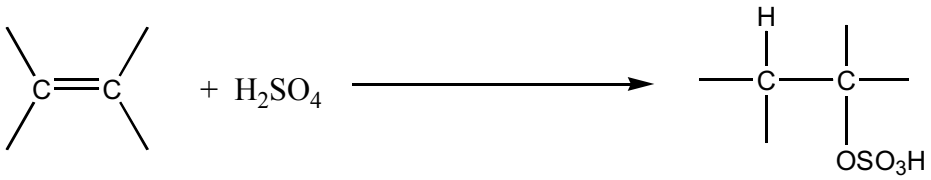
A convenient method of detecting the presence of a terminal carbon-carbon triple bond is through the use of ammoniacal silver nitrate. The terminal hydrogen atom is sufficiently acidic that compounds containing a —C≡C-H group react with ammoniacal silver nitrate to produce a silver salt:



This is a very sensitive test for terminal alkynes. Cloudy precipitate forms in a positive reaction due to a silver salt. The salt product is a dangerous precipitate if allowed to dry. **Note:** product must be decomposed with nitric acid before discarding.

Sulfuric Acid Test

Certain compounds that do not react with dilute acid will react with concentrated sulfuric acid. Evidence for such a reaction occurring is often provided by the formation of a dark solution, an oil, or a precipitate. For example:



Once again, alkanes do not react because of their lack of a functional group. Variable results are obtained with aromatic compounds. Compounds that dissolve in or react with cold concentrated sulfuric acid but not in the solvents 5% HCl, 5% NaOH, 5%$NaHCO_3$ belong together in a class of high carbon # (Mwt.) alcohol, aldehyde, ketone, amide, ester, and unsaturated compound or aromatic hydrocarbon (with several alkyl groups on the benzene ring).

Attention: Some tests may give conflicting or ambiguous results because of impurities in the test reagent or the observation to be made may be subject to misinterpretation. For example, aldehydes often contain trace amounts of its corresponding carboxylic acid.

Chemicals, Equipment, Utilities Required

All equipment used must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
pentane, cyclohexene, phenylacetylene, biphenyl, toluene, bromine in dichloromethane sol'n, Baeyer Reagent, Ammoniacal Silver Test Reagent, Conc. Sulfuric acid., ice wash acetone, chloroform, carbon tetrachloride, nujol	-test tubes, test tube racks -IR Spectrophotometer -KBr salt blocks/disks -mortar and pestle -Pasteur pipettes, Kim-wipes®, -hazardous waste disposal containers (in fume hood)	-115V electrical

About Using the IR Spectrophotometer

- KBr salt blocks are readily fogged and dissolved by water. Use only anhydrous solvents to clean the disks. Store at all times in the dessicator.

Procedure

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

Carry out the tests described below on each of the following substances: pentane, cyclohexene/methylpentenes (use the product you will obtain in Experiment 8), phenylacetylene, biphenyl, toluene, and one of the unknowns if provided.

For each test carried out, record your observations, explain what the observations infer, and write an equation. (See "Write-up" section for suggested format.)

1. Bromine Test

Dissolve three drops (or a few crystals) of the hydrocarbon in 0.5 mL of dichloromethane. Add, dropwise, about 0.5 mL of the bromine in dichloromethane solution. If the brown-red colour persists, stopper the test tube and allow it to stand in light for at least one hour. Test for the evolution of hydrogen bromide using moist litmus paper.

2. Baeyer Test

To three drops (or a few crystals) of the hydrocarbon add, drop by drop, with shaking, about 0.5 mL of a solution made from equal volumes of potassium permanganate (0.03 mol· L^{-1}), and sulfuric acid (3 mol· L^{-1}).

3. Ammoniacal Silver Nitrate Test

In each of four ultra-clean test tubes, use distilled water to dilute 2 mL of (0.3 mol· L^{-1}) silver nitrate solution to 5 mL. Add 2 drops of concentrated ammonia. **(CARE: This solution has a concentration of 14.8 mol· L^{-1}. Use it only in the fume hood. Protect your eyes and hands.)** Shake each test-tube so that the brown precipitate that forms just redissolves. Add 1 drop (or a few crystals) of each of the hydrocarbons to each tube and shake. If a precipitate forms, destroy it with a little concentrated nitric acid before discarding the contents of the tube.

CARE: Concentrated nitric acid has a concentration of 15 mol· L^{-1}. Protect your eyes and hands. Use only in a fume hood.

4. Sulfuric Acid Test

CARE: The sulfuric acid used here has a concentration of 18 mol· L^{-1}. Protect your eyes and hands.

To 1 mL of **cold** concentrated sulfuric acid, *cautiously* add, with shaking, three drops (or a few crystals) of the hydrocarbon. For the test with phenylacetylene, make sure to use a large test tube and perform in the fumehood.

Safety

In addition to the dangers involved when using concentrated sulfuric acid, concentrated nitric acid and concentrated ammonia, you should also be aware of the hazardous nature of the following substances listed below.

Pentane is highly flammable. High concentrations of pentane vapours have a narcotic effect. Liquid pentane is harmful if swallowed or if it gets into the eyes.

Cyclohexene vapour irritates the eyes, skin and respiratory system. The liquid is harmful if swallowed. Highly flammable.

Phenylacetylene is a lachrymator and an irritant! Use only in a fume hood. Wear gloves and eye protection.

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

Toluene is flammable. Prolonged inhalation, ingestion or skin absorption may result in headaches, nausea, vomiting and dermatitis. Avoid contact with the liquid and do not breathe its vapours. Flammable.

Bromine solutions—Bromine is extremely irritant to the eyes, lungs and skin. Poisonous if swallowed. Wear gloves and eye protection. Use only in a fume hood.

Permanganate solutions—Potassium permanganate is a skin irritant. Wear gloves and eye protection.

Silver acetylides are explosive when dry. Destroy by adding concentrated nitric acid.

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

Waste Disposal

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

halogenated compounds—including products from the bromine test
waste permanganate
waste silver
waste concentrated sulfuric acid

Do *not* dispose of any of the substances used in this experiment in any way other than by placing them in the special containers provided.

Part 1 Write-up

Keep the 'Introduction' brief. Do not rewrite the lab manual theory section (pp.100-104 of the CHEM350 lab manual), simply define the purpose of the various tests. The results of this experiment may be presented in the form of a four-column table, as illustrated below. You should attempt to write a conclusion about the prospects of your being able to differentiate between alkanes, alkenes, alkynes and aromatic hydrocarbons using the tests investigated in this experiment. Finally, do not forget to answer the questions at the end of this experiment.

Remember to photocopy you lab report before mailing it to your academic expert for marking.

Test	Observation	Inference	Equation
1.Dissolved 3 drops 1-pentene in 0.5 mL CH_2Cl_2 and added (dropwise) about 0.5 mL Br_2/CH_2Cl_2 solution. 2. Etc.	Red-brown colour of Br_2 disappeared as soon as the two solutions mixed.	Bromine reacts 1-pentene because the latter contains a carbon-carbon double bond.	$CH_3(CH_2)_2CH=CH_2$ $\downarrow Br_2$ $CH_3(CH_2)_2CH\text{-}CH_2Br$ Br

Part 2. Infrared Tutorial:

Interpretation of Infrared Spectra (to be Done at Home)

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). The Unknown Spectra can be found at the end of the CHEM350 Report Book or online at:
   http://science.athabascau.ca/Labs/resources/350Unkns/index.php
   username = auchem350
   password = reaction

Introduction to Infrared Spectroscopy- Theory and Practice

Electromagnetic Radiation

As you read this page, uncountable numbers of photons or 'light particles' are reflecting off its surface and are being absorbed by pigments (i.e. complex organic molecules) in the rod and cone cells in the retina of your eye. Where the ink (i.e. complex organic dye) has absorbed the photons, you perceive a dark area (i.e. letters) due to the lack of photons from that point on the paper.

On a deeper level, photons (and electrons) are actually wave/particle dualities as described by quantum physics. Photons carry only a discrete amount of energy, called quanta, but the amount of energy of a quanta is defined by the equation, $e = h \upsilon = h c/l$ where:

- e = the energy of 1 photon (quanta)
- h = Planck's constant (6.62×10^{-27} erg sec)
- υ = Frequency in hertz (cycles or l per sec)
- c = Speed of light (3×10^{10} cm per sec)
- l = Wavelength in cm

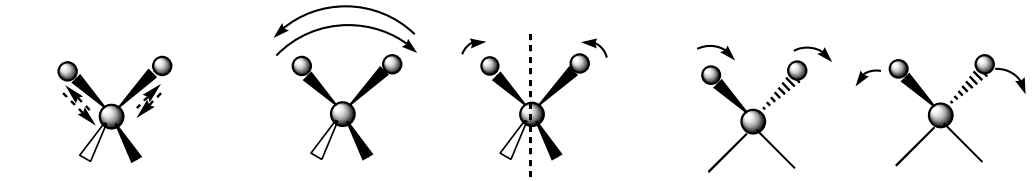
Thus the amount of energy carried by a photon varies directly with its frequency, and because of the relationship between frequency and wavelength, varies inversely with its wavelength. Photons also behave like waves of electromagnetic energy traveling at the speed of light.

Practically speaking however, you need only understand that photons are the messengers that carry the electromagnetic force between electrons and other elementary particles. Electrons, whether free or bound in a covalent bond, are capable of absorbing (or emitting) photons and changing their energy state. This leads to different types of excitation (nuclear transformations, electronic, rotational, nuclear spin changes, bond deformation) depending on the amount of energy carried by the photon. High-energy photons (x-ray, gamma ray, and cosmic ray) can cause ionization of the molecule, while UV photons are involved in electronic interactions. Remember it is the interaction of electrons (via photons) in the outer cloud surrounding atoms that forms the foundation of all chemical reactions.

Infrared Radiation

Infrared radiation is composed of photons with a specific range of wavelengths (7.8×10^{-5} cm to 10^{-2} cm) and frequencies ($\sim 10^{14}$ to 10^{12} Hz). This range includes the near infrared, the infrared and far-infrared regions. The actual wavelengths of interest to most organic chemists are 1.667×10^{-3} cm to 2.5×10^{-4} cm (the 'infrared' region). These wavelengths (λ) are most often expressed as there corresponding wave number (n) where $n = 1/\lambda$, with n measured in cm^{-1}. (e.g. l2.5 to 16.6 μm = 4000 to 600 cm^{-1}).

Infrared carries relatively low levels of energy (e.g. ~1 to 10 kcal/mol) which, when absorbed, result in only bond vibrations like stretching and bending, e.g., rocking, scissoring, wagging, and twisting (i.e., bond deformations).



Stretching Vibration (symmetric or antisymmetric)

(rocking vibration scissoring vibration wagging vibration twisting vibration)

SomeTypes of Bending Vibrations

Every molecule, depending on its make up, is capable of absorbing infrared photons and increasing the intensity of its molecular motions. Different functional groups within the molecule will absorb photons at different infrared wavelengths. Thus when a spectroscopic wavelength scan is performed on an organic molecule, certain λ will be absorbed while other λ will pass through. Once we have the infrared spectrum of a compound, the spectrum can be analyzed and compared with known infrared absorptions for particular functional groups (see Table 8.1).

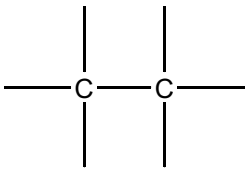
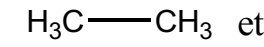
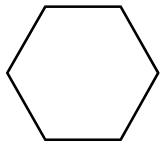
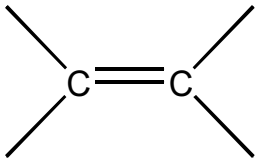
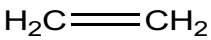
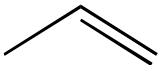
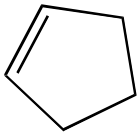
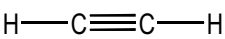
The infrared spectrum for a particular molecule can be very complex, consisting of many absorption bands because of the many possible motions each atom can undergo (a non-linear molecule has 3N-6 normal modes of vibration where N = the number of atoms in the molecule). When analyzing a spectrum, it is important to look at four different regions of the spectrum for the presence or absence of specific absorption peaks.
Note: you are not required to analyze the fingerprint region.

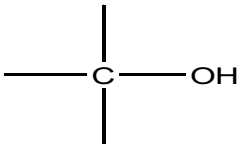
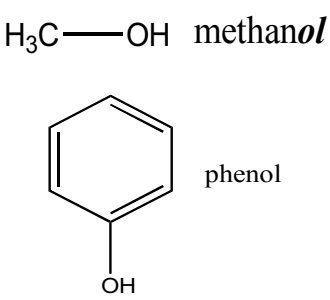
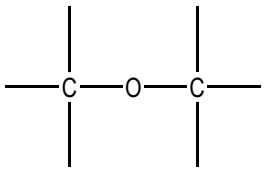
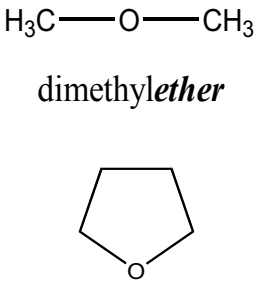
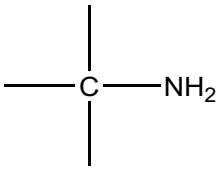
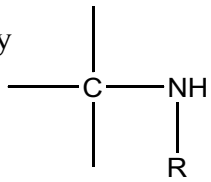
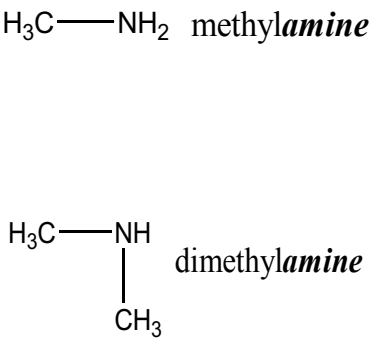
Wavenumber cm^{-1}

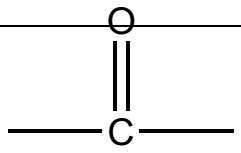
4000	3000	2000	1400	600
N-H O-H sp^2 CH	sp^3 CH	C≡N C≡C	C=C C=O C=N	fingerprint region

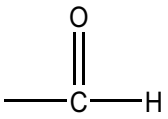
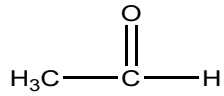
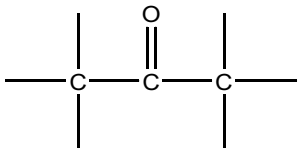
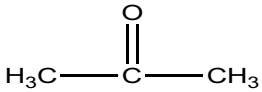
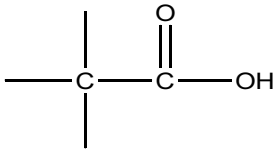
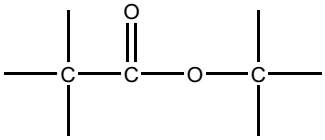
The following pages contain information to help you understand and interpret infrared spectra.

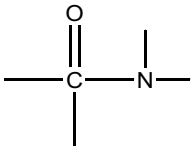
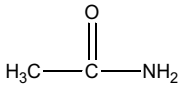
1. a chart showing the structures of various functional groups, which you need to know.
2. the wavenumbers of the functional groups, to help you locate pertinent absorption bands on an infrared spectrum.
3. Diagrams of the shapes and intensities of various infrared absorption bands, which will help in your interpretation of infrared spectra.
4. Finally, your instructor will lead you through the interpretation of sample infrared spectra representative of various functional groups. Unknown spectra are included to allow you to practice on your own. There is a great deal of information to learn, but the more you practice, the easier it becomes to interpret infrared spectra.

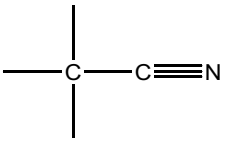
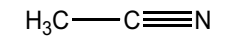
FAMILY NAME	FUNCTIONAL GROUP STRUCTURE	EXAMPLES AND NOMENCLATURE
Alkane	 sp^3 orbitals	 eth***ane***  pent***ane***  cyclohex***ane***
Alkene	 sp^2 orbitals	 eth***ene***  prop***ene***  cyclopent***ene***
Alkyne	 sp orbitals	 eth***yne*** (Acetylene)

Alcohol		
Ether		
Amines	Primary  Secondary 	

Carbonyls: 

Aldehyde		 ethan***al*** (Acetaldehyde)
Ketone		 propan***one*** (Acetone)
Carboxylic Acid		 ethan***oic acid*** (Acetic acid)
Ester		 methyl ethan***oate*** (Methyl acetate)

Amides		 ethan***amide*** (Acetamide)

Nitriles		 ethane***nitrile*** (Acetonitrile)

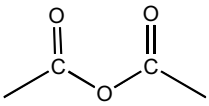
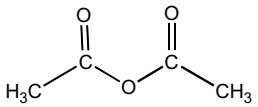
Anhydride		 acetic **anhydride**

Table 6.1 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 (1°)
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}.

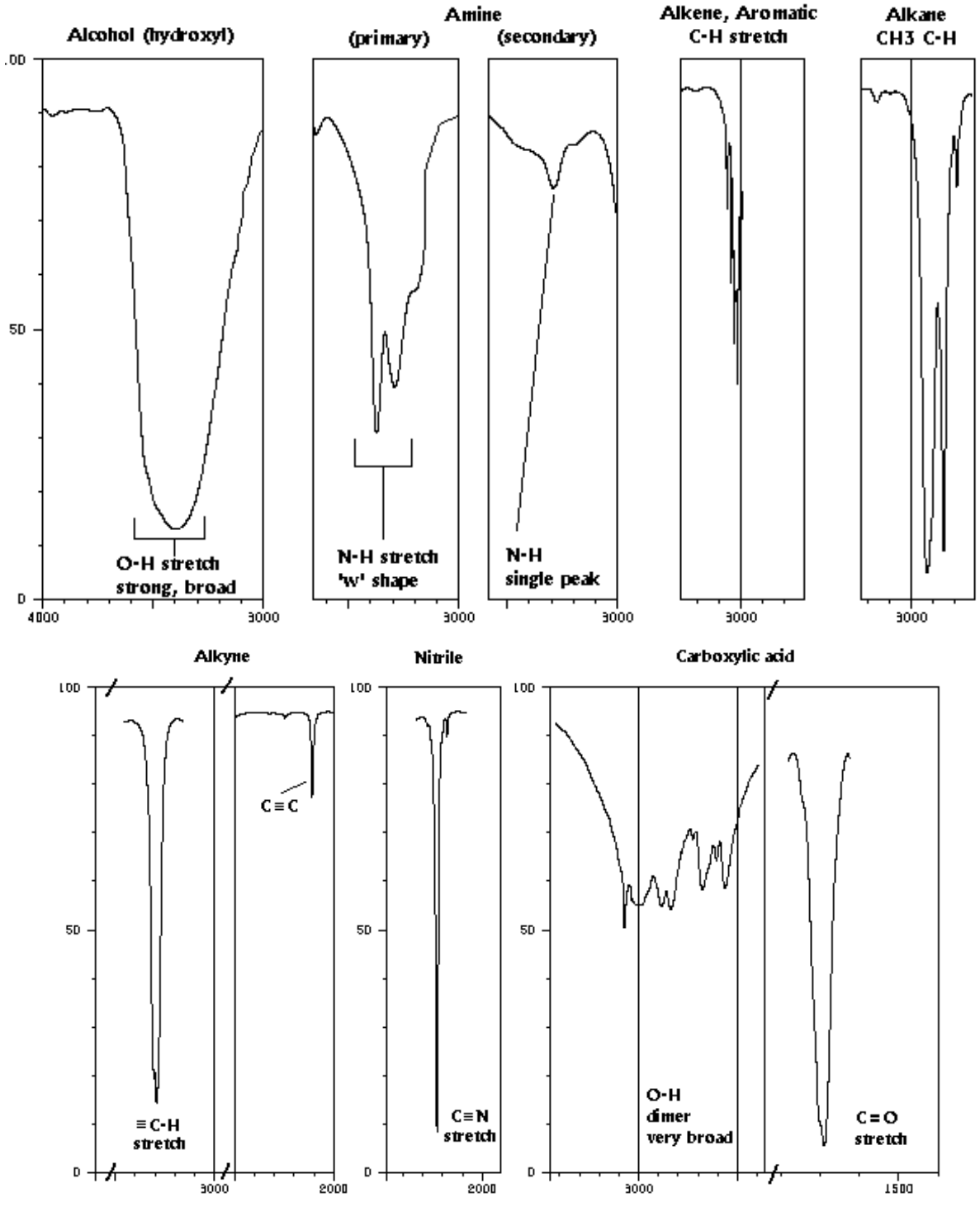
Calculation of the # Degrees of Unsaturation in a Compound

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

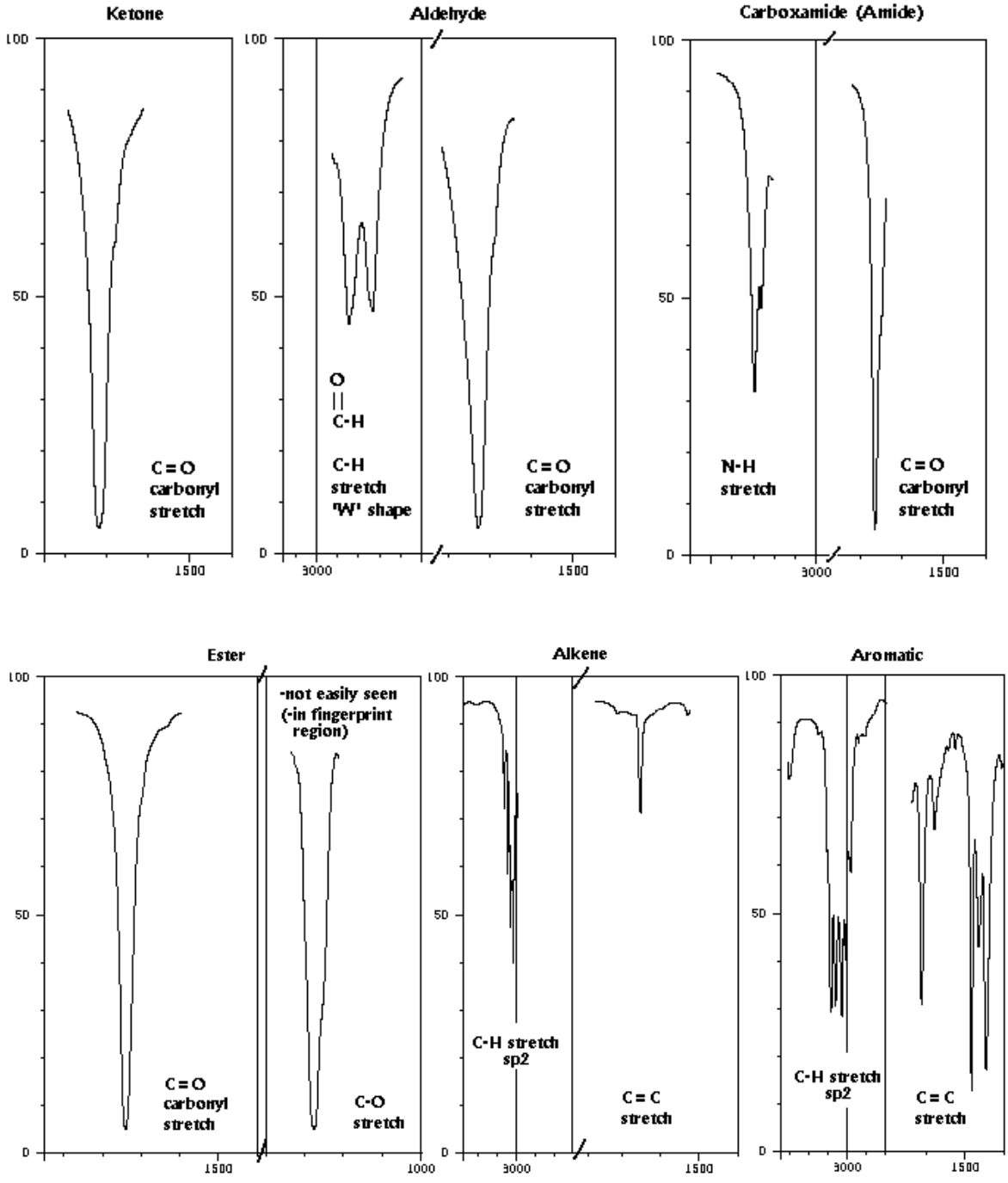
e.g., Therefore, for Compound A, C_7H_{12} = (7) +1 + 1/2(0) - 1/2 (12) - 1/2(0)
= 7 + 1 - 6 = **2** degrees of unsaturation in Compound A.

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

Shapes of Infrared Absorption Bands Observed for Different Functional Groups



Typical Absorption Band Shapes (cont.)



How to Interpret an Infrared Spectrum

Step 1 Divide the infrared spectrum into four main areas (use pencil and ruler and take into account any off-shift in the spectrum's wavenumbers).

i) Above 3000 cm^{-1}
ii) Between 3000 and 2000 cm^{-1}
iii) Between 2000 and 1400 cm^{-1}
iv) Below 1400 cm^{-1} (fingerprint region)

Step 2 Starting at the left of the spectrum, examine the area **above 3000 cm^{-1}**, first looking in the region near 3300 cm^{-1} and record in tabular format the presence/absence of:

i) a broad, very strong absorption band of an **'O-H'**. If present, it means you know that your molecule is at least an **alcohol**.
ii) A broad, weak to medium strength, double or single absorption band of **'N-H'**. If present it means you have an **amine** (1° or 2°) or possibly an **amide**.
iii) A sharp, medium to strong, single absorption band of **'≡C-H'** of a **terminal alkyne**. Note: If present, it means you should also see a 'C≡C' absorption near 2250 cm^{-1}.

After examining the region around 3300 cm^{-1}, look for any sharp, weak to medium absorption just above 3000 cm^{-1} (e.g. 3050 cm^{-1}) resulting from the 'C-H' stretch of a sp^2 hybridized carbon. If present, it means you have a **'C=C-H'** of an alkene or aromatic compound.

Step 3 Next examine the area between **3000 and 2000 cm^{-1}** and record the presence/absence of absorption bands or peaks.

i) First look just below 3000 cm^{-1} (e.g. 2850-2950 cm^{-1}) resulting from the 'C-H' stretch of a sp^3 hybridized carbon. If present, it means you are seeing the **'C-H'** stretch of an **-CH_2 or -CH_3** group. Note: This absorption is not very informative as most organic compounds have -CH_2 or -CH_3 groups.
ii) Then look for the extremely broad peak, actually starting at 3300 cm^{-1} and extending all the way to ~2500 cm^{-1}, caused by the **O-H dimer** between two **carboxylic acid** molecules (COOH). This absorption is probably the most difficult to see as other absorption peaks may be overlapping the broad peak.
iii) Finally look for a sharp, weak to medium peak caused by either **'C≡C'** or **'C≡N'**.
iv) If present, then the compound is an alkyne (might also have the 'C-H' of a terminal alkyne, see step 2 above) or a nitrile.

Step 4 Next examine the area between **2000 and 1400 cm^{-1}** and record the presence/absence of absorption bands or peaks.

i) First look near 1700 cm^{-1} (e.g. 1680-1750 cm^{-1}) for a sharp, strong peak resulting from the **'C=O'** stretch of a **carbonyl**. Note: <u>This absorption is very informative</u> and will be present if your compound is an aldehyde, ketone, ester, amide, or carboxylic acid.
ii) Next look near 1650 cm^{-1} (e.g. 1600-1670 cm^{-1}) for a sharp, weak peak resulting from the **'C=C'** stretch of an **alkene**.
iii) Finally look near 1600 cm^{-1} and 1500 cm^{-1} for a sharp, double peak resulting from the **'C=C'** stretch of an **aromatic ring**.

Step 5 If you dare, you may look in the **fingerprint region** (**area below 1400 cm^{-1}**) and record the presence of absorption bands or peaks.

i) First look near 1200 (1160-1310) cm^{-1} for a sharp, strong peak resulting from the **'C-O'** stretch of an **ester**.
Note: This absorption is very difficult to see and may or may not be present, i.e. conclusive if present, inconclusive if not present.

ii) If you suspect you have an aromatic ring (absorption bands at ~3030 and 1600 and 1500 cm^{-1} present), you may try to discern the substitution pattern of the benzene ring by looking at the strong absorption bands of the **ring 'C-H'** out-of-plane bending vibrations in the region 680-900 cm^{-1}.

Benzene Substitution Pattern	Ring 'C-H' Absorption Bands Present (cm^{-1})
monosubstituted	2 sharp peaks, 730-770, 690-710
ortho disubstituted	1 sharp peak, 735-770
meta disubstituted	3 sharp peaks, 860-900, 750-810, 680-725
para disubstituted	1 sharp peak, 800-860
1,2,3 trisubstituted	2 sharp peaks, 760-780, 705-745
1,3,5 trisubstituted	2 sharp peaks, 810-865, 675-730
1,2,4 trisubstituted	2 sharp peaks, 870-885, 805-825

Ref: McMurry, J., 1992. Organic Chemistry, 3rd ed, Brooks/Cole, p.549-550, (4th ed, p.559)
Nakanishi, K., 1964. Infrared Absorption Spectroscopy, Holden Day p.27.

iii) Again, if you have an aromatic, you may also try to discern the ring substitution pattern of the benzene ring by looking at the very weak overtone-combination absorption bands of the **ring 'C-H'** stretch vibrations in the region 1670-2000 cm^{-1}.

Benzene Substitution Pattern	Ring 'C-H' Overtone Bands Present (cm^{-1})
monosubstituted	4 weak equally spaced and shaped sharp peaks
ortho disubstituted	3 weak irregularly spaced/shaped sharp peaks
meta disubstituted	2 weak sharp peaks + one weak broad peak
para disubstituted	2 weak sharp peaks

iv) If you suspect you have a long straight chain (>4 C) alkane, (absorption bands at 2850-2950 cm^{-1} present but not much else), you may try to see the sharp, weak absorption due to the concerted rocking of >4 $-CH_2$ in a chain. It lies in the region 720 ± 10 cm^{-1}.

Step 6 Finally, you will summarize your results by making a statement about what functional groups you suspect to be present in the molecule or perhaps you will be asked to select from a list of suggested structures, which molecule most likely would generate the spectrum just analyzed.

Instructor Led Group Infrared Analysis Problems

Use the tables below to record your results of the 'Infrared Spectral Analyses' for the following compounds (infrared spectra on pages 124-130 of this lab manual). Label the absorption bands.

Cyclohexanol	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated
>3000 cm^{-1}	1	3331	broad	strong	O-H stretch alcohol
3000-2000 cm^{-1}	2	2932 & 2855	sharp	strong	C-H sp^3 stretch
2000-1500 cm^{-1}	none				
(Fingerprint)	*3*	*1068*	*sharp*	*strong*	*C-O of alcohol*

Functional Group absent: no ≡C-H, no N-H, no sp^2 H-C=, no C≡C, no C≡N, no C=O, no C=C alkene or aromatic

2-methyl-3-butyn-2-ol	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated
>3000 cm^{-1}	1	~3380	broad	strong	O-H stretch alcohol
	2	3303	sharp	strong	
3000-2000 cm^{-1}	3	2876,2938,2987	sharp	med-str.	
	4	2120	sharp	weak	
2000-1500 cm^{-1}	none				

Functional Group absent: no N-H, no sp^2 H-C=, no C≡N, no C=O, no C=C alkene or aromatic

3-buten-2-ol	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated
>3000 cm^{-1}	1	~3350	broad		
	2	3083 & 3012		strong	C-H ____ stretch
3000-2000 cm^{-1}	3		sharp		C-H ____ stretch
2000-1500 cm^{-1}	4	1646			

Functional Group absent: no ≡C-H, no N-H, no C≡C, no C≡N, no C=O, no C=C aromatic

benzhydrol	Absorption Band Code#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated
>3000 cm^{-1}	1	3392-3359	broad		
	2	3049 & 3027	sharp		C-H ____ stretch
3000-2000 cm^{-1}	3	2900	sharp		C-H ____ stretch
2000-1500 cm^{-1}	4	1598,1495,1458	sharp		

Functional Group absent: no ≡C-H, no N-H, no C≡C, no C≡N, no C=O, no C=C alkene

Instructor Led Group Infrared Analysis Problems (cont.)

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

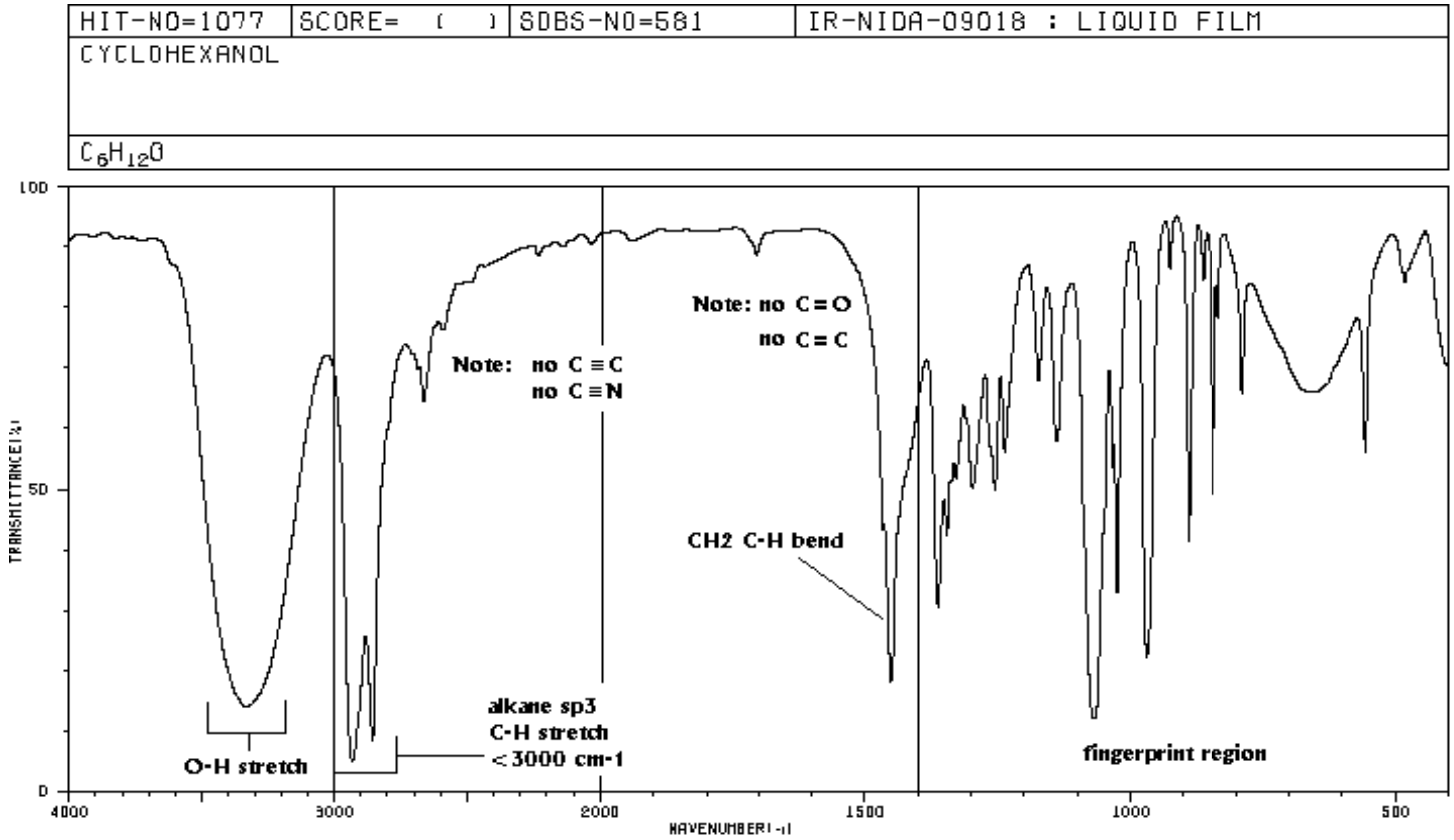
Functional Group absent: no O-H, no ≡C-H, no N-H, no sp^3 C-H, no C≡C, no C≡N, no C=C alkene

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

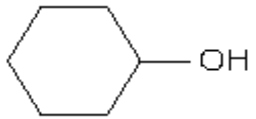
Functional Group absent:

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

Functional Group absent:



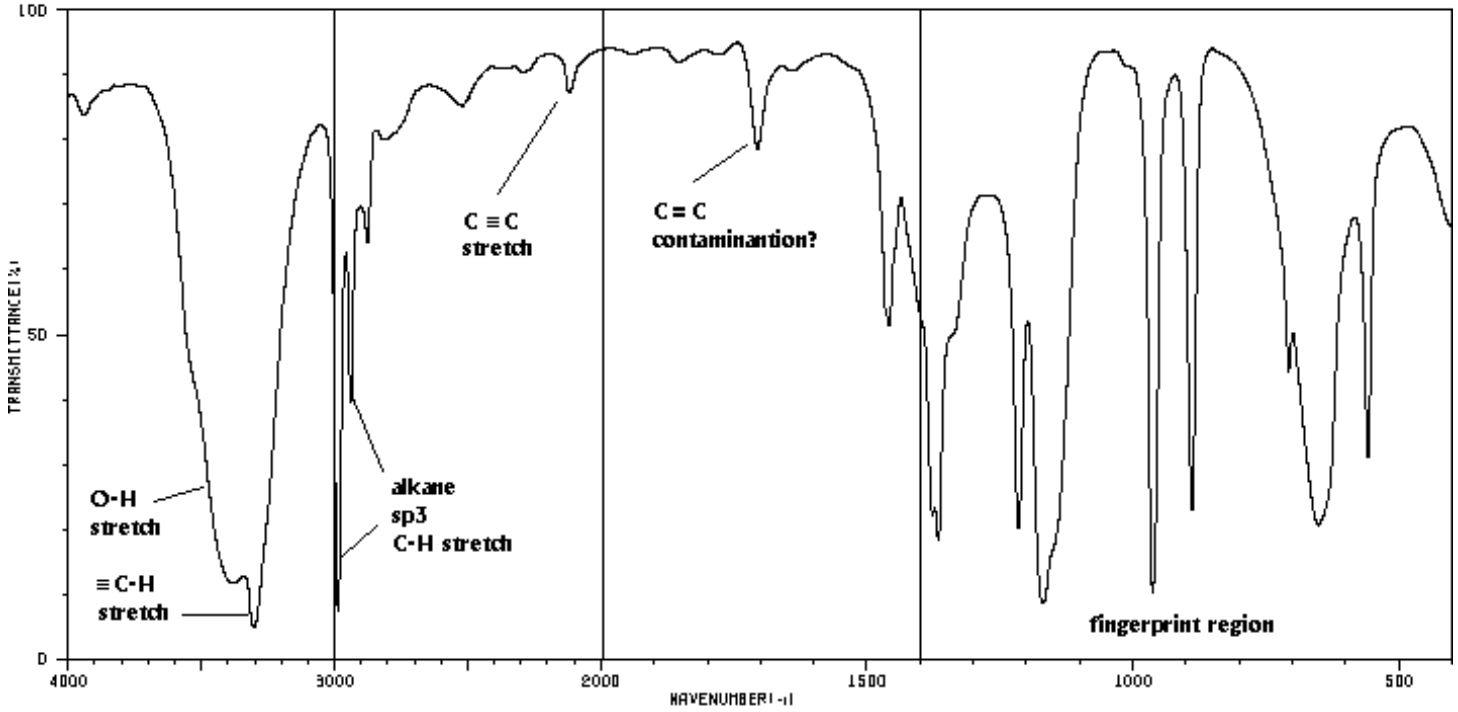
3331	13	1704	86	1256	47	970	21	667	64
2932	4	1467	42	1238	53	926	84	557	53
2855	8	1452	17	1174	86	890	39	482	61
2686	68	1363	29	1140	55	863	81		
2666	82	1346	41	1068	11	845	47		
2588	74	1329	50	1034	52	835	74		
2233	84	1298	49	1025	32	789	64		



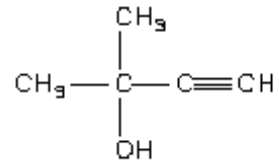
HIT-NO=2057	SCORE= ( )	SDBS-NO=2818	IR-NIDA-00603 : LIQUID FILM

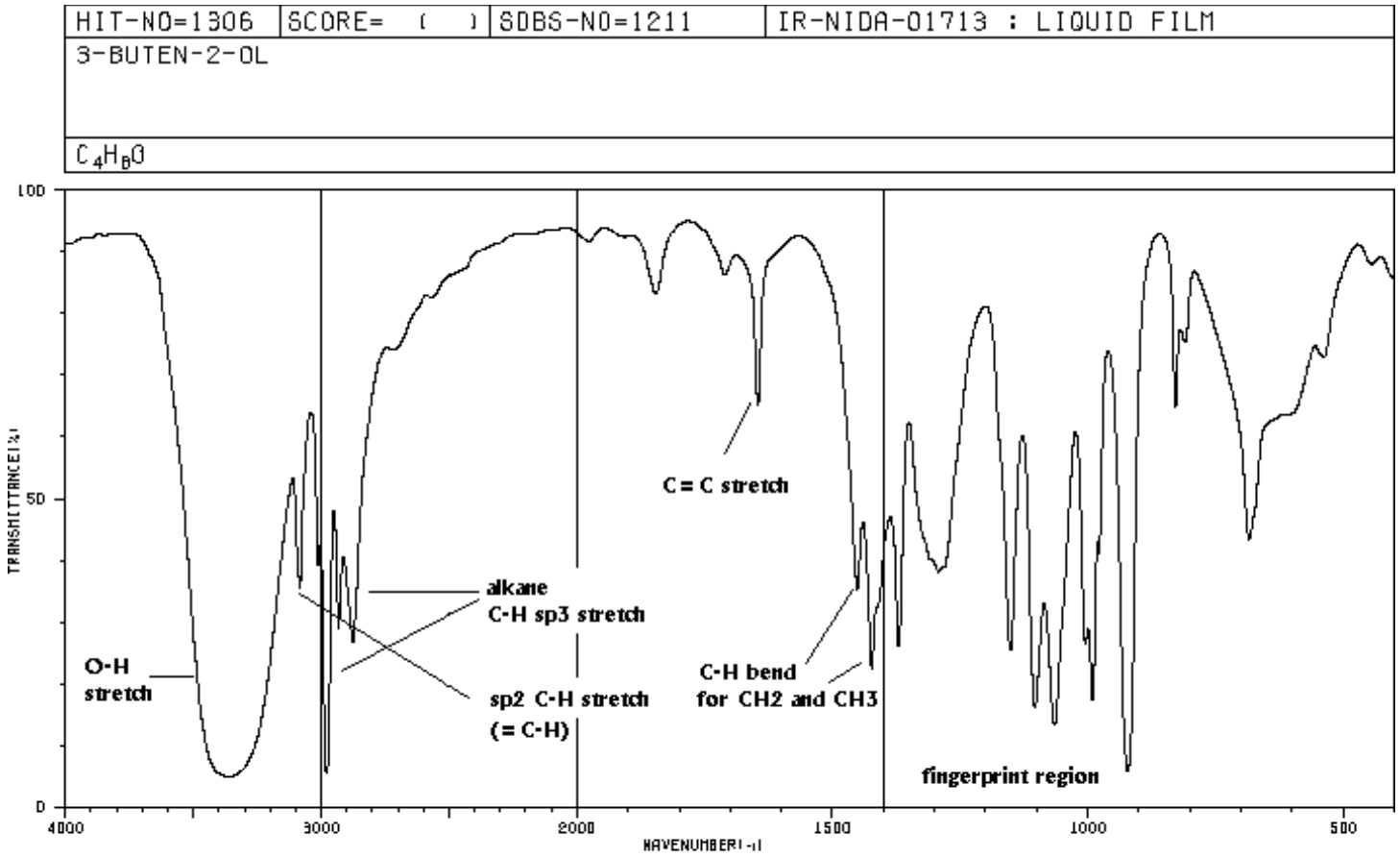
2-METHYL-3-BUTYN-2-OL

C_5H_8O

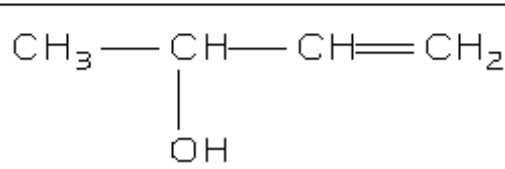


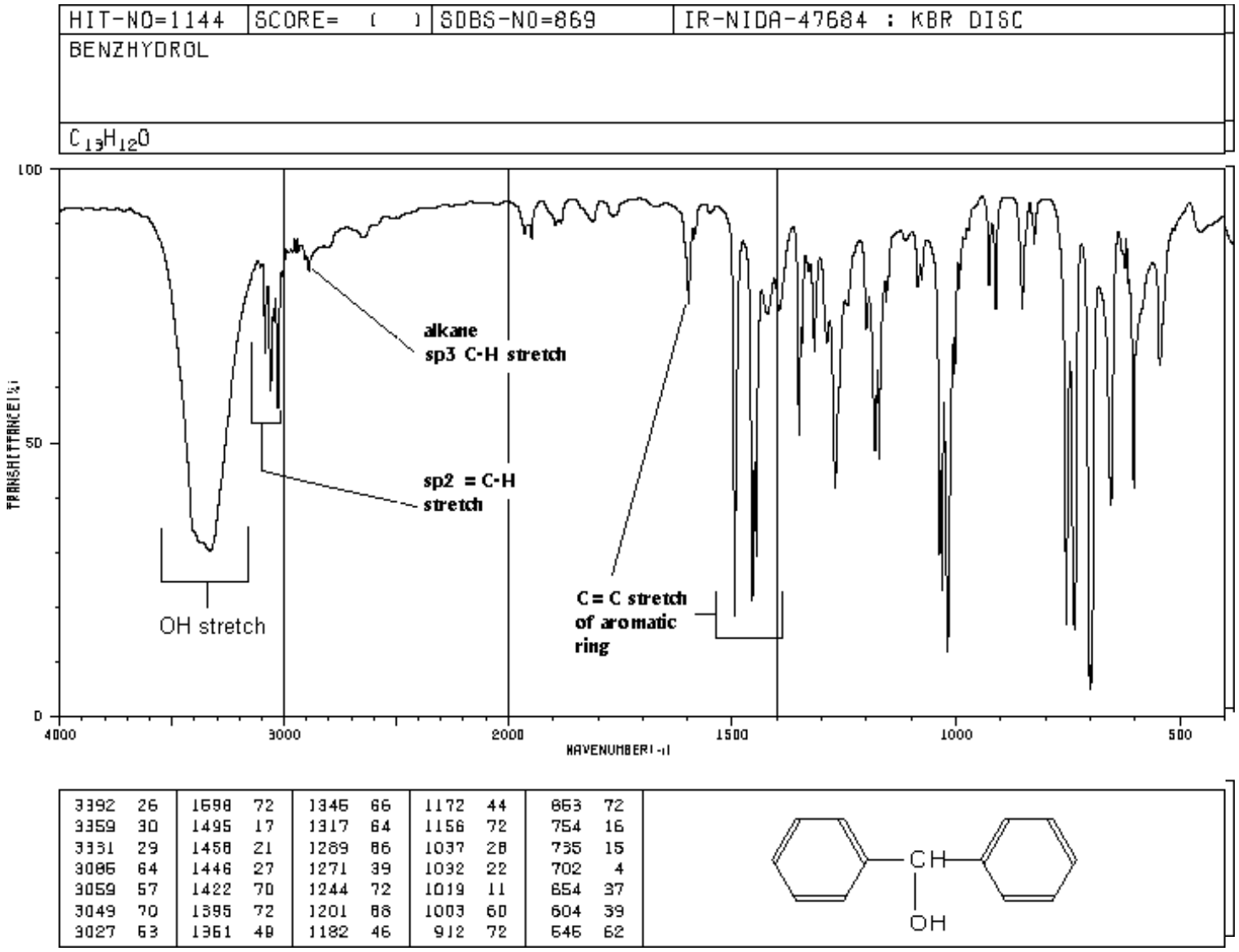
3939	81	2120	84	1170	8
3303	4	1706	74	963	10
2987	7	1465	52	889	22
2938	38	1459	49	708	42
2876	62	1378	21	652	20
2811	77	1368	17	556	30
2619	81	1216	19		





3083	33	1646	62	1066	12	686	41
3012	36	1452	33	1005	24	539	70
2979	4	1424	20	991	15	443	64
2932	26	1371	29	978	30		
2876	24	1292	35	922	5		
1646	79	1152	25	829	60		
1711	81	1103	14	810	72		

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SCORE= ( )
SDBS-NO=869
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BENZHYDROL
C13H12O
100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[cm-1]
alkane
sp3 C-H stretch
sp2 = C-H
stretch
OH stretch
C = C stretch
of aromatic
ring
3392 26
3359 30
3331 29
3086 64
3059 57
3049 70
3027 63
1698 72
1495 17
1458 21
1446 27
1422 70
1395 72
1361 49
1345 66
1317 64
1289 86
1271 39
1244 72
1201 88
1182 46
1172 44
1156 72
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1019 11
1003 60
912 72
863 72
754 16
735 15
702 4
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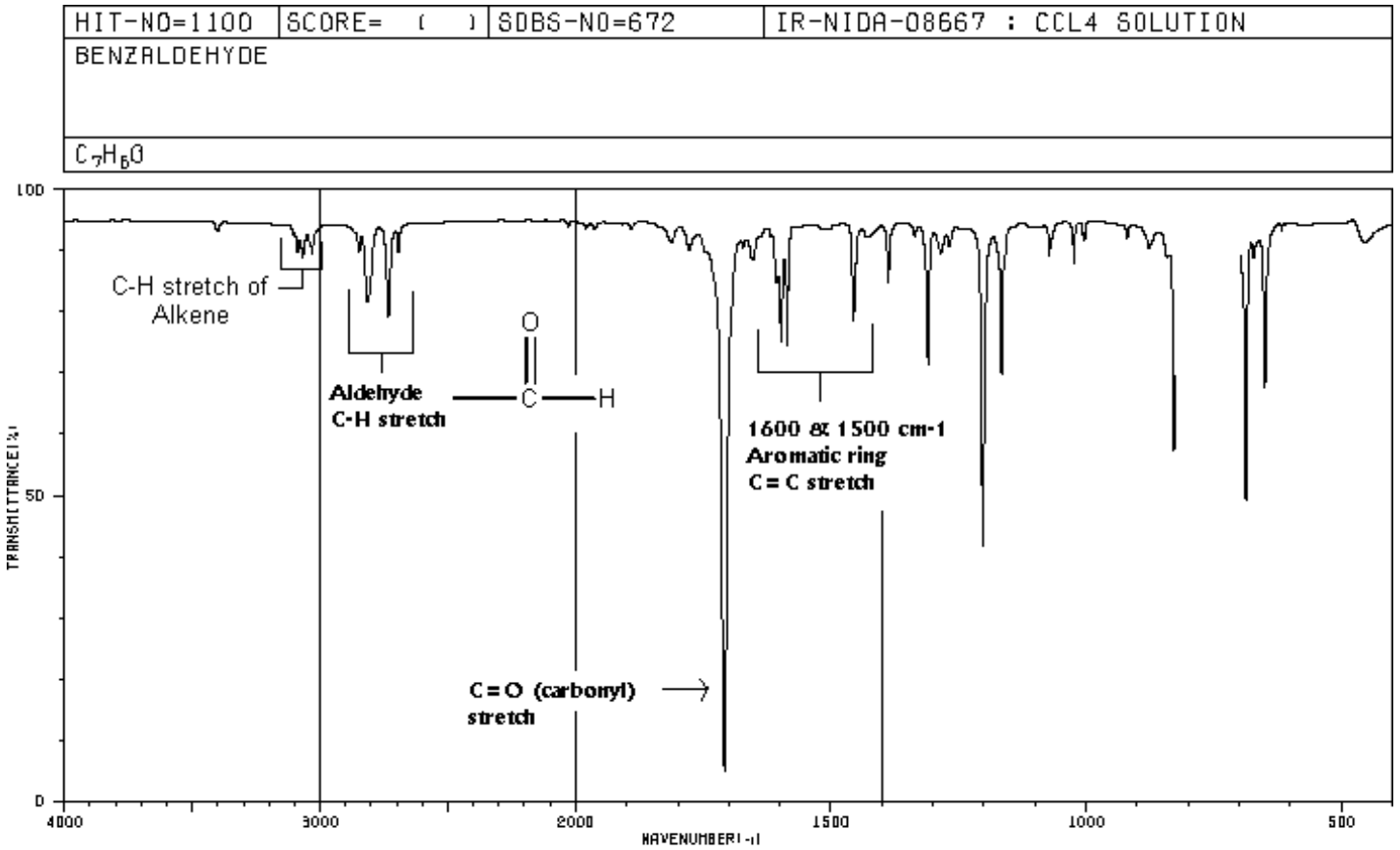
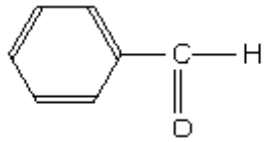
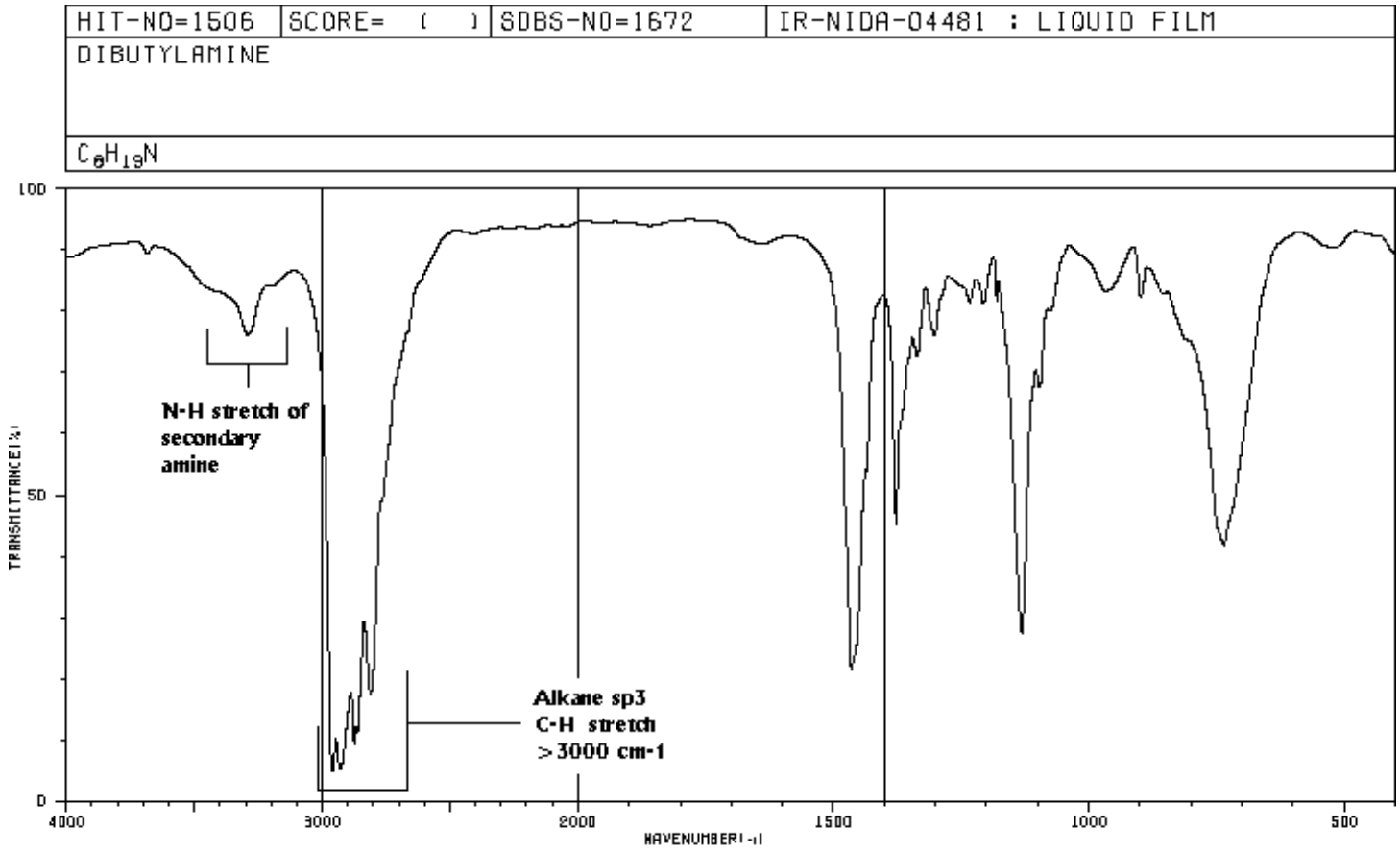
604 39
645 62
CH
OH

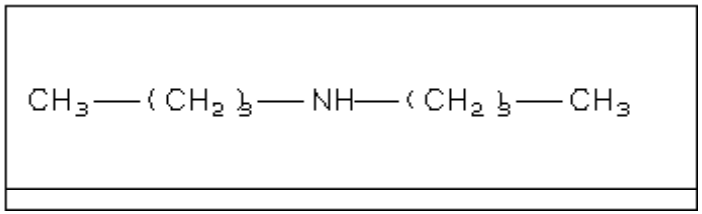


3088	86	1778	86	1388	81	1024	84
3068	86	1709	4	1310	68	828	55
3032	86	1653	84	1285	86	688	47
2847	86	1607	81	1203	39	673	86
2814	79	1598	72	1167	68	650	64
2732	77	1586	72	1160	84		
2693	86	1466	74	1072	86		





3684	86	1466	20	1181	79
3290	72	1378	43	1131	26
2959	4	1338	70	1096	84
2929	6	1302	72	966	79
2874	9	1245	81	961	81
2862	10	1234	79	898	79
2810	16	1206	79	736	41
[illegible]	66	892	41		



Infrared Analysis Practice Problems

Use the tables below to record your results of the 'Infrared Spectral Analyses' of the provided known spectra on pages 133-139 of this lab manual.

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

Functional Group(s) absent:

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

Functional Group(s) absent:

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

Functional Group(s) absent:

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

Functional Group(s) absent:

Infrared Analysis Practice Problems (cont.)

Use the tables below to record your results of the Infrared Spectral Analyses of the provided known spectra.

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

Functional Group(s) absent:

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

Functional Group(s) absent:

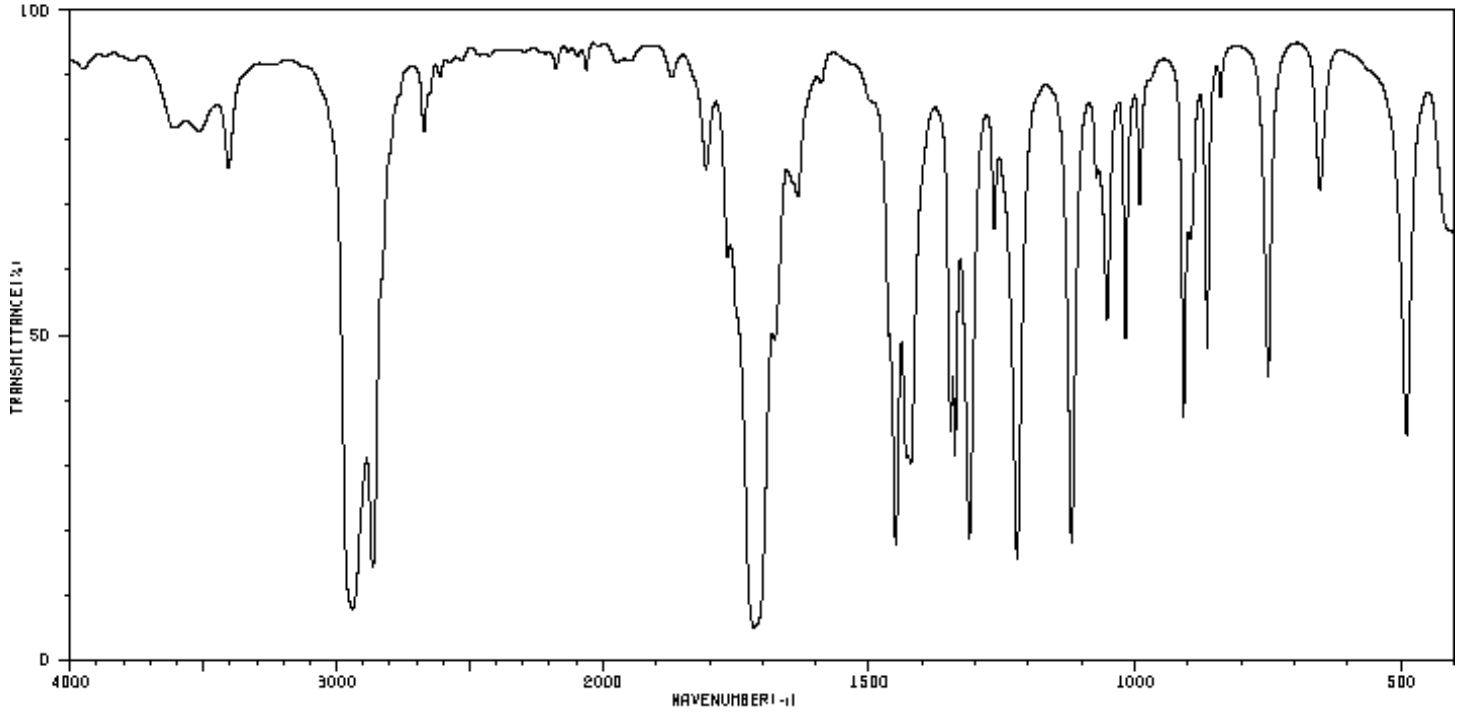
styrene	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

Functional Group(s) absent:

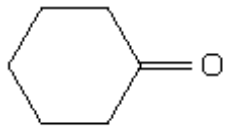
diethyl ether	Absorption Band#	Wavenumber (cm^{-1})	Peak Shape (sharp, broad)	Peak Intensity (strong, medium or weak)	Functional Group Indicated

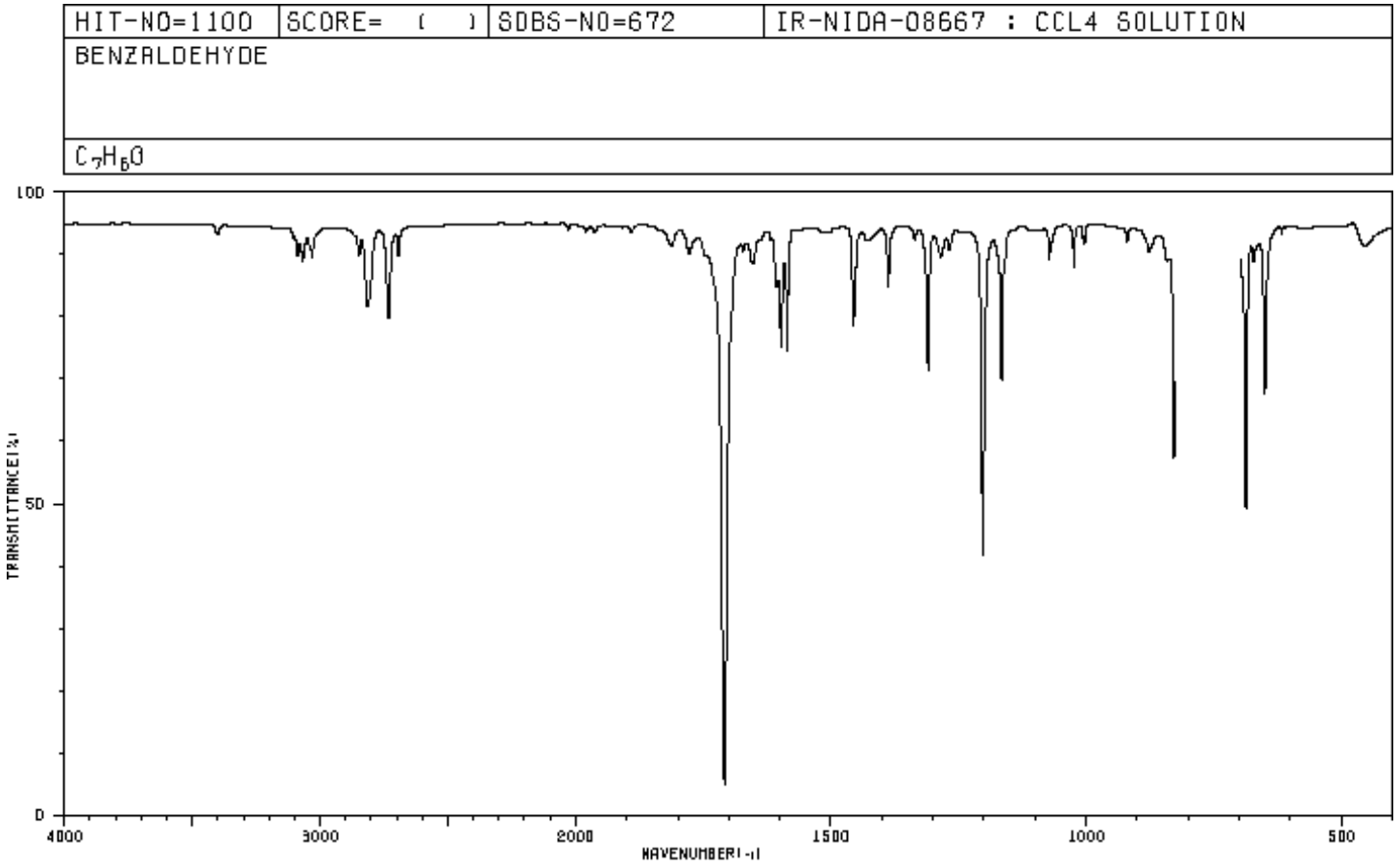
Functional Group(s) absent:

HIT-NO=1070	SCORE= ( )	SDBS-NO=571	IR-NIDA-05262 : LIQUID FILM
CYCLOHEXANONE			
$C_6H_{10}O$			

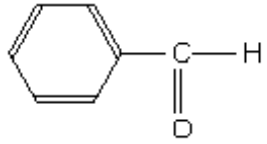


3610	79	2611	86	1460	17	1222	16	896	52
3515	79	1870	86	1429	30	1119	17	864	46
3407	72	1808	72	1422	28	1073	72	839	64
2941	7	1766	60	1347	34	1062	60	760	42
2864	13	1716	4	1338	30	1018	47	652	70
2670	79	1677	47	1311	17	991	68	490	33
2664	84	1634	68	1266	64	909	36		





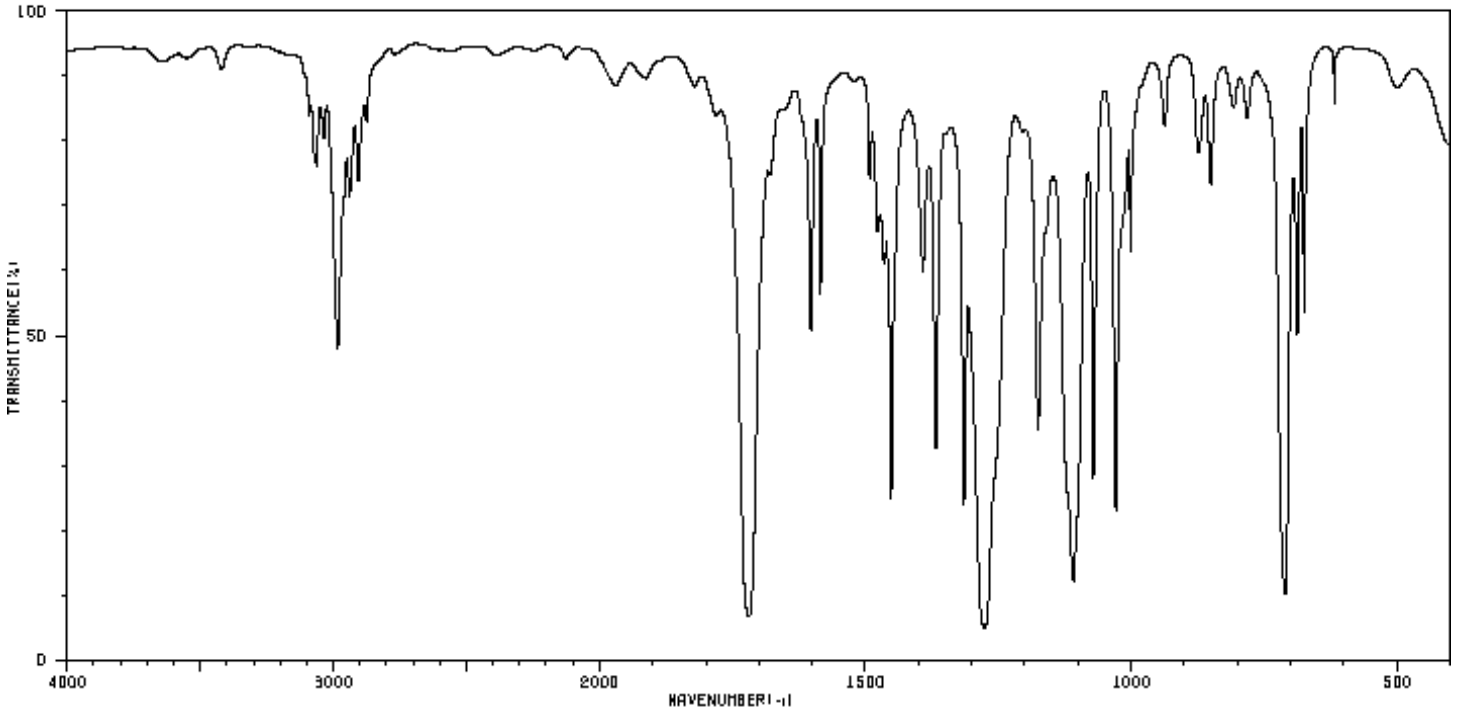
3088	86	1778	86	1388	81	1024	84
3068	86	1709	4	1310	68	828	55
3032	86	1653	84	1285	86	686	47
2847	86	1607	81	1203	39	673	86
2814	79	1598	72	1167	68	650	64
2732	77	1586	72	1160	84		
2693	86	1466	74	1072	86		



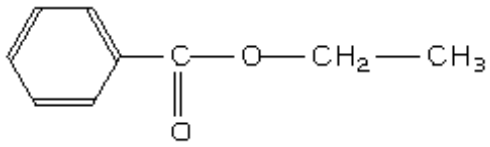
HIT-NO=1451	SCORE= ( )	SDBS-NO=1460	IR-NIDA-04316 : LIQUID FILM

ETHYL BENZOATE

$C_9H_{10}O_2$



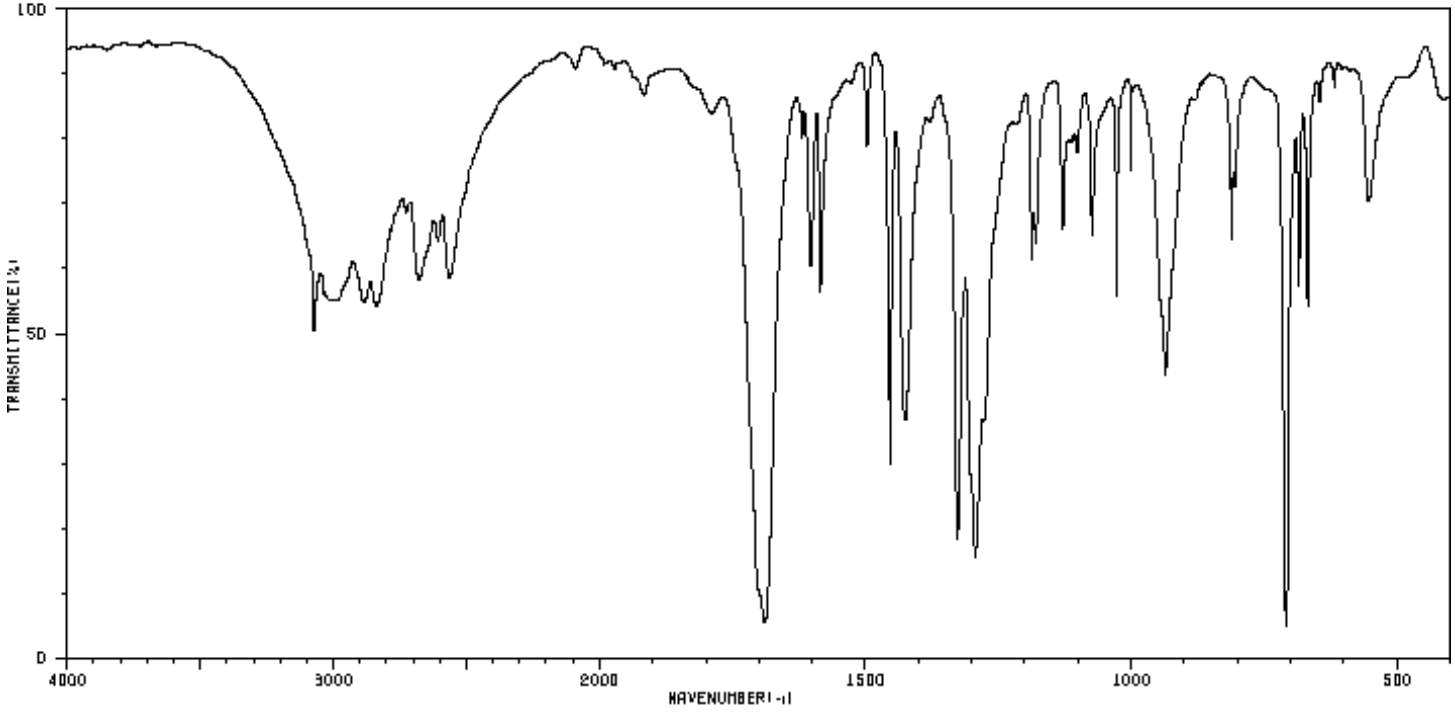
3091	81	1969	84	1466	68	1109	12	807	81
3064	72	1822	84	1452	23	1071	26	782	79
3035	77	1719	6	1392	57	1029	21	711	9
2983	46	1603	49	1368	31	1002	60	688	47
2939	68	1585	53	1315	23	937	79	675	52
2907	70	1492	72	1276	4	873	74	618	61
2874	79	1478	64	1176	34	861	70	606	84



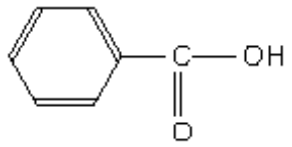
HIT-NO=1081	SCORE= ( )	SDBS-NO=673	IR-NIDA-63340 : KBR DISC

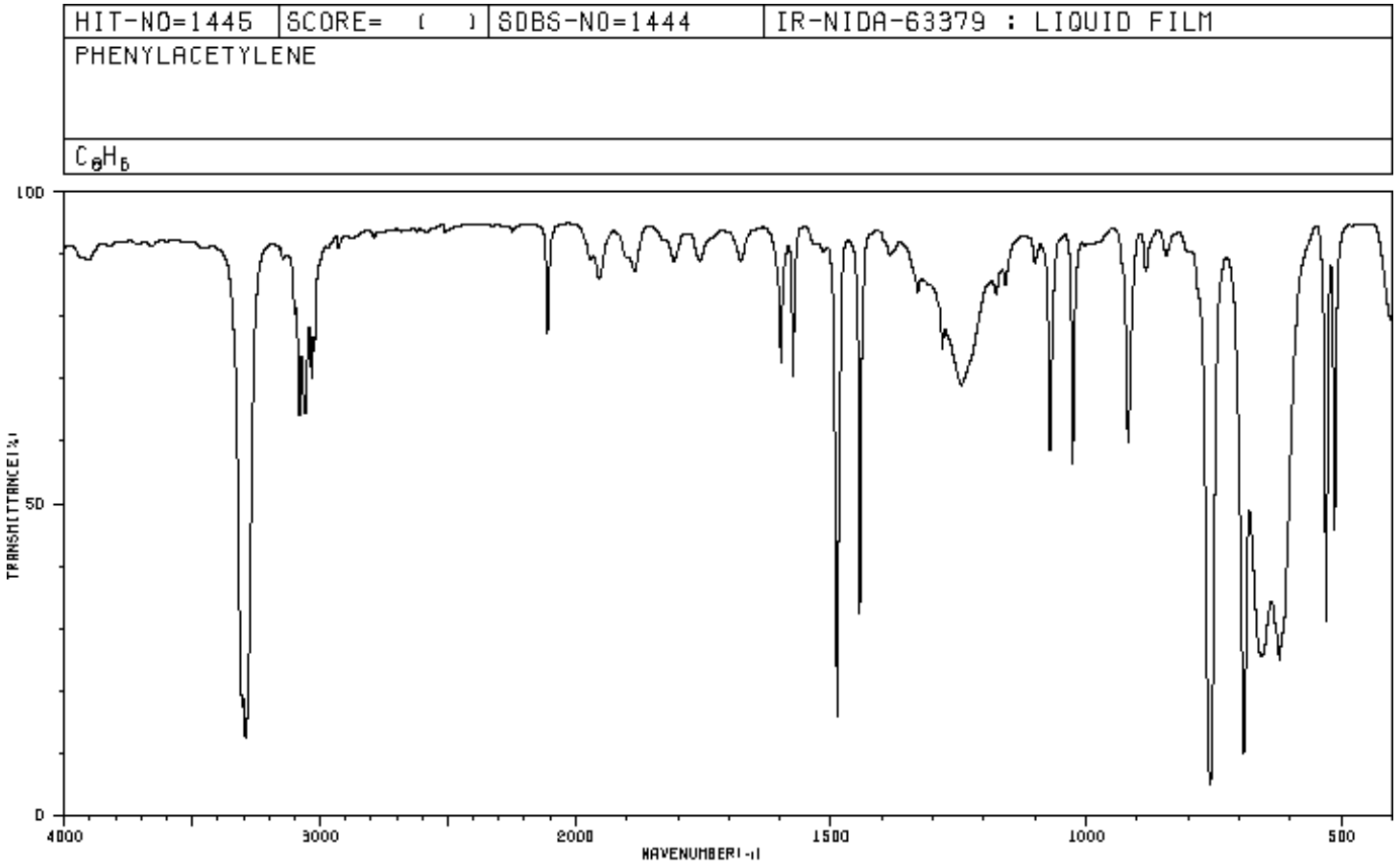
BENZOIC ACID

$C_7H_6O_2$

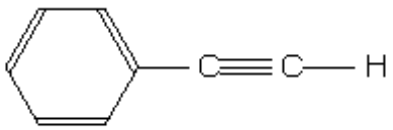


3073	49	2678	67	1426	36	1112	77	936	42
3012	53	2607	62	1327	17	1107	77	812	62
2998	53	2564	57	1294	14	1102	74	805	70
2986	53	1689	6	1187	68	1074	62	708	4
2886	52	1603	58	1180	60	1028	53	685	55
2838	52	1585	59	1129	84	1001	72	667	52
2726	66	1464	28	1118	77	943	60	664	68





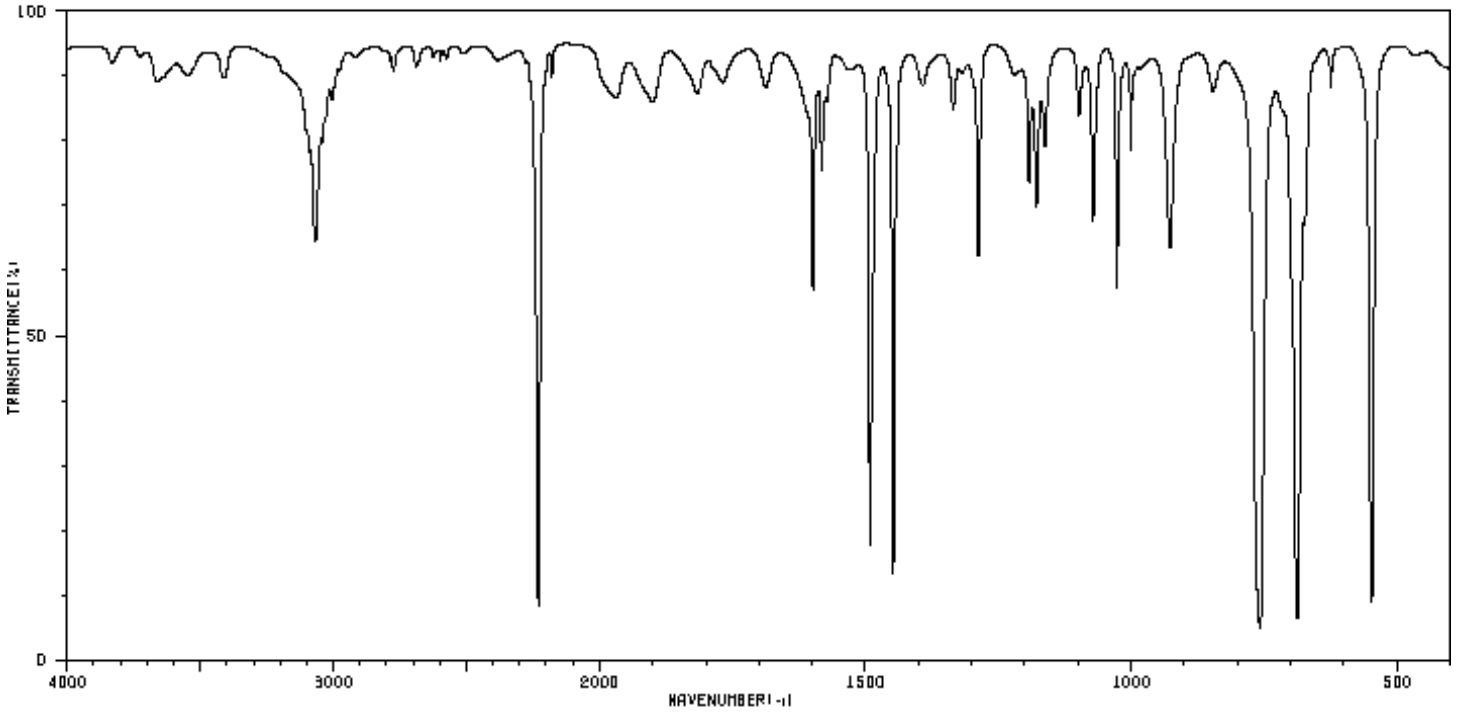
3906	86	2110	74	1674	68	1176	81	843	86
3306	16	1954	84	1488	15	1159	81	757	4
3291	12	1900	86	1444	31	1100	84	692	9
3081	82	1886	84	1386	86	1071	57	666	24
3058	82	1808	86	1331	81	1026	53	621	23
3034	88	1757	86	1282	72	918	57	530	30
3022	72	1698	70	1245	66	883	84	614	43



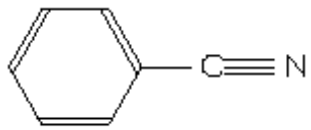
HIT-NO=1114	SCORE= ( )	SDBS-NO=669	IR-NIDA-05064 : LIQUID FILM

BENZONITRILE

C_7H_5N



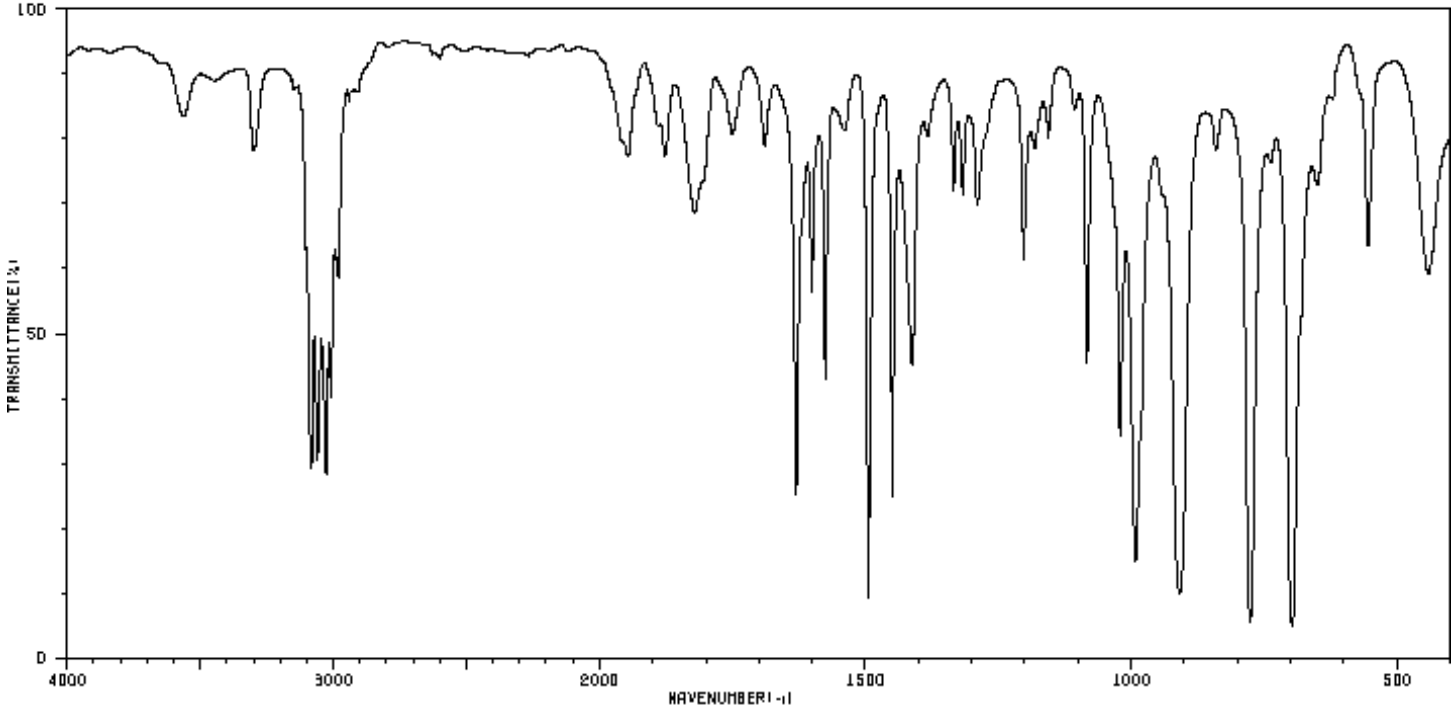
3646	86	2178	86	1582	72	1288	60	1001	74
3412	86	1969	84	1572	81	1193	70	927	60
3088	74	1899	81	1492	17	1178	66	846	64
3066	62	1816	84	1448	12	1163	77	758	4
3004	84	1768	86	1441	72	1098	81	688	6
2256	84	1688	84	1392	84	1072	64	625	64
2230	8	1599	66	1335	81	1027	66	548	8



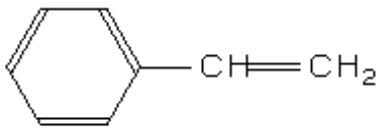
HIT-NO=2170	SCORE= ( )	SDBS-NO=3044	IR-NIDA-10290 : LIQUID FILM

STYRENE

C_8H_8



3299	74	1946	74	1496	9	1202	68	841	74
3082	28	1876	74	1449	23	1182	74	777	5
3060	29	1821	66	1412	43	1156	77	736	72
3027	27	1689	77	1383	77	1083	49	698	4
3009	38	1630	24	1334	70	1021	33	650	70
2980	57	1601	55	1317	68	992	14	555	60
1955	77	1575	41	1290	66	909	9	442	57



Infrared Unknowns Worksheet

Use the tables below to roughly record your results of the 'Infrared Spectral Analyses' for the unknowns (obtained from your instructor or found at the end of this Report Book or online at: http://science.athabascau.ca/Labs/resources/350Unkns/index.php username = auchem350 password = reaction). Please neatly fill out the same table on the unknown spectra and remember to fully label each of the absorption bands identified.

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

Functional Group absent:

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

Functional Group absent:

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

Functional Group absent:

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

Functional Group absent:

Part 2 Write-up

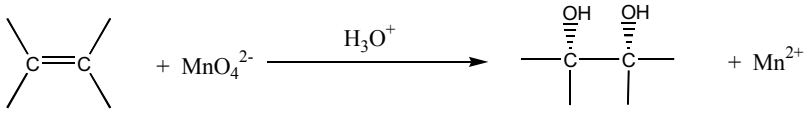
Submit your analyses tables of the 'Instructor Led Group Infrared Analysis Problems' and your analyses tables and spectra for the practice problems. Label your spectra thoroughly.

Also submit your analyses tables and spectra for the unknowns. Label your spectra and clearly indicate the correct structure of the unknowns.

Experiment 6 Questions

Answers are to be submitted with your lab report.

1. The reaction of an alkene with acidic potassium permanganate is an example of a redox reaction. Use the method that you learned in your general chemistry course to write out a balanced equation for the reaction below.



$$a\ C_2H_4 + b\ KMnO_4 + c\ H^+ \text{<------>} d\ C_2H_6O_2 + e\ K^+ + f\ Mn^{+2}$$

Half Rxns.

reduction: ___MnO_4^- + ___H^+ + ___e^- ------>___Mn^{2+} + ___H_2O

oxidation: ___C_2H_4 + ___H_2O ----------> ___$C_2H_6O_2$ + ___ e^- + ___H^+

Bal. Equation: _____

2. The reaction of an alkene with potassium permanganate can also occur in a basic medium, in which case the inorganic product is a brown precipitate of manganese (IV) oxide. (The organic product is again the diol.) Write a balanced redox equation for the reaction of an alkene with alkaline potassium permanganate.

3. What are the major differences you would see in the infrared spectra of an alkane, alkene, and alkyne?

Experiment 7
Extraction of Usnic Acid from Lichen

Preparation

Before beginning this experiment, you should have read the entire experiment and

1. studied the "Stereochemistry" chapter of McMurry's *Organic Chemistry*.

2. completed Experiments 1 through 5.

You may also wish to read "Recrystallization", in Chapter 10 of *The Organic Chem Lab Survival Manual* (Chapters 13 of 3rd ed.).

Objectives

The purpose of this experiment is to

1. isolate an enantiomer of usnic acid, a natural antibacterial organic, optically active compound with a very high specific rotation, found in a native species of lichen called 'Old Man's Beard' (*Usnea* sp.). **Note:** Lichens are fungi/algae symbionts, where the fungus provides a physical support structure and micronutrients for the algal cells while the algal cells provide the fungus with nutrients derived from photosynthesis.

2. learn the technique of liquid solid extraction used in this experiment and the method of two-solvent recrystallization.

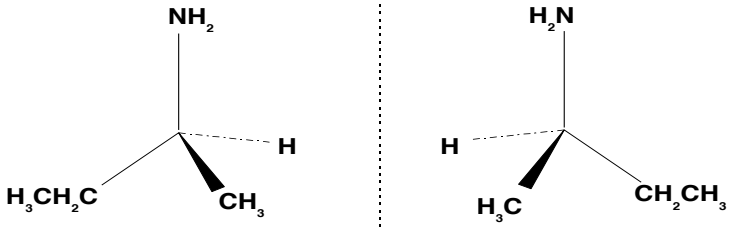
3. determine the specific rotation of the optically active product using a polarimeter, thereby exposing the student to the fundamentals of polarimetry.

Introduction to Natural Products Extractions and Polarimetry

Compounds that contain a carbon atom which is bonded to four different atoms or groups are said to be **chiral** and can exist in two **enantiomeric** forms. Molecular models of these **enantiomers**, or **optical isomers**, are mirror images of one another (see Figure 7.1). Enantiomers have identical physical properties, except that one will rotate plane polarized light to the right, while the other rotates plane polarized light to the left.

Figure 7.1. Line/wedge Diagrams of the two enantiomers of *sec*-butylamine

Because of the similarity in their properties, pairs of



enantiomers would not be separated by the methods used in earlier experiments in this course: e.g., distillation, extraction or recrystallization. One common method of separating enantiomers (i.e., of **resolving a racemic mixture**) is to react the mixture with an optically active reagent so that a pair of **diastereomers** (i.e., stereoisomers that are not mirror images of each other) is formed. In general, diastereomers do differ from one another in their physical properties and can often be separated on the basis of one such property (e.g., solubility in a given solvent). To accomplish this you would have to react a racemic mixture of (±)-*sec*-butylamine with (+)-tartaric acid to produce two diastereoisomeric salts:

(+)-*sec*-butylamine + (+)-tartaric acid -------> (+)-amine-(+)-acid salt
(-)-*sec*-butylamine + (+)-tartaric acid --------> (-)-amine-(+)-acid salt

These two salts can then be separated by repeated crystallizations from water—the salt formed from the (+)-*sec*-butylamine being the least soluble of the two. The salt from the (+)-*sec*-butylamine will be isolated, and the pure (+)-amine regenerated by treating the salt with a strong base.

Another and much simpler way to obtain a pure enantiomer is to find a source which is essentially pure. In this experiment you will attempt to isolate (+) or (-)-usnic acid using a common method for extracting organic compounds from natural sources. Generally a particular lichen will contain only one of the enantiomers of usnic acid, **R** or **S**.

In Experiment 5, we learned the technique **liquid-liquid extraction** for the separation of a mixture of organic solids based on solubility in aqueous versus non-aqueous solvents and acid-base chemistry. In this experiment, another type of extraction method, **solid-liquid extraction**, is used to separate and recover an organic compound (usnic acid) from a complex solid mixture (lichen). The purity of the recrystallized **'chiral'**, (optically active), product is then assessed using polarimetry.

	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, Infrared Spectroscopy	Qualitative Organic Analysis, Infrared Spectroscopy, *(Derivative Formation)**
Separation of Mixtures	Liquid-Liquid Extraction **Solid-Liquid Extraction**	Distillation (simple or fractional)
Drying of Organic Compounds	Vacuum Drying	Pre-drying -'salting out' Drying Agents (e.g. anhydr. $CaCl_2$)

*not done in this course

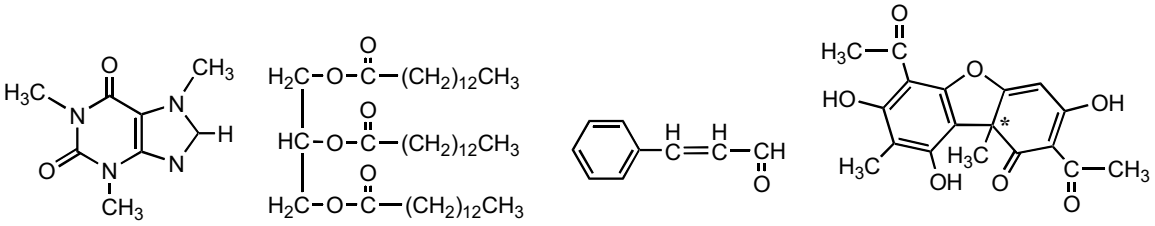
Solid-Liquid Extraction Procedure:

There are only 4 steps involved in performing a solid liquid extraction.

1. Add the unknown mixture and extraction solvent to a vessel.
2. Allow time for the extraction to take place.
3. Gravity filter to remove the unwanted source material
4. Remove the solvent to concentrate the desired extracted solute.

Experiment 7 Background Information

Natural products are of very high interest to chemists. Well-known natural products include caffeine, trimyristin, and cinnamaldehyde.



caffeine trimyristin cinnamaldehyde **usnic acid**

Caffeine can be extracted from tea leaves (2-3% w/w) using boiling water, while trimyristin can be extracted from nutmeg (2-4% w/w) using dichloromethane, and cinnamaldehyde can be extracted from cinnamon using steam distillation. In this experiment, acetone is used to extract usnic acid from the lichen, 'Old Mans Beard'.

After the usnic acid is extracted and concentrated, the product is recrystallized, weighed and then a specific amount placed in the polarimeter and the specific optical rotation determined.

What you will observe when you look through the eyepiece of the polarimeter is that half of the circle will appear dark and the other half light. If the darker half is to the right (relative to the blank), the test substance is dextrorotatory. A darker left half (relative to the blank) indicates a levorotatory substance.

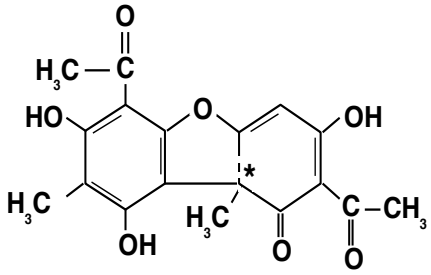


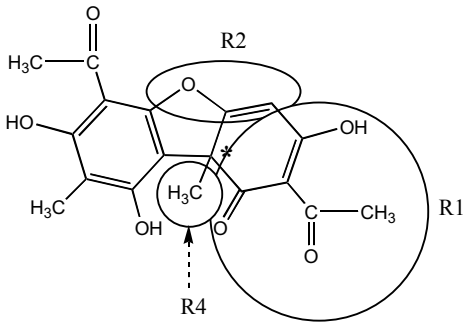
Figure 7.2. Structure of usnic acid (* = chiral or stereogenic C)

Assigning R or S Designations

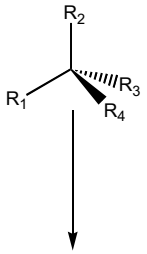
When given a large complicated molecule, especially with ring systems, we advise that you simplify the molecule into arbitrary portions surrounding the chiral centre (see below for R1, R2, R3, R4). Once this is done, follow the Cahn-Ingold-Prelog Sequence Rules to determine R or S configurations:

usnic acid

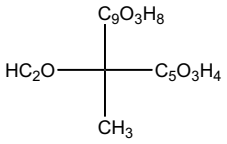
Uncircled atoms =R3



R1 = $C_5O_3H_4$
R2 = C_2OH
R3 = $C_9O_3H_8$
R4 = CH_3
+Chiral C = C
$C_{18}O_7H_{16}$



must orient so that R4 is



Fisher projection of usnic acid
(R or S designation not given)

Cahn-Ingold-Prelog Sequence Rules

1. Rank atoms attached to stereogenic C in order of atomic #, High 1, Low 4. (e.g., Br>Cl>O>N>C>H)
2. If decision cannot be reached, look at second atom of substituent, etc.
3. Multiple bonded C are equivalent to the same # of single bonded atoms.
4. Mentally orient the molecule so that the lowest priority group (R4) is pointing directly back, away from you.

Note: Usnic acid has only one chiral center, and therefore only 2 enantiomers.

Chemicals, Equipment, Utilities Required

All glassware used for solid-liquid extraction must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
lichen (dried and crushed), reagent & HPLC grade acetone, ethanol, L-tartaric acid, distilled water, tetrahydrofuran, ice.	-stirrer-hot Plate, lab jack, retort stands, utility clamps -polarimeter -melting-point apparatus -hazardous waste disposal containers (in fume hood)	-115V electrical, -water aspirator -air-line

About Using the Polarimeter

- The light source for the polarimeter is a very expensive sodium lamp. Do not switch the light source on and off, as this will drastically shorten the life-span of the bulb.

More on Polarimetry

You should already be familiar with the concept of **plane-polarized light** from the theory component of the course. In a **polarimeter**, plane-polarized light of a single wavelength is passed through a sample which, if it is 'optically active', will rotate the plane of polarization in one direction or the other. The light then encounters a rotatable Nicol prism through which it cannot pass until it has been rotated back to its original plane of polarization. Instead of rotating the light back to its original plan of polarization, it is simpler to rotate the Nicol prism so that the plane polarized light may pass through. The angle (and direction) through which the prism must be rotated in order to allow the maximum amount of light to pass is then measured and recorded as the **observed rotation**, α (See Figure 7.3).

α α

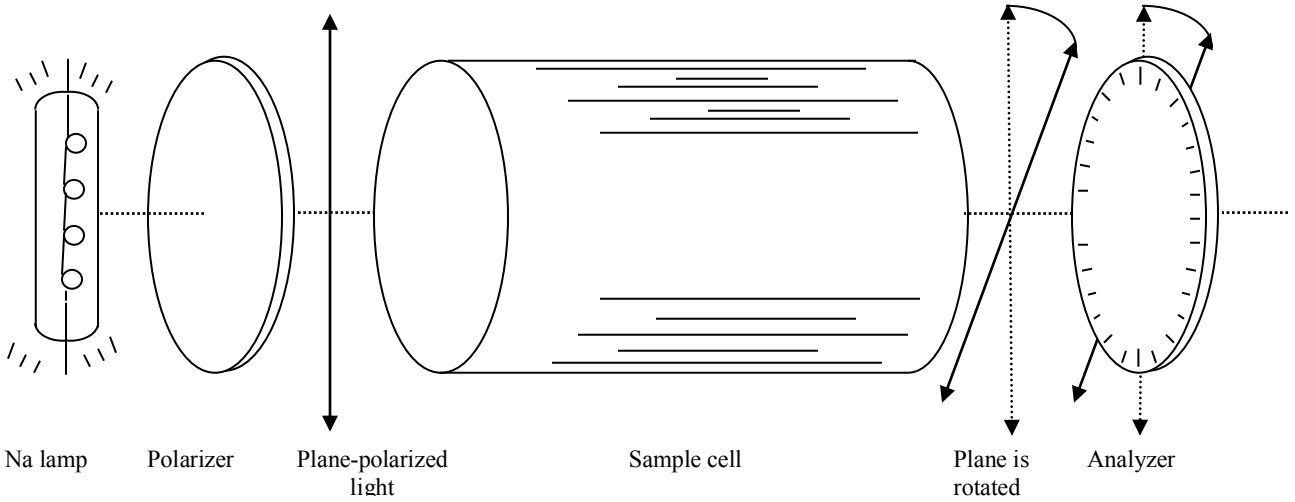


Figure 7.3. Schematic representation of a polarimeter

To be able to make meaningful comparisons between results obtained by different groups of workers, instead of reporting observed rotations, chemists usually report the results of polarimetry measurements in the form of **specific rotation**, $[\alpha]_D^{20}$ where

$$[\alpha]_D^{20} = \frac{\alpha}{L \times d} \quad \text{for a liquid, and}$$

$$[\alpha]_D^{20} = \frac{\alpha}{L \times c} \quad \text{for a solution.}$$

In the above equations, the superscript (20) indicates the temperature at which the measurements were made and the subscript (D) indicates that the measurements were made using the D line obtained from a sodium lamp (i.e., a wavelength of 589.3 nm). The observed rotation is represented by α, and the length of the sample tube (in dm) is presented by L. When the measurement is made on a liquid, it is necessary to know the density of the liquid, d, in $g \cdot mL^{-1}$. When using a solution, the concentration of the solution, c, must be included in the calculation using the units $g \cdot mL^{-1}$. To be complete, the specific rotation must include a sign to indicate the direction of the rotation:

+ for rotation to the right (dextrorotatory), – for rotation to the left (levorotatory).

Procedure

Part A: Extraction of (+ or -)-Usnic Acid

1. Place 10.0 g of previously oven dried (40° C) crushed or cut up lichen into a clean 500 mL Erlenmeyer flask containing a 1" magnetic stirrer and loosely capped with a cork stopper or Parafilm™. To the flask with lichen add 150 mL of acetone.

2. Mix the lichen/acetone mixture for 0.5 hours at room temperature. Frequently resubmerge any lichen that adheres to the sides of the flask.

Part B: Isolation of Usnic Acid

1. **Gravity** filter the mixture, and collect the filtrate in a clean 250 mL Erlenmeyer flask.

2. Evaporate the acetone under a gentle stream of air in the hood with the flask suspended ~1" above a hot plate set on low or use a rotary evaporator (see Exp. 5) to remove almost all the acetone. Allow the last amount of acetone to evaporate at room temperature.

Part C: Purification and Characterization of Usnic Acid

1. Recrystallize the crude usnic acid from as solution of acetone-95% ethanol (10:1). Dissolve the crystals in the minimum amount of hot acetone, and then add the ethanol.

2. Collect the yellow crystals by vacuum filtration, wash with ice cold acetone and dry the crystals on a sheet of filter paper.

3. Weigh the usnic acid to determine your yield, and calculate the percentage of the acid in the lichen by weight.

4. Determine the melting point of the purified usnic acid, confirm the identity of usnic acid by mixed melting point procedure and compare it to the literature.

5. Optional: The instructor may also obtain an IR spectrum of several samples of the purified material, and these will be compared to an authentic sample.

6. While you wait for a suitable moment to determine the specific rotation of the usnic acid, familiarize yourself with the use of the polarimeter by determining the specific rotation of the unknown sample provided.

Part D: Polarimetry-The Specific Rotation of an Unknown Compound

1. Prepare an aqueous solution of the given unknown by dissolving 5 to 6 g of solid (weighed-out on analytical balance) in a 25-mL volumetric flask.

2. Ensure that the polarimeter is set up correctly. The polarimeter should be connected to the control box, the control box should be connected to the step-up transformer, and the step-up transformer should be plugged into a power outlet. The unit is turned on by means of the on-off switch on the control box, and the sodium lamp is lit by pressing the red button adjacent to the on-off switch. At first, when viewed through the eyepiece, the light from the sodium lamp will appear red, but after approximately two minutes the colour will change to bright yellow. When this happens, the unit is ready.

3. Obtain the 200-mm polarimeter tube from the instructor. (**CARE:** This is an expensive item!) Notice that one end of the tube has a smaller diameter than the other. Make sure that the cap on the end with the larger diameter is secure, but not too tight. Remove the cap from the other end (i.e., the end with the smaller diameter), and rinse the tube with distilled water.

4. Secure the tube using a utility clamp and a ring stand. Fill the tube with distilled water. Carefully avoiding the creation of any air bubbles, slide the glass disc across the end of the tube, and screw the cap (including the rubber gasket) onto the end of the tube. Ensure that the outside of the tube is dry, and then insert it into the measuring chamber of the polarimeter with the broader end closest to the eyepiece.

5. Look through the eyepiece and adjust the Vernier scale so that the two half circles that appear are of equal brightness (see Figure 7.4).

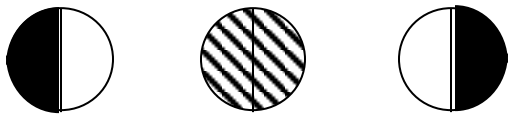


Figure 7.4. Possible views through the eyepiece of the polarimeter

6. Read the Vernier scale. Consult your instructor if you are not sure how to do this, although Figure 7.5 may be of assistance.

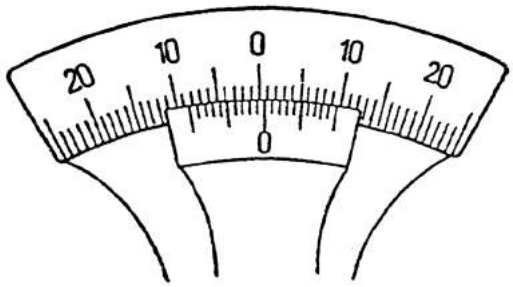


Figure 7.5. Reading the Vernier scale on the polarimeter

In Figure 7.5, the zero of the lower scale is between 0 and 1 on the upper scale. This indicates that the reading is between 0% and 1%. We next look to see which line to the right of the zero on the lower scale coincides with a line on the upper scale. In fact, the seventh line on the lower scale coincides with a line on the upper scale, thus the reading is 0.7%.

Determine the reading several times, approaching the correct adjustment from both possible directions. Your readings will show some variation, record them all and use the mean value in your results. This is a "blank" value and will have to be subtracted from your "test" result. Ideally, the blank value would be 0.0^{o}.

7. Remove the cap from the smaller end of the tube and empty this water into the sink. Rinse the tube with a *small* amount of your test solution. Fill the tube with the test solution as described in step 4 and determine the observed rotation of the sample as described in steps 5 and 6.

Note: when the sample tube is inserted into the polarimeter with the Vernier scale set at the value obtained for the "blank", when you look through the eyepiece, half of the circle will appear dark and the other half light. **If the darker half is to the right, the test substance is dextrorotatory. A darker left half indicates a levorotatory substance.**

8. Place the solution of the unknown in the container provided. Rinse the sample tube with water. Unless you are ready to determine the specific rotation of usnic acid, return the tube to the instructor.

Part E: Polarimetry—The Specific Rotation of Usnic Acid

1. After showing the instructor the usnic acid that you obtained from Part A, weigh-out, on an analytical balance, 80 mg of your sample into a clean 25 mL volumetric flask and add spectral grade tetrahydrofuran (THF) until at the 25.00 mL mark.. If you do not have sufficient usnic acid, combine your product with that of another student or see your instructor.

2. Set up the polarimeter as described in Part D. This time, obtain the "blank" reading using an empty polarimeter tube instead of a tube filled with water. Rinse the tube with a small quantity of (+) or (-) usnic acid, then fill the tube with this substance and determine its observed rotation as described for the unknown compound in Part D. The specific rotation is then calculated using the equation given in the introduction to this experiment.

3. Place the usnic acid in the container provided. Clean the polarimeter tube with acetone and return the polarimeter tube to the instructor.

Safety

Usnic Acid is harmful if swallowed, inhaled or absorbed through the skin. Wear gloves. In case of contact, flush affected area with copious amounts of water. Inv-mus LD50 25 mg/kg.

Acetone (propanone) is an irritant to the eyes, skin and lungs, and harmful to the liver and kidneys if swallowed. Highly flammable. Use in a well ventilated area. TLV (mg/m^3) =1780.

95% Ethanol may contain denaturing substances that enhance its toxicity. Also flammable.

Tetrahydrofuran (THF) or diethylene oxide is harmful if inhaled. Exposure to vapors of THF in excess of 200 ppm in air will result in liver damage. TLV (mg/m^3) =590.

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

Waste Disposal

Solutions containing the usnic acid (i.e., the filtrates from the suction filtrations) should be placed in the container provided.

Write-up and Calculations

This experiment may be written up using the standard preparative format. Keep the "Introduction" and "Procedure" sections brief. Remember to define what is meant by specific rotation. Be sure to include all the numerical data from the polarimetry sections in your report. You should calculate:

1. the specific rotation of the unknown solid.
2. the specific rotation of the usnic acid.
3. the optical purity of the usnic acid.

When calculating the specific rotation, remember to take into account the reading obtained for the blank; for example,

> Observed rotation obtained for the solution of unknown compound = $+6.2^{o}$
> Observed rotation obtained for water = $+0.5^{o}$
> Observed rotation, $[\alpha]$, to be used in calculation = 5.7^{o}

To determine the percentage purity of usnic acid you will need to look up the specific rotation of this substance in an appropriate handbook. **Remember** to photocopy you lab report before mailing it to your academic expert for marking.

Questions

1. Define the difference between diastereomers and enantiomers. Choose a specific example (e.g., glucose/fructose) to help explain your answer.

2. Draw a line/wedge diagrams for the two enantiomers of usnic acid (see Figure 7.1).

For Additional Information

If you have any questions about the operation of the polarimeter, please talk to your laboratory instructor. The instruction booklet for the instrument, *Instruction Manual for Model SR-6 Polarimeter*, should be available for consultation in the laboratory.

Experiment 8
Preparation of Cyclohexene from Cyclohexanol

Preparation

Before beginning this experiment, you should have read through the entire experiment and

1. studied "Alkenes: Reactions and Synthesis" in McMurry's *Organic Chemistry*.

2. obtained a pure sample of cyclohexanol from Experiment 3.

3. reviewed Experiments 3 (simple distillation) and 5 (extractions).

You may also wish to read Chapter 15 of *The Organic Chem Lab Survival Manual* (Chapter 20 in 3rd ed.), particularly the section on Simple Distillation.

Objectives

The purpose of this experiment is to

1. prepare a pure sample of cyclohexene from cyclohexanol using an acid catalyzed dehydration reaction, and

2. acquire more experience with the techniques of simple distillation and liquid-liquid separations, and the use of drying agents.

Introduction to Acid Catalyzed Dehydration Reactions

In the first seven experiments, you have learned several important techniques, all of which are a prerequisite for a chemist carrying out organic synthetic reactions.

	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.

In this experiment you will use several of the above techniques to carry out your first synthetic reaction in the lab (e.g. using a separatory funnel, drying of organic solvents, distillation, boiling point determination). In addition, you will learn how to pre-dry an organic solvent using sodium chloride (a.k.a. 'salting-out').

Review of Distillation Procedure

Remember there are 6 steps to performing a distillation.

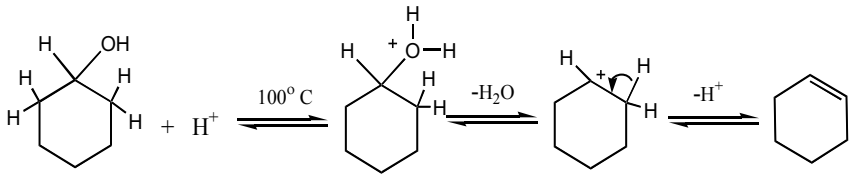
1. Select the heat source (heating mantle, Bünsen burner, steam bath, water bath).
2. Clean, dry and assemble the distillation apparatus. Use joint grease?
   - i) start assembling the apparatus from the bottom up. Use a lab jack.
   - ii) Place the heat source in position. Use lab jack to adjust height.
   - iii) Clamp the distillation flask in position.
   - iv) Place the three way connector into the neck of the distillation flask.
   - v) Place the thermometer adapter into the top of three way connector.
   - vi) Approximately set the height of receiving flask using an utility clamp.
   - vii) Place the condenser into position and secure it with joint clamps.
   - viii) Attach tubing to the water inlet and water outlet of the condenser.
   - ix) Adjust the 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 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 reaction to cool, then disassemble the apparatus. Clean all parts thoroughly with acetone (discard in organic wastes) before washing with soapy water in the sink.

Experiment 8 Background Information

One of the most widely used methods of preparing alkenes is the **acid-catalyzed dehydration** of an alcohol. In this experiment, you will use the sample of cyclohexanol you purified in Experiment 3A. This reaction is a reversible E_1 elimination type reaction (E_1 = elimination, unimolecular) and usually follows Zaitzev's rule. Once the product (cyclohexene) is formed, steps must be taken immediately to safeguard the product from reverting back to the starting reagent. First it is removed from the reaction mixture by distillation. Additional steps are taken in the reaction workup to minimize the formation of side products.

$H^+ = H_3PO_4$ (Mwt = 98.0 g/mol, d=1.7 g/mL, ~14.7 M)

In the first step, protonation of the alcohol, the poor leaving group (-OH) is converted to a better leaving group (-OH_2^+).

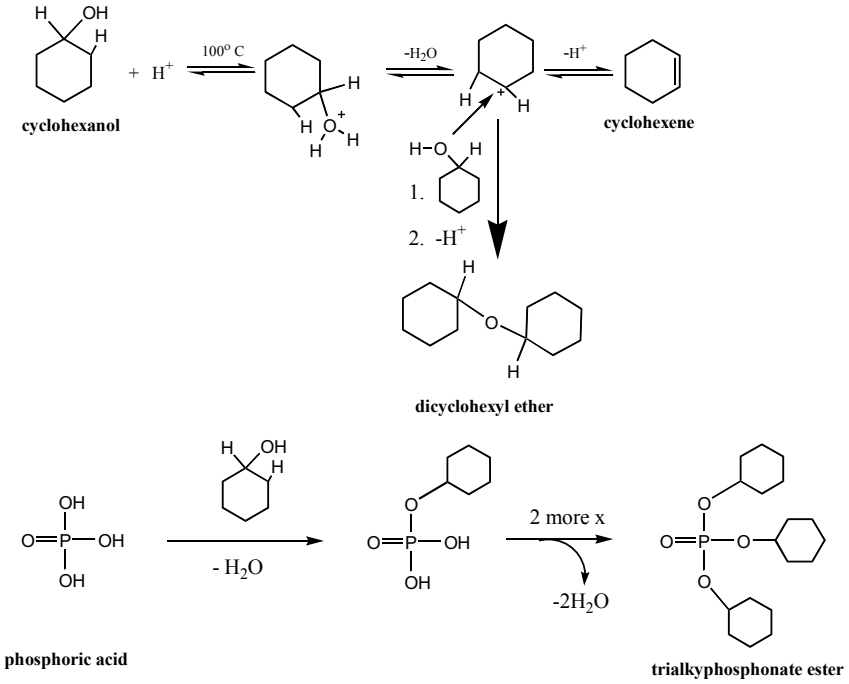


cyclohexanol
Mwt.= 100.16 g/mol
d = 0.963 g/mL
Vol Used =
mol =

cyclohexene
Mwt. = 82.14 g/mol
d = 0.8102 g/mL
Theor.Yield =
Yield =
% Yield =

As you can see, the mechanism consists of a series of equilibria. In our experiment, the overall equilibrium is shifted to the right by the removal of cyclohexene and water from the reaction mixture as they are formed. This is achieved by the process of distillation. Once the crude product is obtained, the cyclohexene must be purified by removing the water and any traces of acid which may still be present. Thus the product is washed with aqueous sodium chloride (i.e., sodium chloride crystals are added to aqueous layer) followed by aqueous sodium carbonate, and then dried over anhydrous calcium chloride. Finally, the cyclohexene is distilled, and the fraction boiling in the range 80—85°C is collected.

Byproducts of acid-catalyzed dehydrations

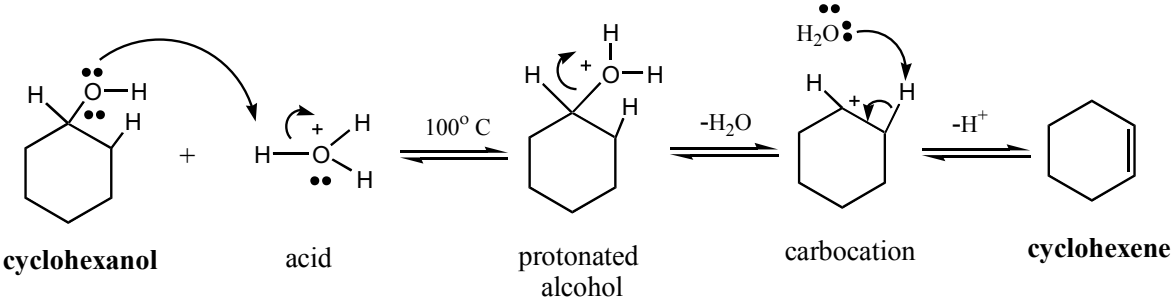


E_1 Reaction Mechanism

The reaction used in the this experiment (cyclohexanol in the presence of 85% phosphoric acid and heat (100°C) occurs via a three step mechanism:

1) protonation of the alcohol oxygen,
2) loss of water to generate a carbocation intermediate, and
3) loss of a proton from the neighbouring carbon atom and formation of a double bond.

Tertiary alcohols will react faster than secondary, which will react faster than primary alcohols (3° > 2° >1°). This is because the tertiary alcohol carbocation is more stable than the secondary or primary carbocations. Please note that fairly harsh conditions were required to form the cyclohexanol carbocation in this experiment. A more sensitive alcohol molecule would not survive such treatment.



In practice, only tertiary alcohols are commonly dehydrated with acid. Phosphorus oxychloride ($POCl_3$) in pyridine at 0° C is routinely used for dehydrating secondary alcohols however this reaction proceeds via an E_2 mechanism (see "Properties of Alcohols", and "Reactions of Alcohols" in McMurry's *Organic Chemistry* for more information).

Chemicals, Equipment, Utilities Required

All equipment used for the reaction must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
cyclohexanol (purified), 85% phosphoric acid, vacuum (glass joint) grease, sodium chloride, 10% sodium carbonate, brine (sat. sodium chloride, anhydrous calcium chloride, ice, distilled water, wash acetone	-graduated cylinders -heating mantle, lab jack, retort stands, utility clamps -distillation apparatus (distillation flask, three way connector, thermometer adapter, condenser, vacuum adapter, receiving flask, boiling stones) -125 mL separatory funnel -hazardous waste disposal containers (in fume hood)	-115V electrical, -cold water supply

About Assembling Distillation Glassware and Using Heating Mantles

- Inspect all glassware for star-cracks (especially the distillation round bottom flask).
- Do not use a heating mantle with a damaged electrical cord.

About The Use of Brine and Drying Agents

- Organic solvents that are wet (have been in previous contact with aqueous solutions) need to be dried before they are distilled. The is achieved by the addition of a solution of saturated sodium chloride (sat. NaCl $_{(aq)}$). The brine helps to draw the bulk of the water from the organic solvent, while also limiting the amount of organic solvent that can dissolve in the brine (i.e., organic solvents are less soluble in brine than in water).
- Once the organic solvent has been pre-dried with brine, the final trace water can be bound by the addition of a suitable drying agent. The drying agent then can be removed by gravity filtration or decantation. Be careful. The over addition of a drying agent can significantly reduce your yield.

Procedure for Cyclohexene Synthesis

You must complete at least steps 1-8 before stopping.

A. Reagent and Equipment Preparation

1. Use graduated cylinders to measure out 21 mL of cyclohexanol (previously distilled in Experiment 3) and 5 mL of 85% phosphoric acid into a 100-mL round bottom flask. **Caution:** 85% phosphoric acid is corrosive and viscous. Wear gloves, protect your eyes and work with it in the fume hood. Pipette carefully.

2. Add a few boiling stones, and then attach the flask to a simple distillation apparatus (see *The Organic Chem Lab Survival Manual*, pp. 103-109; pp.189-194 in 3rd ed.), making sure that the thermometer has been positioned correctly (see Experiment 3). Note that the collecting vessel is a 50-mL round bottom flask, cooled in an ice-water bath.

B. Reaction

3. Start the cooling water circulating through the condenser, and begin to heat the reaction mixture using a heating mantle.

4. As the cyclohexene begins to distil, the control on the heating mantle should be adjusted so that the temperature of this distilling vapour does not exceed 100°C. Record the temperature changes you observe and correct them for barometric pressure.

C. Quenching the Reaction

5. When only a few millilitres of liquid remain in the distilling flask, stop the distillation by lowering the lab jack and removing the heating mantle. The appearance of white fumes in the distillation flask is a good indication that the distillation has proceeded far enough. **Remember:** Never try to distil to dryness! Proceed immediately to the next step.

D. Reaction Workup/Product Recovery

6. Add solid sodium chloride to the distillate until no more salt will dissolve. The sodium chloride should be added little by little using a spatula, and the flask would be shaken after each addition.

7. Add enough 10% sodium carbonate solution to make the solution in the flask basic to litmus. **(Take care: Some gas may be evolved.)** Transfer the neutralized mixture to a separatory funnel and separate the two layers. The aqueous layer should be drained through the stopcock and the upper layer poured through the neck of the separatory funnel into a 125-mL Erlenmeyer flask.

8. Wash the organic layer in the separatory funnel with 10 mL of brine (=saturated sodium chloride). Remove and discard the wash/aqueous layer.

9. Add 2 to 3 g of anhydrous calcium chloride to the cyclohexene in the Erlenmeyer flask. Place a cork in the mouth of the flask, and swirl the contents occasionally as the cyclohexene dries over a period of 10 to 15 minutes. The cyclohexene should be clear when all the water has been removed. While you are waiting, clean your condenser and prepare to carry out another simple distillation.

E. Product Purification and Analysis

10. Gravity filter (or decant) the dry cyclohexene into a clean, dry 50-mL round bottom flask, and add a few boiling stones. Distil the cyclohexene, collecting the fraction that boils over a range of 80-85^{o}C (corr.). Note: Remember that the boiling point of your product needs to be corrected for barometric pressure.

F. Product Analysis

11. Determine the yield (mass) of cyclohexene obtained, and calculate your percentage yield. Optional: Perform infrared spectroscopy on the sample. Determine the density of your sample by also measuring the volume of product (d=m/v), and determine the refractive index (n_D^{20}).

12. Transfer the sample to a suitably labelled screw cap vial and submit it to your instructor. Save this sample as it is needed for use in Experiment 6.

Safety

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

Cyclohexene vapour irritates the eyes, skin and respiratory system. The liquid is harmful if swallowed. Highly flammable.

Phosphoric acid burns the skin and eyes, and causes serious internal injury if swallowed. Wear gloves and eye protection.

Sodium chloride and **sodium carbonate** do not normally constitute a safety hazard, but you should treat all chemicals with respect.

Saturated sodium chloride (brine) does not normally constitute a safety hazard, but you should treat all chemicals with respect.

Calcium chloride (anhydrous) is an irratant and is hygroscopic. Wash away any dust with lots of water.

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

Waste Disposal

Cyclohexanol/phosphoric acid residues should be placed in the container provided for this purpose.

The **aqueous layer from the separation** may be washed down the sink with plenty of water.

The **cyclohexene residue** from the final distillation should be placed in the bottle labelled "Organic Wastes: Non-halogenated."

Write-up

This experiment should be written-up using the standard format for preparative experiments (see the "Reports" section of this *Laboratory Manual*.)

Remember to photocopy you lab report before mailing it to your academic expert for marking.

Questions

Answers to be submitted with report.

1. What is the purpose of adding 10% sodium carbonate solution to the distillate in step 7 of the procedure?

2. Identify two possible by-products that could be formed from cyclohexanol in this experiment. [**Hint:** You may have to search through your textbook to find what other reactions can occur between an alcohol and a concentrated mineral acid (e.g. phosphoric acid).]

Experiment 8 Optional
Preparation of Methylpentenes from 4-methyl-2-pentanol

Preparation

Before beginning this experiment, you should have read through the entire experiment and

1. studied "Alkenes: Reactions and Synthesis", in McMurry's *Organic Chemistry*.

2. reviewed Experiments 3 (simple distillation) and 5 (extractions).

You may also wish to read Chapter 15 of *The Organic Chem Lab Survival Manual* (Chapter 20 in 3rd ed.), particularly the section on Simple Distillation.

Objectives

The purpose of this experiment is to

1. prepare a mixture sample of methylpentenes from 4-methyl-2-pentanol using an acid catalyzed dehydration reaction, and

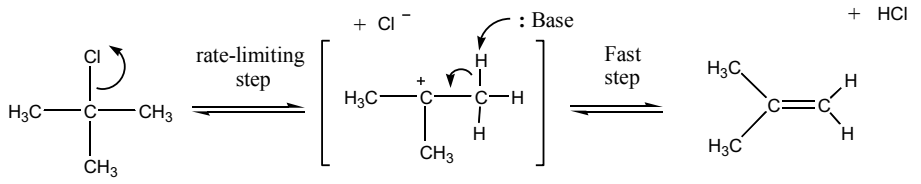
2. acquire more experience with the techniques of simple distillation and liquid-liquid separations, and the use of drying agents.

3. Learn about online control of a GC and perform GC analysis on your final product.

Optional Experiment 8 Background Information

Reactions of alcohols (R-OH) can be either: **C-O** bond reactions or **O-H** reactions. In this experiment, a C-O bond is broken, along with a neighbouring C-H bond, dehydration (-H_2O) of the alcohol occurs, and an alkene π bond is formed. It is important to review preparation of alkenes and reactions of alkyl halides for S_N1, E_1, S_N2, E_2 mechanisms.
E1 = elimination-unimolecular mechanism (analogous to the S_N1 mechanism). Two steps are involved for alkyl halides and 3 steps for alcohols.

E1 Example - Loss of HCl from a tertiary alkyl halide



(no geometric requirement because halide and hydrogen are lost in separate steps)

(Zaitsev's rule followed)

Some general characteristics of E1 reactions are:
Reactivity via the E1 mechanism is: Tertiary > Secondary > Primary
First order kinetics shown, consistent with a spontaneous dissociation process.
No deuterium isotope effect seen.
The E1 reaction has no geometric requirement because of the two separate elimination steps.

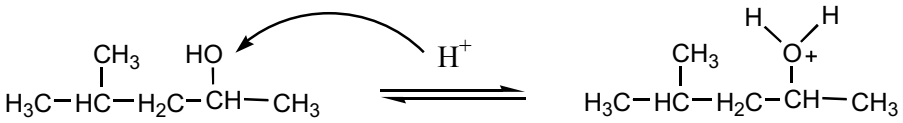
Limitations of E1 Reaction: Acid-Catalyzed Dehydrations

Competition can occur with S_N1 reaction if reaction conditions are not 'controlled' (when protic solvents, non-basic nucleophiles are used). Mixtures of products form with the E1 reaction (also S_N1). Unsymmetrical reagents and rearrangements possible (hydride and methyl shifts).This mechanism works well with only tertiary alcohols, less better with secondary (requires more harsh conditions e.g., 75% H_2SO_4, 100° C), and needs extremely harsh conditions (95% H_2SO_4, 150° C) for acid-catalyzed reaction to work with primary alcohols. (Reactivity via the E1 mechanism is: Tertiary > Secondary > Primary)

The reaction proceeds using a 3 step process: 1. protonation, 2. carbocation formation, and 3. double bond formation.

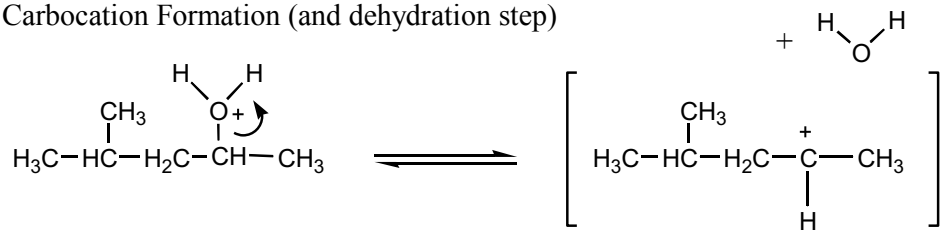
Methylpentene isomers via acid-catalyzed dehydration reaction of 4-methyl-2-pentanol in 3 steps:

1. Protonation by Acid-Catalyst

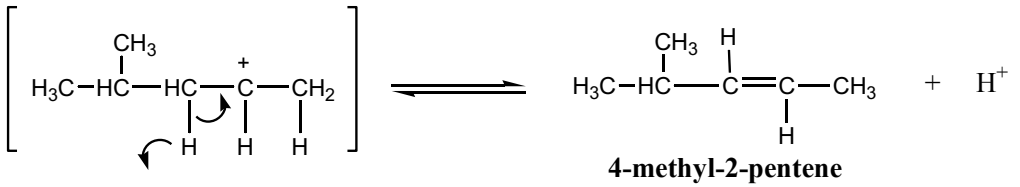


4-methyl-2-pentanol

2. Carbocation Formation (and dehydration step)

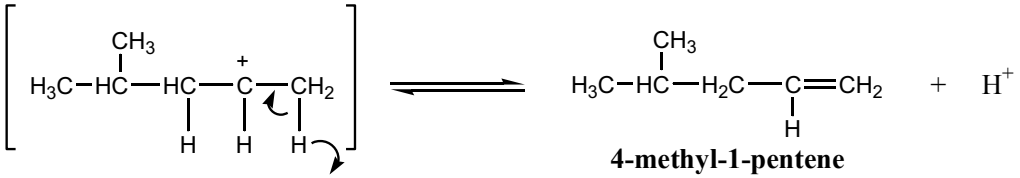


3. Double Bond Formation (with rearrangements and regeneration of catalyst)



4-methyl-2-pentene

or

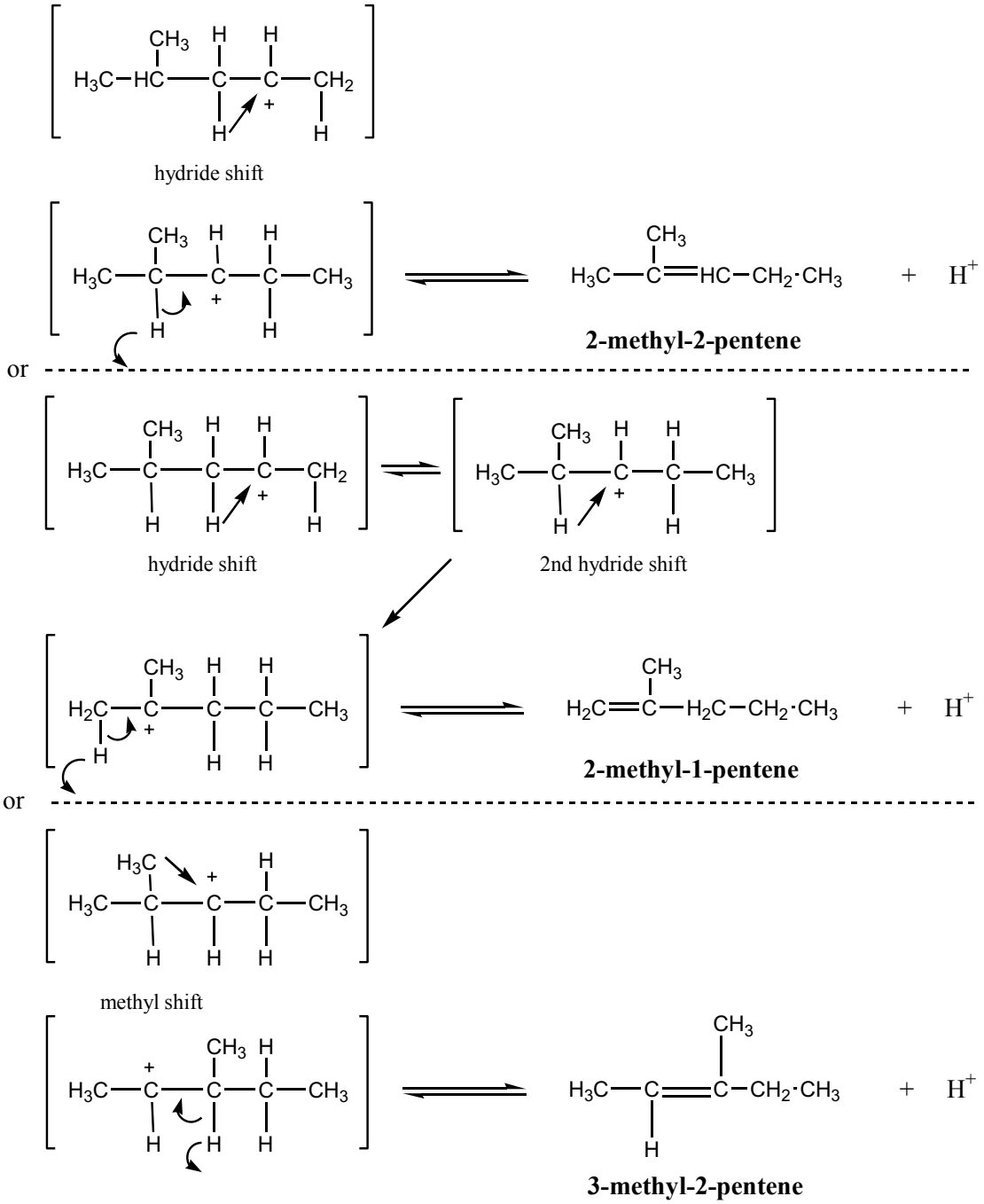


4-methyl-1-pentene

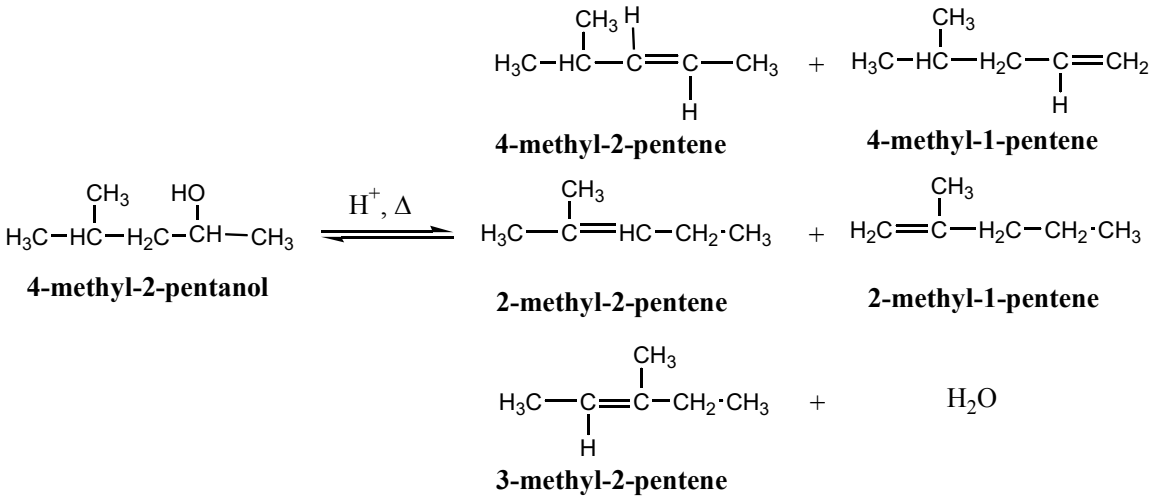
or ...

Other methylpentene isomers via hydride (:H$^-$) or methyl shifts:

4. Double Bond Formation (with hydride shift rearrangements and regeneration of catalyst)



Exp. 8 Overall Acid Catalyzed Dehydration Reaction of 4-methyl-2-pentanol



Methylpentene Isomers

About Assembling Distillation Glassware and Using Heating Mantles

- Inspect all glassware for star-cracks (especially the distillation round bottom flask).
- Do not use a heating mantle with a damaged electrical cord.

About The Use of Brine and Drying Agents

- Organic solvents that are wet (have been in previous contact with aqueous solutions) need to be dried before they are distilled. The is achieved by the addition of a solution of saturated sodium chloride (sat. NaCl (aq)). The brine helps to draw the bulk of the water from the organic solvent, while also limiting the amount of organic solvent that can dissolve in the brine (i.e., organic solvents are less soluble in brine than in water).
- Once the organic solvent has been pre-dried with brine, the final trace water can be bound by the addition of a suitable drying agent. The drying agent then can be removed by gravity filtration or decantation. Be careful. The over addition of a drying agent can significantly reduce your yield.

Chemicals, Equipment, Utilities Required

All equipment used for the reaction must be clean and free of any organic contamination.

Chemicals	Equipment	Utilities
4-methyl-2-pentanol (purified), conc. sulfuric acid, distilled water, 10% sodium hydroxide, brine (sat. sodium chloride), anhydrous calcium chloride, ice, wash acetone, vacuum (glass joint) grease	-graduated cylinders -heating mantle, lab jack, retort stands, utility clamps -distillation apparatus (distillation flask, three way connector, thermometer adapter, condenser, vacuum adapter, receiving flask, boiling stones) -125 mL separatory funnel -hazardous waste disposal containers (in fume hood) -Varion Gas Chromotograph	-115V electrical, -cold water supply

Alternate Procedure for Methylpentenes Synthesis

You must complete at least steps 1-9 before stopping.

A. Reagent and Equipment Preparation

1. Use graduated cylinders to measure out 0.40 mol of concentrated sulphuric acid (conc. H_2SO_4 = 18M, using L = mol/M, L = 0.4 mol/18M = 0.022L or 22 mL) and add it to 20 mL distilled water in a 100mL round bottom flask. Mix well and allow to cool back to room temperature.
   Caution: conc. sulfuric acid is very corrosive. Wear gloves, protect your eyes and work with it in the fume hood. Pipette carefully.

2. Slowly add 0.15 mole of 4-methyl-2-pentanol (commercially supplied) all the while gently swirling the mixture in the 100mL round bottom flask.

3. Add a few boiling stones, and then attach the 100-mL round bottom flask to a simple distillation apparatus (see *The Organic Chem Lab Survival Manual*, pp. 103-109; pp.189-194 in 3rd ed.), making sure that the thermometer has been positioned correctly (see Experiment 3). For the receiving/collecting vessel, use a 125-mL separatory funnel.

B. Dehydration Reaction

4. Start the cooling water circulating through the condenser, and begin to slowly heat the reaction mixture using a heating mantle (setting ~3-4), collecting all the distillate up to 75° C. Record the temperature changes you observe and correct them for barometric pressure.

C. Quenching the Reaction

5. When the distillate temperature exceeds 75° C, stop the distillation by lowering the lab jack and removing the heating mantle. Proceed immediately to the next step.

D. Reaction Workup/Product Recovery

6. Wash the organic layer in the separatory funnel with 10 mL of 10% NaOH. Remove and discard the wash/aqueous layer.

7. Wash the organic layer in the separatory funnel with 10 mL of distilled water. Remove and discard the wash/aqueous layer.

8. Wash the organic layer in the separatory funnel with 10 mL of brine (=saturated sodium chloride). Remove and discard the wash/aqueous layer.

9. Add 2 to 3 g of anhydrous calcium chloride to the crude methylpentenes in the Erlenmeyer flask. Place a cork in the mouth of the flask, and swirl the contents occasionally as the crude methylpentenes dries over a period of 10 to 15 minutes. The crude methylpentenes should be 'clear' when all the water has been removed. While you are waiting, clean your condenser and prepare to carry out another simple distillation (use dry equipment).

E. Product Purification and Analysis

10. Gravity filter or decant the dry crude methylpentenes into a clean, dry 50-mL round bottom flask, and add a few boiling stones. Connect the flask to the simple distillation apparatus using a tared 25 mL round bottom flask in an ice bath as the receiving flask.

11. Distil the crude methylpentenes, collecting the fraction that boils over a range of 25-75^{o} C (corrected). Record the actual boiling point range and barometric pressure.

F. Product Analysis

12. Determine the yield (mass) of purified methylpentenes obtained, and calculate your percentage yield. Optional: Perform Online Gas Chromatography on the sample (see procedure below).

13. Transfer the sample to a suitably labelled screw cap vial and submit it to your instructor. Save this sample as it is needed for use in Experiment 6.

Gas Chromatography Procedure and Analysis

14. Using a clean Pasteur pipette, place a small amount of sample (< 1mL) into the special auto-sampler GC vial provided by the instructor. Receive the 'vial code' and write the code number for your product vial here:_____. You will use this code when you access the GC online, to perform your analysis.

15. Run a ___ μL sample of the product mixture on the gas chromatograph and calculate the relative % concentration of each compound in the product mixture using the areas for each peak.

16. Compare your results to the following reference values, arranged in order of ascending retention times:

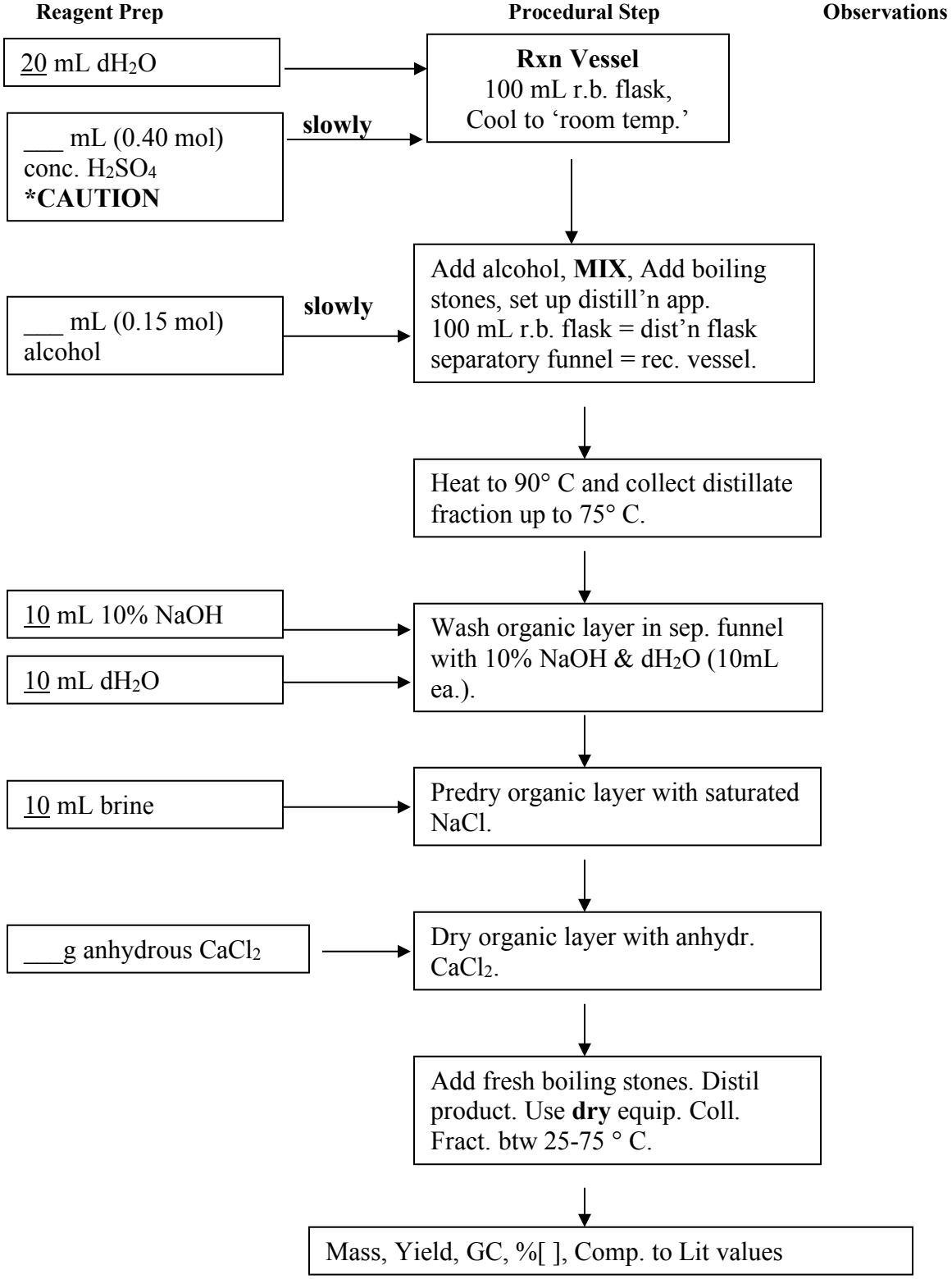
Name of Compound	**Literature Area %**
4-methyl-1-pentene	5.2
cis and *trans*-4-methyl-2-pentene	69.4
2-methyl-1-pentene	3.8
2-methyl-2-pentene	19.7
cis and *trans*-3-methyl-2-pentene	1.9

Ref: Nienhouse, E.J., 1969. A Unique Laboratory-Lecture in Organic Chemistry, *Journal of Chemical Education* **46**(11), pp.765-766.

Gas Chromotography Procedure and Tutorial

Please follow the "Instructions for AU Student Access" on the http://www.remotelab.ca website.

CHEM350 Exp. 8 Optional Reaction Flowchart



Safety

4-methyl-2-pentanol is flammable and irritating to the skin and eyes, and is harmful if inhaled or ingested. Flash point = 41° C.

Methylpentenes is flammable (Flash point = ~ –20° C) and irritating to the skin and eyes, and is harmful if inhaled or ingested.

Concentrated sulfuric acid burns the skin and eyes, and causes serious internal injury if swallowed. Wear gloves and eye protection.

10% Sodium hydroxide is corrosive and will cause burns to the skin and eyes, and causes serious internal injury if swallowed. Wear gloves and eye protection.

Saturated sodium chloride (brine) does not normally constitute a safety hazard, but you should treat all chemicals with respect.

Calcium chloride (anhydrous) is an irratant and is hygroscopic. Wash away any dust with lots of water.

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

Waste Disposal

4-methyl-2-pentanol residues (highly acidic!) should be placed in the bottle labelled "Organic Wastes: Non-halogenated."

The **aqueous layer from the separation** may be washed down the sink with plenty of water.

The **methylpentenes residue** from the final distillation should be placed in the bottle labelled "Organic Wastes: Non-halogenated."

Write-up

This experiment should be written-up using the standard format for preparative experiments (see the "Reports" section of this *Laboratory Manual*.)

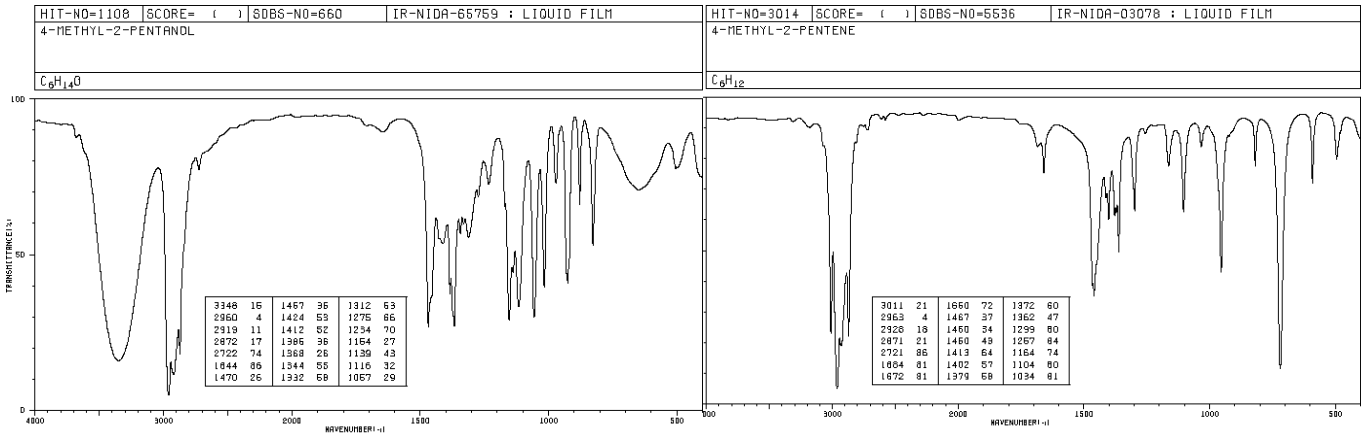
Remember to photocopy you lab report before mailing it to your academic expert for marking.

Questions

Answers to be submitted with report.

1. What is the purpose of adding 10% sodium hydroxide solution to the distillate in step 6 of the procedure? If necessary use reaction equation(s) to fully explain your answer.

2. Would infrared spectroscopy analysis be of any use in identifying the methylpentenes product? Briefly explain your answer.



Experiment 9
The Nitration of Acetanilide

Preparation

Before beginning this experiment, you should have

1. studied "Structure Determination: Mass Spectrometry and Infrared Spectroscopy", "Benzene and Aromaticity", and "Chemistry of Benzene: Electrophilic Aromatic Substitution" in McMurry's *Organic Chemistry*.

2. completed Experiments 1 through 5.

3. read through the details of this experiment and prepared a flow chart for the procedure to be followed.

You may also wish to read Chapter 29 of *The Organic Chem Lab Survival Manual* (Chapter 32 in 3rd ed.), and

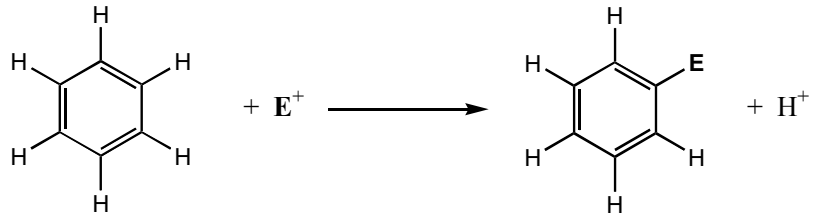
Objectives

The purpose of this experiment is to provide the student with a practical example of an aromatic electrophilic substitution reaction, and to illustrate how the two isomeric products can be separated through recrystallization using an appropriate solvent. An introduction to the practical aspects of infrared spectroscopy is provided when the student obtains and compares the infrared spectrum of the reactant, acetanilide, and the product, 4-nitroacetanilide.

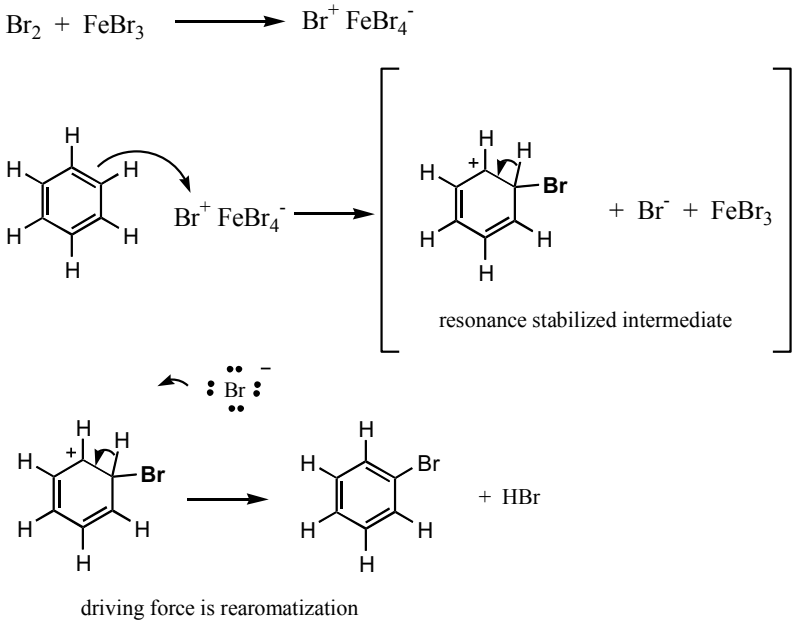
Introduction to Electrophilic Aromatic Substitution Reactions

You already know that aromatic rings are less reactive than alkenes to electrophiles. Recall that in Experiment 8, the alkene, cyclohexene, reacted instantly with electrophile Br_2 in dichloromethane, but biphenyl and toluene did not.

The electrophilic aromatic substitution reaction (polar type reaction) is the most important reaction of aromatic compounds. Think of an aromatic ring as a region of high electron density (nucleophilic = electron donating), since it contains six pi electrons in a cyclic conjugated system. Imagine that the pi electrons are in circular clouds above and below the ring, making them very accessible to attack by an electrophile (electron accepting). When using the proper conditions, an electrophile (E^+) will react with an aromatic ring and substitute for one of the hydrogens:



Electrophilic aromatic substitution reactions can be thought to occur in three phases. The first step is to generate the electrophile, the second is the nucleophilic on the electrophile to generate a resonance stabilized carbocation, and the third is the rearomatization of the ring.



Experiment 9 Background Information

In this experiment, you will use the sample of acetanilide purified in Experiment 2. The acetanilide (acetamido group is ortho-para directing) is dissolved in glacial acetic acid (which stabilizes the molecule and prevents it from degrading into aniline (a meta director), and then reacted with the strong electrophile, nitronium ion (NO_2^+). The nitronium ion is formed when nitric acid and sulfuric acid react as follows (sulfuric acid is the stronger acid and therefore gives up its proton while nitric acid acts like a base and accepts a proton):

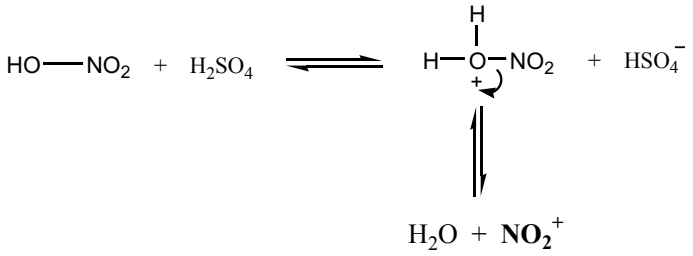
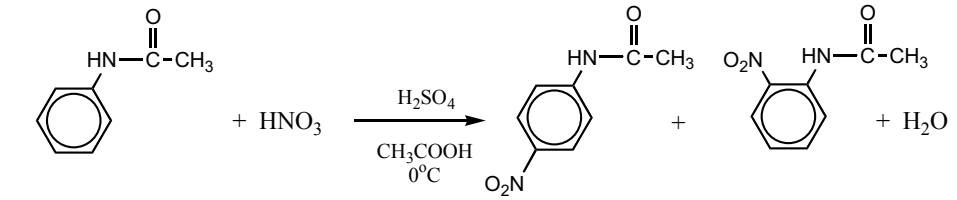


Figure 9.1: Formation of the nitrating reagent.

The overall reaction of acetanilide with nitric acid is shown below. Which is the limiting reagent?:



acetanilide
mp = 114.3° C
Mwt.= 135.17 g/mol
moles =

nitric acid
M = 15.4 M
moles =

***p*-nitroacetanilide**
mp = 216° C
Mwt. = 180.16 g/mol
moles=
Theor.Yield =

o-nitroacetanilide

Figure 9.2: Overall reaction of acetanilide forming *p*-nitroacetanilide.

More Background Information

In order to perform a desired synthesis, organic chemists often need to introduce a nitro group ($-NO_2$) into an aromatic ring. This goal is usually achieved by reacting the aromatic substrate with a nitrating mixture, often consisting of a mixture of concentrated nitric and sulfuric acids. The reactive species in the nitrating mixture is the nitronium ion, (NO_2^+), which is a strong electrophile and readily attacks aromatic systems (see Figure 9.3).

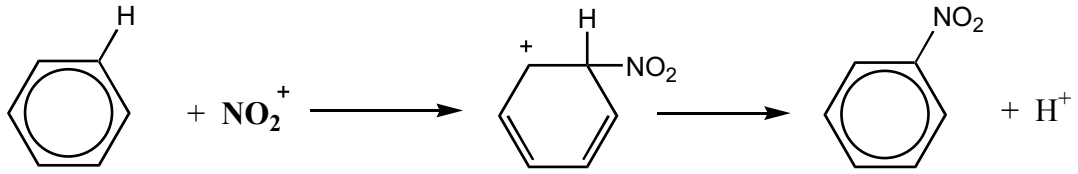


Figure 9.3: Mechanism of the nitration of benzene

The introduction of a nitro group into an aromatic ring is often an important step in an organic synthesis. Once introduced, the nitro group can be easily reduced to an amino group, and the amine can subsequently be converted to a variety of compounds via the formation of a diazonium salt (see "Aliphatic Amines" in McMurry's *Organic Chemistry*). However, the rather drastic conditions needed to bring about an electrophilic aromatic substitution can place limitations on this general approach.

For example, aniline is so susceptible to oxidation that the nitric acid present in the nitrating mixture would oxidize most of the aniline before nitration could take place. Also, the anilinium ion that would be formed in the strongly acidic medium (see Figure 9.4) contains the deactivating, meta-directing NH_3^+ substituent. Thus, even if

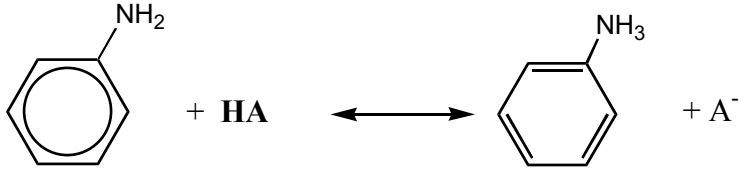


Figure 9.4: Formation of the anilinium ion from aniline

the oxidation of aniline could be prevented, the direct nitration of this compound would yield *m*-nitroaniline rather than the *ortho*- and *para*-substituted products. How, then, could a chemist prepare *p*-nitroaniline? One solution is to "protect" the sensitive amino group by acetylation, to nitrate the acetanilide so formed, and to hydrolyze the *p*-nitroacetanilide to *p*-nitroaniline. This sequence of reactions is shown in Figure 9.5 (next page).

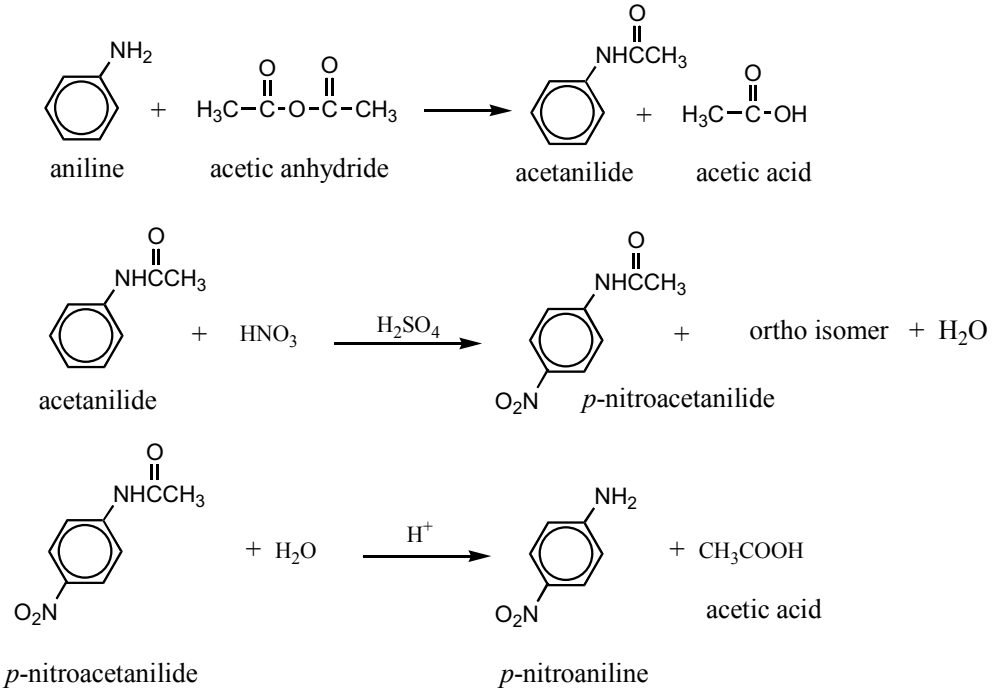
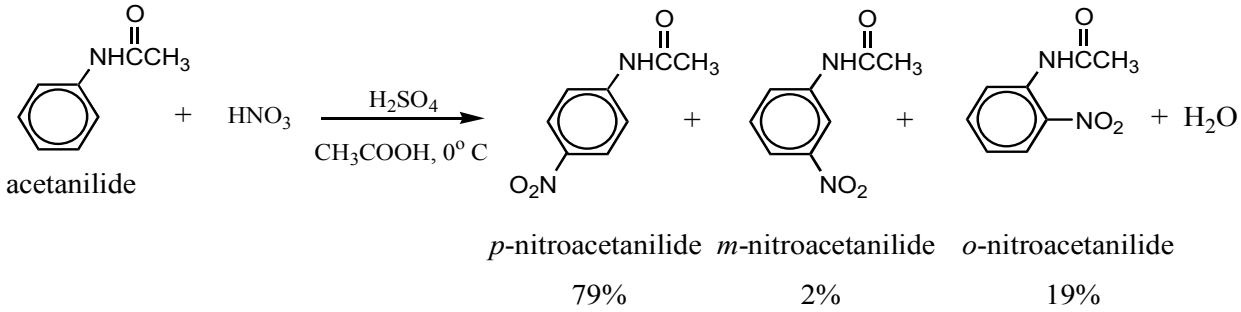


Figure 9.5: The preparation of *p*-nitroaniline

In this experiment you will perform only the middle portion of this sequence; that is, the



nitration and purification of acetanilide (see Fig. 9.6).

Figure 9.6: Preferred direction of nitration of acetanilide.

Note: the type of substituents in aromatic compounds have an effect on electrophilic substitution. The acetamido (CH_3CONH-) group is a moderately activating group (so is the methoxy group (CH_3O-) while the amino (-NH_2) and hydroxyl (-OH) are strong activating groups. The nitro group (-NO_2) is a strong deactivator). Activating groups are *ortho-para* directors and deactivating groups are *meta* directors.

Infrared Spectroscopy

A general introduction to infrared spectroscopy can be obtained by reading "Structure Determination: Mass Spectrometry and Infrared Spectroscopy" Sections in *Organic Chemistry*, and Chapter 29 of *The Organic Chem Lab Survival Manual* (Chapter 32 in 3rd ed.). In the latter source, pay particular attention to the section headed "The Nujol Mull" (p. 208 or p.303 in 3rd ed.) as this is the type of sample that you will be using.

Do not worry too much about the details of operating the spectrometer. Your instructor will provide you with specific instructions for the instrument that is available at your particular lab site. (A Pye Unicam SP3-200 if you complete your laboratory work in Athabasca, or a Hewett Packard FTIR at N.A.I.T.)

Chemicals, Equipment, Utilities Required

All glassware used must be clean of any organic contamination (**especially acetone**).

Chemicals	Equipment	Utilities
acetanilide (purified) acetic acid (glacial) nitric acid (conc.) sulfuric acid (conc.) ice distilled water ethanol wash acetone	-stirrer/hotplate, lab jack, retort stands, utility clamps, latex gloves -Büchner funnel & adapter, filter flask, Whatman #1 filter paper circle, sample vial + label -recrystallization (flat bottom) dish -melting-point apparatus -hazardous waste disposal containers (in fume hood)	-115V electrical, -water aspirator

About Concentrated Acids

- **Dilute all conc. acids** to < 3M using cold water before rinsing down the drain.
- **Always add acid to water (AtoW).**

For example, say you have 10 mL of unused conc. sulfuric acid left over after measuring out all you needed for the reaction. To dispose of the unwanted sulfuric acid you must calculate how much to dilute it before rinsing it down the drain.

Given: conc. sulfuric acid is 18 M.

Therefore the number of moles you have to dispose of = 18M × 0.01L = 0.18 moles.

To dilute it to < 3M, you must place it into a minimum of 'x' L of water.

Since M = moles/L, then L = moles/M

L = 0.18 moles/3 M = 0.06 L or **60 mL** of water.

Treat all glassware that has come into contact with concentrated acids with extreme care. Small amounts of the acid are coating the surface and must be diluted and rinsed away. To rinse away the acid

1. in a sink, turn on the water, cold and slow flow.
2. pointing the opening of the vessel *away* from you, place the acid contaminated glassware beneath the stream of water until near overflowing. Dump the contents down the drain and flush the glassware 2 more times with the water.
3. finally, clean the glassware with hot soapy water, rinse with hot water, and >3 times with distilled water. Dry with acetone and air-dry or oven dry to allow the acetone to evaporate before using the glassware for measuring more reagents. This is particularly important in this experiment, as any trace acetone will react with the nitronium ion, producing a coloured impurity.

Procedure

1. Carefully add 3 mL of concentrated nitric acid (15 mol· L^{-1}) to 4 mL of concentrated sulfuric acid (18 mol· L^{-1}) in a **very clean** smaller flask. Cool the resulting nitrating mixture to room temperature. Have the flask clamped into position in the ice bath to keep the flask from tipping over!

   Caution: Nitric acid, sulfuric acid and the nitrating mixture are highly corrosive. Wear gloves, protect your eyes, and work in a fume hood. Excess nitric and sulfuric acid measured out should be properly disposed. See your instructor.

2. Place 10 mL of concentrated (i.e., 18 mol· L^{-1}) sulfuric acid contained in a 125-mL Erlenmeyer flask and cool in an ice-water bath.

   Caution: Sulfuric acid is extremely hazardous. Wear gloves and proper eye protection.

3. Meanwhile, ask your instructor for the acetanilide that you purified in Experiment 2. Dissolve about 7.0 g of the acetanilide in 7 mL of glacial (i.e., 100%) acetic acid by warming the two substances together in a small Erlenmeyer flask in a fume hood (use setting 2 on hot plate).

   Caution: Acetic acid is corrosive and its vapour is extremely irritating. Wear gloves, protect your eyes, and work in a fume hood.

   Cool the solution until crystals just begin to form, then warm slightly to redissolve, and then pour the solution slowly, with stirring, into 10 mL of concentrated (i.e., 18 mol· L^{-1}) sulfuric acid contained in the 125-mL Erlenmeyer flask, which is being kept cool in an ice-water bath (from step 2 above).

   Continue to cool the solution to about 5° C (this can take ~30 min). Use lots of ice, and swirl frequently.

4. Use a Pasteur pipette to **slowly transfer** the nitrating mixture prepared in step 1 to the Erlenmeyer flask containing the acetanilide solution prepared in step 3. Swirl the flask continuously during the addition and keep the temperature of the mixture below 20° C by cooling in an ice-water bath.

5. When all the nitrating mixture has been added, allow the reaction mixture to stand at room temperature for 30 minutes.

6. Add the reaction mixture slowly, with stirring, to a mixture of 100 mL of water and 25 g of ice in a 400-mL beaker. (You should have a frothy, pale-yellow slurry.)

7. Collect the solid by suction filtration (refer to Experiment 2, if necessary). Break up the solid with a spatula, being careful not to tear the filter paper, and wash the solid with cold water.

8. Remove the solid from the Büchner funnel and transfer it to a 400-mL beaker. Add 100 mL of distilled water and stir vigorously. Collect the solid by suction filtration and again wash with cold water.

9. Repeat step 8. Use blue litmus paper to test the wash water collected in the filter flask to see if it is still acidic. If it is, you should repeat step 8 again.

10. When the wash water is no longer acidic, press the solid between two filter papers until it is as dry as possible and then allow it to dry in air.

11. Determine the mass of crude *p*-nitroacetanilide obtained. Recrystallize the product using a 4:1 mixture of ethanol and water. You should expect to use about 100-150 mL of solvent. Remember that using either too much or too little solvent will reduce your final yield.

12. When your product is dry (you may have to leave it drying in air until your next laboratory session), determine its yield and melting point.

13. Ask your instructor to assist you in obtaining an infrared spectrum of both your starting material (acetanilide) and your product (4-nitroacetanilide).

14. Store your sample in a suitably labelled sample vial and hand it to your instructor for grading and possible use in a subsequent experiment.

Safety

Acetanilide was formerly used as a dusting powder, as a mild antiseptic and anesthetic. It can be harmful if taken internally.

***p*-Nitroacetanilide** is not considered to be particularly hazardous; however, you should avoid allowing this compound to come into contact with your skin or eyes. Wash your hands before eating.

Concentrated nitric acid is a corrosive liquid with an irritating vapour. Protect your hands and eyes. Use only in a fume hood.

Concentrated sulfuric acid is very corrosive to eyes, skin and other materials. Wear gloves and protect your eyes.

Glacial acetic acid can cause burns. Its vapour is irritating to the skin and eyes. Wear gloves and use only in a fume hood. Poisonous if swallowed.

Ethanol can be poisonous if swallowed. The denaturing substances present in laboratory ethanol increase its toxicity. Highly flammable.

Waste Disposal

Excess concentrated nitric and sulfuric acid measured out during Step 1 of the procedure must be neutralized before discarding. **See your instructor for the procedure**.

The acidic filtrate and washings from the suction filtrations should be diluted with copious amounts of water and washed down the drain.

The ethanol/water mixture from the recrystallization should be placed in the container provided.

Write-up

This experiment should be written up using the standard format for "preparative type" experiments. Do not forget to report the mass of acetanilide used, the mass of crude *p*-nitroacetanilide obtained, and the mass, percentage yield and melting point of the recrystallized product. Tabulate your data wherever possible.

Remember to photocopy you lab report before mailing it to your academic expert for marking.

Questions

Answers to be submitted with your lab report.

1. During the nitration of acetanilide (Step 4 of the procedure), care is taken to keep the reaction mixture cool. What do you think might be the consequences of allowing the reaction mixture to become too warm?

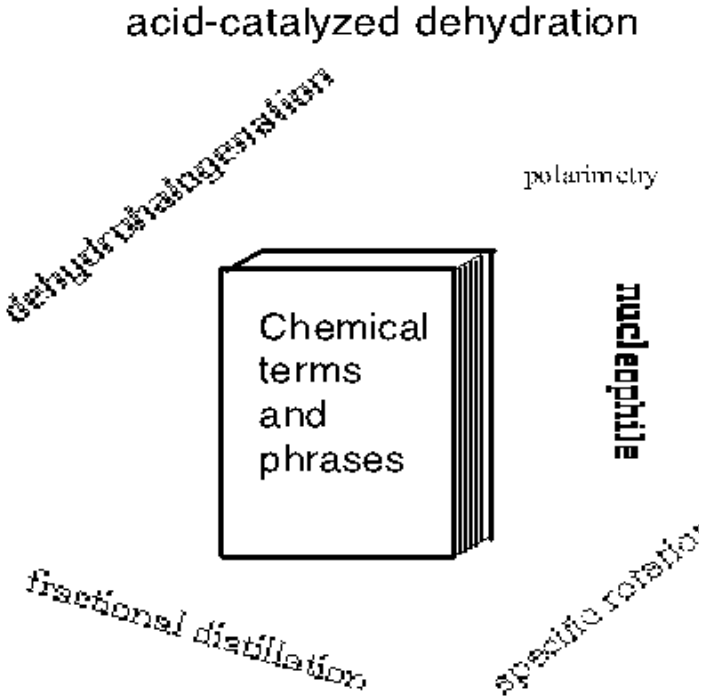
2. What organic compound (other than ethanol) would you reasonably expect to isolate from the ethanol/water mixture that was used to recrystallize your 4-nitroacetanilide?

ATHABASCA UNIVERSITY

CHEM350

ORGANIC CHEMISTRY I

Glossary 2009-2012



Chem 350 Glossary of Terms and Phrases

absolute configuration that the R enantiomer is dextrorotary and that S enantiomer is levororotary. J.M. Bijvoet in 1949-1951 proved conventions are correct using X-ray spectroscopic methods on tartaric acid salts.

absorb to take up a substance in bulk.

absorbance is the common logarithm of the reciprocal of the transmittance of a pure solvent or Absorbance =2-log(%Transmittance)

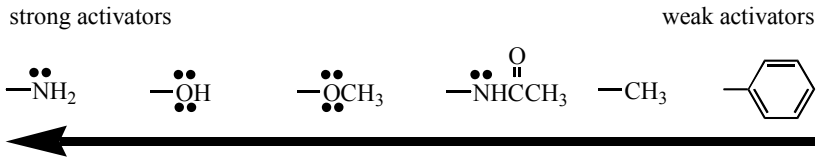
acetanilide (mp. 114-116° C) is an odourless compound in the form of white, shining crystalline leaflets or a white crystalline powder. It is soluble in hot water, alcohol, ether, chloroform, acetone,glycerol and benzene. Used as a rubber accelerator, in the manufacture of dyestuffs and intermediates, as a precursor in pencillin manufacture and as a painkiller.

acetone (aka 2-propanone, CH_3COCH_3), is a clear, colorless, volatile, extremely flammable liquid, miscible with water, used as a solvent and reagent.

achiral molecule (a-ky´-rul, Gr. a*cheir*= 'away from' handed), a type of molecule that is superimposable on its mirror image. It is not optically active and does not exist as a pair of enantiomers.

activated charcoal a water insoluble carbon powder added during hot gravity filtrations to adsorb (i.e., remove) high molar mass (coloured) impurities from the product. (see also recrystallization). If your product is coloured, do not use!

activating group is a substituent on an aromatic ring which increases the reactivity of the aromatic ring towards electrophilic substitution relative to benzene.



alcohol(s) (R-OH, IUPAC ending = ol, functional group name = hydroxyl) are organic derivatives of water. They have higher water solubilities (one hydroxyl group can solubilize 3-4 'C'-atoms) and boiling points than hydrocarbons of similar molecular weight (see Table 6.2) due to intermolecular hydrogen bonding. The alcohols can be primary, secondary, or tertiary depending on the number of carbon atoms attached to carbon bonded to the hydroxyl. Compounds that contain more than one hydroxyl group are call polyhydric alcohols (2OH=glycols or diols, 3OH=triols).

Physical Properties of Some Alcohols:

Name	Formula	Mol. Wt.	Mp (°C)	Bp (°C)	Sp. gravity
methyl alcohol (methanol)	CH_3OH	32.04	-97	64.7	0.792
ethyl alcohol (ethanol)	CH_3CH_2OH	46.07	-114	78.3	0.789
n-propyl alcohol (1-propanol)	$CH_3CH_2CH_2OH$	60.11	-126	97.2	0.804
isopropyl alcohol (2-propanol)	$CH_3CHOHCH_3$	60.11	-88	82.3	0.786
ethylene glycol	$HOCH_2CH_2OH$	62.07	-12	198	1.11
n-butyl alcohol (1-butanol)	$CH_3(CH_2)_3OH$	74.12	-90	117.7	0.810
isobutyl alcohol	$(CH_3)_2CHCH_2OH$	74.12	-108	107.9	0.802
sec-butyl alcohol (2-butanol)	$CH_3CH_2CHOHCH_3$	74.12		99.5	0.808
t-butyl alcohol	$(CH_3)_3COH$	74.12	25	82.5	0.789
n-pentyl alcohol (1-pentanol)	$CH_3(CH_2)_4OH$	88.15	-79	137.3	0.814
phenol	C_6H_5OH	94.11	43	181.7	1.058
n-hexyl alcohol (1-hexanol)	$CH_3(CH_2)_5OH$	102.2	-52	155.8	0.820
cyclohexanol	$C_6H_{11}OH$	100.2	25.1	161.1	0.962
n-heptyl alcohol (1-heptanol)	$CH_3(CH_2)_6OH$	116.2	-34	176	0.822
n-octyl alcohol (1-octanol)	$CH_3(CH_2)_7OH$	130.2	-16.7	194.4	0.820
n-nonyl alcohol (1-nonanol)	$CH_3(CH_2)_8OH$	144.3	-5.5	213.5	0.827
n-decyl alcohol (1-decanol)	$CH_3(CH_2)_9OH$	158.3	7	229	0.830

1-undecanol	$CH_3(CH_2)_{10}OH$	172.3	19	243	0.830
lauryl alcohol (1-dodecanol)	$n\text{-}C_{12}H_{25}OH$	186.3	24	259	0.831

Boiling Point (Bp) of Other Hydrocarbons:

Name	Formula	Mol.Wt.	Bp (°C)
ethane	CH_3CH_3	30.07	-89
ethanal	CH_3CHO	44.05	20.8
propane	C_3H_8	44.11	-42
propanal	CH_3CH_2CHO	58.08	48.8
butane	C_4H_{10}	58.12	0
pentane	C_5H_{12}	72.15	36
diethyl ether	$CH_3CH_2OCH_2CH_3$	74.12	34.5
pentanal	$CH_3(CH_2)_3CHO$	86.14	103
hexane	C_6H_{14}	86.18	69

In syntheses, alcohols are versatile and can be converted into many aliphatic compounds. Reactions of alcohols can be divided into 2 types: C-O bond attacks (e.g., dehydration of alcohols to alkenes, alcohols to alkyl halides), and O-H bond attacks (e.g., alcohols to ethers, alcohols to tosylates, alcohols to carboxylic acids).

Preparation of alcohols can occur by many means. e.g., (1) hydration or hydroboration of alkenes (2) reduction of carbonyl groups and acid derivatives, (3) Grignard addition.

aliphatic hydrocarbons (Gr. *aleiphar* = fat), one of two major broad categories of organic compounds (aliphatic or aromatic), originally meant that the compound's chemical behaviour was 'fat-like', it now means a compound reacts like and alkane, alkene, alkyne or one of their cyclic counterparts.

alkanes (straight chain = C_nH_{2n+2}, cycloalkanes = C_nH_{2n}, IUPAC ending = ane, no functional group name, only C-C single bond, aka parrafin =Lat. *parum affinis* = slight affinity, or aliphatic =Gr. *aleiphas* = fat) are hydrocarbons in which all of the carbon atoms are sp^3 hybridized and all the carbon-carbon bonds are single bonds resulting from the overlap of two tetrahedral carbon sp^3 orbitals (1.54 ± 0.01 angstroms, 85 ± 3 kcal/mol). The C-H bonds are also all nearly constant (1.09 ± 0.01 angstroms, 95 ± 3 kcal/mol).

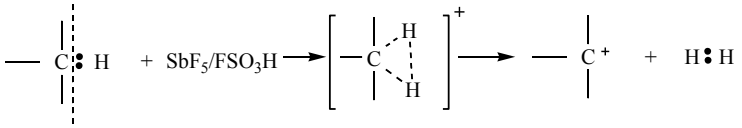
Some physical constants of n-alkanes (=homologous series) are:

Name	Formula (C_nH_{2n+2})	Mol. Wt.	Mp (°C)	Bp (°C)	(d^{20}_4) density	n_D^{20}
methane	CH_4	16.04	-183	-161.5		
ethane	CH_3CH_3	30.07	-172	-88.6		
propane	$CH_3CH_2CH_3$	44.11	-188	-42.1		
n-butane	$CH_3CH_2CH_2CH_3$	58.12	-135	-0.5		
n-pentane	$CH_3(CH_2)_3CH_3$	72.15	-130	36.1	0.626	1.3575
n-hexane	$CH_3(CH_2)_4CH_3$	86.18	-95	68.7	0.659	1.3749

Alkanes, although fairly unreactive, can undergo a few reactions:

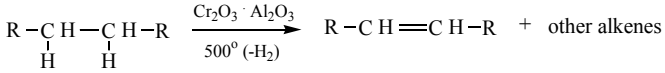
1. Polar reactions of Alkanes

i. Heterolytic cleavage

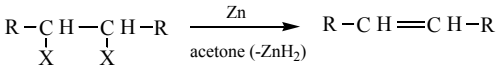


heterolytic cleavage of sigma bond | superacid | pentacoordinate carbon compound | carbocation

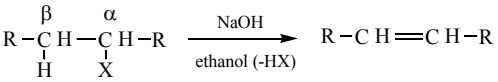
ii. Dehydrogenation (elimination reaction via catalyst)



iii. Dehalogenation (elimination reaction of vicinal (vic) dihalide)

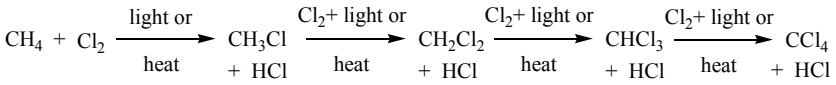


iv. Dehydrohalogenation (β–elimination reaction of alkyl halides)

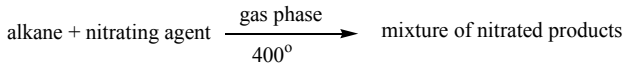


2. Radical reactions of Alkanes

i. Halogenation (via chain reaction)



ii. Nitration (via chain raction)



alkene(s) (C_nH_{2n}, IUPAC ending = ene, functional group name = C-C double bond, $R_2C{=}CR_2$, *aka* olefin =Lat.=*oleum*, oil + *facere*, to make) are hydrocarbons that contain one or more carbon-carbon double bonds. They are also referred to as unsaturated compounds. The carbon-carbon double bond is due to sp^2 hybridization, it is composed of a sigma bond and a pi bond (1.33 ± 0.01 angstroms, 152 ± 3 kcal/mol). Alkenes have planar geometry, restricted bond rotation (i.e., cis-trans isomers) and the geometry of the alkene can be described by the E,Z system using the Cahn-Ingold-Prelog sequence rules for nomenclature. Some physical constants of alkenes are:

Name	Formula (C_nH_{2n})	Mol. Wt.	Mp (°C)	Bp (°C)	d^{20}_4 density	n_D^{20} RI
ethylene	CH_2CH_2	20.05	-169	-103.7		1.363
propene	CH_2CHCH_3	42.08	-185.2	-47.4	0.5193	1.3567
1-butene	$CH_2CHCH_2CH_3$	56.12	-185.3	-6.3	0.5951	1.3962
1-pentene	$CH_2CH(CH_2)_2CH_3$	70.14	-138	30.0	0.6405	1.3715
1-hexene	$CH_2CH(CH_2)_3CH_3$	84.16	-139.8	63.3	0.6731	1.3837
cyclohexene	C_6H_{10}	82.15	-103.5	83.0	0.8102	1.4465

Unlike alkanes, alkenes are very reactive and can be converted into many aliphatic compounds. Reactions of alkenes are predominated by their electron-rich double bond and their reactions with electrophiles: e.g., addition of HX where the orientation of electrophilic addition is generally governed by Markovnikov's rule and Hammond's postulate. Reactions with other electrophiles (X_2, HOX, BH_3) may give rise to anti-stereochemistries and non-Markovnikov syn additions.

Preparation of alkenes is predominated by elimination reactions. e.g., (1) dehydration of alcohols (2) dehydrohalogenations (3) dehydrogenation (4) Hofmann elimination, (5) Cope elimination, (6) acetate pyrolysis, (7) tosylate elimination, and (8) Wittig reaction.

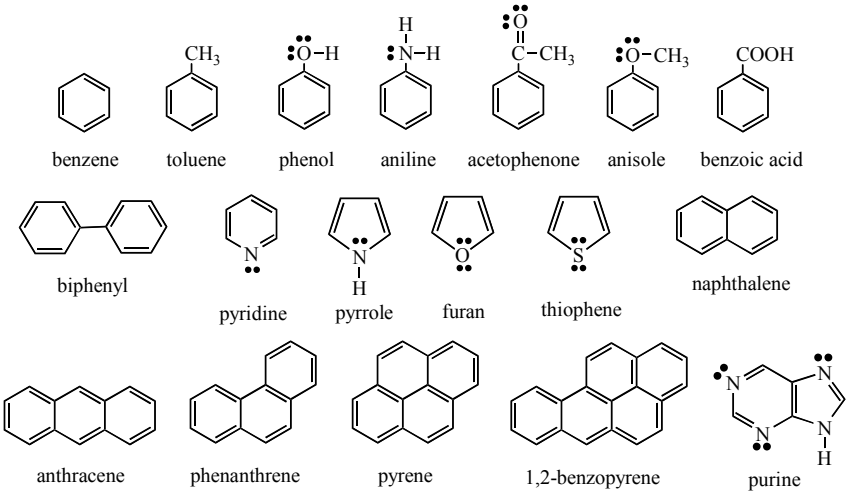
alkynes (C_nH_{2n-2}, IUPAC ending = yne, functional group name = C-C triple bond, aka acetylenes, are hydrocarbons that contain one or more carbon-carbon triple bond. They are also referred to as unsaturated compounds. The carbon-carbon triple bond is due to the overlap of two *sp* hybridized carbon atoms; it is composed of one strong sigma bond and two weaker pi bonds (1.20 angstroms, 196 kcal/mol). Simple alkynes have linear geometry, and therefore cannot exhibit cis-trans isomerism. Boiling points, melting points and sp.gravities of simple alkynes are normally slightly higher than the corresponding alkanes and alkenes due to their rod like structure. Some physical constants of alkynes are:

Name	Formula (C_nH_{2n})	Mol. Wt.	Mp (°C)	Bp (°C)	d^{20}_4 density	n_D RI
acetylene(ethyne)	CHCH	26.04	-81.8	-83.6	0.6208	1.0005
propyne	CH_3CCH	40.07	-101.5	-23.2	0.7062	1.3863
1-butyne	$CH_3CH2CCH$	54.09	-125.7	8.1	0.691	1.3962
1-pentyne	$CH_3(CH_2)_2CCH$	68.13	-90	39.3	0.695	1.3852
1-hexyne	$CH_2(CH_2)_3CCH$	82.15	-132	71	0.7155	1.3989

As a general rule, alkynes react with electrophilic reagents similar to alkenes although at a slower rate.

anti addition(s) a term used to describe the stereochemistry of an addition reaction, it refers to the addition of substituents to opposite faces of a double bond resulting in trans products.

aromatic compound(s) (C_nH_{2n-6}, contain an aromatic ring, base names: benzene, phenol, toluene, aniline, acetophenone, anisole, biphenyl) are a class of organic compounds that have a low carbon-hydrogen ratio and tend to be fragrant in nature. Aromatic compounds may also be heterocyclic (e.g., pyridine, pyrrole, furan, and thiophene) or polycyclic (e.g., naphthalene, anthracene, phenanthrene, pyrene and benzopyrene) or polyheterocyclic (e.g., purine).



aromatic orientation substituents on an aromatic ring can affect the orientation of the reaction depending on whether or not the substituent is an ortho, meta, or para directing group.

aromatic reactivity substituents on an aromatic ring can affect the reactivity of the ring relative to benzene depending on whether or not the substituent is an activating or deactivating group.

asymmetric carbon refers to a 'C' atom bonded to four different groups. Note: the presence of a asymmetric 'C' in a molecule only suggests the possibility that a molecule will be chiral. see also 'chiral center'.

azeotrope is a mixture with a constant boiling point. e.g., 96% ethanol:4% water mixture boils to dryness at a constant temperature. Further definition includes a minimum boiling azeotrope (it boils off first, then the other components) and maximum boiling azeotrope (other components come off first, the azeotrope boils off last).

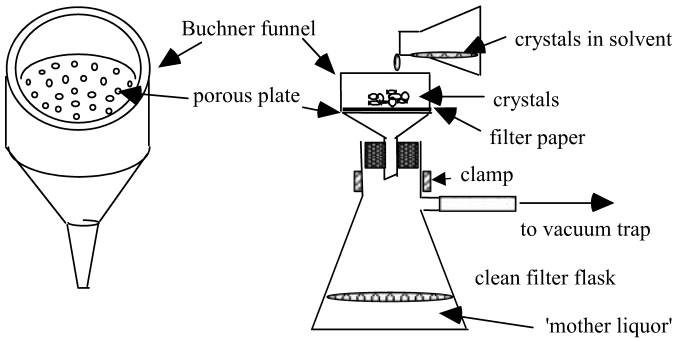
Barometric pressure correction The observed boiling point of a liquid must be corrected for barometric pressure using the following formula, or by using an nomograph.

Bp (corr.) = observed bp +((760 mm Hg – obs. Bar.Press mm Hg)/10) × 0.5° C

boiling point an important physical property of organic compounds, the boiling point of a compound is the temperature at which the liquid and gaseous phases of the compound are in equilibrium. It is also the temperature at which the vapour pressure of a liquid becomes equal to the external pressure. Note: 'boiling range' is more correct as a small temperature difference occurs between the time a compound starts to vapourize and when vapourization is completed. The boiling point must be corrected for barometric pressure.

boiling stones or boiling chips are small granules of inert material (often silica) which are added to solutions/solvents to prevent bumping during boiling of the liquid. The stone provides extra points of nucleation where vaporization can take place = bubble formation (see also 'bumping of liquids').

Büchner funnel a funnel primarily used for separating crystals of product from the ice cold liquid solvent above them. Used in conjunction with vacuum filtration. (see also vacuum filtration and recrystallization).



bumping of liquids refers to a dangerous, massive, instantaneous vaporization of heated liquids caused by localized hot spots in the reaction vessel and resulting in splashes of hot liquid being thrown from the reaction vessel. Bumping can be alleviated by using boiling stones.

Cahn-Ingold-Prelog sequence rules a method of specifying the configuration of chiral carbon atoms (R or S configuration). The rules are as follows:

1. Rank the atoms directly attached to the chiral center in order of decreasing atomic number. The group with highest atomic number is ranked first, the group with lowest atomic number is ranked fourth.
2. If a decision about priority cannot be reached by applying rule 1., work outwards to the first point of difference.
3. Multiple bonded atoms are considered as if they were an equivalent number of singly bonded atoms. i.e., -CHO substituent = $-CH(OC)_2$.

The method requires that you mentally orient the molecule so that the group with lowest priority is pointing directly back, away form you.

carbocation a tri-valent carbon intermediate which has only six electrons in its outer shell and carries a formal positive charge. It is an electrophile that can accept an electron pair from a nucleophile. It is sp^2 hybridized and planar. see also electrophilic additions, Markovnikov's Rule, Hammond postulate, S_N1 reactions.

chiral molecule (ky´-ral, Gr. *cheir*=hand), a type of molecule that has a nonsuperimposable mirror image.

chiral centers one of the causes of chirality, refers to a 'C' atom bonded to four different groups. Note: the presence of a chiral center in a molecule only suggests the possibility that a molecule will be chiral. see also 'asymmetric carbon'.

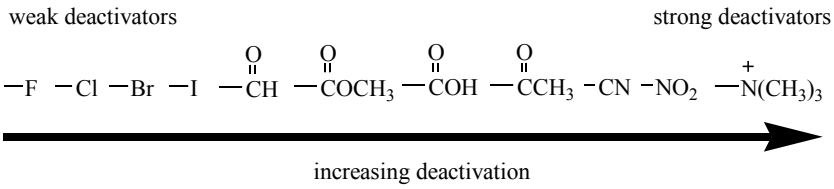
column holdup is the volume of retained liquid on the internal surfaces of the distillation system.

concentration a term which refers to the amount of solute dissolved in a given amount of solvent or solution. e.g., see molarity, molality, normality, parts per million, weight percentage.

condensation turning a vapour into a liquid by cooling a compound below its boiling point.

condenser is a jacketed glass column of jointware used in distillations. Cold water can be circulated through the condenser and causes condensation of vapour.

deactivating group is a substituent on an aromatic ring which decreases the reactivity of the aromatic ring towards electrophilic substitution relative to benzene.



dehydration, acid-catalyzed a type of E_1 elimination-polar reaction, the mechanism consists of a series of equilibria and involves the attack of an electrophile on a alcohol oxygen, loss of water to form a carbocation intermediate, and finally the elimination of a proton next to a cationic carbon atom. The reaction follows Hammond postulate and, like base-induced dehydrations, Zaitsev's rule normally).

reactivity order = tertiary R_3COH > secondary R_2CHOH > primary RCH_2OH

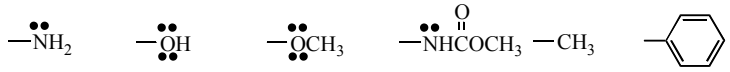
It is a commonly preferred method for the conversion of an alcohol to an alkene.

dextrorotary (Lat. *dextrorsum*=towards the right), a term to describe optically active molecules that rotate polarized light to the right (+).

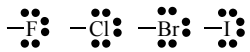
diastereomers are stereoisomers that are not enantiomers. i.e., not mirror images of each other.

directing substituents substituents on an aromatic ring can be three types: (1) ortho- and para-directing activators, (2) ortho- and para-directing deactivators and (3) meta-directing deactivators.

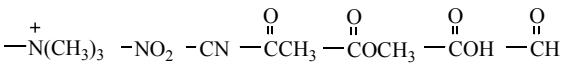
***ortho*- and *para*-directing activators** (resonance effect greater than inductive effect)



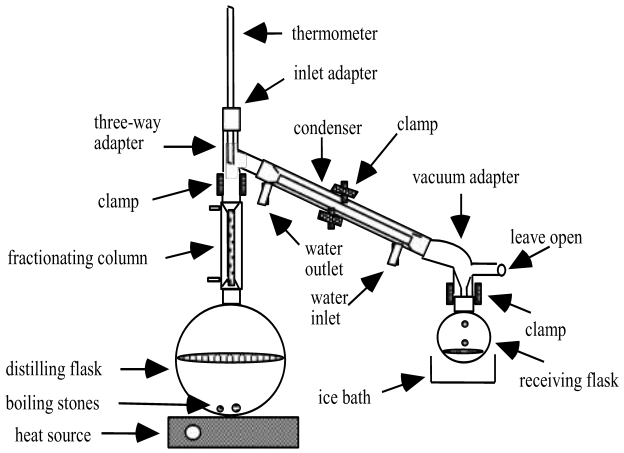
***ortho*- and *para*-directing deactivators** (inductive effect greater than resonance effect)



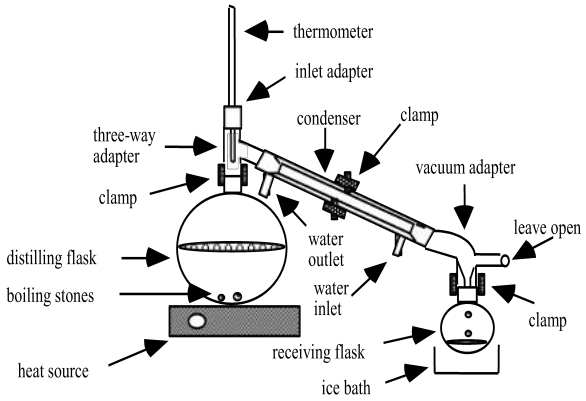
***meta*-directing deactivators**



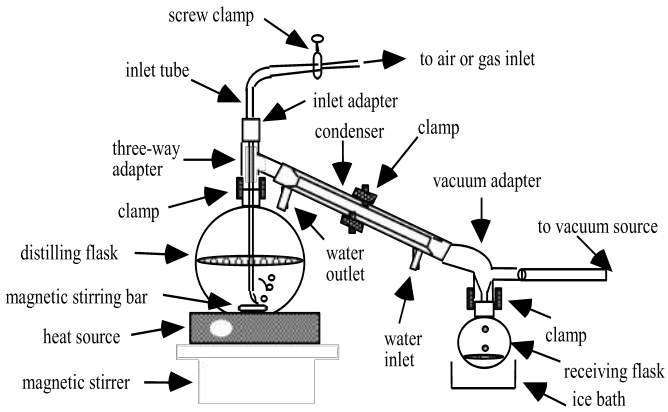
distillation, fractional a method for the separation of volatile compounds from a mixture of two or more miscible liquids with boiling points that differ by less than 25^{o} C. Employs the use of a fractionating column and occurs at atmospheric pressure.



distillation, simple a simple and effective method for the purification of a volatile liquid product from impurities with at least 25^{O} C difference in boiling point and non-volatile impurities. The crude liquid product is heated to a boil in a still pot (flask) and the vapours rise and are condensed into a receiver flask. Usually only refers to distillations below 150^{O} C and at 1 atmosphere of pressure.



distillation, vacuum usually only refers to distillations of liquid with a boiling point above 150^{O} C at 1 atmosphere of pressure. It is a method for the purification of a volatile heat-labile liquid product from its miscible impurities with at least 25^{O} C difference in boiling point and non-volatile impurities. The crude liquid product is heated to a boil in a still pot (flask) and the vapours rise and are condensed into a receiver flask.



drying agent used to dry wet solvents (solvents saturated with water). Some examples and their characteristics are:

	Drying Agent	Capacity/Efficiency:	Drying Compatibility:
1.	calcium chloride,	large/low	not good for alcohols, amines, phenols
2.	potassium carbonate	fair/fair	not good for acidic materials
3.	disodium sulfate	large/ slow and low	good with organic solvents
3.	magnesium sulfate	large/good and rapid	good with organic solvents
4.	calcium sulfate	large/good	good with organic solvents
5.	potassium hydroxide	large/v.g. and rapid	good for amines
6.	sodium metal	small/v.g and v.fast	good only for relatively dry solvents not good with acidic protons, halocarbons (violent rxns).
7.	phosphorous pentoxide	small/v.g and v.fast	good only for relatively dry solvents not good with alcohols, ketones, amines or acids
8.	metal hydrides (CaH_2)	small/v.g and v.fast	good only for relatively dry solvents not good for cmpds. with acidic H, C-hetro-atom, double bonds, or chlorocarbons (violent reactions)

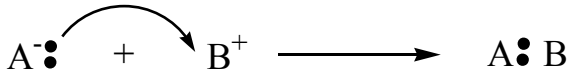
-small amounts of the drying agent are added to the material to be dried and the liquid then allowed to stand in a closed vessel. The drying agent is removed by gravity filtration or decantation.

E_1 reaction (E_1 = elimination, unimolecular) is one of four main polar reaction mechanisms in organic chemistry. More specifically, elimination reactions of alkyl halides. It is analogous to the S_N1 reaction. All E_1 eliminations occur by spontaneous dissociation of a halide and loss of a proton from the carbocation intermediate (rate limiting step). Occurs under solvolysis conditions in the absence of added base and shows first-order kinetics. Strongly affected by solvent, leaving group, and substrate structure. Shows no geometric requirement in the substrate.

E_2 reaction (E_2 = elimination, bimolecular) is one of four main polar reaction mechanisms in organic chemistry. More specifically, elimination reactions of alkyl halides. It is analogous to the S_N2 reaction. In E_2 eliminations, the base removes a proton at the same time as the leaving group dissociates and the reaction shows second-order kinetics. Strongly affected by solvent, type of nucleophile/base, leaving group, and substrate structure. Anti-periplanar geometry of substrate is preferred.

electrophile (electrons+.Gr. *phile*= attracted to) is an 'electron-loving' reagent with electron-poor sites that form a bond by accepting a pair of electrons from an electron-rich reagent. The term is specifically used when bonds to carbon are involved. Correlated to Lewis acids but refers to relative rates of organic polar reactions whereas Lewis acids are referring to relative equilibrium constants.

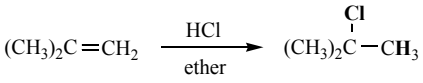
Examples of electrophiles are: alkyl halides, X^+, H^+, HX, Hg^{+2}, $AlCl_3$, BF_3.



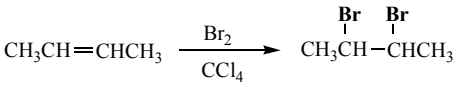
Nucleophile (electron-rich) Electrophile (electron-poor)

electrophilic additions a type of polar reaction. All proceed by an attack on an electrophile by an electron-rich double bond. Some examples are:

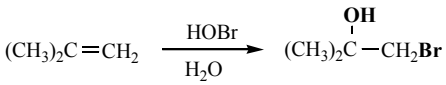
1. Addition of HX (X= Cl, Br, or I)



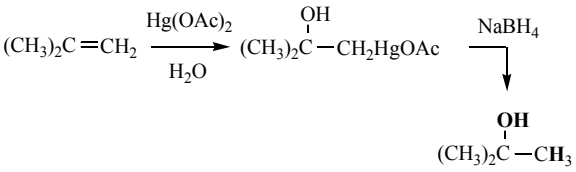
2. Addition of X_2 (X= Cl, or Br)



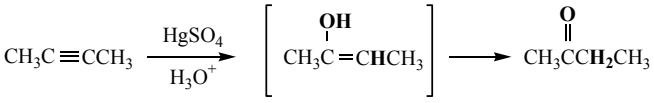
3. Halohydrin formation: Addition of HOX(X= Cl, Br or I)



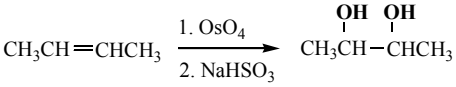
4. Hydration by oxymercuration: Addition of -Hg-OH



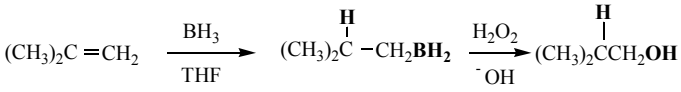
5. Alkyne hydration:



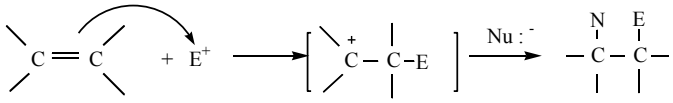
6. Hydroxylation by Osmium Tetroxide:



7. Hydroboration:



Rxn Mech.

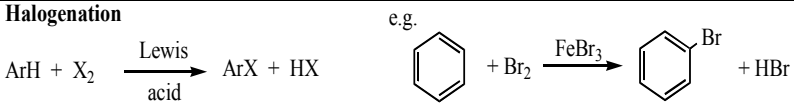


cation intermediate

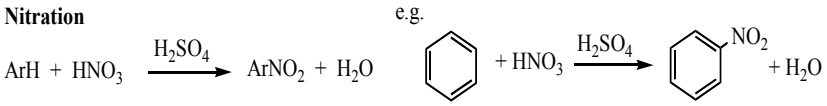
where E^+ = electrophile (H^+, X^+, or Hg^{2+}) and $Nu:^-$ = nucleophile ($HO:^-$ or $X:^-$)

electrophilic aromatic substitution perhaps the single most important type of reaction of aromatic compounds. They all proceed via a common two step mechanism. It involves the attack of an electrophile by an aromatic ring (pi electrons of the aromatic ring) and the formation of a carbocation intermediate. The loss of a proton is the second step. Overall the electrophile substitutes for one of the hydrogens. Because of its resonance forms, benzene will undergo electrophilic substitution reactions rather than addition reactions typically shown by alkenes. There are six primary types of electrophilic substitution reactions that are of importance:

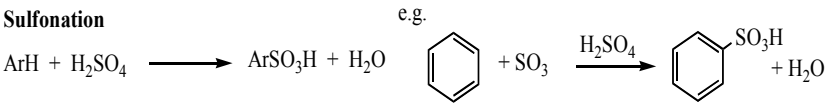
1. Halogenation



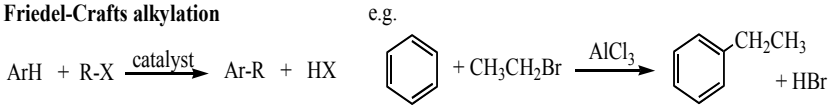
2. Nitration



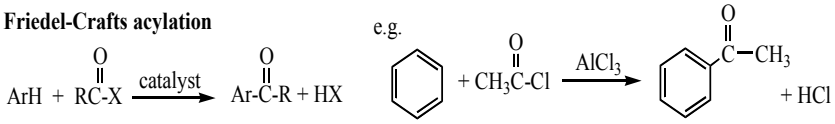
3. Sulfonation



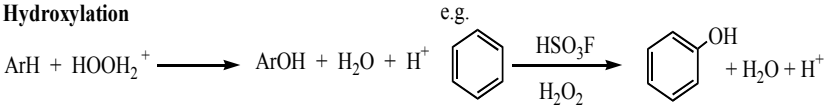
4. Friedel-Crafts alkylation



5. Friedel-Crafts acylation

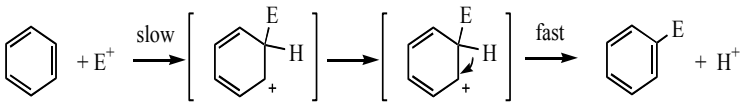


6. Hydroxylation



Phenol (67% Yield)

General mechanism for electrophilic aromatic substitution:



-a bimolecular reaction showing second order kinetics (Rxn Rate = k[ArH][E^+]). The rate limiting step is the formation of the carbocation intermediate.

emergent stem error emergent stem error occurs when a thermometer is not immersed to its recommended depth (see engraved line on stem, 76 mm from the bottom of the bulb). Corrected by the formula: emergent stem correction (to be added to t_1) = $0.00017 \times N(t_1-t_2)$ where N = length in degrees of exposed mercury column, t_1 = observed temperature, t_2 = temperature at middle of exposed column.

emulsion in chemistry, it refers to the appearance of a 'cloud of small droplets/particles' suspended in solution instead of two distinct layers in separatory funnels during extractions.

enantiomers (Gr. *enantio*=opposite) or optical isomers are stereoisomers that are nonsuperimposable mirror images of each other.

eutectic mixture (pron. yu-'tek-tik, Gr. *eutektos* = easily melted) is a mixture (i.e., an alloy or solution) having the lowest melting point possible. The melting point of an eutectic mixture has a sharp range which can be confused with that of a pure compound.

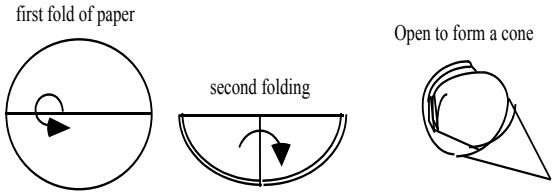
extraction a technique used in organic chemistry to separate components of an organic mixture. It refers to removing a component from a mixture of soluble components. It takes advantage of the difference in solubility of a substance in two immiscible liquids. The four classes of compounds commonly extracted are:

Compound Class	Examples:	Extract into:	Recover with:
1. Strong Acids	mineral, organic acids	sat.Na-bicarbonate	HCl (conc.)

2. Weak Acids	phenols, sustit.phenols	10% NaOH (aq)	HCl (conc.)
3. Organic Bases	aniline, triethylamine	10% HCl (aq)	NH_4OH, NaOH
4. Neutral Organic	amides, hydrocarbons	dichloromethane	same

extraction, back- a technique used in organic chemistry to recover a component from a solvent in which it is partially soluble in. (see also extraction).

filter cone a way of quickly folding filter paper for use in gravity filtrations:



filter flask or 'suction flask' is an thick walled Erlenmeyer flask with a side arm on the neck which is used in conjunction with a Büchner funnel and water aspirator for collecting crystals of product . (see also vacuum filtration and recrystallization).

filter paper for clarifying solutions, collecting precipitates and crystals in gravity and vacuum filtrations. Common brand name Whatman™. Choice of 6 porosities from course to fine:

Whatman Grade#	Porosity	Flow rate	Surface	Particle Retention
Whatman 4	coarse	Fast 12s	smooth	20-25 μ
Whatman 1	medium	Med. 40s	smooth	11 μ
Whatman 2	med-Fine	Med. 55s	smooth	8 μ
Whatman 2V	medium	Med. 55s	sm.pleated	8 μ
Whatman 3	coarse	Slow 90s	sm.grained	6 μ
Whatman 5	fine	Slow 250s	sm.dense	2.5 μ

Remember to choose the right size of circle diameter for funnel.

Fischer projections named after Emil Fischer (1852-1919) as a standard method for depicting the 3-dimensional arrangement of atoms (i.e., configuration) in 2-dimensions (on paper). The tetrahedral carbon atom is represented by the intersection of two perpendicular crossed lines. Horizontal lines are bonds coming out of the page while vertical lines represent bonds going into the page.

Movements of the projections on paper allowed are:

(1) Rotate 180^o but not 90^o or 270^o and

(2) Hold any one group steady and rotate the other three clockwise or counterclockwise.

Assignment of R,S configurations to Fischer projections governed by the following rules:

(1) Assign priorities to the four substituents.

(2) Perform one of the allowed motions to place the lowest priority group at the top of the Fischer projection.

(3) Determine the direction of rotation in going from priority 1 to 2 to 3 to 4 and assign R or S configuration.

fore-run is the low-boiling point material collected from a distillation. The volume is measured and the fore-run is usually discarded.

fraction(s) what a fractional distillation separates components into.

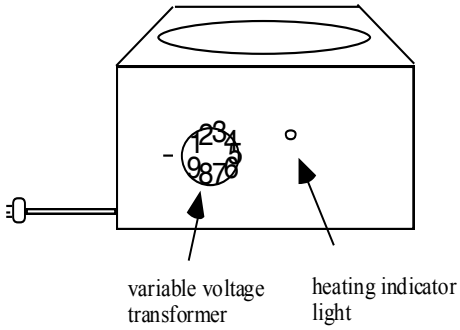
fractionating column very similar to the condenser except it is wider and it has projections at the end to help hold in the packing material (glass beads, glass helices, ceramic pieces, metal chips or twistings).

functional group(s) are structural features, composed of an atom or group of atoms with a characteristic chemical reactivity, which are part of a larger molecule that aid in the classification of organic compounds. Examples of functional groups are: C=C double bond, $R_2C=O$ carbonyl, -OH hydroxyl, C-X halide, C-OH alcohol, NO_2 nitro, $O=C-NH_2$ amide, NH_2 amine.

gas one of three common phases of matter (others are solids and liquids), it has no fixed shape or volume. Note: volumes of gases vary greatly with changes in temperature or pressure.

Hammond postulate proposed by George Simms Hammond (1921-) in 1955, an important explanation of the interplay between reactivity and stability of carbocations intermediates and the effect on the structure of the final product. "The more stable carbocation should form faster than the less stable one."

heating mantle a electrical heat source with an external or built in variable voltage transformer depending on the model.



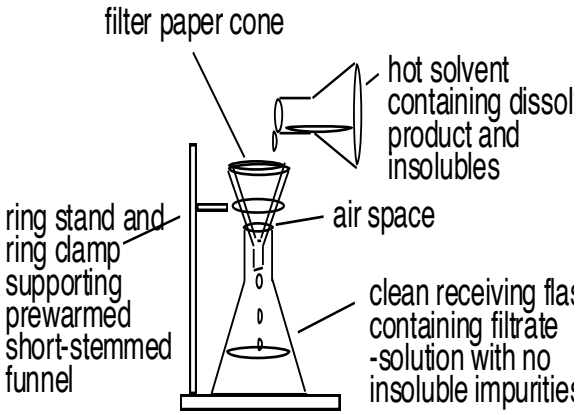
HETP or **h**eight **e**quivalent to 1 **t**heoretical **p**late is the length of fractionating column that equals one simple distillation.

homogeneous mixture or solutions that are a single phase in which a solution occurs and may be solid, liquid or gaseous. It has or any subsample of the mixture has the same set of intrinsic properties; each property of course dependent on the composition of the mixture.

homologous series a series of compounds that differ from one another by a constant unit (e.g.,, $-CH_2$ in alkanes).

homologs what members of a homologous series are called.(e.g.,, methane and ethane are homologs).

hot gravity filtration a method used during the purification and recrystallization of product to remove impurities less soluble than the product. Hot solvent containing dissolved product is poured through filter paper in a prewarmed (100-120° C) short-stemmed funnel and the filtered liquid is collected in a clean, dry receiving flask. Insolubles and boiling chips are retained on the filter. (see also recrystallization).



hydride shift a type of structural rearrangement that can occur during a reaction involving the formation of a carbocation.

hydrocarbon(s) are a family of organic compounds, containing only hydrogen and carbon, which can be subdivided into several groups based on the type of bond that exists between carbon atoms. Alkanes (contain all C-C single bonds), alkenes (contain one or more C-C double bonds), alkynes (contain one or more C-C triple bonds).

ice bath or more correctly, a 'water-ice' bath. Temperature 0-4° C. A flat bottomed vessel containing mostly water with some ice cubes which is used to cool solutions in flasks. i.e., during recrystallization.

immiscible pairs of liquids that do not mix in any proportions are said to be immiscible. E.g., water-hexane solvent system. The solubility of water in hexane is negligible. (i.e., water is immiscible in hexane).

inductive effect an electron-withdrawing effect important in the understanding of aromatic reactivity. Inductive effects are caused by the intrinsic electronegativity of atoms and to dipoles present in functional groups and involve donated or withdrawing electrons in sigma bonds or through space.

interface is the borderline between to immiscible liquids.

intrinsic properties are attributes which distinguish matter from all other types of matter. E.g.,, density, color, physical state, melting point, boiling point, refractive index, specific rotation, IR spectrum etc.

isomer a general term for compounds related to each other in one of two ways: as structural isomers or stereoisomers. Structural (constitutional) isomers have identical molecular formulas but differ in their atoms bonding sequence (e.g.,, butane and 2-methylpropane). Stereoisomers have identical molecular formulas and their atoms bonding sequence is the same. Stereoisomers differ in that their atoms are arranged differently in space. E.g., cis-trans isomers are a type of stereoisomer.

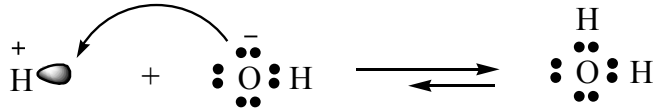
IUPAC system International Union of Pure and Applied Chemistry's system of nomenclature for organic molecules where each different compound has a different name. Has a set of rules which provides names for more than 2 million organic molecules plus millions more yet to be synthesized. E.g.,, For unbranched alkanes:
Rule 1. The base name of any group relates to the total number of carbon atoms in the group.

layer(s) refers to the formation of two phases when insoluble liquids are mixed together. i.e., The less dense top layer (light phase) floats on top the more dense lower layer (heavy phase).

leverorotary (Lat. *Laevus*=on the left hand), a term to describe optically active molecules that rotate polarized light to the left (-).

Lewis acid is a substance that accepts an electron pair.

Some Lewis acids are H_3O^+, BF_3, $AlCl_3$, $TiCl_4$, $ZnCl_2$, $FeCl_3$, and $SnCl_4$.



Hydronium ion (Lewis acid) electron accepting | Hydroxide ion (Lewis base) electron donating | Water

Lewis base is a substance that donates an electron pair (see also Lewis acid). Some examples of Lewis bases are hydroxides, amines, ethers, alcohols and ketones (O and N containing organic compounds). Not to be confused with nucleophiles. For instance, ethoxide ion ($CH_3CH_2O^-$) is a stronger base than ethylmercaptide ion ($CH_3CH_2S^-$) (K_a C_2H_5OH = ~10^{-18}, K_a C_2H_5SH = ~10^{-12}) however in many cases the ethylmercaptide ion is the stronger nucleophile.

liquid one of three common phases of matter (others are solid and gas), it has no fixed shape but does have a 'constant' volume. Note: volumes of liquids do not change greatly with changes in temperature or pressure.

Markovnikov's rule named after Vladimir Vassilyevich Markovnikov (1833?-1904), who published a paper in 1868 entitled "Materials on the Question of a Mutual Effect of Atoms in Chemical Compounds" in which he formulated an empirical rule for predicting the additions of hydrogen halides to asymmetrical alkenes. The modern rule was proposed in 1905 and states that 'in the ionic addition of an unsymmetrical reagent (e.g., HX) to an alkene, the positive portion (acid hydrogen) of the adding reagent bonds to the carbon with fewer alkyl substituents (or more hydrogen atoms) so as to produce a more stable carbocation. Then the negative portion (X group) always bonds to the carbocation (more alkyl substituted carbon or less hydrogenated carbon)'.

melting point an important physical property of organic compounds, the melting point of a compound is the temperature at which the solid and liquid phases of the compound are in equilibrium. Note: 'melting range' is more correct as a small temperature difference occurs between the time a compound starts to melt and when melting is completed.

meso compunds are compounds that are superimposable on their mirror images by virtue of a plane of symmetry, yet contain chiral centers, e.g., *cis* 1,2-dibromocyclopropane.

methyl shift a type of structural rearrangement that can occur during a reaction involving the formation of a carbocation.

minimum solvent the amount of solvent (usually hot) required to just dissolve the solute.

mixed melting point a method used to help find the identity of an unknown compound. Based on the premise that when an organic compound is impure, its melting point is lowered. i.e., mix genuine stock reagent with the unknown and if the melting point of the mixture is the same as the unknown, the identity of the unknown is that of the stock reagent. If it is different, then try again with another stock reagent!

mixed-solvent system used to recrystallize product when one cannot find a single solvent which completely dissolves your product. e.g., water:ethanol. Water:ethanol behaves like water at low temperatures, and it acts like ethanol at high temperatures.

miscible pairs of liquids that mix in all proportions are said to be miscible. e.g.,, water-acetone, water-methanol, water-ethanol, water-propanol solvent systems. the solubility of water in ethanol is ∞. All ratios of mixtures results in one dissolving completely in the other (i.e., water is completely miscible in acetone).

molality (abbr.=m) is the concentration of a solution expressed as moles of solute per kg of solvent. Note: the molality of a solution does not vary with temperature because masses do not change with temperature.

molarity (abbr.=M) is the concentration of a solution expressed as moles of solute per liter of solution. Note: the molarity of a solution changes with temperature because of expansion and contraction of the solution.

molar solution contains 1 mol or g mol wt. of the solute in 1 L of solution.

mole (abbr. = mol) the amount of substance of a system which contains as many elementary units (atoms, molecules, ions, electrons, other particles or groups of other particles) as there are atoms in 0.012 kg of carbon 12. i.e., Avogadro's number (6.0221367×10^{23}) of elementary units.

molecule is the smallest unit quantity of matter in a substance which can exist by itself and retains all the properties of the original substance.

molecular weight is the sum of the atomic weights of all the atoms in a molecule.

mole fraction (abbr.=X_A) is an expression of concentration of a component (A), defined as the number of moles of a component A divided by the total moles of all components.

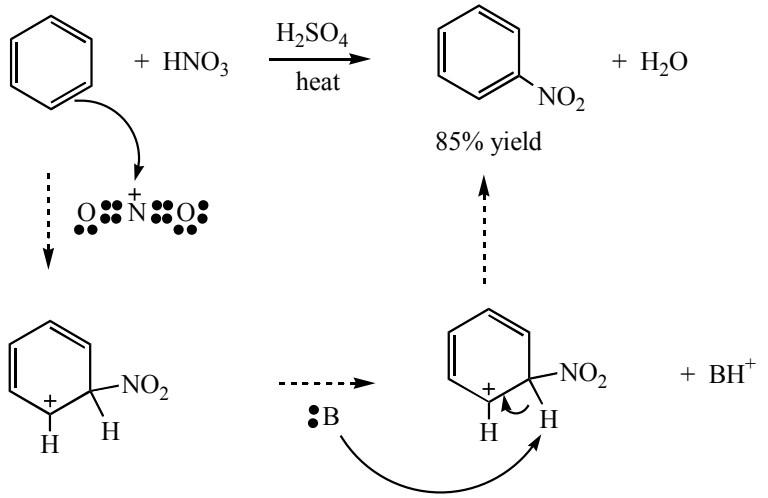
$$X_A = \frac{\text{moles component A}}{\text{total moles of all components}}$$

Note: The sum of all mole fractions for a given solution must = 1.

MSDS **M**aterial **S**afety **D**ata **S**heet is part of WHMIS (see below). These sheets give 'complete' details on the physical properties of the chemical, possible health effects that are produced upon exposure, preventative measures, etc.

nitrating mixture a mixture of concentrated sulfuric and concentrated nitric acid which results in the formation of nitronium ions (NO_2^+), a strong electrophile which readily attacks aromatic systems.

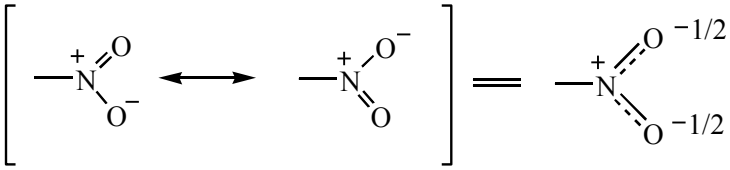
nitration addition of a nitro group (-NO_2), into an organic system. Proceeds via an electrophilic substitution reaction mechanism analogous to halogenations.



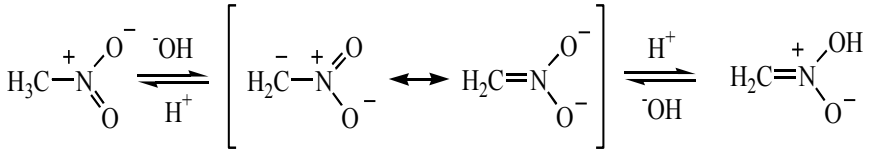
B: = H_2O, HSO_4^- or NO_3^-

nitro group

a nitro group (-NO_2) is electronically similar to a carboxylate anion (-CO_2^-) and can have two equivalent resonance forms:



The nitro group is highly electronegative and nitro compounds are polar compounds of high boiling points but low water solubility. A nitro group is capable of stabilizing a negative charge on an adjacent atom; thus nitromethane is sufficiently acidic to dissolve in aqueous sodium hydroxide



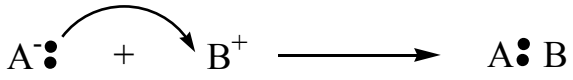
Nitromethane
pK_a 15

aci-Nitromethane

nucleophile

(nucleus+.Gr. *phile*= attracted to) is an 'nucleus-loving' reagent with electron-rich sites that form a bond by donating a pair of electrons to an electron-poor reagent. The term is specifically used when bonds to carbon are involved. Correlated to Lewis bases but refers to relative rates of organic polar reactions whereas Lewis bases are referring to relative equilibrium constants.

Nucleophiles can be negatively charged (:$^-$Nu=:$^-$OH, :$^-$H, :X^-, NO_2^-, R3C:-), or neutral (:Nu-H= H_2O, ROH, :NH_3, R-NH_2). Note: If neutral, the nucleophile must be attached to a hydrogen atom which can be eliminated.



Nucleophile (electron-rich) Electrophile (electron-poor)

oiling out

a phrase to describe the formation of an oil instead of crystals which can occur during recrystallization from a mixed-solvent system. It often happens when the boiling point of the recrystallization solvent is higher than the melting point of the compound

optical activity

was discovered by Jean Baptiste Biot (1774-1862), a French physicist at Collège de France, in 1815. He observed that naturally occurring organic compounds (sugar, camphor) rotate the plane of polarization of an incident beam of polarized light.

optical isomers

see enantiomers. Discovered by Louis Pasteur in 1848 while studying crystals of sodium ammonium tartrate salts.

parts per billion

(abbr.=ppb) is an expression of concentration for very dilute solutions, similar to ppm, where the mass of solute in solution is divided by the total mass of solution all times 1 billion (e.g., 1μg/kg):

$$\text{ppb} = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 10^9$$

parts per million (abbr.=ppm) is an expression of concentration for dilute solutions, similar to weight percentage, where the mass of solute in solution is divided by the total mass of solution all times 1 million (e.g., 1mg/kg):

$$\text{ppm} = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 10^6$$

phase refers to portions of matter that are uniform in composition and in intrinsic properties.

plane-polarized light light obtained when passed through a polarizer. Polarized light consists of light waves oscillating in a single plane. Ordinary light is unpolarized since its electromagnetic waves oscillate in an infinite number of planes at right angles to the direction of light travel.

polarimeter an instrument used to measure the amount of optical rotation of optically active organic molecules.

polar reactions one of three fundamental types of organic chemical reactions (see also radical reactions, pericyclic reactions). Polar reactions can be classified into several general categories:

(1) Electrophilic addition reactions
(2) Elimination reactions
(3) Electrophilic aromatic substitution reactions
(4) Nucleophilic substitution reactions
(5) Nucleophilic aromatic substitution reactions

Polar reactions are between electron rich reagents and electron poor reagents. They are heterolytic processes and involve an even-numbered-electron species.

protecting group a group added to a sensitive or interfering functional group to protect it in a reaction with a reagent intended for a second functional group. Use of a protecting group involves three steps: (1) formation of an inert derivative, (2) performing the wanted reaction, and (3) removal of the protecting group.

e.g.,, protecting a sensitive amino group by reacting it with acetic anhydride (acetylation).

-protecting an alcohol with dihydropyran and converting the alcohol to a tetrahydropyranyl (THP) ether.

-protecting a carbonyl group by reacting it with ethylene glycol and conversion to an acetal.

pure compound a pure compound has a sharp melting point (1-2^{o} C). An impure compound has a broad depressed melting point.

racemic mixture (proun. ray-ceé-mic, Lat. *racemus*=cluster (of grapes)), or racemate is a 50:50 mixture of chiral enantiomers denoted by (±). Optical rotation is zero.

Raoult's Law defines the partial pressures of A and B vapors above a solution containing components A and B:

Raoult's law states that: $P_A = X_A P^o_A$ and $P_B = X_B P^o_B$

where P_A is the vapor pressure of the solution,

X_A is the mole fraction of the solvent, and

P^o_A is the vapour pressure of the pure solvent

-solutions that obey Raoult's law are called 'ideal solutions'.

R configuration (R abbr. for Lat. *rectus*=right) refers to the direction of travel (clockwise) around a chiral center in order of rank of substituents. (see also Cahn-Ingold-Prelog sequence rules).

recovery the final step of the extraction procedure, it is when the component is forced back out of solution by neutralization of the extraction medium.

recrystallization an important method of purification of organic compounds. It involves 5 steps: (1) dissolving the impure compound in minimum hot solvent, (2) performing hot gravity filtration after adding activated charcoal, (3) slowly cooling the filtrate, first to room temperature and then to 4^{o} C, (4) collecting the purified product crystals by vacuum filtration and rinsing the crystals with a small volume of ice-cold solvent and finally (5) drying the purified product.

reflux ratio (R) R is the ratio of the volume of condensate formed at the top of the column and returned to the system to the volume removed as distillate.

$$R = \frac{\text{volume of condensate returned to the column}}{\text{volume of condensate removed as distillate}}$$

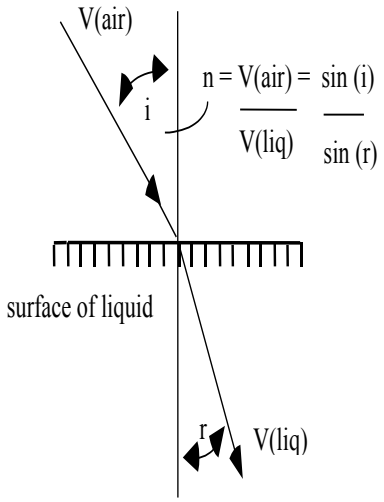
refractive index (abbr.= n_D^{20}) a specific physical property of liquids that therefore can be used in the identification of unknown compounds and to detect small quantities of impurities. It is based on the fact that light travels at a different velocity in liquid (V_{liq}) than in air (V_{air}).

The refractive index is inversely proportional to the temperature (it increases with decreasing temperature). This can be compensated for by using the following equation:

$n_D^{20} = n_D^{x} + (Temp_x - 20^{o}\text{ C}) \times 0.00045^{o}\text{ C}^{-1})$ where:

n_D^{x} = the measured refractive index at temperature x

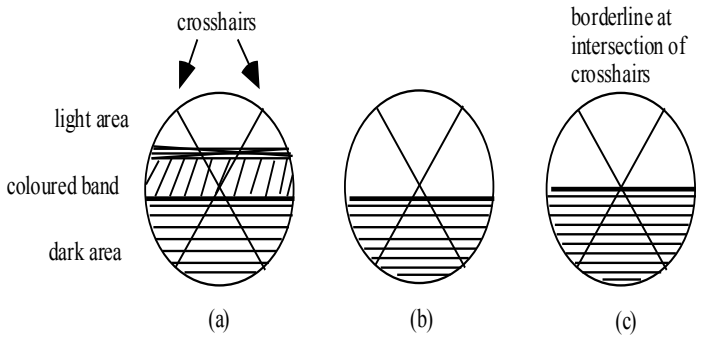
$Temp_x$ = the temp. of the sample at time of measurement



Light is refracted as it passes from air into a liquid.

refractometer a device used for the measurement of refractive index. It uses a sodium D line light source and can be temperature compensated to 20^{o} C. The machine must also be adjusted for chromatic aberration (by 'achromatizing the borderline'). Views through eyepiece of refractometer are seen below:

In (a) below, a coloured band appears between the light and dark areas. Reduce this coloured band to a minimum by rotating the compensator drum/dial just below the eyepiece. Now the eyepiece should look like (b). The final step before reading the refractive index is to adjust the borderline between the light and dark areas (using the side handwheel) so that it crosses the intersection of the two crosshairs as shown in (c).



regiospecific reactions (Lat. *rego* = to rule or govern) refers to reactions that from a standpoint of orientation tend to give predominately one addition product when or two or more possible isomeric products might have been formed.

resonance effect an electron effect important in the understanding of control of aromatic orientation. Resonance effects are caused by donating or withdrawing electrons and involve electrons in p-orbitals and aromatic ring pi electrons. Note: Some activators of aromatic rings (-OH, $-OCH_3$, $-NH_2$) show inductive effects due to their electronegativity but their resonance electron-donation effect is far greater and therefore they activate the aromatic ring.

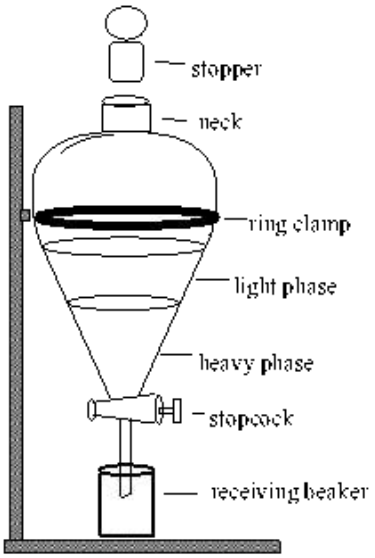
rotary evaporator an apparatus used for the evaporation of relatively large volumes of solvent. It uses a vacuum to keep the temperature low during the evaporation process.

salting out refers to the use of salt (note: sol. NaCl in ice cold water is 36g/100mL) to alter the ionic strength of water and thereby reduce the solubility of an organic compound which is partially soluble in water.

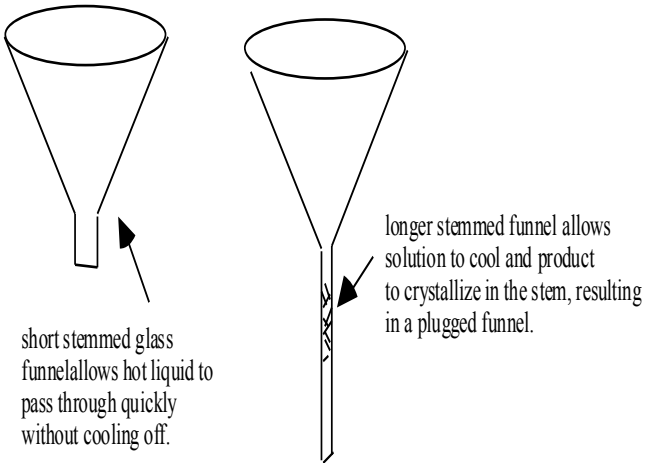
S configuration (S abbr. for Lat. *sinister*=left) refers to the direction of travel (counterclockwise) around a chiral center in order of rank of substituents. (see also Cahn-Ingold-Prelog sequence rules).

second crop a way of increasing the yield of purified product. It involves 5 steps: (1) saving the filtrate from the vacuum filtration and reducing the volume of solvent by boiling. Steps (2)-(5) are the same as for recrystallization. Note: the second crop is often not as pure as the first crop of crystals.

separatory funnel (a.k.a. 'sep funnel') used for extractions and separations of immiscible liquids. The bottom/heavy layer is let out the bottom by opening the stopcock and the top/light layer is poured out the top of the funnel.



short-stemmed funnel or 'stemless funnel' is a funnel primarily used for hot gravity filtrations. (see also hot gravity filtrations and recrystallization). The short-stem allows for the hot filtered product to pass quickly into the collection/receiving flask without crystallizing.



sigma (s) plane a kind of plane of symmetry used to study molecular conformations. It is a mirror plane that bisects a rigid object so that one-half of the object coincides with the reflection in the mirror of the other half. No molecule possessing a plane of symmetry can be chiral (i.e., no chiral molecule has a plane of symmetry). e.g.,, water has two (σ) planes, ammonia has three.

S_N1 reaction (S_N1 = substitution, nucleophilic, unimolecular) is one of four main polar reaction mechanisms in organic chemistry. More specifically, nucleophilic substitution reactions of alkyl halides. It is analogous to the E_1 reaction. S_N1 reactions occur via a carbocation intermediate (sp^2 hybridized, planar species; achiral) and result in varying degrees of racemic mixtures or rarely complete racemization (e.g., 80:20 or 50:50 mixture of enantiomers respectively). This is because the nucleophile may attack the carbocation 'equally' well from either side. The S_N1

reaction shows first order kinetics (Rate= k[RX]) with the rate-limiting step involving the formation of the carbocation intermediate. The S_N1 reaction is favoured by any factor that stabilizes the high-energy carbocation intermediate (Hammond postulate) and is not affected by the nature of the attacking nucleophile (solvolysis). The reaction is favoured by the leaving group that's the most stable (Tosylate$^-$>I:$^-$>Br:$^-$>Cl:$^-$>H_2O:), and the solvent used (fast in polar protic solvents, slow in non-polar solvents).

S_N2 reaction (S_N2 = substitution, nucleophilic, bimolecular) is one of four main polar reaction mechanisms in organic chemistry. More specifically, nucleophilic substitution reactions of alkyl halides. It is analogous to the E_2 reaction. In S_N2 reactions, there is a change (inversion) of configuration at the chiral center (nucleophile back-side attacks substrate from a position 180^o away from the leaving group), the reaction shows second order kinetics (Rate= k[RX][Nu:$^-$]) and takes place in a single step without intermediates. The S_N2 reaction is subject to alkyl steric effects, is affected by the nature of the attacking nucleophile, the leaving group (same as S_N1 reactions), and the solvent used (slow in protic, fast in polar aprotic solvents).

solid one of three common phases of matter (others are liquid and gas), it has fixed shape and volume. Note: volumes of solids change very little in with changes in temperature or pressure.

solute in a solution, they are the components which are dissolved in the solvent.

solution is a homogeneous mixture of two or more substances.

solvation refers to the interaction of an ion with solvent molecules.

solvent in a solution, it is the component in greater abundance.

solvolysis in reactions, it refers to the solvent serving as both reaction medium and nucleophile. Has a strong effect on reaction rate. Important in many S_N1 reactions and the effect is explained by the Hammond postulate, and solvation and polarity (dielectric constants).

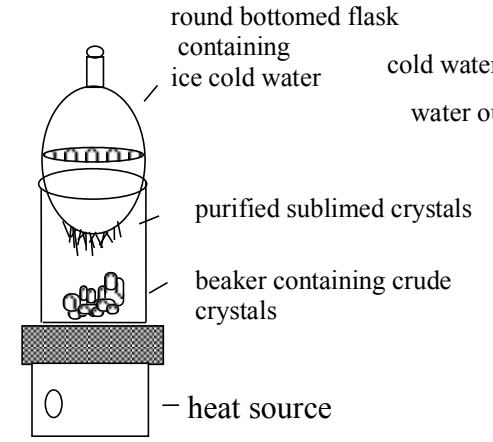
specific rotation $[\alpha]_D$ = standardized intrinsic physical property of optically active compounds. Defined as the observed rotation of light of 5896 angstroms wavelength (the yellow sodium D line) when passed through a sample path length of 1 decimeter (dm=10cm) with a sample concentration of 1 g/mL.

$$\text{Given: } [\alpha]_D^{20} \text{ for a solution} = \frac{(\alpha - \alpha_{blank})}{\text{STL (dm)} \times c}$$

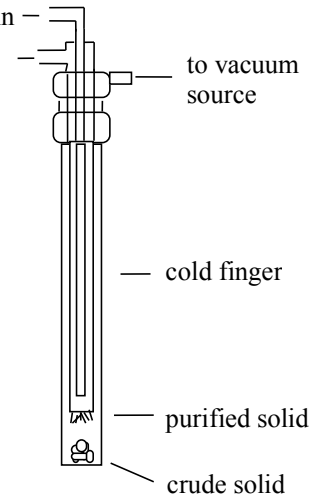
where α = observed rotation, α_{blank} = obs.rotation of solvent, STL=Sample Tube Length in dm, and c = conc. of sol'n (g/mL).

stereoisomers one of two types of isomer. They are compounds with identical chemical formula that have their atoms connected in the same order but differ in the spatial arrangement of those atoms.

sublimation (to sublime =the direct conversion of a solid to a vapour) is a procedure used for the purification of compounds that sublime. The impure solid is gently heated and the vapours of pure compound are collected on a cool surface.



crude sublimation apparatus



cold finger sublimator

suspension is a liquid mixture in which fine particles of a solid substance are dispersed or suspended.

sweating of solvent a result of escaping solvent previously trapped in the crystalline lattice.

symmetrical reagent in alkene addition reactions, it refers to a reagent that has identical parts to add to a double bond (e.g., H_2 or X_2).

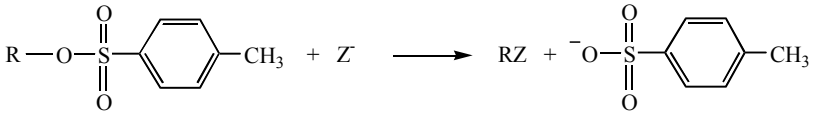
syn addition(s) a term used to describe the stereochemistry of an addition reaction, it refers to the addition of substituents to the same face of a double bond resulting in cis products.

theoretical plates an efficiency term used for fractionating columns where each theoretical plate is equivalent to one simple distillation.

thermometer calibration a procedure performed to correct for defects in accuracy in a thermometer used for melting point and boiling point determinations. Suggested standards are ice water (mp 0^{o} C), hydrocinnamic acid (mp 47-49^{o} C), acetanilide (mp 113-115^{o} C), adipic acid (mp 152-154^{o} C) and *p*-hydroxybenzoic acid (mp 215-217^{o} C).

throughput in reference to distillations, it is the maximum volume of distillate that can be obtained per unit of time while still maintaining equilibrium throughout the fractionating column

tosylate is an alkyl *p*-toluenesulfonate ester. It is a very good leaving group in nucleophilic substitution reactions.

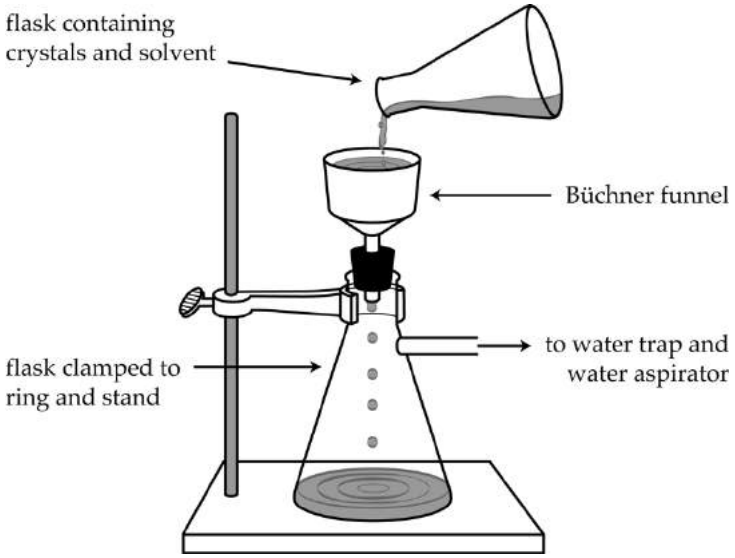


an alkyl tosylate Nucleophile tosylate leaving group

trituration a method for solidifying an 'oiled out' organic compound. It involves 4 steps: (1) removing a small sample of the oil with a Pasteur pipette and placing a few drops on a clean watch glass, (2) Add a few drops of solvent that the compound is known to be insoluble in, (3) using a glass rod beat (triturate) the solvent-oil mixture until it forms a crystalline solid and finally (4) use these crystals to seed the rest of the oil and cause the oil to crystallize.

unsymmetrical reagent in alkene addition reactions, it refers to a reagent that has non-identical parts to add to a double bond (e.g., H_2O, HOX or HX).

vacuum filtration or suction filtration, is a common method of collecting crystalline product. (see also recrystallization). It involves the use of a Büchner funnel, filter paper, filter flask and water aspirator (with water trap).

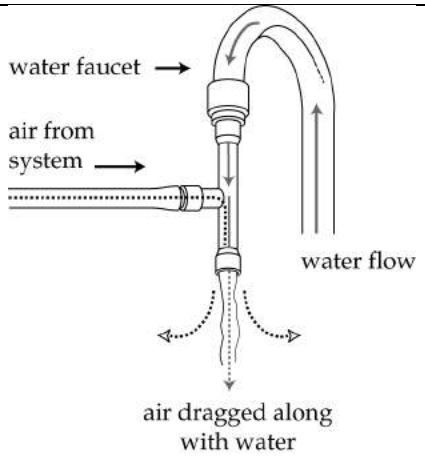


van der Waals forces intramolecular forces between non-polar molecules. They operate over very short distances and result from the induced polarization of the electron clouds in molecules. i.e., Temporary dipole moments in one molecule causes a temporary opposite dipole moment in another and a tiny attraction occurs between the two molecules. The cumulative effect of a very large number of these tiny attractive force interactions explains why molecules exist in a liquid state rather than a gaseous state. Note: These forces increase as molecule size increases.

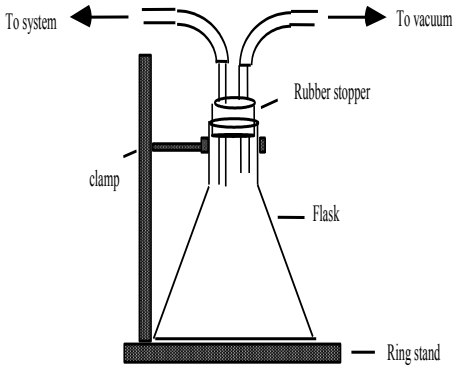
vaporization turning a liquid into a vapour by heating a compound to its boiling point.

washing a technique used in organic chemistry to purify a component which has been extracted from an organic mixture.

water aspirator a small device attached to a water faucet. It is used to create an inexpensive source of vacuum for use in vacuum filtrations.



Water Trap a safety apparatus used to prevent the back flow of water from a water aspirator into the filter flask during vacuum filtration.



Weight percentage abbr.=Wt.%, w/w, a quantitative expression of concentration, in parts per hundred, and is defined as the mass of the component in solution divided by the total mass of solution, all times 100%. Can also be expressed as w/v defined as the mass of the component in solution divided by the total volume of solution, all times 100%.

$$\text{Wt\% (w/w)} = \frac{\text{mass of component in soln}}{\text{total mass of soln}} \times 100\%$$

WHMIS **W**orkplace **H**azardous **M**aterials **I**nformation **S**ystem (WHMIS) is a national system intended to provide laboratory personnel with uniform information on chemicals used in the workplace. Its three main features are: (1) chemical manufacturers supply a label outlining the products hazards and recommend emergency procedures, (2) the manufacturer provides a Material Safety Data Sheet (MSDS) for each hazardous product, and (3) Employers provide an appropriate education program for all workers who work with hazardous chemicals.

Zaitsev's rule	(proun.= *Sayt zeff*), formulated by Alexander M. Zaitsev (1841-1910).Rule paraphrase = 'Base-induced elimination reactions generally give the more substituted alkene product'.

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Compound Name	Chemical Formula	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Refract. Index	Hazardous Properties*
acetanilide	$CH_3CONHC_6H_5$	S	135.17	113-115			Toxic, irritant
acetanilide,4-methyl	$CH_3CONHC_6H_4CH_3$	S	149.19	149-151			Irritant
acetanilide, *p*-nitro	$CH_3CONHC_6H_4NO_2$	S	180.16	216			Irritant
acetanilide, *o*-nitro	$CH_3CONHC_6H_4NO_2$	S	180.16	94	1.419		Irritant
acetanilide, *m*-nitro	$CH_3CONHC_6H_4NO_2$	S	180.16	154-156			Irritant
acetic acid, glacial (17.4 M)	CH_3CO_2H	L	60.05	118.1	1.049		Corrosive, hygroscopic
acetic acid, *p*-ethoxyphenyl	$C_2H_5OC_6H_4CH_2CO_2H$	S	180.2	87-90			Irritant
acetic anhydride	$(CH_3CO)_2O$	L	102.09	140	1.082	1.3900	Corrosive, lachrymator
acetone	CH_3COCH_3	L	58.08	56.5	0.7899	1.3590	Flammable, irritant
acetone, diethylamino	$(C_2H_5)_2NCH_2COCH_3$	L	129.2	64/16mm	0.832	1.4250	Irritant
acetophenone	$C_6H_5COCH_3$	L	120.15	202	1.030	1.5325	Irritant
activated carbon		S					(see charcoal)
allyl alcohol (2-propen-1-ol)	$CH_2=CHCH_2OH$	L	58.08	96-98	0.854	1.4120	Highly Toxic, flammable
ammonia (14.8 M)	NH_3	L	17.03		0.90		Corrosive, lachrymator
ammonium hydroxide (14.8 M)	NH_4OH	L	35.05		0.90		Corrosive, lachrymator
aniline	$C_6H_5NH_2$	L	93.13	184	1.022	1.5860	Highly toxic, irritant
aniline, 4-bromo	$BrC_6H_4NH_2$	S	172.03	62-64			Toxic, irritant
aniline, 4-chloro	$ClC_6H_4NH_2$	S	127.57	72.5			Highly toxic, irritant
aniline, *o*-ethyl	$CH_3CH_2C_6H_4NH_2$	L	121.18	210		1.5590	Toxic, irritant
aniline, 2-ethoxy	$CH_3CH_2OC_6H_4NH_2$	L	137.18	231-233	1.051	1.5550	Irritant, light sens.
aniline, 4-methyl	$CH_3C_6H_4NH_2$	L	107.16	196	0.989	1.5700	Toxic, irritant
aniline, 3-nitro	$NO_2C_6H_4NH_2$	S	138.13	114			Highly toxic, irritant
aspirin (see salicylic acid, acetate)	$CH_3CO_2C_6H_4CO_2H$	S	180.16	138-140			Irritant, toxic
benzaldehyde	C_6H_5CHO	L	106.12	179.5	1.044	1.5450	Hi.toxic, cancer susp.agnt
benzaldehyde, 4-methyl	$CH_3C_6H_4CHO$	L	120.15	204-205	1.019	1.5454	Irritant (*p*-tolualdehyde)
benzaldehyde,4-methoxy	$CH_3OC_6H_4CHO$	L	136.15	248	1.119	1.5730	Irritant, (anisaldehyde)
benzaldehyde, 4-nitro	$NO_2C_6H_4CHO$	S	151.12	106			Irritant
benzene	C_6H_6	L	81.14	80.1	0.908	1.4990	Flamm., cancer susp.agnt
benzene, bromo	C_6H_5Br	L	157.02	155-156	1.491	1.5590	Irritant
benzene, chloro	C_6H_5Cl	L	112.56	132	1.107	1.5240	Flammable, irritant
benzoate, ethyl	$C_6H_5CO_2C_2H_5$	L	150.18	212.6	1.051	1.5050	Irritant
benzoate, methyl	$C_6H_5CO_2CH_3$	L	136.15	198-199	1.094	1.5170	Irritant
benzocaine, or 4-aminobenzoic acid, ethyl ester,	$H_2NC_6H_4CO_2C_2H_5$	S	165.19	88-92			Irritant
benzoic acid	$C_6H_5CO_2H$	S	122.12	122.4			Irritant
benzoic acid, 4-acetamido	$CH_3CONHC_6H_4CO_2H$	S	179.18	256.5			Irritant
benzoic acid, 4-amino	$H_2NC_6H_4CO_2H$	S	137.14	188-189	1.374		Irritant
benzoic acid, 3-chloro	$ClC_6H_4CO_2H$	S	156.57	158			Irritant
benzoic acid, 4-chloro	$ClC_6H_4CO_2H$	S	156.57	243			Irritant
benzoic acid, 3-hydroxy	$HOC_6H_4CO_2H$	S	138.12	210-203			Irritant
benzoic acid, 4-hydroxy	$HOC_6H_4CO_2H$	S	138.12	215-217			Irritant
benzoic acid, 2-methyl	$CH_3C_6H_4CO_2H$	S	136.15	103-105			See also *o*-toluic acid
benzoic acid, 4-methyl	$CH_3C_6H_4CO_2H$	S	136.15	180-182			See also *p*-toluic acid
benzoic acid, 4-nitro	$O_2NC_6H_4CO_2H$	S	167.12	239-241			Irritant
benzonitrile	C_6H_5CN	L	103.12	191	1.010	1.5280	Irritant
benzophenone	$(C_6H_5)_2CO$	S	182.22	49-51			Irritant
benzoyl chloride	C_6H_5COCl	L	140.57	198	1.211	1.5530	Corrosive, toxic
benzyl alcohol	$C_6H_5CH_2OH$	L	108.14	205	1.045	1.5400	Irritant, hygroscopic

Compound Name	Chemical Formula	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Refract. Index	Hazardous Properties*
benzyl amine	$C_6H_5CH_2NH_2$	L	107.16	184-185	0.981	1.5430	Corrosive, lachrymator
benzyl chloride	$C_6H_5CH_2Cl$	L	126.59	179	1.1002		Hi.toxic, cancer susp.agnt
biphenyl	$C_6H_5C_6H_5$	S	154.21	69-71	0.992		Irritant
boric acid	H_3BO_3	S	61.83		1.435		Irritant, hygroscopic
Brady's Reagent	$(NO_2)_2C_6H_3NHNH_2$	L	See hydrazine, 2,4-dinitrophenyl				
bromine	Br_2	L	159.82	58.8	3.102		Highly toxic, oxidizer
butanal	$CH_3CH_2CH_2CHO$	L	72.11	75			Flammable, corrosive
1,3-butadiene, E,E-1,4-diphenyl	$C_6H_5C_4H_4C_6H_5$	S	206.29	153			Irritant
butane, 1-bromo	$CH_3CH_2CH_2CH_2Br$	L	137.03	101.3	1.276	1.4390	Flammable, irritant
butane, 2-bromo	$CH_3CH_2CHBrCH_3$	L	137.03	91.3	1.255	1.4369	Flammable, irritant
butane, 1-chloro	$CH_3CH_2CH_2CH_2Cl$	L	92.57	78.4	0.886	1.4024	Flammable liquid
butane, 2-chloro	$CH_3CH_2CHClCH_3$	L	92.57	68.2	0.873	1.3960	Flammable liquid
1-butanol	$CH_3CH_2CH_2CH_2OH$	L	74.12	117-118	0.810	1.3990	Flammable, irritant
2-butanol	$CH_3CH_2CHOHCH_3$	L	74.12	99.5-100	0.807	1.3970	Flammable, irritant
2-butanone	$CH_3CH_2COCH_3$	L	72.11	80	0.805	1.3790	Flammable, irritant
2-butanone, 3-hydroxy-3-methyl	$(CH_3)_2C(OH)COCH_3$	L	102.13	140-141	0.971	1.4150	Irritant
1-butene, 3-chloro-	$CH_3CH(Cl)CH=CH_2$	L	90.55	62-65	0.900	1.4155	Flammable, lachrymator
3-buten-2-ol	$CH_2=CHCH(OH)CH_3$	L	72.11	96-97	0.832	1.4150	Flammable, irritant
n-butyl butyrate	$C_3H_7CO_2C_4H_9$	L	144.21	164-165	0.871	1.4060	Irritant
3-butyn-2-ol, 2-methyl	$CH{\equiv}CC(CH_3)_2OH$	L	84.12	104	0.868	1.4200	Flammable, toxic
calcium carbonate	$CaCO_3$	S	100.09		2.930		Irritant, hygroscopic
calcium chloride, anhydr.	$CaCl_2$	S	110.99		2.150		Irritant, hygroscopic
camphor (1R, +)	$C_{10}H_{16}O$	S	152.24	179-181	0.990	1.5462	Flamm., irritant
carbon dioxide, solid	CO_2	S	44.01	-78.5(subl.)			Frost bite burns
carbon tetrachloride	CCl_4	L	153.82	76	1.594		Susp. cancer agent
charcoal (Norit)		S	Decolourizing agent, used in recrystallizations				Irritant
chloroform	$CHCl_3$	L	119.38	61.3	1.500		Highly toxic
cinnamaldehyde, *trans*	$C_6H_5CH=CHCHO$	L	132.16	246(decomp)	1.048	1.6220	Irritant
cinnamic acid, trans	$C_6H_5CH=CHCO_2H$	S	148.16	135-136			Irritant
crotonaldehyde	$CH_3CH=CHCHO$	L	70.09	102.4	0.846	1.4365	Highly toxic, flammab.
cyclohexane	C_6H_{12}	L	84.16	80.7	0.779	1.4260	Flammable, irritant
cyclohexane, bromo	$C_6H_{11}Br$	L	163.06	166.2	1.324	1.4950	Flammable, irritant
cyclohexane, methyl	$C_6H_{11}CH_3$	L	98.19	101	0.770	1.4220	Flammable, irritant
cyclohexene	C_6H_{10}	L	82.15	83	0.811	1.4460	Flammable, irritant
cyclohexanol	$C_6H_{11}OH$	L	100.16	161.1	0.963	1.4650	Irritant, hygroscopic
cyclohexanone	$C_6H_{10}(=O)$	L	98.15	155.6	0.947	1.4500	Corrosive, toxic
cyclohexanone, 4-methyl	$CH_3C_6H_9(=O)$	L	112.17	170	0.914	1.4460	Corrosive, toxic
cyclopentane	C_5H_{10}	L	70.14	49.5	0.751	1.4000	Flammable, irritant
cyclopentane, bromo	C_5H_9Br	L	149.04	137-138	1.390	1.4881	Flammable
cyclopentanone	$C_5H_8(=O)$	L	84.12	130.6	0.951	1.4370	Flammable, irritant
dichloromethane	CH_2Cl_2	L	84.93	40.1	1.325	1.4240	Toxic, irritant
diethyl ether (see ethyl ether)	$C_2H_5OC_2H_5$	L	74.12	34.6	0.708	1.3530	Flammable, toxic
1,4-dioxane	$C_4H_8O_2$	L	88.11	100-102	1.034	1.4220	Flamm., cancer susp.agnt
diphenylmethanol	$(C_6H_5)_2CH(OH)$	S	184.24	65-67			Irritant

Compound Name	Chemical Formula	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Refract. Index	Hazardous Properties*
ethyl acetate	$CH_3CO_2C_2H_5$	L	88.11	76-77	0.902	1.3720	Flammable, irritant
ethyl alcohol, anhydrous	CH_3CH_2OH	L	46.07	78.5	0.785	1.3600	Flammable, poison
ethyl ether, absolute	$CH_3CH_2OCH_2CH_3$	L	74.12	34.6	0.708	1.3530	Flammable, irritant
fluorene	$C_{13}H_{10}$	S	166.22	114-116			Irritant
formaldehyde (sol'n)	HCHO	L	30.03	96	1.083	1.3765	suspect. cancer agent
formamide, N,N-dimethyl	$HCON(CH_3)_2$	L	73.10	149-156	0.9487	1.4310	suspect. cancer agent
furfuryl amine	$(C_4H_3O)CH_2NH_2$	L	97.12	145-146	1.099	1.4900	Irritant
gold	Au	S	196.97	1064	19.28		Expensive/valuable
***n*-hexane**	$CH_3(CH_2)_4CH_3$	L	86.18	69	0.659	1.3750	Flammable, irritant
hydrazine, 2,4-dinitrophenyl	$(NO_2)_2C_6H_3NHNH_2$	70% soln	198.14				Flammable, irritant
hexanes	C_6H_{14}	L	86.18	68-70	0.672	1.3790	Flammable, irritant
hydrochloric acid, conc. 12 M	HCl	L	36.46		1.20		Corrosive, highly toxic
iodine	I_2	S	253.81	133	4.930		Corrosive, highly toxic
lichen		S					Allergin
ligroin (high bp petrol. ether)	C_6-C_7 (light naphtha)	L		60-80	0.656	1.3760	Flammable, irritant
Lucas Reagent		Solution	of hydrochloric acid/zinc chloride (from zinc dust)				Toxic, irritant
magnesium (metal)	Mg	S	24.31	651	1.75		Flammable
magnesium oxide	MgO	S	40.31		3.58		Moist. sens., irritant
magnesium sulfate, anhydrous	$MgSO_4$	S	120.37		2.660		Hygroscopic
magnesium sulfate, 7-hydrate	$MgSO_4.7H_2O$	S	246.48		1.670		(epsom salt)
manganese dioxide	MnO_2	S	86.94	535 (dec.)	5.026		Oxidizer, irritant
methanol, anhyd.	CH_3OH	L	32.04	64.5	0.791	1.3290	High. toxic, flammable
methanol, diphenyl	$(C_6H_5)_2CH(OH)$	S	184.24	69			Irritant
methanol, triphenyl	$(C_6H_5)_3C(OH)$	S	260.34	164.3			Irritant
methylene chloride	CH_2Cl_2	L	84.93	40.1	1.325	1.4230	See dichlormethane
mineral spirits (light kerosene)	C_{12}-C_{14}	L		179-210	0.752	1.4240	Flammable, irritant
naphthalene	$C_{10}H_8$	S	128.17	80.5			Flamm., susp.cancer agent
nitric acid (conc. 15.4 M)	HNO_3	L	63.01		1.400		Corrosive, oxidizer
2-octanone	$CH_3(CH_2)_5COCH_3$	L	128.22	173	0.819	1.4150	Irritant
pentane	C_5H_{12}	L	72.15	36.1	0.626	1.3580	Flammable, irritant
2-pentanol, 4-methyl	$C_6H_{14}O$	L	102.18	132	0.802	1.4110	Irritant
3-pentanol	$C_2H_5CH(OH)C_2H_5$	L	88.15	115/749mm	0.815	1.4100	Flammable, irritant
3-penten-2-one, 4-methyl	$(CH_3)_2C{=}CHCOCH_3$	L	98.15	129	0.858	1.4450	Flammable, lachrymator
1-pentene, 2-methyl	C_6H_{12}	L	84.16	62	0.682	1.3920	Flammable, irritant
1-pentene, 4-methyl	C_6H_{12}	L	84.16	53-54	0.665	1.3820	Flammable, irritant
2-pentene, 2-methyl	C_6H_{12}	L	84.16	67	0.690	1.400	Flammable, irritant
2-pentene, 3-methyl	C_6H_{12}	L	84.16	69	0.698	1.4040	Flammable, irritant
2-pentene, 4-methyl	C_6H_{12}	L	84.16	57-58	0.671	1.3880	Flammable, irritant
petroleum ether, (Skelly B)	Mixt. of C_5-C_6	L		35-60	0.640		Flammable, toxic
petroleum ether, hi bp (ligroin)	Mixt. of C_6-C_7	L		60-80	0.656	1.3760	Flammable, toxic
phenethyl alcohol	$C_6H_5CH_2CH_2OH$	L	122.17	221/750mm	1.023	1.5320	Toxic, irritant
phenol	C_6H_5OH	S	94.11	40-42	1.071		Highly toxic, corrosive
phenol, 2,4-dimethyl	$(CH_3)_2C_6H_3OH$	S	122.17	22-23	1.011	1.5380	Corrosive, toxic
phenol, 2,5-dimethyl	$(CH_3)_2C_6H_3OH$	S	122.17	75-77	0.971		Corrosive, toxic
phenylacetylene	$C_6H_5C{\equiv}CH$	L	102.14	142-144	0.930	1.5490	Flamm., cancer susp.agent
phenylmagnesium bromide	C_6H_5MgBr	L	181.33		1.134		Flammable, moist.sensit.
phosphoric acid (85%, 14.7 M)	H_3PO_4	L	98.00		1.685		Corrosive

Compound Name	Chemical Formula	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Refract. Index	Hazardous Properties*
potassium chromate	K_2CrO_4	S	194.20	968	2.732		Canc.susp.agent, oxidizer
potassium dichromate	$K_2Cr_2O_7$	S	294.19	398			Hi.toxic, canc.susp.agent
potassium hydroxide	KOH	S	56.11				Corrosive, toxic
potassium iodide	KI	S	166.01	681	3.130		Moist.sens., irritant
potassium permanganate	$KMnO_4$	S	158.04	d<240	2.703		Oxidizer, corrosive
propane, 2-chloro, 2-methyl	$(CH_3)_3CCl$	L	92.57	50	0.851	1.3848	Flammable
propane, 2-nitro	$(CH_3)_2CHNO_2$	L	89.09	120	0.992	1.3940	Canc.susp.agent, flamm.
2-propanol, 2-methyl-	$(CH_3)_3COH$	L	74.12	82.3	0.7887		Flammable, irritant
propionate, ethyl	$C_2H_5CO_2C_2H_5$	L	102.13	99	0.891	1.3840	Flammable, irritant
propionic acid	C2H5CO2H	L	74.08	141	0.993	1.3860	Corrosive, toxic
rosaniline hydrochloride	$C_{20}H_{14}(NH_2)_3Cl$	Solution	337.86	250 (dec)			Susp. cancer agent
salicylic acid	$HOC_6H_4CO_2H$	S	138.12	158-160			Toxic, irritant
salicylic acid, acetate ester	$CH_3CO_2C_6H_4CO_2H$	S	180.16	138-140			Irritant, toxic
Schiff's Reagent		Solution	of roseaniline hydrochloride & sulfur dioxide				Toxic
silane, tetramethyl	$Si(CH_3)_4$	L	88.23	26-28	0.648	1.3580	Flammable, hygroscopic
silica, sand	SiO_2	S	60.09	NA			abrasive
silver nitrate	$AgNO_3$	S	169.88	212	4.352		Highly toxic, oxidizer
sodium acetate	CH_3CO_2Na	S	82.03				hygroscopic
sodium acetate, trihydrate	$CH_3CO_2Na\ 3H_2O$	S	136.08	58	1.45		Hygroscopic
sodium bisulfite	$NaHSO_3$	S			1.480		Severe irritant
sodium borohydride	$NaBH_4$	S	37.38	400			Flam. solid, corrosive
sodium bicarbonate	$NaHCO_3$	S	84.01		2.159		Moist. sensitive
sodium carbonate	Na_2CO_3	S	105.99	851	2.532		Irritant, hygroscopic
sodium chloride	NaCl	S	58.44	801	2.165		Irritant, hygroscopic
sodium dichromate, dihydrate	$Na_2Cr_2O_7.2H_2O$	S	298.00		2.350		Hi.toxic, cancer susp.agent
sodium hydrogen carbonate	$NaHCO_3$	S	84.01		2.159		See sodium bicarbonate
sodium hydroxide	NaOH	S	40.00				Corrosive, toxic
sodium iodide	NaI	S	149.89	661	3.670		Moist.sens., irritant
sodium metabisulfite	$Na_2S_2O_5$	S	190.10		1.480		Moist.sens., toxic
sodium methoxide	$NaOCH_3$	S	54.02				Flam. solid, corrosive
sodium sulfate	Na_2SO_4	S	142.04	884	2.680		Irritant, hygroscopic
styrene	$C_6H_5CH{=}CH_2$	L	104.15	146	0.909		Flammable
styrene, β-bromo	$C_6H_5CH{=}CHBr$	L	183.05	112/20mm	1.427	1.6070	Irritant
sucrose	$C_{12}H_{22}O_{11}$	S	342.30	185-187	1.5805		Tooth Decay!
sulfur dioxide	SO_2	Gas	64.06	-10 bp			Nonflamm, corrosive
sulfuric acid (conc. 18 M)	H_2SO_4	L	98.08		1.840		Corrosive, oxidizer
sulfurous acid	H_2SO_3	L	82.08		1.030		Corrosive, toxic
L-tartaric acid	$HO_2CC_2H_2(OH)_2CO_2H$	S	150.09	171-174			Irritant
tetrahydrofuran	C_4H_8O	L	72.11	65-67	0.889	1.4070	Flammable, irritant
tetramethylsilane	$Si(CH_3)_4$	L	88.23	26-28	0.648	1.3580	Flammable, hygroscopic
tin	Sn	S	118.69		7.310		Flammable solid, moist.sens.
Tollen's Reagent		L	See ammonia + silver nitrate				
toluene	$C_6H_5CH_3$	L	92.14	110.6	0.867	1.4960	Flammable, toxic
toluene, 4-nitro	$NO_2C_6H_4CH_3$	S	137.14	52-54	1.392		Hi.toxic, irritant
o- or 2-toluic acid	$CH_3C_6H_4CO_2H$	S	136.15	103-105			Probable irritant
p- or 4-toluic acid	$CH_3C_6H_4CO_2H$	S	136.15	180-182			Probable irritant
triethylphosphite	$(C_2H_5O)_3P$	L	166.16	156	0.969	1.4130	Moist. sens., irritant

Compound Name	Chemical Formula	Solid (S) or Liquid (L)	Formula Weight	MP or BP (°C)	Density (g/mL)	Refract. Index	Hazardous Properties*
triphenylmethanol	$(C_6H_5)_3C(OH)$	S	260.34	164.3			Probable irritant
urea	NH_2CONH_2	S	60.06	135	1.335		Irritant
(-) usnic acid	$C_{18}H_{16}O_7$	S	344.32	198			Toxic
(+) usnic acid	$C_{18}H_{16}O_7$	S	344.32	201-203			Toxic
water	H_2O	L	18.02	100		1.33	Will burn skin when hot
water, ice	H_2O	S/L	18.02	0	1.00		Frostbite, hypothermia
xylenes	$CH_3C_6H_4CH_3$	L	106.17	137-144	0.860	1.4970	Flammable, irritant
zinc dust	Zn	S	65.37	419.5			Flammable, moist.sens.
zinc chloride	$ZnCl_2$	S	136.28	283	2.91		Corrosive, toxic.

*Be sure to consult the chemical's MSDS for more specific detail on hazardous properties.

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