Chemistry 361, Fall 2016
Principles of Organic Chemistry Laboratory

Instructor: Dr. John Markiewicz
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Lab Class: Tuesday/Thursday 2:00-4:50 pm
Room 465 (Detailed schedule below)

Office Hours: M 2-3 pm; W 10-11 am; Th 5-6 pm; or by appointment. I welcome drop-in visits, but I cannot guarantee that I will be available to help you during non-office hours.

Course Objectives: Introduce you to basic laboratory skills and provide you with experience in interpreting experimental data. Provide laboratory experience that emphasizes and reinforces the principles and concepts of chemistry in CHM 355 and 356.

University Policies: By enrolling in this course, you agree to the University Policies listed below. Please read the full text of each policy by going to www.marshall.edu/academic-affairs and clicking on "Marshall University Policies." Or, you can access the policies directly by going to www.marshall.edu/academic-affairs/policies/. Academic Dishonesty/Excused Absence Policy for Undergraduates/Computing Services Acceptable Use/Inclement Weather/Dead Week/Students with Disabilities/Academic Forgiveness/Academic Probation and Suspension/Academic Rights and Responsibilities of Students/Affirmative Action/Sexual Harassment

Catalog Description: An introduction to experimental organic chemistry with emphasis on fundamental techniques and their application to the preparation and identification of organic compounds.

Required Materials:

1. Custom Laboratory textbook by Pavia, D, Lampman, G, Kriz, G and Engel, R, *Introduction to Laboratory Techniques: A Microscale Approach, 5th edition*. This manual is only available in the bookstore. The custom manual is designed to lighten the financial burden to students compared to purchasing the full text book.
2. Safety goggles
3. Bound laboratory notebook (such as mead notebooks that are available from common office supply stores). If you purchase a notebook without pre-written page numbers, please fill these in by hand before beginning any experiments.

4. Bring a roll of paper towels to use in lab. MU does NOT provide paper towels (sorry) and you will definitely need some!
   Recommended: lab coat or old long-sleeve shirt

Laboratory Policies:

1. Anyone who has not signed the statement acknowledging one's full understanding of the required safety measures will not be permitted to work in the laboratory.
2. Use care in following the directions of your instructor and laboratory text. Do not alter the experimental procedures without being instructed to do so by the instructor or the TA's.
3. Know the locations of all safety equipment in the laboratory. You will be tested on this.
4. All injuries, no matter how trivial, must be reported to the instructor immediately.
5. Academic dishonesty will not be tolerated. Students engaging in academic dishonesty will be sanctioned as per the university policy.
6. Only "Excused Absences", as defined in the policy, can be made up. The proper procedure is to notify me (by e-mail, phone, or in person) as soon as possible; any medical documentation has to be submitted directly to the Dean of Student Affairs (MSC 2W38) who will then notify me. Note that one lab grade will be dropped in computing your score. If you miss a laboratory it will become your drop grade. If you miss more than one lab, you will be given a zero on that lab if your absence was not excused. If you have excused absences for more than one lab and do not make them up, you will be given an incomplete in the course so you can make up the missed labs in a later semester.

Support Services

Marshall University offers a variety of support services to students:

- Tutoring Center Online
- Writing Center Online
- Libraries
- Textbook Service
- Disabled Student Services
- Campus Resources
- Technical Help
- VISTA Help

"Policy for Students with Disabilities: Marshall University is committed to equal opportunity in education for all students, including those with physical, learning and psychological disabilities. University policy states that it is the responsibility of students with disabilities to contact the Office of Disabled Student Services (DSS) in Prichard Hall 117, phone 304 696-2271 to provide documentation of their disability. Following this, the DSS Coordinator will send a letter to each of the student's instructors outlining the academic accommodation he/she will need to ensure equality in classroom experiences, outside assignment, testing and grading. The

instructor and student will meet to discuss how the accommodation(s) requested will be provided. For more information, please visit http://www.marshall.edu/disabled or contact Disabled Student Services Office at Prichard Hall 11, phone 304-696-2271.

Dress Code (for your safety)

1. Protective eye goggles must be worn in the laboratory at all times. Failure to do so will constitute sufficient grounds for dismissal from the laboratory. Keep your safety glasses in your drawer so you don't forget them at home! You are responsible for obtaining a pair of safety goggles.
2. Clothing: Slacks or dresses cut below the knee must be worn.
3. Shoes covering the bridge of the foot and toes must be worn. NO Sandals!
4. Students with long hair should wear it tied back during the lab.

You will not be allowed to work in the lab while violating rules 1-3. If you commute to school, please consider keeping a spare set of lab-appropriate cloths in your car, so you will not miss lab if you accidently come underdressed.

Although the university policy does not cover the following items, these recommendations are strongly encouraged: Do not wear contact lenses (glasses preferred). Avoid wearing nylon stockings or other garments that can melt to your skin in the event of a fire. Minimize the amount of exposed skin below your neck. Consider buying a lab coat or brining in an old long-sleeve shirt that you will keep in your drawer and wear only during the lab.

Absences

Only "Excused Absences", as defined in the policy, can be made up. The proper procedure is to notify me (by e-mail, phone, or in person) as soon as possible; any medical documentation have to be submitted directly to the Dean of Student Affairs (MSC 2W38) who will then notify me. Note that one lab grade will be dropped in computing your score. If you miss a laboratory it will become your drop grade. If you miss more than one lab you will be given a zero on that lab if your absence was not excused. If you have excused absences for more than one lab and do not make them up, you will be given an incomplete in the course so you can makeup the missed labs in a later semester.

Grading Policy

Three Tests	60% (20% each test; see schedule below)
Lab Reports	25%
Notebook and safety quiz	15%

The grading scale used in this course will be:

A= 90-100, B=80-89.99%, C= 70-79.99%, D= 60-69.99%, F= less than 60%

Tests

Tests make up a large portion of your grade. You will learn the material from reading the textbook, participating in the pre-lab lectures, and by completing the experiment. The lab reports serve as a method to review the material and identify areas where you require additional reading. To prepare for tests, you must attend the scheduled review sessions. You should review your pre-lab lecture notes and the product evaluation reports before the review sessions. **If you are absent on a test day then you will need to make up the test within one week or you will receive a zero for the test.**

Lab reports

Lab reports are due one week after completing a lab at the beginning of the class. If a lab is turned in late, there is a 10-point deduction. Lab reports will not be accepted when they are more than one week late. You will receive a grade of zero for the lab report if you turn it in after one week.

Notebook:

Except for the first day of class, you will be given a notebook quiz after the prelab lecture of each class. In order to do well on this quiz, you must prepare your notebook to accept data from your experiment before coming to lab. See "The Laboratory Notebook" for more details. The quiz will consist of 12 random questions about the procedure you are doing and the procedure you previously completed. After the prelab lecture, a TA or myself will ask you the questions, and you will need to point to the place in your notebook where the question can be answered. A good notebook should answer at least 10 questions correctly, and you can still receive full credit if two of the questions cannot be answered by what is already written in your notebook. Some of these questions may appear nit-picky, but sometimes small details make a large difference when making new discoveries, and that is one thing this course prepares you to do. You will not know the questions before taking notes, so be as thorough as you can. A question regarding toxicity/safety precautions from the MSDS is a common question.

CHM 361, Fall 2016

Schedule of Experiments

Date	Exp #	Description
23-Aug		Check-in
25-Aug	3A	Sulfanilamide
30-Aug	20/21	TLC; read Technique-20 (benzil, benzophenone, benzoin)
1-Sep	handout	Reduction of benzophenone w/$NaBH_4$
6-Sep	handout	Extraction of caffeine from Pepsi/Coke
8-Sep	23C	*t*-Pentyl chloride
13-Sep		**Review test 1**
15-Sep		**Test 1**
20-Sep	11B	Acetaminophen
22-Sep	11B	Acetaminophen
27-Sep	41	Nitration of methyl benzoate
29-Sep	24A	Exp 24/24A 4-Methylcyclohexene
4-Oct	24A	Exp 24A 4-Methylcyclohexene IR spectra
6-Oct	31B	Camphor reduction
11-Oct	46b, 32A	Nylon; benzoin condensation
13-Oct	32A-B	Preparation of benzil
18-Oct		**Review for test 2**
20-Oct		**Test 2**
25-Oct	37	Tetraphenylcyclopentadienone
27-Oct	37	Tetraphenylcyclopentadienone
1-Nov	33A	Triphenylmethanol (part 1)
3-Nov	33A	Triphenylmethanol (part 2)
8-Nov	Handout	Deprotection of acetal using I_2
10-Nov	Handout	Deprotection of acetal using I_2
15-Nov	Handout	Hydrogenation Solventless
17-Nov	Handout	Hydrogenation Solventless
22-Nov		Thanksgiving Break
24-Nov		Thanksgiving Break
29-Nov	Handout	Determining relative rates of hydrogenation A
1-Dec	Handout	Determining relative rates of hydrogenation B
6-Dec		**Review test 3**
8-Dec		**Test 3**

Tips on keeping a good notebook

The Laboratory Notebook

1. Authenticity, Credibility and Accuracy

When a scientist does an experiment, it is important that he or she keep accurate records of that experiment. These records are kept in a laboratory notebook. In this course, and in academic and industrial research laboratories, it is considered very important that you make every effort to insure that these records are accurate, relatively permanent, and not easily altered or modified. In addition to documenting what you did, your notebook should document when you did the work. To achieve these goals, you will be required to:

A. have a bound notebook (pages sown in) with consecutively numbered pages.

(You can buy notebooks specially made for this purpose from the book store. As an alternative, you may use a common bound notebook such as a Mead Composition (Marble) Notebook. Graph ruled preferred but not required. Spiral and loose-leaf notebooks are *not* acceptable since it is too easy to lose and/or delete or add pages. As noted earlier, if you bought a notebook that did not have page numbers printed by the factory, you may write these by hand in ink. You must number up to 100 pages by the first notebook quiz.)

B. record your observations in permanent ink.

(Records done in pencil are too easily modified).

C. record your observations and results directly into the notebook as you do the experiment;

(It is not acceptable to copy data on a piece of paper and then transfer the data to the notebook. It is very poor practice to record observations from memory after completing an experiment.)

D. clearly indicate the date that all work was performed;

(Each experiment should begin with a date. Your observations should be entered in chronological order. If the experiment continues for more than one day, a new date should be entered when further observations are made.)

E. correct any errors by drawing a single line through the error and then entering the correct data.

(*i.e.* "The reaction mixture was heated at the boiling point of the solvent for ~~35~~ 45 minutes.")

(Erasures are not acceptable.)

2. Style and Grammar

Most scientific writing uses the past tense and passive voice, and avoids first person statements. This style of writing may not be as natural to you as using the first person, active voice. Unlike poetry or literature for entertainment, scientific writing should convey information without added emotion and it should not leave anything to interpretation. Statements like "luckily the product was recovered in high yield" are inappropriate. Instead, write "the product was recovered in 85% yield." Do not write "I transferred the reaction mixture to a separatory funnel, and then I washed it with two 15-mL portions of 10% NaOH." Instead, write "The reaction mixture was transferred to a separatory funnel and washed with two 15-mL portions of 10% NaOH."

You should write the procedure as you do the experiment and record observations directly as you see them. It is unacceptable to write everything at the end of the lab period or later after you go home. Many scientists write the procedure as one or multiple paragraphs. In this course, you are encouraged number each step. I will understand that after each step, you worked for a *short* amount of time before recording the next step and accompanying observations. If you chose, you may write out the procedure before coming to class by drawing a line down the middle of the page. Write the procedure with numbered steps one the left side. Write the observations and any changes to the right side.

3. Contents

The cover or first page of laboratory notebooks should be clearly labeled with the name of the investigator. You should leave one or two pages blank at the beginning of the notebook so a table of contents can be added. Thus, you may start the first experiment on page 4.

You should also put your name and date at the beginning of each experiment. The date should appear at the top of each page. If a page is used on more than one day, indicate where one day ends and another begins. The format of the entries for individual experiments will vary depending on the type of experiment. In this course, the objectives of the experiments fall in to three groups, isolation or purification of organic compounds, preparation of organic compounds, and identification of organic compounds. Suitable formats for each of the three types of experiment are shown below.

Do not leave large spaces between experiments. Any open spaces should have line drawn through them to prevent someone from adding additional data after the experiment is closed.

Notebook Format for Purification or Separation Experiments

Your Name Date

Title

I. Introduction

   a. purpose

   b. data table with references (more details below)

   (See Technique 29, Guide to the Chemical Literature, in your laboratory manual for examples of how to cite references)

II. Experimental (You should describe the experiment as you did it. Include sufficient detail so that another person with a similar chemical background to your own could repeat the work without referring to the text. Record any observations made during the experiment.)

III. Results and Discussion

IV. Conclusions

V. Exercises or Assigned Questions

Notebook Format for Synthetic Experiments

Your Name Date

Title

I. Introduction

a. purpose

b. a balanced equation for the main reaction

c. the mechanism of the main reaction

d. equations for any significant side reactions

e. data tables with references (You may make one table; however, you may find it useful to prepare two or three tables: one for reactants, solvents, and catalysts etc. A separate table for products, and side products. Each of these tables should include the molecular weight, CAS (Chemical Abstract Service) number, and physical properties for each compound. The reactants table should also include the amount used in the appropriate measured quantity (usually grams, milligrams, or milliliters) and in moles or millimoles. The products table should also include the amount of product obtained, the theoretical yield and percent yield. You must also include information that demonstrates that you read and understood the safety data sheet (also called SDS or MSDS), which can be found the internet. For example, search "1-bromobutane sds" in google. Any supplier who sells the chemical must include a copy when you purchase them, and they often have online versions. The introduction and the data tables should be prepared before the laboratory period. However, you should leave blank space for the amounts used and obtained. This data can be added at the appropriate time. At the end of the experiment, place dashes or NA in any blank spaces.

II. Experimental

(You should describe the experiment as you did it. Include sufficient detail so that another person with a similar chemical background to your own could repeat the work without referring to the text. At this point in the course, you may assume that the reader has had an introduction to the techniques for isolation and purification of organic compounds. Suppose that a fractional distillation is required to purify the products of a synthetic reaction. It is unnecessary to describe the details of how to do a fractional distillation. You may assume the reader knows how to assemble the glassware, position the thermometer and regulate the water flow through the condenser etc. The type and length of column used in the distillation should be included in the notebook since this varies from one experiment to another. Record any observations made during the experiment.)

III. Results and Discussion (In addition to the usual discussion of the experiment, this section should contain a detailed calculation of the theoretical and percent yields for the synthesis.)

IV. Conclusions

V. Exercises or Assigned Questions

Notebook Format for Qualitative Analysis Experiments

Your Name Date

Title

I. Introduction

(Your introduction should include a discussion of the classification tests and derivatives that can be used to identify the type of compounds given as unknowns. Include balanced equations were appropriate.)

II. Experimental

(You should do all of the relevant classification tests and the preparation of at least two derivatives. You should describe the experiments as you did them. Include sufficient detail so that another person with a similar chemical background to your own could repeat the work without referring to the text. You should include a brief description of what was actually observed during classification tests. That is, it is not adequate to say that you did a test and it was positive or negative. Describe the observed result and then draw the appropriate conclusions as to whether the test was positive or negative.)

III. Results and Discussion

(This section should present an overview of the logic you used to identify the unknown and needs to be expanded considerably from previous experiments. Include a table of the classification tests done and the results. Point out the conclusion drawn from each classification test performed. In some situations, you will need to draw conclusions based on more than one test. Based on the boiling point or melting point of your unknown and the results of the classification tests, you should prepare a list of possible compounds that could be your unknown. Point out how you used the derivatives to identify the unknown. Any inconsistencies in your data should be discussed.)

IV. Conclusions

(Identify the unknown and include the unknown number. If you cannot identify the unknown, do not guess. Unsupported conclusions will be penalized if they are right or wrong. If you can limit the unknown to a list of possible compounds, do so.)

The following is an example of an exceptional notebook kept by Prof. Larry Schmitz

Larry Schmitz *Jan. 11, 2001*

Date each page of your work.

Synthesis of n-Butyl Bromide

Include your name and Title each experiment.

I. Introduction

The purpose of this experiment is to prepare a sample of n-butyl bromide according to the following equation:

a brief statement of purpose.

$$CH_3CH_2CH_2CH_2OH + NaBr + H_2SO_4 \text{ ------> } CH_3CH_2CH_2CH_2Br + H_2O + NaHSO_4$$

a balanced equation.

The reaction proceeds via an S_N2 substitution on the protonated alcohol as shown below.

$$CH_3CH_2CH_2CH_2OH + H_2SO_4 \text{ ------> } CH_3CH_2CH_2CH_2O^+H_2 + HSO_4^-$$

$$CH_3CH_2CH_2CH_2O^+H_2 + Br^- \text{ ------> } CH_3CH_2CH_2CH_2Br + H_2O$$

Mechanism

Side reactions that might accompany this reaction are elimination to form an alkene and/or condensation to yield and ether.

$$CH_3CH_2CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2CH{=}CH_2 + H_2O$$

$$2\ CH_3CH_2CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3 + H_2O$$

side reactions.

Table of Reactants and Products/Side Products

Data tables must have boarders

Compound	*1-butanol*	*NaBr*	*H_2SO_4*	*1-bromobutane*	*1-butene*	*di-n-butyl ether*
*CAS number**	71-36-3	7647-15-6	7664-93-9**	109-65-9	106-98-9	142-96-1
*molecular wt.**	74.1 g/mol	102.9 g/mol	98.1 g/mol**	137.0 g/mol	56.1 g/mol	130.2 g/mol
*mp or bp**	bp = 117.2 °C	mp = 747 °C	bp = 290 °C**	bp = 101.6 °C	bp = -6.3 °C***	bp = 142 °C
*Density**	0.810 g/mL	—	1.84 g/mL**	1.27 g/mL	—	0.77 g/mL
volume	1.35 mL	—	2.0 mL	—	NA	NA
mass	1.134 g	2.4 g	—	1.709 g	NA	NA
moles	0.0153 mol	0.023 mol	0.037 mol	0.01247 mol	NA	NA
equivalents	1 (limiting)	1.5	2.5	0.8153	NA	NA
*Safety*****	irritant	toxic, do not eat	extremely corrosive, take extra care to avoid contact with skin and eyes	toxic, irritant, corrosive	flammable gas, do not inhale *****	toxic, irritant

Put a dash or NA where data is not written or applicable

* *Except where noted, data obtained from: R.C. Weast, ed. Handbook of Chemistry and Physics. 70th ed. Boca Raton, FL: CRC Press 1989.*

Write the introduction before lab

Include references to appropriate literature.

Jan. 11, 2001

*** Obtained from www.chem.exper.com; checked on Wikipedia*
**** Obtained from Sigma-Aldrich chemical catalog*
***** Except where noted, data obtained from Science Lab.com*
****** Obtained from praxair.com*

II. Experimental

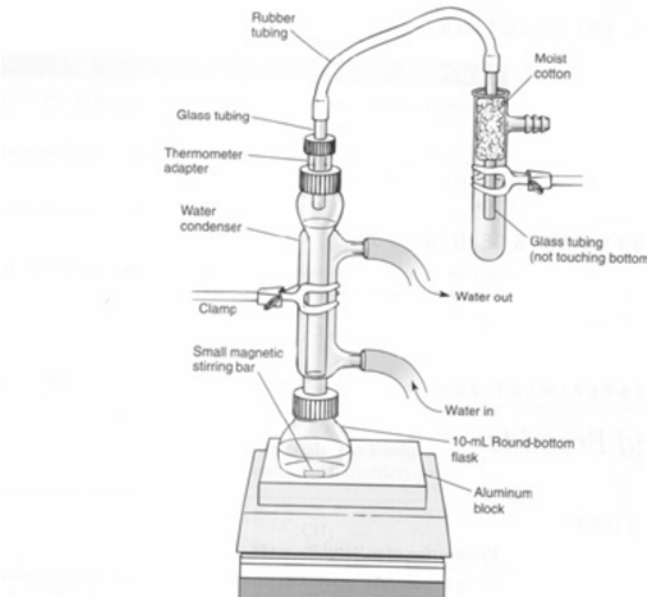
The synthesis was carried out using the method of Pavia, Lampman, Kriz and Engel. Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. Introduction to Organic Laboratory Techniques, a Microscale Approach; 3rd Ed.; Saunders: New York, 1999.

To a preweighed 10-mL round-bottom flask was added 1.4 mL of 1-butanol.

Wt. of Flask:	*19.657 g*
Wt. of Flask and 1-butanol:	*20.791 g*
Wt. of 1-butanol:	*1.134 g*

Procedure

1) 2.4 g of sodium bromide and 2.4 mL of water were added to the 1-butanol.
2) The mixture was cooled in an ice bath.
3) 2.0 mL of concentrated sulfuric acid was added dropwise.
4) The flask was attached to a reflux apparatus with an HBr trap as shown below.



5) The mixture was stirred, heated to its boiling point and allowed to reflux for ~~65~~ 70 minutes.

If you cite a website, you must double check with another website. If the data are still wrong, you risk missing points on your notebook quiz

Bring your notebook with you when you weigh items on the balance

Included your observations in the experimental section.

Use the passive voice and past tense when describing the work you did.

Record data in your notebook as you do the experiment.

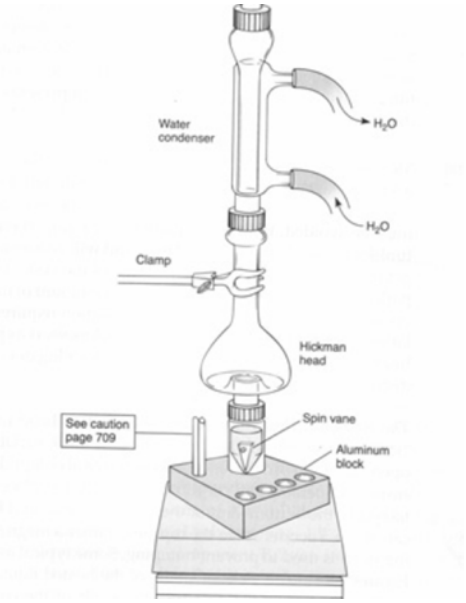
Use diagrams if they help make your meaning clear.

Jan. 11, 2001

6) *Most of the lower layer he reaction mixture was allowed to cool until the apparatus could be touched without burning oneself. Two layers formed in the flask.*
7) *Most of the lower layer was removed with a Pasteur pipet. A drop of water was added to the lower layer and was found to be miscible with the lower layer. The lower, aqueous, layer was discarded. The upper layer was transferred to a 5 mL conical vial and a small amount of additional aqueous layer was removed with a Pasteur pipet.*
8) *The remaining layer was extracted with 2 mL of 9M sulfuric acid by adding the acid to the vial, gently shaking, venting, allowing the layers to separate and removing the bottom layer with a Pasteur pipet. A drop of water added to the bottom layer was miscible with it confirming that is was the aqueous layer. The aqueous layer was discarded.*
9) *2 mL of water was added to the organic layer, the vial capped, shaken and the layers allowed to separate. The lower layer was removed and placed in a clean vial. The upper layer was miscible with an added drop of water. The upper layer was discarded.*
10) *The organic layer was washed with saturated aqueous sodium bicarbonate by adding 2 mL of the bicarbonate solution to the organic layer in several portions, capping and shaking the vial with frequent venting.*
11) *The layers were allowed to separate and the lower layer was removed and placed in a clean vial. The upper layer was miscible with water and was discarded.*
12) *Three microspatula fulls of anhydrous sodium sulfate was added to the organic layer, the vial capped and allowed to stand for about 5 minutes until the organic layer was clear.*

Jan. 12, 2001

13) *The organic layer was transferred to a clean and dry distillation apparatus consisting of a 3 mL vial and a Hickman still head as shown below.*



Included your observations in the experimental section.

Use the passive voice and past tense when describing the work you did. Note that "I" and "we" are never used.

Record data in your notebook as you do the experiment.

Be sure to keep the date correct. Update as needed

Use diagrams if they help make your meaning clear.

14) The distillation apparatus was heated with a hot plate. The product was periodically removed from the Hickman still as it distilled and placed in a clean preweighed vial.

15) The distillation was discontinued when only a drop remained in the distilling vial.

Wt. of the vial: 35.350 g
Wt. of the vial and product: 37.059 g
Wt. of the product: 1.709 g

The boiling point of the purified product was obtained using the microscale boiling point procedure of Pavia et. al., and was found to be 101 °C. Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. Introduction to Organic Laboratory Techniques, a Microscale Approach; 3rd Ed.; Saunders: New York, 1999, pp. 586-589. The infra-red spectrum of the product was obtained as a thin film of a neat sample between silver chloride plates using a Midac model M1700 Fourier transform spectrophotometer.

Be sure to include enough detail to allow the reader to repeat your spectral work as well as your synthetic work.

III. Results and Discussion

Calculations:

Moles of 1-butanol = 1.134 g (1 mol / 74.1 g) = 0.01530 mol
Moles of sodium bromide = 2.4 g (1 mol/102.9 g) = 0.023 mol
Moles of sulfuric acid = 2.0 mL (1L /1000 mL) (18 mol/L) = 0.036 mol
Since the stoichiometry is 1:1:1 the limiting reagent is 1-butanol.
Theoretical Yield = 0.01530 mol butanol (1 mol butyl bromide/ 1 mol butanol) (137.0 g/mol) = 2.096 g
% Yield = (1.709 g / 2.096 g) 100% = 81.53%

Be sure to include units in your calculations.

Use significant figures appropriately

The product, n-butyl bromide, was obtained in relatively high yield (81.53%). Allowing for some loss of the actual product during purification, this means that only small amounts of the expected side products could have formed. The observed boiling point and IR spectrum indicate that the product was relatively pure. The observed boiling point was close to the literature boiling point (101 vs. 101.6 °C, respectively). Allowing for the fact that atmospheric pressure in Huntington is generally slightly less than 760 mm Hg, this is good agreement. The IR spectrum does not show bands that would be expected if the product were contaminated with starting material or side products. The absence of OH stretching bands (3200 - 3500 cm^{-1}), C=C (1640 -1670 cm^{-1}), and =C-H stretches (3020 - 3100 cm^{-1}), and C-O stretches (1050 - 1250 cm^{-1}) demonstrate the lack of substantial amounts of 1-butanol, 1-butene, and di-n-butyl ether, respectively.

Discussion.

IV. Conclusions

Relatively pure n-butyl bromide was obtained in 82% yield from the reaction of 1-butanol and sodium bromide catalyzed by sulfuric acid.

brief conclusion