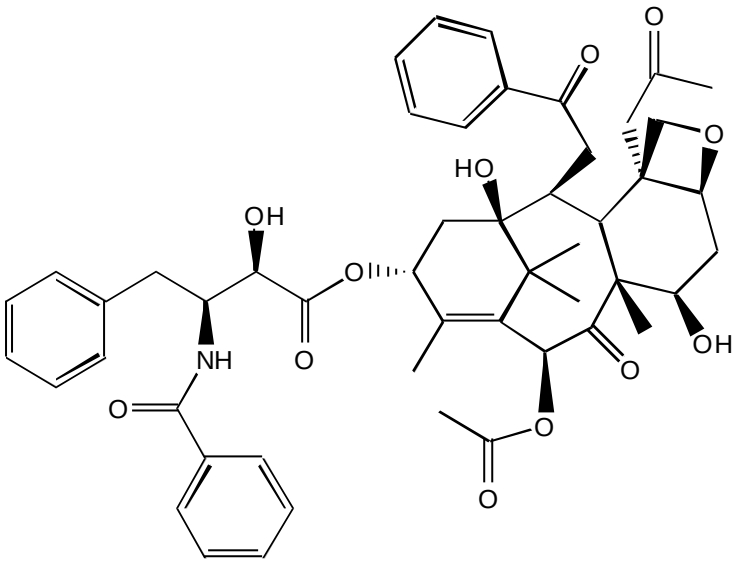
Chem 141

Organic Chemistry Laboratory Manual



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Introduction

Organic Chemistry is an applied science that is best understood through laboratory work. However, to quickly understand the central concepts at play within Organic Chemistry, lectures provide a faster method of presentation. It would be ideal to learn all Organic Chemistry through laboratory experiences. Time does not allow us this luxury.

The experiments for Chem 141/142 are designed to supplement the course work and provide real experience with concepts presented in class. To gain the full potential from your lab time you should be fully prepared. This manual was developed and will be improved to best prepare you and future Organic Chemistry students. Read the experimental procedure in full prior to each laboratory. Additionally, accompanying videos have been recorded to help your preparations. These can be downloaded and are tremendously helpful. I recommend you watch the video after you have read the full experimental procedure.

Attendance

Students must attend the lab section to which they are assigned. If more than 2 labs are missed, for any reason, you will receive an **F** in the course. Official documentation of sickness or family crisis is required if a lab is missed. Unexcused absences will result in a ZERO grade for that laboratory experiment.

Lab Supplies

The following items must be purchased before attending your first laboratory period.

1. Safety glasses: Protective eyewear that meets OSHA requirements can be purchased from the bookstore, these are stamped "Z87" on the temple earpiece. If safety glasses do not fit over your regular glasses you must wear safety goggles. Safety goggles are bigger and can be purchased at the bookstore. CONTACT LENSES are a potential health hazard and should only be worn in the lab if you have no other type of corrective lenses. If you wear contact lenses you must wear goggles with them, and inform your Teaching Assistant (TA).

If you forget your eye protection, goggles can be rented from the 1st floor stockroom A143.

Safety glasses or goggles must be worn by everyone once any experiment has started in the bench areas of the lab. Students not observing this rule will receive a ZERO for that experiment and asked to leave.

2. Laboratory notebook: A copy of each report will be given to your TA each week. The bookstore sells lab notebooks that have copy sheets between each written page. This style of notebook will not need to be photocopied as you can just tear the copied pages out to submit to your TA. This saves time and money photocopying each lab report.

3. Breakage card: A breakage card will NOT be required in the new STEM building.

Health and Safety in Chemistry Labs.

We all manage risk in our everyday lives. We use our judgment to control the risk and stay comfortable in our different environments.

Chemistry labs are an uncommon environment to our everyday lives; however, managed carefully and responsibly the laboratory should be healthy and safe. The best precaution against accidents is good preparation. Read the full experiment and watch the associated video. Work slowly and methodically through your instructions and keep track of your steps and progress. Maintain a clean and tidy work space (either in the hood or on your benchtop). Ask questions of your TA if there is anything that is unclear or seems unsafe to you. Wear gloves and a lab coat if necessary. Wash your hands before you leave the lab.

Spills

Spills can happen to everyone dealing with chemicals. Therefore, only full coverage shoes are permitted in the lab. Sandals and open-toed shoes are not permitted.

If any spill occurs let your TA know. Try to consider the potential hazards; are there any open flames (such as Bunsen burners) in the area? Is there a reactivity issue with another reagent close-by? Try to stop the spill from spreading by using a spill kit or paper-towels to absorb the spill and contain it. Chemical and dry waste created from spills should be disposed of through UVM's Environmental Safety Department, not in the trash. Please ask your TA for assistance.

Chemical Hazards and Exposure

No eating, drinking or smoking is permitted in the laboratory due to the danger of ingesting toxic chemicals. Be sure you understand the risk associated with each chemical. Never taste a chemical. Read the labels on the bottles carefully and slowly. If this is your first time using a chemical refer to the MSDS (Material Safety Data Sheet) for full information on the chemical's associated risks. http://ccinfoweb.ccohs.ca/msds/search.html . If a chemical container is unlabelled, notify your TA at once, do not assume that you know the contents.

If you spill a chemical onto yourself, immediately flush and wash the area with water for 15 minutes. If the exposure covers a large area of your body, use the emergency shower provided in each laboratory, rinse for 15 minutes and seek medical attention. For eye exposures use the eyewash station and flush the eye for at least 15 minutes. Report all chemical exposures to your TA immediately.

For a more detailed overview of chemical hazards and exposures, refer to "Working Safely in the Laboratory with Chemicals", pages 5- 23.

Physical Hazards

Fires can occur in a laboratory. Small fires can be extinguished by covering the container with foil or even a book to starve the fire of oxygen. Tell your TA immediately that you have fire. If the fire is not controlled evacuate the room, sound the fire-alarm and then evacuate the building. Check for the safety of your classmates.

Evacuation

If there is a spill, fire or a gas leak that requires the laboratory be evacuated, leave immediately. Do not return for your bag, notes or wallet. Stay together. Stay with your classmates and pass around a sheet of paper adding your name and contact information

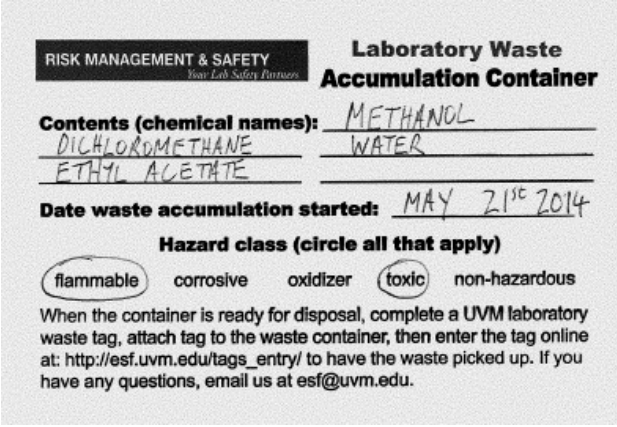
(address and contact phone number) to the list. You may be asked to gather in the hallway or leave the building in an orderly fashion. If you are asked to leave, ensure the Fire Alarm has been sounded.

Waste Management

The UVM Department of Environmental Safety manages the collection and disposal of all chemical waste generated on campus. During the normal laboratory time you will generate materials that require special handling so as not to contaminate the trash or Lake Champlain (via wastewater treatment). The waste materials that require special disposal will be clearly identified within each experiment. Please help protect our drinking water, community and the environment by carefully following waste disposal instructions.

Once you are finished with a procedure (either one step or the whole experiment) be sure to follow the Waste Management section for each lab experiment. You should keep track of the waste you accumulate throughout each experiment. Keep it clearly labeled, in a safe location to avoid spills. During your clean-up assess the nature of the waste; hazardous or non-hazardous. Depending on the particular hazard class; flammable, corrosive, oxidizer and/or toxic, dispose of the waste in the appropriately labeled container. Chemical waste containers will be available in the hoods with a yellow label as shown below.

Check the YELLOW label !!!


RISK MANAGEMENT & SAFETY
Your Lab Safety Partners

Laboratory Waste
Accumulation Container

Contents (chemical names): METHANOL
DICHLOROMETHANE
WATER
ETHYL ACETATE

Date waste accumulation started: MAY 21ST 2014

Hazard class (circle all that apply)

flammable corrosive oxidizer toxic non-hazardous

When the container is ready for disposal, complete a UVM laboratory waste tag, attach tag to the waste container, then enter the tag online at: http://esf.uvm.edu/tags_entry/ to have the waste picked up. If you have any questions, email us at esf@uvm.edu.

1) Add your waste to the container only if it matches at least one of the chemicals listed on the label.

If there is no issue with chemical compatibility you may add additional chemicals to the waste bottle not already noted. Be sure to write any additional waste chemicals on the laboratory waste accumulation label.

2) Never overfill the bottle. Only fill to 90% of the bottle capacity. Pour slowly through a funnel to ensure none of your waste spills during disposal. If you spill, wipe up any mess and make sure the label is still legible. Let your TA know that you spilled.

Waste is generally segregated into Acids in one container, Organic solvents in another and Solid wastes/ metals in a separate container. If a waste container is not available for your waste ask your TA about starting another container. With your TA's advice, fill out

the lab waste accumulation label (see above) as completely as possible. Spare yellow lab waste accumulation labels will be available in the pigeon holes by the blackboard.

3) Label any waste containers with a sticker and fill in the waste names on the label.

Some waste materials (paper-towels from cleaning bench-tops) or food-based wastes that are not contaminated with hazardous chemicals can be disposed of in the trash. If you have any doubt about appropriate chemical waste disposal ask your TA. No points will be deducted for asking about waste disposal. Take your time during clean-up.

Your actions impact our environment, inside and outside the lab. Your actions also affect UVM's compliance with the laws that govern the use and management of hazardous materials. These laws are complicated by the fact that there are 4 separate government entities that define a hazardous material. OSHA (and related state agencies) identifies those materials that pose a hazard to workers who are required to use the material. The EPA (and related state agencies) identifies those materials that pose a hazard when released into the air, soil or water. The City of Burlington regulates the materials that can go into the sewer system. The Department of Transportation regulates those materials that pose any hazard during transportation. Each agency has their own scope of who is covered under their regulation and their own definitions of a hazardous material.

For instance, EPA defines a corrosive material as having a pH<2.0 or >12.5 and prohibits these from drain disposal. The Burlington sewer use prohibits discharges <5.0 or >10.5. OSHA considers the destruction of the tissue of an albino rabbit while DOT allows consideration of the corrosion rate of steel.

Grading

Prelab quiz:

Prior to attending lab you must complete the prelab quiz on Blackboard.

Prelab:

As part of your lab write-up you should prepare a few notes outlining your plan for the lab period. This will be incorporated into your full Lab Report.

Objective: Plan for the experiment. What you hope to achieve in a few brief sentences. A brief explanation, in your own words, explaining your step-by-step process for the lab period (bullet points would be sufficient).

Lab report:

During the lab period take accurate notes of your actual procedure. Make particular notes of any deviations from the procedure noted in the manual. Mention if this was useful or not. You should also note any significant transformations during the experiment "then the reaction turned pink.", "long needles of crystals started to form" etc. Use your own words to best describe the situation as it evolves.

After the lab you should write up a full report for the experiment. The lab report should consist of the following areas:-

Objective: Your prelab notes are sufficient for this.

Method: Actual method followed and any significant deviations.

Data and Results: Clearly present weight or volumes of synthesized compound or any data generated during the experiment.

Calculations and Conclusions: Present any graphs or yields. In full sentences describe the results of your experiment. Explain how your results relate to the objective, any errors, whether your experiment was a success and what could be improved.

Post-lab questions:

After the experiment is completed you must complete the postlab questions on Blackboard, prior to the next session. These questions will be designed to be a little more involved and require a little research and thought. You may be asked about a mechanism or the broader application of the experiment outside the teaching lab arena.

Pre-lab notes =	2
Pre-lab quiz (Blackboard) =	3
Full Report =	8
Technique =	2
Post-lab questions (Blackboard)=	5
Total	20 points per lab

Lab 1

Determination of Alcohol content of Wine by Fractional Distillation

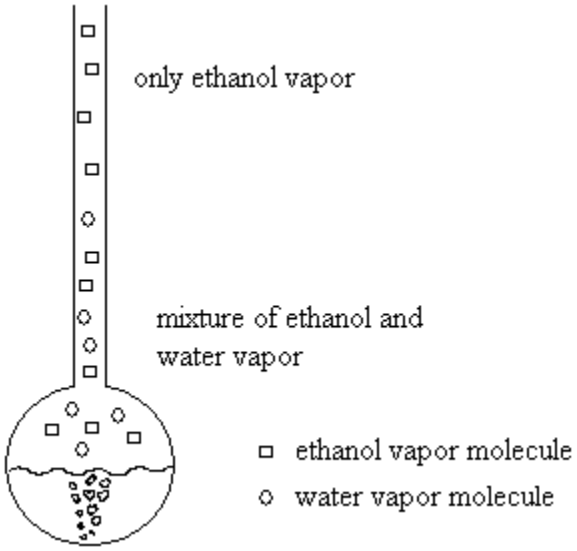
Introduction

If a mixture of ethanol and water are warmed you might expect the more volatile (lower boiling) ethanol to boil first and then the water. This is not exactly true. As the mixture is warmed all the molecules within the flask will gain energy. In fact some water molecules will gain sufficient energy to boil at a lower temperature than normal. Pure ethanol boils at 78ºC. Pure water boils at 100 ºC. However, as a 50:50 mixture with ethanol, the water will boil at a much lower temperature, 87 ºC.

This presents a problem; how can two liquids be easily separated? We will see in a later experiment that if the liquids form two layers (similar to oil and water in salad dressing), the layers can be separated by pouring one off and leaving the other behind. However, if the liquids are capable of dissolving in each other, as ethanol and water do, then a different technique will be required.

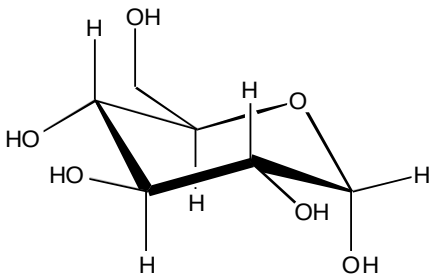
Distillation is an ancient art used to purify liquids for medicinal properties. Distillation is part of the process by which gasoline is removed from a complex mixture of organic compounds known as crude oil. The apparatus has two main components; the fractionating column and the condenser. The condenser's role is fairly apparent. The vapors that are escaping from the top of the fractionating column are cooled by the outer layer of the condenser and reform into a liquid dripping down the condenser to be collected and measured.

The role of the fractionating column is a little more subtle and complex. First we need to visualize the vapors escaping from the surface of the liquid in the flask as a mixture of both ethanol and water. As the vapors reach the fractionating column the vapors start to cool. The water has a higher boiling point and so condenses first. The ethanol vapor continues up the column. Some water vapor is still able to climb up the column. However, as the surface becomes cooler and cooler the water is no longer able to stay in the vapor phase and all the remainder condenses to form liquid. The only remaining vapors are molecules of ethanol.



Wine is the fermented juice of grapes or some other fruit such as apple, cherry or blackberries. The act of fermenting sugars to form ethanol is performed by yeast (a naturally occurring fungus). Grapes often have a white coating of yeasts on the outside of their skins. Specialized yeasts are prepared by vintners to perfect the flavors and alcohol content desired. Generally, wine yeast can generate 18% ethanol (by volume) depending on the sugar content of the juice. The carbon dioxide generated is either allowed to escape or retained to give the wine a bubbly/sparkling effect like champagne. The reaction is as follows:-

Glucose



$C_6H_{12}O_6$

Yeast

Ethanol

$2\ C_2H_5OH + 2CO_2$

Objective

The task for this lab is to deduce the alcohol content of table wine by performing fractional distillation of 50ml of wine. The temperature at the still-head will be monitored to track the temperature of the vapors exiting the fractionating column. A graph of the vapor temperature versus volume of distillate collected will be drawn.

Experimental Procedure

1. Set up a fractional distillation apparatus as illustrated in Figure 1 at the end of this experiment. The apparatus must be set high enough that a sand bath heating mantel can be placed under the distillation flask.
2. Disconnect the fractionating column and pour 50ml wine into the round bottom flask to be heated. Measure the wine accurately using a measuring cylinder. Add 2 or 3 boiling chips to allow even boiling and prevent bumping. Empty any sand from the heating mantel and raise it to neatly fit around the round bottom flask. Reattach the fractionating column.
3. Check that a slow trickle of water is flowing through your condenser and turn on the power to your heating mantel by turning the variac box to 4.
4. Control the power to the heating mantel with the variac box. A good distillation rate is about 1 drop per second.
5. Note the temperature at the still-head for every 1ml of liquid collected. Collect 1-2ml past 100°C.

Results

1. Draw a graph of volume (x-axis) vs. temperature (y-axis).
2. From the graph predict the amount of ethanol collected and as a result the percentage (by volume) of the wine that was ethanol.
3. Compare your result to the label of the wine explain any difference.

Waste Management

1. The distillate that was collected from the condenser is non-hazardous can be discarded down the sink.
2. The contents of the round bottom flask used for boiling is non-hazardous and can be discarded down the sink.
3. Wash the round bottom flask with soap and water to remove any remaining residue. Rinse the fractionating column with plenty of water to remove any residue.

NOTE.

1. Plug the heating mantel into the variac box **NOT** directly into a wall outlet.
2. Make sure the thermometer is just below the level of the condenser.
3. Ensure all the ground glass joints are clean and snug. Use a blue Keck clamp to secure any crucial joints. Keck clamps only work in one direction, check.
4. Collect the distillate into a 10ml graduated cylinder to track the volume accurately. Empty it periodically.
5. Do not consume any water or ethanol distilled in this lab. Previous experiments performed by Chem 141 students will have contaminated the glassware and as a result the distillates are unfit for human consumption.

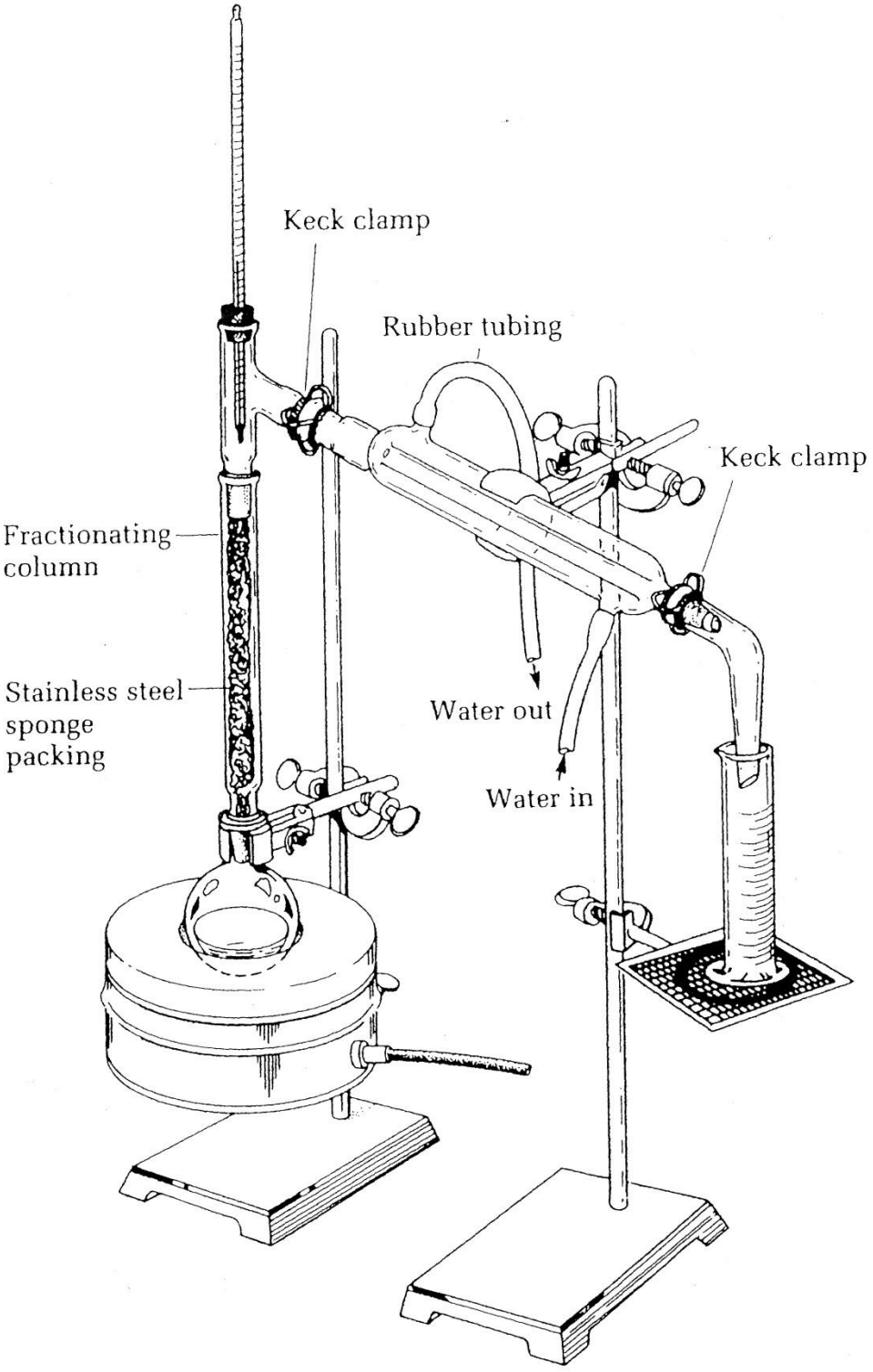


Figure (1)
Fractional Distillation Setup

Lab 2

Component Analysis of Common Analgesic Tablets by Thin-Layer Chromatography

Introduction

Chromatography is a broad title given to the separation of a mixture by its interaction with a media of a different phase. In this experiment we will separate the pain-killing compounds found in over-the-counter drugs and deduce the active ingredients by comparison to standard solutions of the compounds.

Different functional groups differ in polarity and the strength of their interaction with a polar solid, in this experiment. When very polar compounds such as an amine or an alcohol, in solution, pass over a polar solid, an equilibrium will establish; some of the alcohol will bind to the solid and some will continue to flow with the solvent. The equilibrium will slow the progress of the polar sample through the solid on the surface of the TLC plate. A less polar functional group will flow with the eluting solvent and proceed more quickly through the solid. This principle will allow the alcohol or amine to be separated from a compound with less polar functional groups, such as alkanes or alkenes.

Thin-layer chromatography is the separation of a small sample mixture on a silica surface. This is an example of liquid-solid chromatography. The sample of interest is washed through the solid by an eluting solvent termed the eluent. A thin-layer of silica is evenly spread on the surface of a sheet of foil (often called the "TLC plate") and acts as the solid. The silica is a polar solid. Polarity is the key to an effective separation. The polarity of the solid, the sample components and the eluting solvent must be correct to allow for an effective separation. The two main types of solids used for TLC are alumina and silica. We will use silica for this experiment. Eluting solvents can vary widely depending on the samples to be eluted. Methanol, water and ethanoic acid are the most polar eluent options. Ethyl acetate and diethyl ether have more moderate eluent polarity. Hexanes are the least polar eluent commonly used for TLC. Combinations of these solvents can be mixed to tune the rate of elution of the sample components. Fast elution will cause the sample components to blur together at the elution front. If the rate of progress of the sample is too slow the components of the mixture may not pass through the solid at all.

An adequate flow rate of elution is achieved by the capillary action of the eluent climbing the TLC plate. This will be a consistent rate depending on the thickness of the silica so should be constant between students and runs. As the components of the mixtures start to interact with the silica an equilibrium is established between each component and the silica and their flow across the TLC plate will vary providing separation.

TLC is very versatile with the following applications:-

1. *Monitoring a reaction*:- The disappearance of a starting material spot and appearance of the product spot on the TLC plate can be used as a method to check the progress of a reaction.
2. *Determining the number of components of a mixture*:- An effective separation will give a crude understanding of the composition of a mixture.
3. *Comparison to a known compound*:- If a spot on a TLC plate is inline with a known compound it is a good indication the mixture has the known compound as one component.

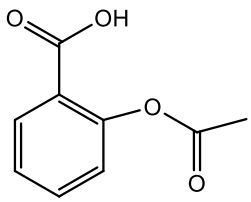
Analgesics, such as aspirin, ibuprofen and acetaminophen, reduce pain without decreasing consciousness or awareness. These drugs have their own methods of action and as such very precise roles in decreasing pain. To affect an overall approach to pain control these drugs are often mixed by pharmaceutical companies and sold under a brand-name. Standard solutions of the active ingredients of these over-the-counter drugs have been prepared to compare to the compounds noted in your samples.

An analgesic tablet will be ground with ethanol to extract the active ingredients. A very small drop of your analgesic tablet will be placed on the sample baseline of the TLC plate using a capillary tube. The drop should result in a wet spot no larger than 2mm. A very small drop of each of the standards will be placed on the baseline and marked. The TLC plate will then be lowered into a beaker with a few milliliters of eluent at the bottom of the beaker. The eluent should evenly cover the bottom of the plate but only reach about half-way to the sample baseline. The beaker will then be covered and the eluent will begin to climb the silica. Once the eluent reaches the top of the TLC plate the solvent front should be marked immediately and the sample and standard spots visualized with a UV lamp and marked. The ratio of the sample height to solvent front R_f will need to be calculated for each spot so be sure to mark each one.

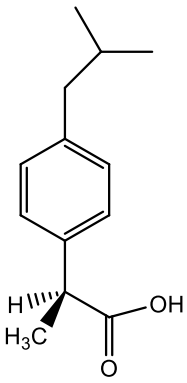
$$R_f = \text{(distance to spot) / (distance to solvent front)}$$

Objective

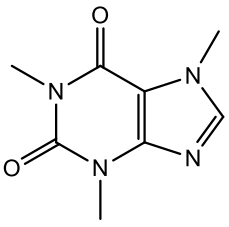
Three TLC plates will be performed by each student. The first plate will contain each OTC analgesic (Advil, Excedrin, Tylenol and Anacin). The second TLC will contain each standard (caffeine, ibuprofen, acetaminophen, and acetylsalicylic acid). The The third plate will confirm the components of one OTC analgesic, that seems to contain multiple ingredients, by cospotting. Spots will be visualized by UV light and the R_f values calculated and recorded.



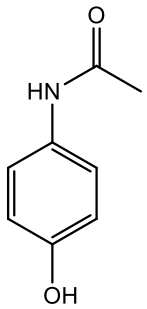
Aspirin
(acetyl salicylic acid)



Ibuprofen
S(+)-2-(4-isobutylphenyl)-propanoic acid



Caffeine



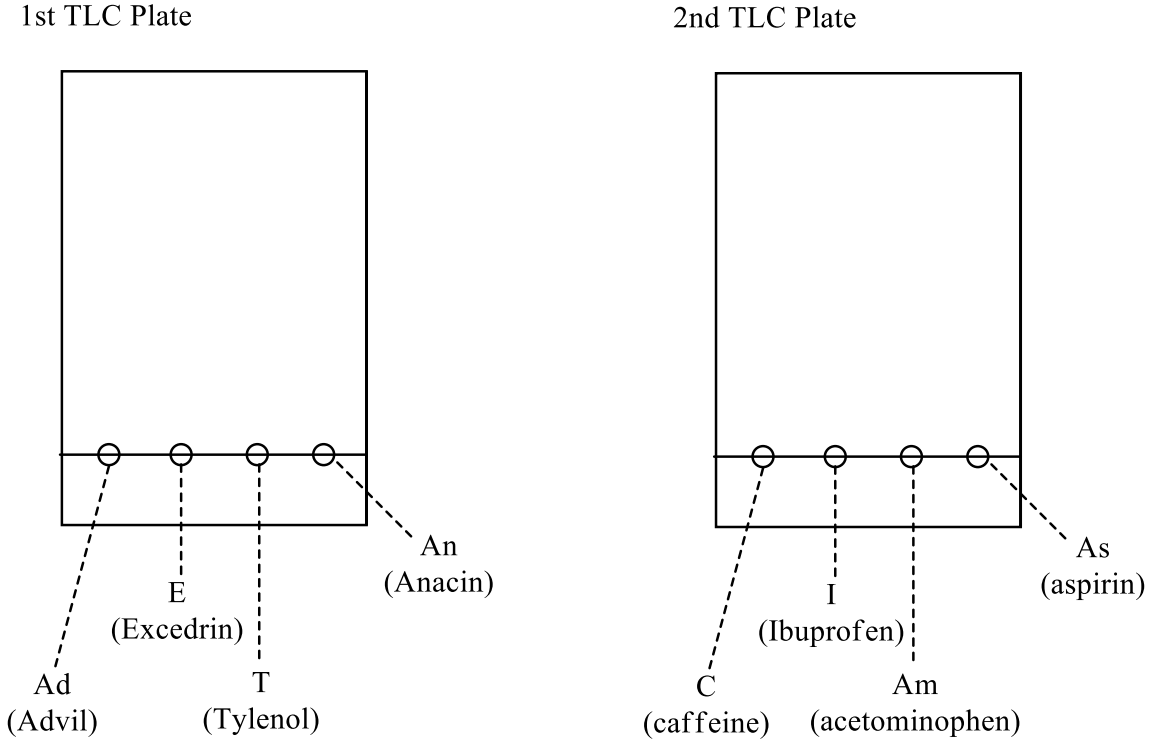
Acetaminophen
(4-acetamidophenol)

Experimental Procedure

1. First, capillary tubes for spotting the samples and standards must be pulled from glass Pasteur pipettes. Hold the pipette at either end and heat the middle of the pipette in the lower blue cone of a hot Bunsen burner flame. As the glass begins to glow orange gently

wiggle the ends. Once the glass becomes the consistency of gum remove the pipette from the flame and pull the ends. The pipette should stretch to form a long thread. This requires practice. You will need two 30cm sections of capillary tube to spot all the samples and standards for this experiment.

2. Use a pencil (NOT a pen) to draw the sample baseline 1cm from the bottom of a 5x6cm silica gel TLC plate. Label 4 spots with the code letters noted on the illustration below.



3. Pour 5ml of the eluent (95% ethyl acetate/5% acetic acid) into the bottom of a 250ml beaker, cover and leave to sit while the TLC plate is spotted. This allows the eluent to saturate the air within the beaker and will help the TLC proceed more quickly.

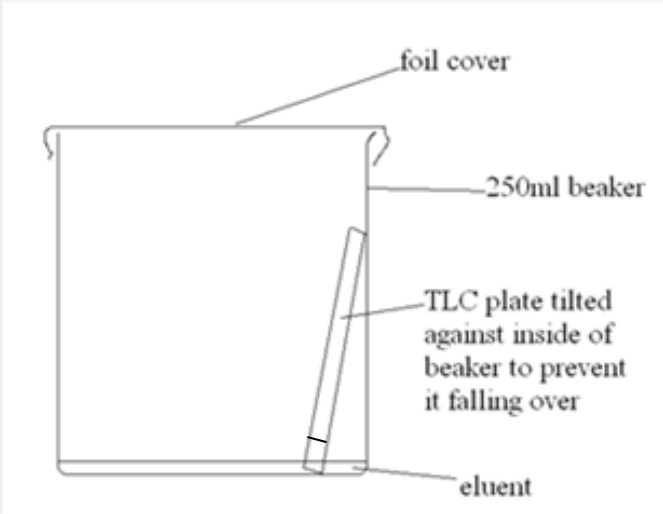
4. Place one crushed tablet of each analgesic into separate test-tubes. Crush by using a mortar and pestle or crushing between weigh papers. Add 3mL of ethanol to each test-tube.

5. Break the end of a capillary tube and ensure it looks even and has no ragged, jagged spikes. Dip the, now smooth, end of the capillary tube into your ethanol/tablet solution.

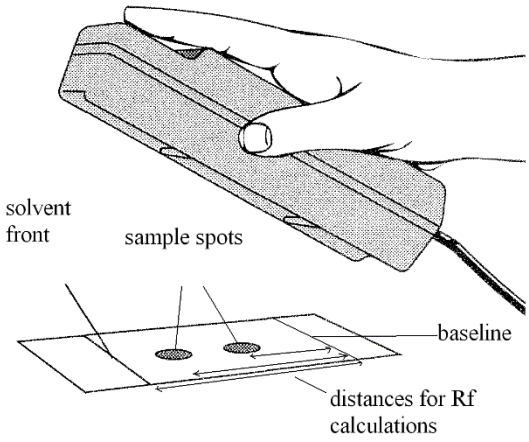
6. Very gently and lightly spot the TLC plate ONCE with the tablet solution. Break off the end of the capillary and discard into a beaker for broken glass. (At the end of the lab period dispose of all your broken glass in the box at the front of the lab).

7. Spot each analgesic on their respective marked positions on the TLC plate. Between each spot, break off the end the capillary tube to ensure the various solutions do not mix.

8. Use the UV lamp to visualize the spots. Ensure the spots are not touching and there is sufficient sample and standard deposited on the baseline. Check with your TA if you are not sure.



9. Place the TLC plate in the beaker with the sample end in the eluent. The eluent should not splash over the baseline. You should be able to see the eluent climb up the silica.
10. Once the eluent has reached 1-2cm from the top of the TLC plate remove it from the beaker. Immediately mark the location of the solvent front with a pencil line.
11. Use the UV lamp to visualize the location of the sample and standard spots. Circle the spots with a pencil. Initial the TLC plate and show your TA.
12. Repeat the procedure for the second TLC plate using the standard analgesic solutions.



Visualizing results with UV lamp

13. Calculate R_f values for each spot and use the co-spotting method to decipher the analgesic composition among those spots that are not readily apparent (both visually and by R_f value). This is done by running three lanes; spot the analgesic on the first mark, both the analgesic and standard solution on the second mark directly on top of one another, and only the standard solution on the third mark. If the OTC analgesic and standard solution are inline, without doubling of spots, then it can be concluded that the spotted standard is found in the spotted analgesic. If the co-spot lane shows two distinct spots then the standard is not a component of the analgesic.

14. Do this for all spots that have inconsistent R_f values (especially streaking compounds). You may perform more than one co-spotting series on one plate or repeat this method for each OTC analgesic. Be aware that some analgesics may contain greater than one active ingredient and thus may require more than one co-spot.

Results and Calculations.

1. Draw an illustration of your TLC plates in your notebook.
2. Calculate the R_f values for all the spots for both plates. Present these results in a table for easy comparison.
3. Compare your results to the actual analgesic composition (labeled on each analgesic box) and determine if the TLC correctly determined the components of each tablet and if the co-spotting method upheld or refuted the composition.

Waste Management

The eluent (ethyl acetate and acetic acid) and ethanol in this experiment are regulated by the EPA as hazardous wastes because they are ignitable below 140 deg F.

1. The eluent waste containing ethyl acetate and acetic acid is flammable. Discard of in the waste container labeled ethyl acetate, acetic acid and ethanol.
2. TLC plates may be contaminated with ethyl acetate and acetic acid. Discard as dry hazardous waste in the solid waste container. Do not mix solid and liquid wastes.
3. Any remaining ethanol/tablet solution is flammable and therefore hazardous. Because ethanol is organic and flammable, it is compatible with both ethyl acetate and acetic acid. Discard in the hazardous waste container from step 1 of this section. Add "ethanol" to the contents on accumulation label if it is not listed.
4. Broken glass - pipettes and capillary tubes should be placed in the broken glass box at the front of the laboratory.

Note

1. Keep track of which Pasteur pipettes are hot. Do not try to pick up a pipette that has just been heated in a Bunsen burner!
2. Ultraviolet (UV) light is damaging to eyes. Luckily safety glasses filter UV and are sufficient protection. Do not shine the UV lamp into unprotected eyes.

Lab 3

Extraction of an Antibiotic

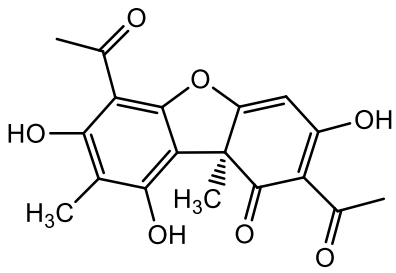
Introduction

The extraction of compounds from plant and animal sources is a lead for the pharmaceutical industry in search of new medications. Often the natural products uncovered have undesirable side-effects or lower than desired efficacy. The modification of the structures of natural products can lead to improved pharmokinetics or improved specificity.

Extractions are performed by many of us on a daily basis as we brew coffees and teas. Essentially we are using hot water to extract the tasty water soluble esters and flavors from the solids (and some caffeine).

Lichens are a symbiotic relationship between a fungus and an algae. The fungi were originally considered be only useful in the absorption of water, to the point they were considered almost parasitic. However, it has become clear that the fungus is responsible for the generation of a very important chemical defense agent, usnic acid. Several lichens native to New England have been shown to have antibiotic properties and usnic acid has been shown to be the agent responsible for this biological activity.

Lichens have been used medicinally for thousands of years. There is evidence the Egyptians viewed lichens as medicines. Usnic acid has been found to be useful as an antibiotic with activity against several Gram-positive bacteria including skin infections and tuberculosis. There have been reports that usnic acid can cause liver problems.



Usnic acid
MW= 344 g/mole
mp= 204ºC

Objective

Usnic acid will be extracted into acetone (2-propanone) from the lichen Old Man's Beard (*usnea spp)*. The product will be crystallized by evaporating the solvent and adjusting the polarity by the addition of water. The resultant crystals will be filtered. The purity of the product will be assessed by a melting range determination.

Experimental Procedure

1. Weigh 4 grams of lichen and place in a 150 ml beaker.
2. Add 50ml of acetone to the 150ml beaker.
3. Stir and crush the lichen in the acetone with a stir-rod or spatula for 15 minutes.
4. Remove the pieces of lichen from the acetone by filtering through a glass funnel with a folded filter paper (15cm) into a 125ml Erlenmeyer flask.

5. Clean the 125ml beaker and transfer the contents of the Erlenmeyer flask.
6. Add two boiling sticks and place the beaker on a hotplate (in the hood) and warm to boiling (setting #4 is usually sufficient).
6. Evaporate almost all the acetone. A layer approximately 2-3mm deep at the bottom of the beaker is all that is required. Some solid may be noted at the meniscus.
7. Remove the beaker from the heat and remove the boiling sticks. Return to your bench area.
8. Add 2-4 drops of cold water until a slight cloudiness is noted.
9. After the flask has cooled on the bench-top for approximately 3 minutes, filter the small yellow crystals using a Buchner funnel, a vacuum flask (125ml) and an aspirator to apply a vacuum. Use the illustration on page 23 as a guide.
10. Weigh the crystals and calculate a percentage of the lichens that is usnic acid. Note the melting point of the crystals.

Results and Calculations.

1. Yield should be noted by weighing the crystals formed and comparing to the initial weight of the lichens.
2. Melting range of the usnic acid should be noted.

Waste Management

The usnic acid generated in this experiment is not regulated as hazardous waste. Acetone is regulated by the EPA as hazardous wastes because they are ignitable below 140 deg F.

1. The filter paper with ground lichens, from Step 4 of the experiment, is non-hazardous and can be disposed of in the trashcan.
2. The filtrate from step 9 of the experiment contains acetone and is flammable. Dispose of as hazardous waste in the waste container labeled with the respective chemical contents.
4. The usnic acid crystals are non-hazardous so can discarded into normal trash.
5. The vacuum flask used for filtration can be washed with soap and water to remove residue. Any acetone used to rinse should be discarded of as hazardous waste.

NOTE

Do not consume any usnic acid prepared during this experiment. No FDA approval for the consumption of usnic acid has been given. Previous experiments performed by Chem 141 students will have contaminated the glassware and as a result the products are unfit for human consumption.

Lab 4

Extraction and Recrystallization

Introduction

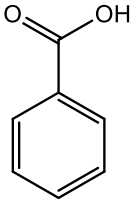
The extraction of a chemical of interest is an ancient technique performed as routinely in a kitchen as it is in a laboratory. The act of passing hot water over coffee grounds is extraction. We are extracting the soluble esters (responsible for the pleasant flavor) and the caffeine from the solids of the coffee. The preparation of tea is similar. These are both examples of solid/liquid extractions.

Organic chemists routinely use liquid/liquid extractions to purify one compound from a mixture. A sample will be dissolved in a solvent that accommodates all the components of the mixture. An aqueous (water-based) solution of acid or base is added to ionize one component of the mixture drawing only that one component into the water layer. This removes one compound from the mixture. The water layer can then be removed using a separatory funnel. The pH of the water layer can then be adjusted to generate the non-polar form of the organic compound. This would remove any salts and allow for a routine recrystallization.

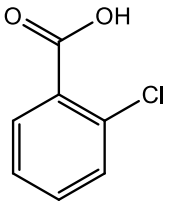
Recrystallization is a second technique that will be employed today to affect the purification of the carboxylic acid and neutral compound. Solubility is temperature dependent. If a solution is warmed it is better able to dissolve more solute. The sample should be dissolved in a minimal volume of warm solvent. As the solvent cools the solute (sample) will no longer remain in solution and begin to form crystals. If the crystals form slowly, with no disturbance, no contaminates should co-crystallize with the desired compound.

Objective

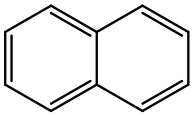
A carboxylic acid will be extracted from a neutral compound. The carboxylate will be protonated and back extracted into ether. The solvent will be removed and the carboxylic acid recrystallized. The neutral compound will also undergo recrystallization to further purify it. Melting points will be used to identify the compound and indicate purity.



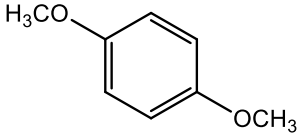
benzoic acid
mp 123ºC



2-chlorobenzoic acid
mp 141ºC



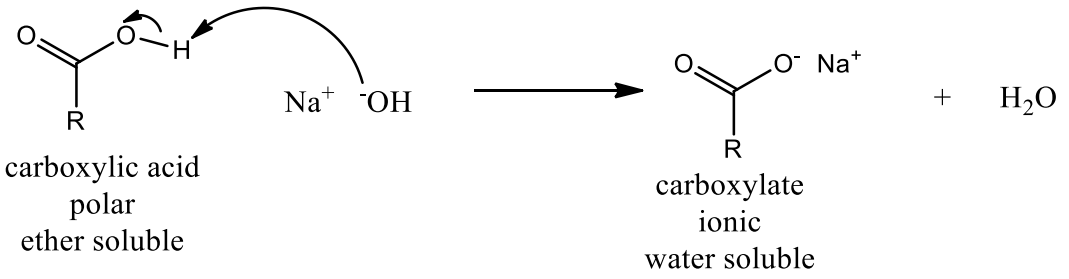
naphthalene
mp 82ºC



1,4-dimethoxybenzene
mp 57ºC

Mechanism

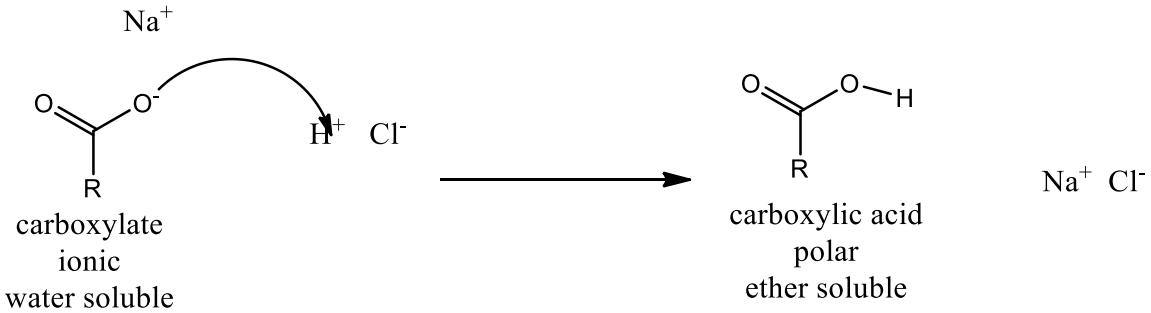
Deprotonation of carboxylic acid



carboxylic acid
polar
ether soluble

carboxylate
ionic
water soluble

Protonation of carboxylate



carboxylate
ionic
water soluble

carboxylic acid
polar
ether soluble

Experimental Procedure

1. Dissolve 2g of the sample mixture in methyl *t*-butyl ether (30ml) in a 125ml Erlenmeyer flask.
2. Pour the solution into a separatory funnel supported in a ring stand.
3. Add 10ml of 2M sodium hydroxide to the separatory funnel.
4. Shake the funnel with the stopper firmly closed for a full minute. Vent through the stopcock to prevent pressure building up.
5. Place the separatory funnel back in the ring-stand. Remove the stopper.
6. Drain the lower water layer and set aside in an Erlenmeyer flask labeled “Acid”.
7. Drain the remaining ether layer into an Erlenmeyer flask labeled “Neutral”.

Recrystallization of "Acid" Flask:- Carboxylic acid.

1. Pour contents of "Acid" flask into the empty separatory funnel.
2. Add 12ml of 2M hydrochloric acid. A white cloud/milky solid should form, if not add more hydrochloric acid 15-25ml may be required.
3. Add 20ml of methyl *t*-butyl ether to the separatory funnel.
4. Put the stopper back in the top of the separatory funnel and shake to dissolve the carboxylic acid into the ether layer.
5. Pour the lower water layer into new flask labeled "W1" and keep aside until the end of the experiment.
6. Pour the upper ether layer into a dry 125ml Erlenmeyer flask, add a boiling stick, and place in the warm (not hot) hot-plate in the hood.
7. Allow the ether to boil off until there is a minimal volume of the solution coating the bottom of the Erlenmeyer flask. Do not allow the flask to boil to dryness.
8. Add 3ml of methanol and warm to boiling. The sample should fully dissolve.
9. Allow the flask and its contents to cool to room temperature, sometimes this step needs an ice bath to cool.
10. Take the weight of a filter paper of suitable size for a Buchner funnel.
11. Slowly filter the crystals and take the weight of the filter paper and dry crystals. You will need to use a suction flask with a side-arm connected to the aspirator to pull the solution through the filter paper.
12. Scrape the crystals off of the filter paper from the Buchner funnel onto a larger piece of filter paper, the 11 cm papers work well. Fold the paper in half with the crystals inside (like a taco). Rub the sides back and forth to dry the crystals.
13. Weigh the filter paper and crystals. By difference, to the initial weight of the filter paper, you will be able to determine your yield.
14. Push the open end of a melting point tube down into the crystals, turn the melting point tube the right way up and tap the crystals to the bottom of the tube.
15. Use a melting point apparatus to determine the melting range of the crystals and thus the identity of your carboxylic acid.

Recrystallization of "Neutral" Flask:- Neutral compound

1. Add a boiling stick to flask labeled "Neutral" and place on the warm (not hot) hot-plate in the hood.
2. Allow the ether to boil off until there is a minimal volume of the solution coating the bottom of the Erlenmeyer.
3. Do not allow the flask to boil to dryness.
4. Add 3ml of methanol and warm to boiling. The sample should fully dissolve.
5. Pour hot contents into a clean dry test-tube to allow crystals to form.
6. Allow the test-tube and its contents to cool to room temperature, again sometimes this step requires an ice-bath to cool.
6. Take the weight of a filter paper of suitable size for a Buchner funnel.
8. Filter the crystals and take the weight of the filter paper and dry crystals. You will need to use a suction flask with a side-arm connected to the aspirator to pull the solution through the filter paper. Scrape the crystals off of the filter paper from the Buchner funnel onto a larger piece of filter paper, the 11 cm papers work well. Fold the paper in half with the crystals inside (like a taco). Rub the sides back and forth to dry the crystals.

9. Weigh the filter paper and crystals. By difference, to the initial weight of the filter paper, you will be able to determine your yield.
10. Push the open end of a melting point tube down into crystals, turn the melting point tube the right way up and tap the crystals to the bottom of the tube.
11. Use a melting point apparatus to determine the melting range of the crystals and thus the identity of your neutral compound.

The methods for recrystallizing the carboxylic acid and the neutral compound are the same from step 7 of the carboxylic acid. If you are careful and keep track of the flasks you can run these steps in tandem. Boil off the ether from both flasks at the same time, add methanol to both flasks, warm at the same time, etc.

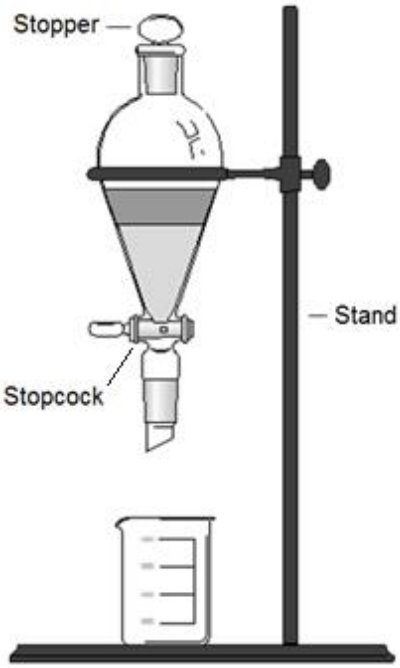
Results and Calculations

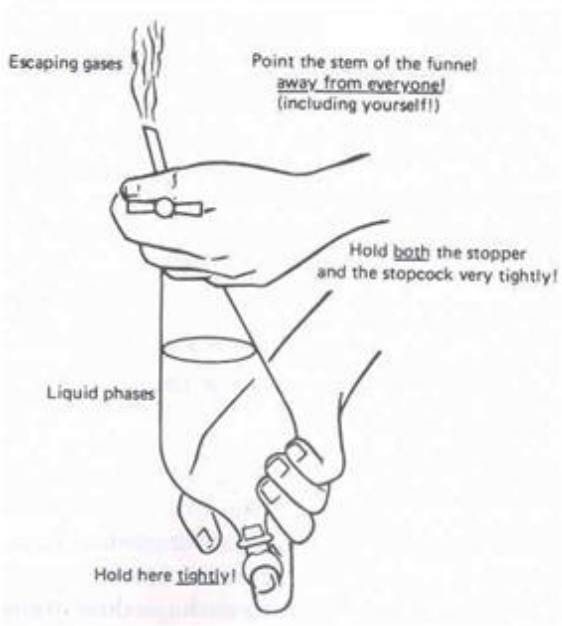
1. Deduce the yield as a percentage yield for both the carboxylic acid and the neutral compound.
Percentage Yield= ((mass of crystals)/ 1g) x100%
2. Report the melting ranges of your crystals.
3. Record the letter label of your unknown and deduce the identity of your carboxylic acid and the neutral compound by comparison to the melting points for benzoic acid or 2-chlorobenzoic acid and 1,4-dimethoxybenzene or naphthalene.

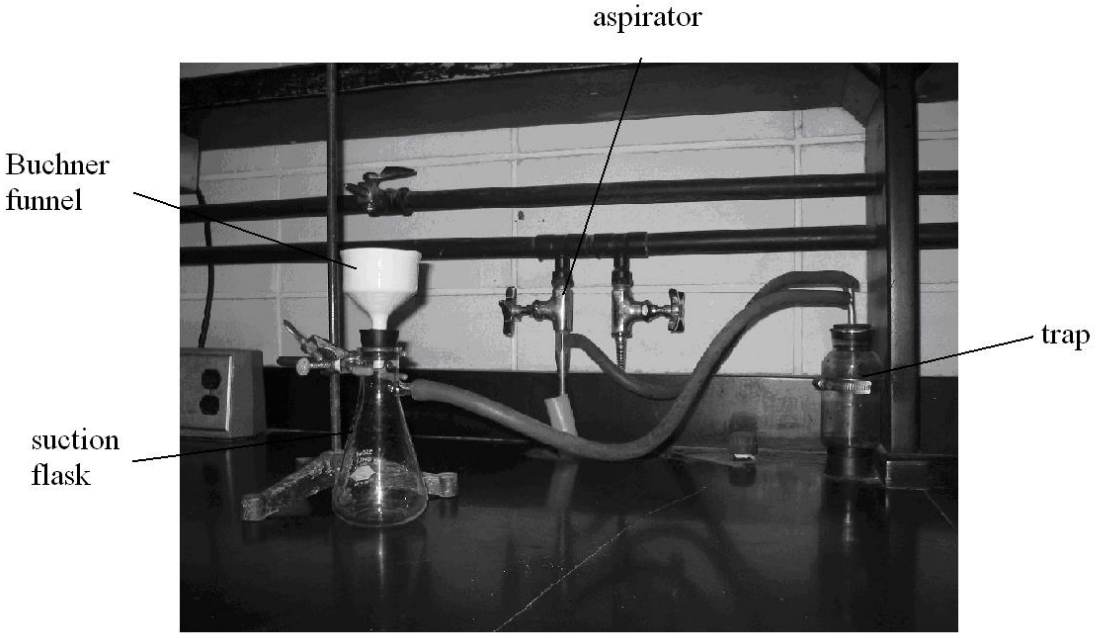
Waste Management

The following chemicals utilized or produced in this experiment are regulated as by the EPA hazardous waste because they are ignitable below 140 deg F: methyl t-butyl ether, dimethoxybenzene, methanol and acetone. Hydrochloric acid and sodium hydroxide are also regulated as hazardous waste because both are corrosive, with a pH < 2 or pH >12.5 respectively.

1. Because the water layer (W1) may be contaminated with ether, which is flammable, and hydrochloric acid, which is corrosive, it should be disposed of as hazardous waste.
2. Methanol, used for recrystallization, is flammable and should also be disposed of as hazardous waste. Discard in the waste container from step 1 of this section.
3. Wash the separatory funnel with soap and water. If it is dirty with organic residue use acetone to rinse. Because acetone is flammable, discard of as chemical waste in the waste container from step 1 of this section. If it is not listed, add acetone to the contents on the label.
4. Discard crystals (benzoic acid, 2-chlorobenzoic acid, naphthalene, 1,4-dimethoxybenzene) and filter paper in the solid waste container. Do not mix solid and liquids.
5. Place used melting point tubes in the broken glass box at the front of the lab, NOT in the trashcan.


Stopper
Stand
Stopcock


Escaping gases
Point the stem of the funnel away from everyone! (including yourself!)
Hold both the stopper and the stopcock very tightly!
Liquid phases
Hold here tightly!


aspirator
Buchner funnel
trap
suction flask

Lab 5

An Exercise with Molecular Models

In this laboratory period, we will use molecular models to investigate some three dimensional properties of molecules. This experiment will be graded but you may work in groups. There are prelab questions for this lab. But not prelab write-up is required.

We will look at **conformations** of acyclic (non-cyclic) compounds, **constitutional isomers** in acyclic compounds with the same molecular formula, **stereoisomers** in cyclic compounds, and identify **axial** and **equatorial** bonds in cyclohexanes. If time permits you may also examine other conformations of cyclohexanes.

I. Conformations.

1. Ethane. Construct two models of ethane and arrange one in a fully staggered conformation and the other in a fully eclipsed conformation.

a) Draw both of these conformations using the Newman, "sawhorse" and dash-wedge drawing conventions.
b) Locate all the planes of symmetry in the two conformations.
c) By how many degrees must one rotate one carbon atom with respect to the other to carry a staggered conformation into an eclipsed conformation (or vice versa).
d) By how many degrees must one rotate one carbon atom with respect to the other to carry one staggered conformation into another staggered conformation (or one eclipsed conformation into another eclipsed conformation).
e) What are the H-C-C-H dihedral angles in the two conformations.

2. Propane. Replace one of the hydrogens in an ethane model with a methyl group to make a model of propane.

a) Arrange the model in a fully staggered conformation and draw a Newman Projection of the conformation.
b) Arrange the model in a fully eclipsed conformation and draw a Newman Projection of the conformation.
c) Locate all the planes of symmetry in the two conformations.

3. Butane. Replace one of the methyl group hydrogens in your propane model with a methyl group to make a model of butane. For the following manipulations, sight down the central (C_2-C_3 bond):

a) Arrange the model in the conformation in which the two methyl groups are eclipsed (Syn conformation) and draw a Newman Projection.
b) Rotate either C_2 or C_3 by 60° to bring the model to a Gauche conformation and draw the Newman Projection.

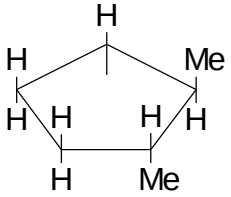
c) Starting with the Gauche conformation, rotate either C_2 or C_3 until the dihedral angle between the methyl groups is 180° and draw the Newman Projection of the resulting Anti conformation. By how many degrees did you rotate one of the carbons to achieve this rotational transformation?

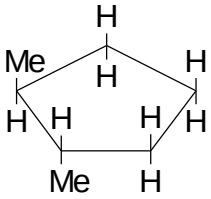
II. Constitutional Isomers.

Retain your model of butane from the previous exercise and make a model of isobutane from another model of propane by replacing an internal hydrogen with a methyl group. Arrange the models of the two constitutional isomers in their most stable conformations and visually inspect them for similarities and differences. What are your observations?

III. Stereoisomers.

a) Make a model of the *cis*-1,2-dimethylcyclopentane and locate the plane of symmetry in the molecule.
b) Make two models of *trans*-1,2-dimethylcyclopentane.





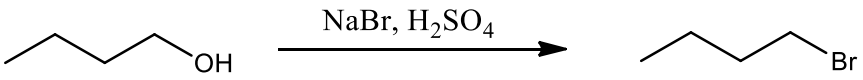
Is there a plane of symmetry in either of these structures?
c) What is the relationship between the *cis* and *trans*-1,2-dimethylcyclopentanes?
d) What is the relationship between the two *trans*-1,2-dimethylcyclopentanes?

IV. Axial and Equatorial Bonds in Cyclohexanes.

a) Make a model of the chair conformation of cyclohexanes and identify which C-H bonds are axial and which C-H bonds are equatorial. It may be useful to use different colored atoms to identify axial vs equatorial.
b) Replace one of the axial hydrogens with a methyl group and examine the model for nonbonded interactions.
c) Interchange the axial methyl group and an equatorial hydrogen on the same carbon atom to place the methyl group in an equatorial position and examine the model for nonbonded interactions.
d) Execute several "ring flips" on your model of methylcyclohexane to simultaneously interconvert all the equatorial and axial bonds, and examine how this affects nonbonded interactions.

Lab 6

Synthesis of 1-Bromobutane (S_N2)



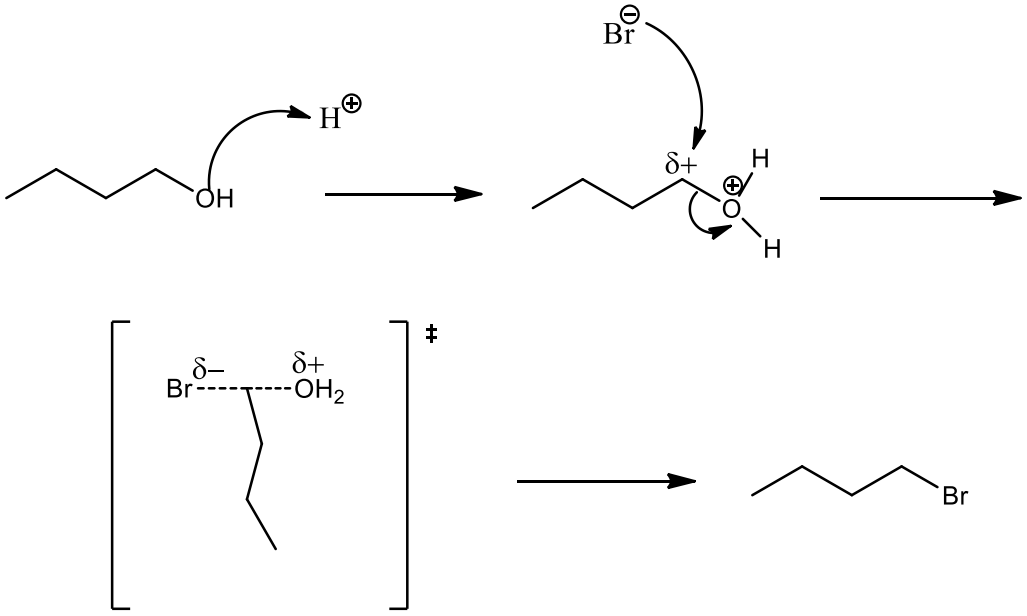
1-butanol
MW= 74 g
bp= 118ºC

1-bromobutane
MW= 137g
bp= 101ºC

Introduction

A S_N2 is a nucleophilic ($_N$), substitution (S) that is bimolecular rate dependent (2). The initial rate of reaction will be due to the concentration of both the substrate and the nucleophile; the alcohol and bromide ion (Br^-), respectively, in this experiment. The basicity of the leaving group will also affect the progress of the reaction. The use of strong acid will allow the protonation of the hydroxyl. Water (H_2O) is a much weaker base so is a better leaving group than hydroxide (^-OH).

Mechanism



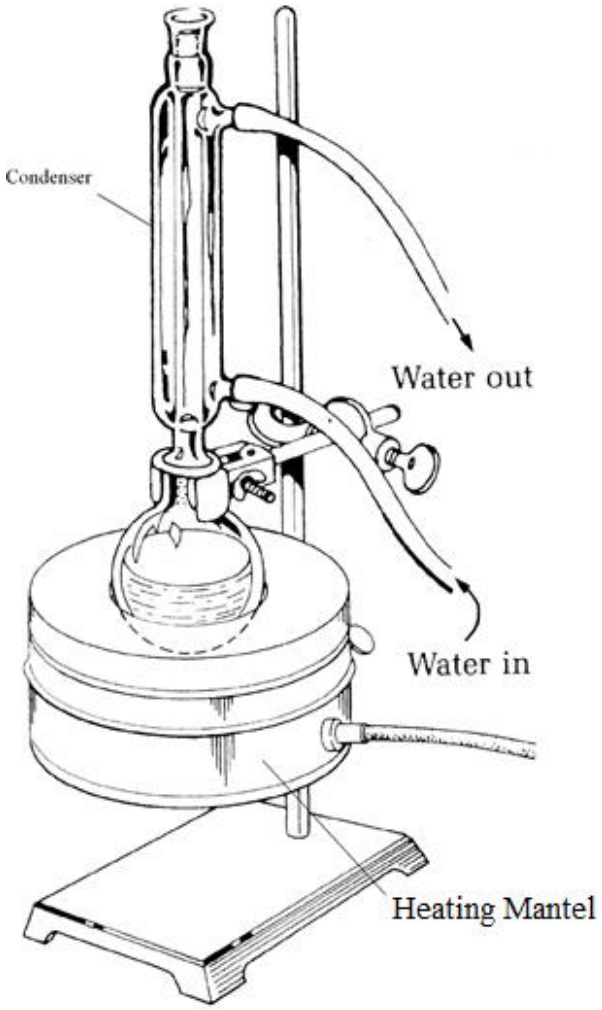
Objective

Bromobutane will be synthesized by refluxing 1-butanol with sodium bromide and sulfuric acid. Purification of the reagents will be performed by distillation and extraction. A Beilstein test will be used to show the presence of the halide.

Experimental Procedure

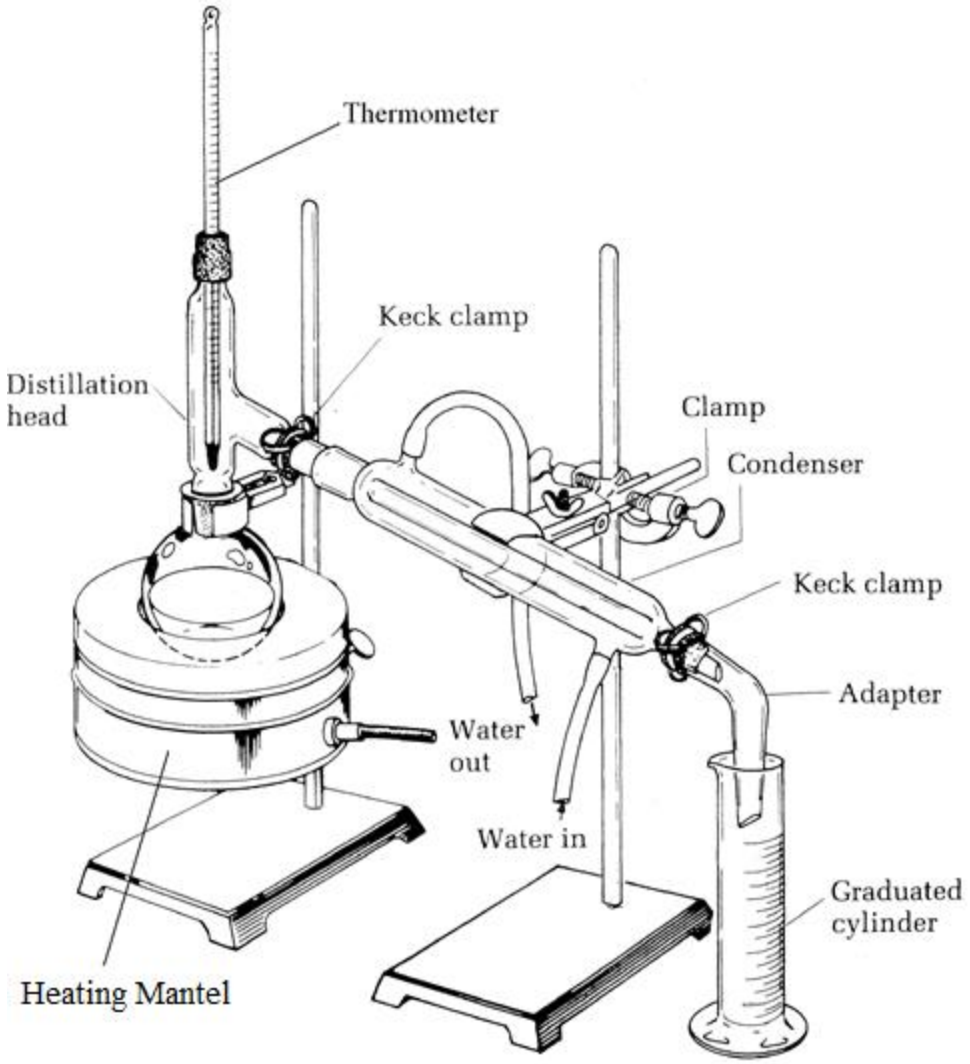
1. Add 3 boiling chips to a 150ml round bottom flask.
2. Add 7g of sodium bromide, 7.5ml of water and 5ml of 1-butanol.
3. Cool the round bottom flask in an ice-water bath for 2 minutes.
4. Cautiously add the 6ml of concentrated sulfuric acid over 5 minutes. Add very small drops. Swirl the flask in the ice-water bath between each addition.

Reflux



5. Attach the flask directly to the bottom of the condenser and attach with a blue Keck clamp.
6. Raise a heating mantel underneath the round-bottom flask.
7. Ensure a steady stream of water is flowing through the condenser and warm the reaction to a steady boil by plugging the sand-bath into the variac box and turning the dial to 4.
8. Reflux the reaction for 35 minutes.
9. Lower the sand-bath and allow cooling for 1 minute. If the reaction is still boiling after 1 minute then dunk the flask in your ice-water bath.

Distillation



10. Disconnect the condenser and install a simple stillhead and proceed with a simple distillation.
11. Ensure the water is still flowing through the condenser as a steady stream and raise the heating mantel under the reaction flask.
12. Turn the dial on the variac box to 4.
13. Once the temperature at the stillhead reaches 115ºC all the bromobutane will have been distilled and the sand-bath can be lowered.
14. Record the yield.
15. Dip a clean piece of copper wire into your product liquid. Allow the product to evaporate.
16. Place the wire in the blue cone of a light Bunsen burner flame. Note any color change to the flame.

Results and Calculations

1. Record the weight of 1-bromobutane and calculate the percent yield.
2. Note any change in the flame color of the Bunsen burner, for the starting material and product.

Waste Management

The following chemicals utilized or produced in this experiment are regulated by the EPA as hazardous waste because they are ignitable below 140 deg F: 1-butanol and 1-bromobutane.
Sulfuric acid and sodium hydroxide are regulated as a hazardous wastes because they have a pH <2 and pH > 12.5 respectively.

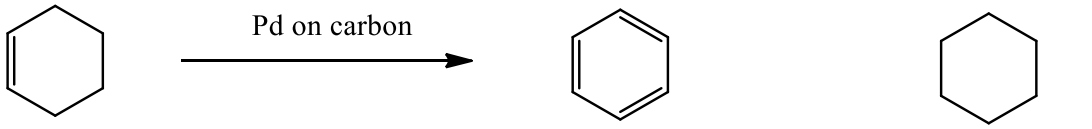
1. Because the acidic residue in the round bottom flask is corrosive it should be disposed of in the hazardous waste container labeled water, 1-bromobutane, sulfuric acid, sodium bromide, 1-butanol. The empty flask can then be washed with soap and water.
2. The water layers set aside from the extraction contain small amounts of alkenes that are flammable so these solutions should be added to the waste container from step 1 of this section.
3. The remaining 1-bromobutane is flammable so should be discarded in the appropriately labeled waste container.

Notes

1. Sulfuric acid is very corrosive. You should wear gloves whenever you are handling this reagent or the round-bottom flask.
2. The sand-bath should be plugged into the variac box not the wall outlet.
3. Remove the stopper before you try to drain a layer from the separatory funnel.

Lab 7

Catalytic Hydrogenation



cyclohexene
MW= 82 g/mole
bp= 83ºC

benzene
MW= 78 g/mole
bp= 79ºC

cyclohexane
MW= 84 g/mole
bp= 80.7ºC

Introduction

Hetergenous catalysts are crucial for many chemical reactions. The utility of heterogeneous catalysts is that the catalyst is in a different phase from the substrate chemical (solid catalyst vs. liquid substrate, solid catalyst vs. gas substrate). For instance, in this experiment the palladium will be embedded on carbon and is a solid. The substrate, cyclohexene, is a liquid. This allows the catalyst to be easily removed from the reaction by filtration.

Gasoline refineries often use heterogeneous catalysts to crack long alkyl chains into the shorter octane fractions required for gasoline. Generally, the catalyst is mounted to a surface, and the substrate, crude oil, is passed over the surface.

The catalytic converter installed in the exhaust system of a car is a solid supported catalyst acting on the gaseous emissions from the engine. This alternative heterogeneous catalyst (gas/solid) reduces the gaseous emissions from internal combustion engines responsible for acid rain nitrogen oxides (often called NOx).

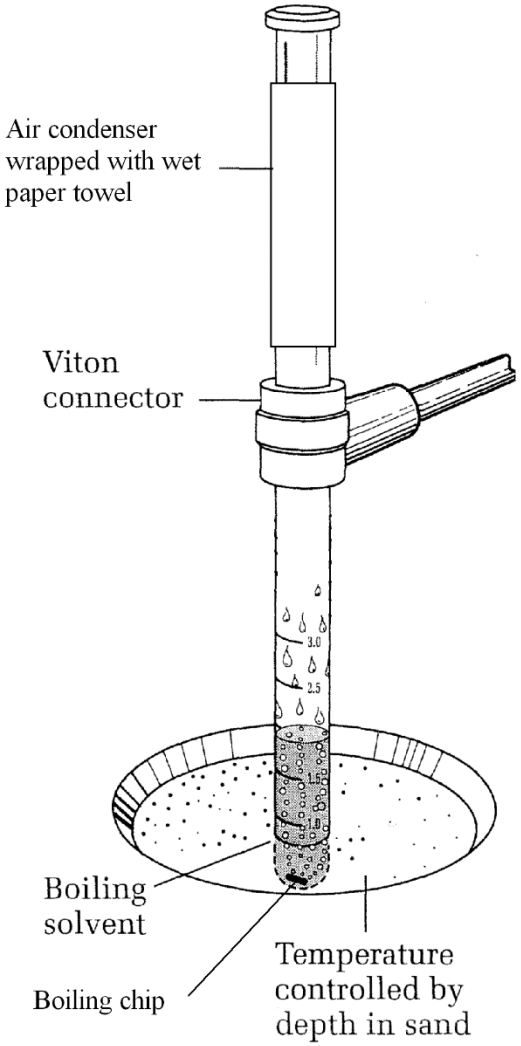
Cyclohexene can act as a hydrogen donor and an acceptor. Palladium metal is capable of adsorbing hydrogen atoms and transferring the hydrogen to a new molecule. This transfer of hydrogen allows for the transformation of the more reactive alkene into either an alkane or benzene (stabilized by aromaticity).

Objective

Cyclohexene will be heated with palladium on carbon. Transfer hydrogenation with the adsorbed hydrogen on the palladium will generate benzene and cyclohexane. The result will be an unsaturated product, benzene, and a fully saturated product, cyclohexane. Gas-chromatography (GC) will be used to determine the ratio of the two products and the yield of the products.

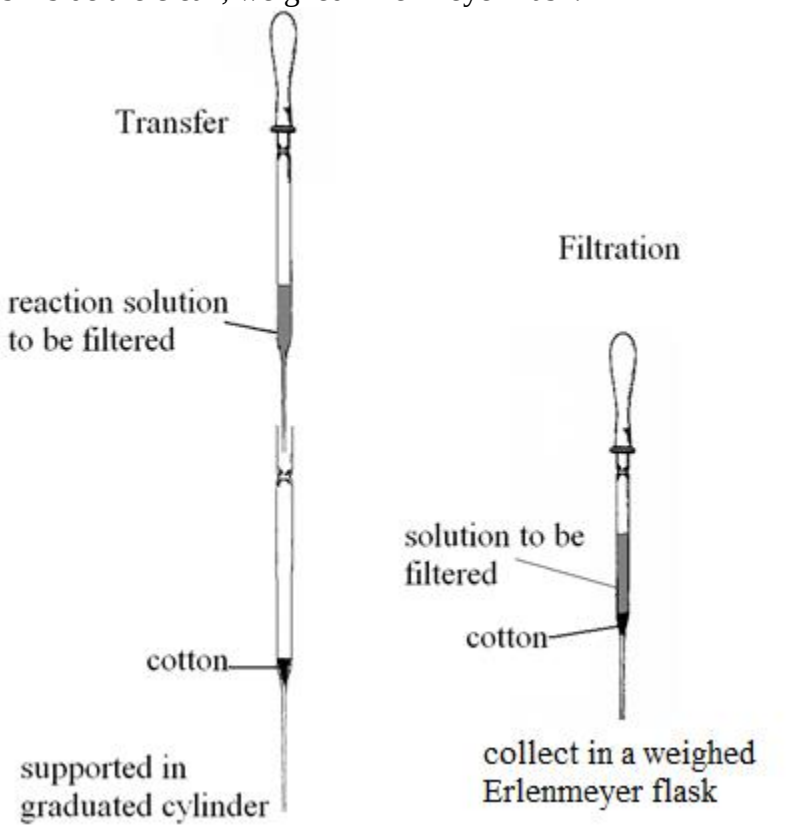
Experimental Procedure

1. Weigh 0.100g of palladium/carbon and place in a test-tube.
2. Add 1.6ml of cyclohexene to the test-tube and two boiling chips.
3. Attach the test-tube holder and an air condenser (open-ended tube).
4. Wrap the outside of the condenser with a wet paper towel and hold in place with a test-tube clamp.
5. Clamp the assembly to a ring stand and place the test-tube in a sand-bath.



6. Plug the sand-bath/heating mantel into a variac box and turn the dial to 3.
7. Warm the reaction mixture to boiling for 15 minutes.
8. Control the rate of boiling by removing the test-tube form the sand-bath if the boiling becomes too violent.
9. After the 15 minutes remove the test-tube from the sandbath and allow to cool for 2-3 minutes.
10. Filter off the catalyst. This is done by placing a small plug of cotton into a Pasteur pipette. Place this pipette in a clean, weighed graduated cylinder.
11. Use a second pipette to suction the reaction solution from the test-tube and squirt it into the top of the pipette with the cotton.

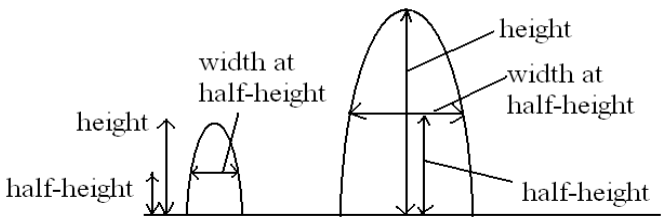
12. Transfer the rubber bulb to the pipette with the cotton and gently squeeze the bulb. The cyclohexene/benzene/cyclohexane solution will squirt out the bottom of the pipette so make sure it is inside the clean, weighed Erlenmeyer flask.



13. Reweigh the Erlenmeyer flask. By difference to the original weight of your Erlenmeyer flask, calculate your yield.
14. Take a gas-chromatogram.

<u>Results and Calculations</u>
1. Calculate your yield.
2. Cyclohexane elutes first then cyclohexene and benzene elutes last.
3. Calculate the area of each peak on the Gas-Chromatogram. Measure the height of each peak (in centimeters). Divide the height by two (eg. 32cm/ 2= 16cm) this is "half-height". Mark that half-height for each peak. Measure the width of each peak at half-height.

Area of peak= width at half-height x height



4. Deduce the ratio of cyclohexane to benzene.

5. Deduce the ratio of product areas to total area. This is the overall yield of product (or percent conversion).

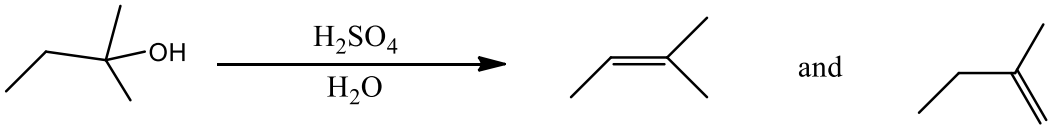
Waste Management

The following chemicals utilized or produced in this experiment are regulated by the EPA as hazardous waste because they are ignitable below 140 deg F: cyclohexene, cyclohexane, benzene, palladium on carbon and acetone.

1. Because palladium on carbon and acetone are flammable, rinse any remaining palladium on carbon with acetone into the hazardous waste container labeled cyclohexene, cyclohexane, benzene, palladium on carbon and acetone.
2. Place used pipettes in the broken glass box at the front of the lab.
3. Any pipettes contaminated with palladium on carbon will be handled as solid waste and collected in a container in the fume hood. Ensure a yellow waste accumulation sticker is attached to an appropriate container.
4. Any remaining cyclohexene, benzene and cyclohexane is flammable so should be disposed of in the chemical waste container from step 1 of this section.

Lab 8

Alkenes by Acid-catalyzed Dehydration of an Alcohol



2-methyl-2-butanol
MW= 88.15 g/mole
bp= 102ºC
den.=0.805 g/ml

2-methyl-2-butene
MW= 70.14 g/ml
bp= 38.57ºC
den.= 0.662g/ml

2-methyl-1-butene
MW= 70.14 g/ml
bp= 31.16ºC
den.= 0.662g/ml

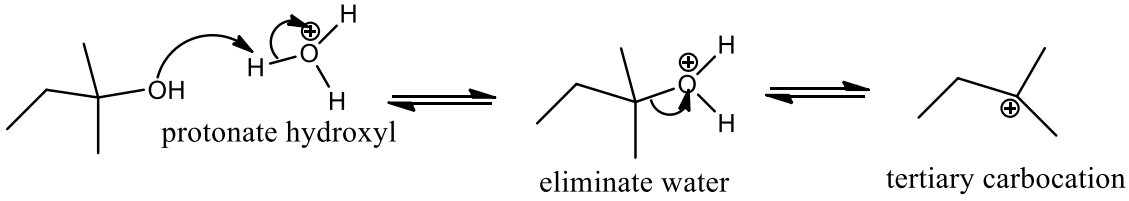
Introduction

Tertiary alcohols dehydrate through an acid-catalyzed E1 mechanism to form alkenes (see page 619 of class text). The preference for the resultant alkenes follows Zaitsev's Rule. Gas/liquid chromatography (GC) will be used to deduce the ratio of the two possible alkenes that form.

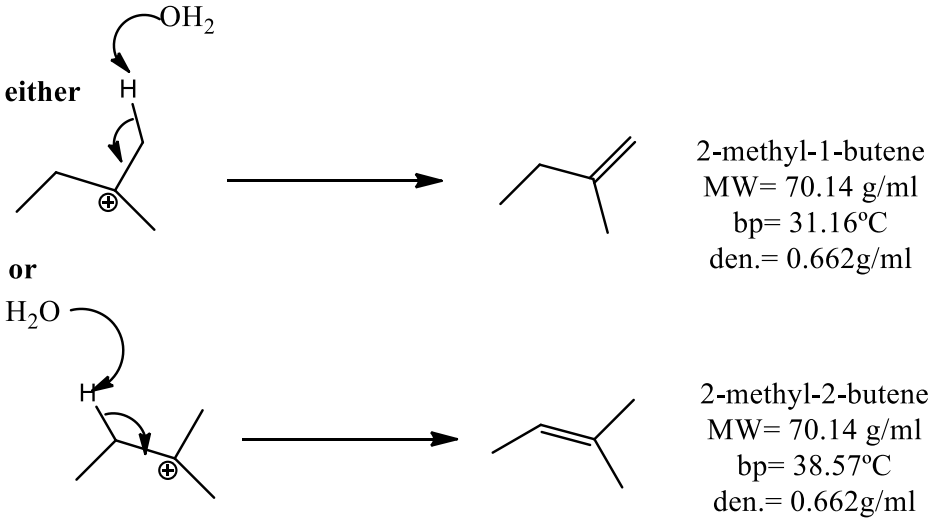
Zaitsev's rule predicts the more substituted alkene will be favored. The formation of a tertiary carbocation allows for the deprotonation to occur at either adjacent carbon. The result is two possible alkene products.

Mechanism

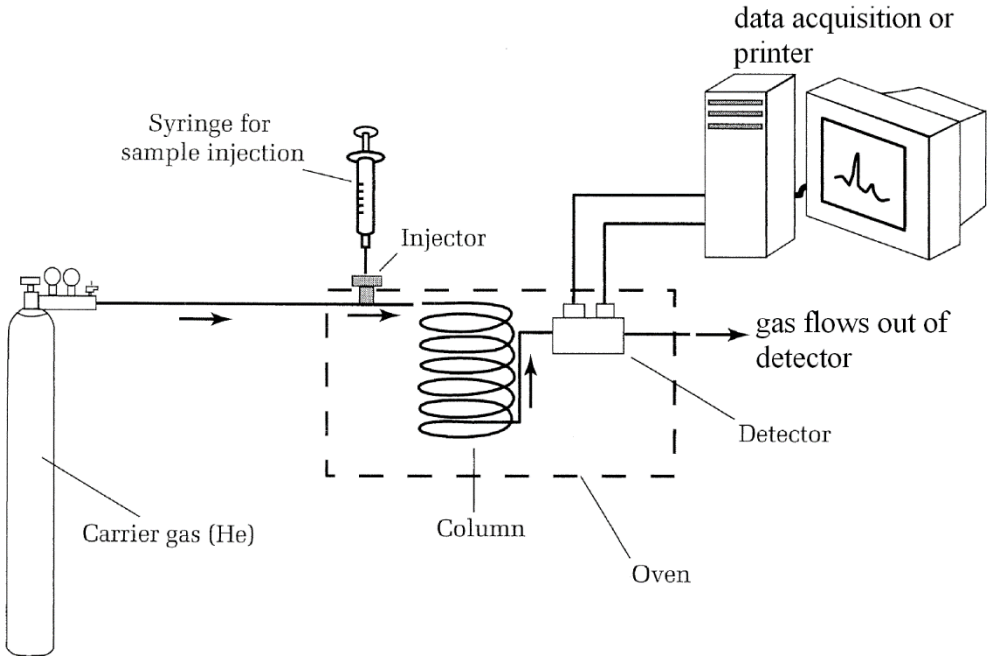
Formation of Carbocation



Two alternate pathways



GC is a chromatographic technique that follows similar principles noted with TLC. The eluent for GC is an inert carrier gas (nitrogen or helium). The sample is heated to form a gas and interacts with a grease (liquid) supported within the column. The volatility of the sample will determine the rate of elution. The lower boiling sample will exit the column first. When paired with mass spectrometry GC can become a very powerful tool for analysis. The applications are both clinical and environmental; blood can be analyzed for contamination or ground water can be analyzed for salt composition.



Objective

Reflux 2-methyl-2-butanol with sulfuric acid resulting in the dehydration to two alkenes. Fractional distillation will allow separation from the acid and any remaining alcohol. The distillate will be analyzed by GC to determine the ratio of the two alkenes produced.

Experimental Method

The alkenes generated by this reaction are volatile so can easily evaporate. Set-up your equipment before combining the reagents to reduce the amount of material lost to evaporation.

1. Weigh your graduated cylinder used for collection. This will allow you to deduce your yield of alkenes.
2. Assemble the fractional distillation equipment as illustrated on the next page. Cool the graduated cylinder in ice-water to prevent evaporation of your alkenes.
3. Cool the flask and add 6ml of 6M sulfuric acid. Be careful!! This is corrosive.
4. Cool the flask and sulfuric acid solution in an ice-water bath.
5. Slowly pour 9ml 2-methyl-2-butanol (in three batches) into the round bottom flask. Swirl between additions. Add two boiling chips.
6. Reinstall the flask into the reflux/distillation apparatus.

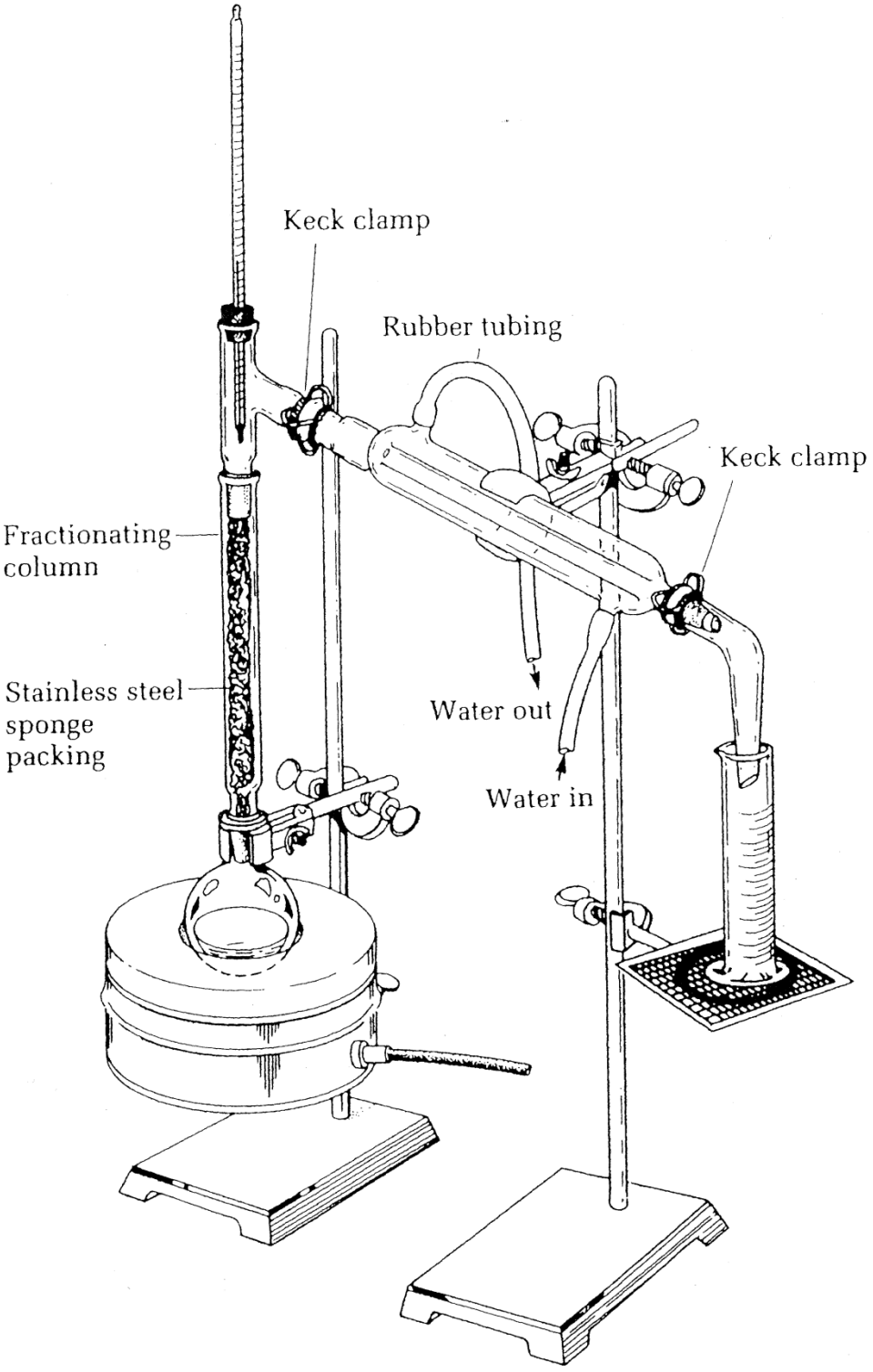


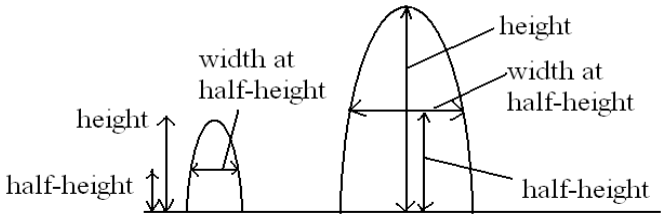
Figure (1)
Fractional Distillation Setup

7. Ensure the water supply to the condenser is turned on. Plug the heating mantel into the variac and set to 3-4.
8. Collect approximately 10ml of alkenes. The temperature at the still-head should remain at ~35ºC.
9. Weigh your measuring cylinder. This will give your yield.
10. Inject a sample of your alkenes into the GC. See your TA for assistance.

Results and Calculations

1. The crude yield of the alkenes can be calculated by weighing the 10ml cylinder and noting the weight after collecting the alkenes.
2. Calculate the areas of each peak. Measure the height of each peak (in centimeters). Divide the height by two (eg. 32cm/ 2= 16cm) this is "half-height". Mark that half-height for each peak. Measure the width of each peak at half-height.

Area of peak= width at half-height x height



3. The ratio of the two areas is equivalent to the ratio of the two alkenes.

Waste Management

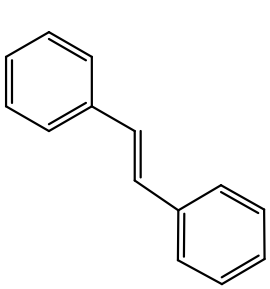
The following chemicals utilized or produced in this experiment are regulated by the EPA as hazardous waste because they are ignitable below 140 deg F: 2-methyl-2-butanol, 2-methyl-2-butene and 2-methyl-1-butene. Sulfuric acid is regulated as hazardous waste because it is corrosive, with a pH < 2.

1. The strongly acidic residue in the round bottom flask below the fractionating column must be carefully poured into the hazardous waste container in the hood labeled acid waste (water, sulfuric acid, 2-methyl-2-butanol, 2-methyl-1-butanol). To protect yourself from exposure to corrosives, you should wear gloves whenever you are handling this reagent or the round-bottom flask.
2. The fractionating column should be thoroughly rinsed with water.
3. Because alkenes are extremely flammable, dispose of any waste containing alkenes in the hazardous waste container labeled 2-methyl-2-butene and 2-methyl-1-butene.
4. Any organic residue on your glassware should be first washed with soap and water and then rinsed with acetone. Please add acetone to the chemical contents if it is not listed.

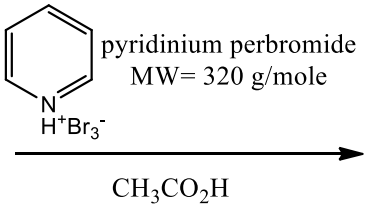
Lab 9

Synthesis of an Alkyne: Addition-Elimination

Addition:



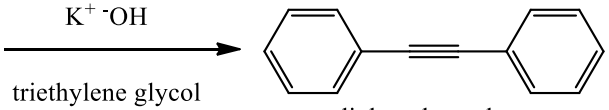
E-stilbene
MW = 180 g/mole
mp = 123-125 ºC



A
mp= 236-237 ºC

Elimination:

A



diphenylacetylene
MW = 178 g/mole
mp = 61 ºC

Introduction

You have learned that carbon-carbon π-bonds (e.g. an alkene) are areas of high electron density and are thus nucleophilic. If a sufficiently reactive electrophile is present, then an alkene can react with it. Keeping in mind that pyridinium perbromide is a convenient source of molecular bromine (Br_2), review your Chem. 141 notes to predict the identity of the compound missing from the schemes above (i.e. **A**) and include this information in your pre-lab.

Objective

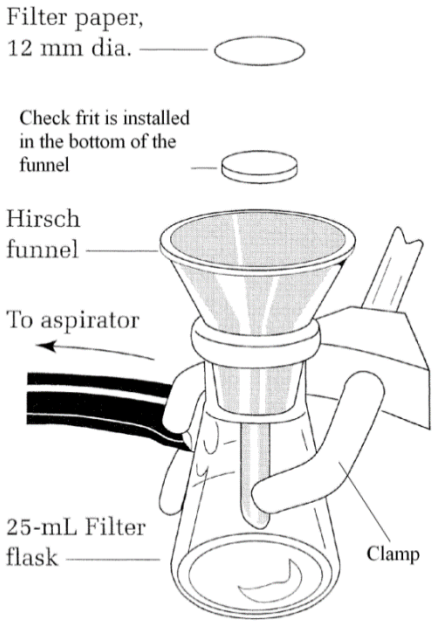
This two-step synthesis will allow the conversion of an alkene to an alkyne by way of an intermediate that can undergo a double elimination when heated with strong base. Purification of both intermediate **A** and the final product (diphenylacetylene) will be achieved by crystallization. Be sure to determine yields for both the intermediate **A** and the final product. You will obtain a melting point for the diphenylacetylene you isolate to provide an indication of purity.

Experimental Procedure

Addition

1. Add 0.1 g of pyridinium perbromide to a test tube from your microscale kit.
2. Add 50 mg of (E)-stilbene and 1 mL of acetic acid (ethanoic acid) to the reaction tube.
3. Warm the reaction tube in the water bath (setup for you in the hood) for 5 minutes while stirring intermittently.
4. Allow the mixture to cool for 2 minutes in a test tube rack and then cool it further in an ice-water bath to ensure full crystallization.

5. Collect the crystals by suction filtration using a pre-weighed filtration apparatus (suction filter and filter paper).



6. Rinse the crystals with approximately 3 mL of ice-cold methanol and then allow the vacuum to draw air through the crystals to dry (~2 minutes). Scrape the crystals off of the filter paper from the Buchner funnel onto a larger piece of filter paper, the 11 cm papers work well. Fold the paper in half with the crystals inside (like a taco). Rub the sides back and forth to dry the crystals.
7. Weigh the crystals of intermediate **A**.

Elimination

1. Preheat a sand bath by plugging it into a variac box set at 2. (REMEMBER: Never plug a sand bath into a wall outlet!)
2. Place 80 mg of your intermediate **A** in a clean and dry reaction tube.
3. Add 1 pellet of potassium hydroxide and 0.5 mL of triethylene glycol.
4. Insert a thermometer to monitor temperature and to stir.
5. Heat the reaction in the sand bath while stirring gently with the thermometer; the reaction needs to reach 160-170 ºC for 5 minutes.
6. After 5 minutes at 160-170 ºC remove the reaction tube from the sand bath and allow it to cool in a test tube rack until the tube can be handled comfortably.
7. Slowly add 2-3 mL of water using the thermometer to stir thoroughly during the addition.
8. Cool the reaction in an ice water bath for 5 minutes to allow crystals to from completely.
9. Collect the crystals by suction filtration using a pre-weighed filtration apparatus (suction filter and filter paper).
10. Rinse the crystals with 5 drops of ice-cold methanol (do not use more methanol or it will dissolve the product) and allow the vacuum to draw air through the crystals to dry them.
11. Weigh the crystals and take a melting point as an indication of purity.

Results and Calculations

1. Record the weights of both intermediate **A** and diphenylacetylene and calculate percent yields.
2. Record the melting range of your diphenylacetylene and comment on its purity by comparison to the literature value.

Waste Management

In this experiment, acetic acid is regulated as hazardous waste because it is ignitable below 140 °F. Potassium hydroxide is regulated because it is corrosive and has a pH > 12.5.

1. Dispose of the filtrate (liquid in bottom flask from filtration) in the waste container labeled potassium hydroxide, triethylene glycol, water, acetic acid, bromide ions.
2. Dispose of any excess intermediate **A** and diphenylacetylene crystals in the solid waste container in the hood. Do not mix solids and liquids.
3. Dispose of filter papers in the solid waste container from step 2 of this section.
4. Rinse any organic residue from glassware with acetone. Because acetone is flammable collect these washings and dispose of them in the waste container from step 1 of this section.

Notes

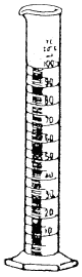
1. Do not try to break the potassium hydroxide pellets.
2. Use gloves when handling potassium hydroxide pellets as they are very corrosive. Mention any spill of potassium hydroxide to your TA immediately.

Glassware and Equipment

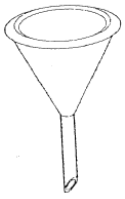
beaker

Erlenmeyer flask

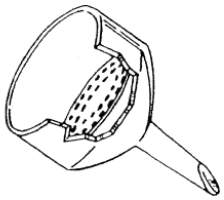
suction flask



graduated cylinder

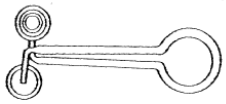


short stem funnel

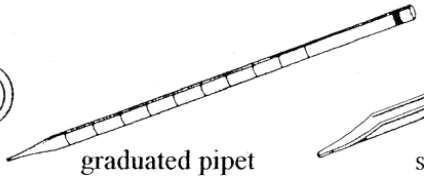


Buchner funnel

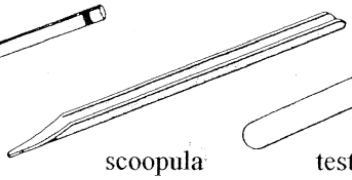
separatory funnel



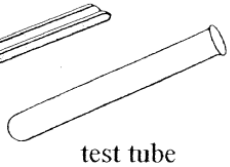
pinch clamp



graduated pipet

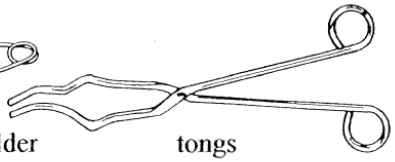


scoopula



test tube

test tube holder

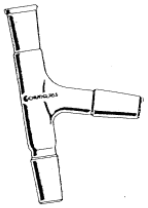


tongs

watch glass

dropper bulb

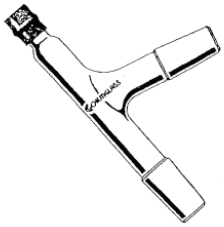
Keck clamp



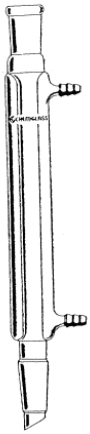
two way connector

+ thermometer adapter & neoprene sleeve

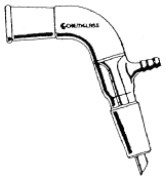
or



two connector & neoprene sleeve



condenser



vacuum adapter

round bottom