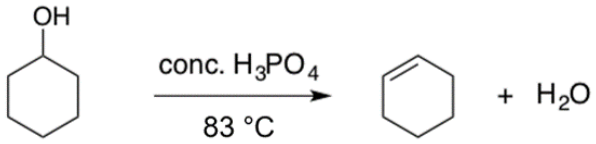
Activity 6: Dehydration of Cyclohexanol: Synthesis and Purification by Distillation

The Experiment



Lab Activity Goal

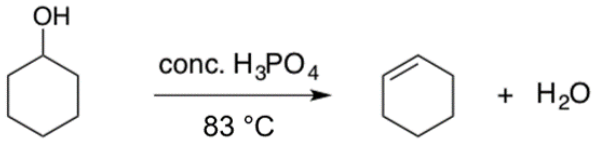
Synthesize cyclohexene by the acid-mediated dehydration (E1 elimination) of cyclohexanol. The cyclohexene product will be isolated by simple distillation of the reaction mixture. The cyclohexene product will then be analyzed using a classical chemical test, TLC, and by IR spectroscopy. NMR spectra of cyclohexanol, cyclohexene, and a mixture will be analyzed.

Pre-Laboratory Assignment

See the Activity 6 Pre-Lab Preparation and Outline document in Labflow.

Experimental Procedure

Part 1. Synthesis and Distillation of Cyclohexene



1. Place about 10 mL of cyclohexanol in a 100-mL round bottom flask. Record the exact volume that you measured.

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2. Add 12 mL of 85% phosphoric acid and a few **black charcoal** boiling chips. (Regular Boileezers™ stones will dissolve in the phosphoric acid.) Follow your instructor's directions on how to handle the phosphoric acid.
3. Set up a simple distillation apparatus (refer to Figure 1). The round bottom flask should be clamped firmly to the monkey bars at a height that allows for the heating mantle and the **raised** lab jack to fit below. The raised lab jack needs to be high enough that "*lowering it down*" will allow a hot heating mantle to be easily slid out from under the round bottom flask (secured to the monkey bars). Use a 50-mL round bottom flask immersed in an ice-water bath as the receiver flask.
4. Once your instructor checks that your apparatus is set up correctly, begin heating.

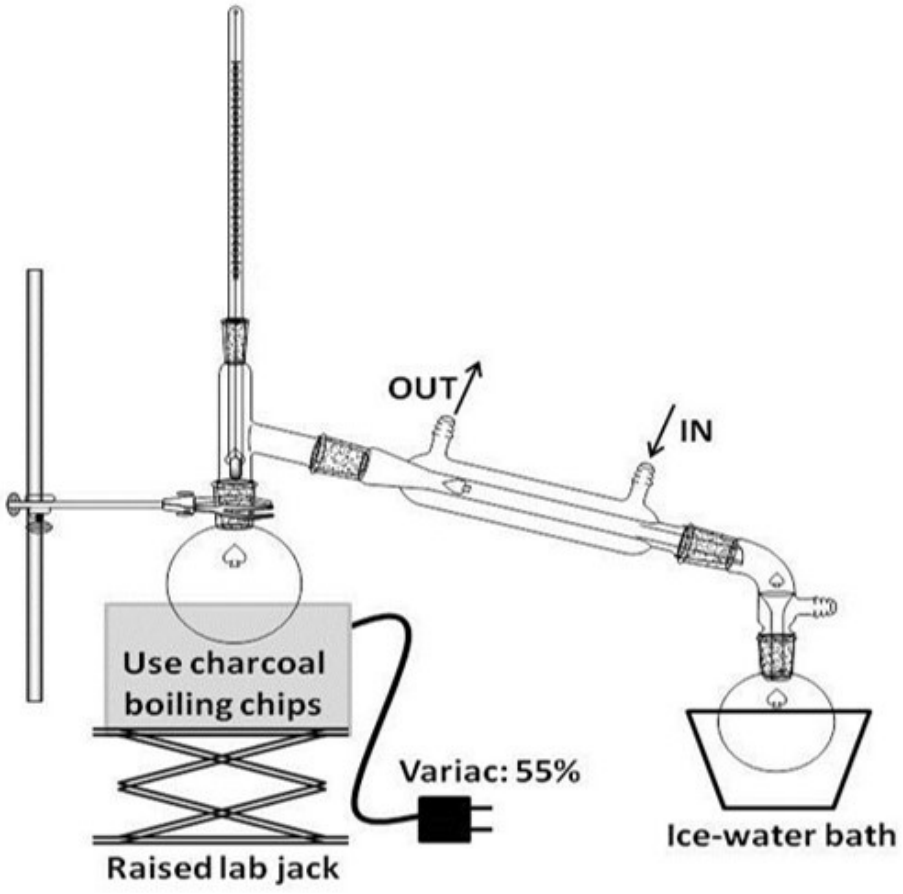

Figure 1. Distillation apparatus set-up

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Important: Safety Pause

When using electrical heating methods, it is critical to use the Variac to control the amount of heat added to your reaction mixtures. When running reactions at elevated temperatures, it is advisable to keep the hood sashes closed when possible.

Safety Pause

5. Monitor the thermometer carefully to make sure the vapor temperature does not exceed 83 °C. If the vapor begins to get too hot, adjust the Variac. If necessary, lower the heating mantle. Record the temperature when the distillation is stable (there is a constant flow of distillate into the receiver, and the thermometer reading is steady). Note: Distilling at 83 °C allows the cyclohexene to distill while leaving most unreacted cyclohexanol and phosphoric acid behind in the reactor flask/distilling pot.
6. Stop heating by lowering the lab jack when you have 5-10 mL of liquid left in the reactor. **NEVER DISTILL TO DRYNESS!**
7. Transfer the product to the **small** separatory funnel from your drawer. Obtain about 5 mL of 10% $Na_2CO_{3(aq)}$. Rinse the receiver flask with a small amount of the Na_2CO_3 solution and then transfer the contents to the separatory funnel. Transfer the remaining Na_2CO_3 solution to the funnel.

Important: Safety Pause

Mixing in a separatory funnel can increase pressure which, as always, requires frequent venting IN THE HOOD. It is especially critical to vent when gaseous products are being formed.

Safety Pause

- The aqueous Na_2CO_3 will neutralize any phosphoric acid that distilled over to the receiving flask. This will result in an exothermic acid/base reaction and the formation of carbon dioxide gas. Thus, great care must be taken to properly vent the separatory funnel. **Immediately vent** the separatory

funnel into the hood **before you begin swirling.** Then, swirl gently and vent often in the hood.

- Where is your product? Where is the aqueous layer?

NOTE: Water can sometimes be dissolved in organic compounds. Non-polar organic compounds may contain small quantities of water while more polar compounds (e.g., alcohols, carboxylic acids, etc.) can contain significant quantities of water). Steps 8 and 9 will remove any water that may remain in the cyclohexene.

8. Keep the cyclohexene product in the separatory funnel and wash it twice with two separate portions of 10 mL saturated NaCl solution.
   - The saturated NaCl solution contains Na^+ and Cl^- ions, which increases the ionic strength of aqueous solution significantly. This, in turn, minimizes the solubility of water in the organic phase and vice versa, making the two phases in the separatory funnel even more immiscible.
9. Transfer the product to a 25-mL Erlenmeyer flask and dry over anhydrous Na_2SO_4 to remove trace amounts of water. A cloudy, slightly turbid solution is an indicator of this trace water. You should initially add no more than a small, pea-sized quantity of Na_2SO_4 crystals. Move on to the next step while you wait for the Na_2SO_4 crystals to absorb the water in your cyclohexene product.
10. While waiting about 10 minutes for the Na_2SO_4 to absorb/remove any remaining water from the organic product, weigh a small round bottom flask **with stopper** held upright in a small beaker (see Figure 2).
11. After checking to see if the Na_2SO_4 removed trace water from your cyclohexene product (by seeing if your product is no longer turbid), decant the *dried* product into your pre-weighed flask, place it back in the beaker, and weigh the whole set again **with the stopper in place**. The perfect decantation maximizes the product transferred without including any Na_2SO_4.

Figure 2. Weighing your cyclohexene product.

12. Calculate the mass of the final product and then the percent yield of your reaction. **Note that you will need your weighed product for three tests (TLC, Bromine, and IR) in Parts 2, 3, and 4.** Complete all three tests before disposing of your product.

Part 2. TLC Analysis of Purified Cyclohexene

In this part of the laboratory, you will use Thin Layer Chromatography (TLC) techniques that you learned in Activity 4 to analyze the purity of the distilled cyclohexene.

Pro-tip

Cyclohexene is volatile and consequently will evaporate off your plate rather quickly. Thus, once your TLC plate is spotted with cyclohexene it should be developed immediately. Additionally, once your TLC plate is developed it should be visualized/stained as soon as possible (see step 6).

1. Prepare a TLC chamber using 30% ethyl acetate in hexanes as the eluent. Do this BEFORE you prepare your TLC plate.
2. Prepare a TLC plate with three lanes.
3. Use a capillary tube to add the reactant and product samples to your plate as shown in the figure to the right. Remember the origin line must be above the solvent level in the development chamber. Remember not to gouge the silica coating as you prepare your plate.

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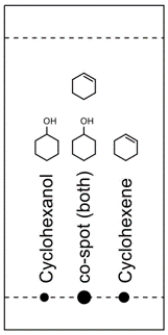

- **Cyclohexanol** – Your instructor will provide you with a solution of the cyclohexanol. DO NOT use pure cyclohexanol- only a small amount is necessary. Spot the cyclohexanol lane AND the co-spot lane.
- **Co-Spot –** The co-spot is used to draw comparisons and help differentiate spots in the reactants or products with similar R_f. In this lane, add BOTH cyclohexanol solution and cyclohexene.
- **Cyclohexene** – You may spot your product directly on the plate. Note that this is not a dilute solution, so much less will be required. Do not add too much or your TLC will have a large streak. Alternately, you may prepare a solution with a few drops of your cyclohexene dissolved in 1 to 2 mL of hexanes.

4. Place your TLC plate in the chamber carefully. Make sure the origin is above the solvent.
5. Once your TLC is developed, remove the plate from the chamber and **immediately** mark the solvent front so you can later calculate the R_f of your spots.
6. Take your developed plate to the "staining station" where one of your instructors will submerge it into a permanganate solution at least as deep as your plate's solvent front. Compounds on your plate that can be oxidized will slowly change color as the purple permanganate is reduced to a yellow-brown manganese (IV) oxide species.
    - Allow your plate to dry on a watch glass or a paper towel. Do not set it down directly on the bench. Do not touch it with your bare fingers. It can chemically react with your skin the same way it reacts with the organic compounds on your plate.

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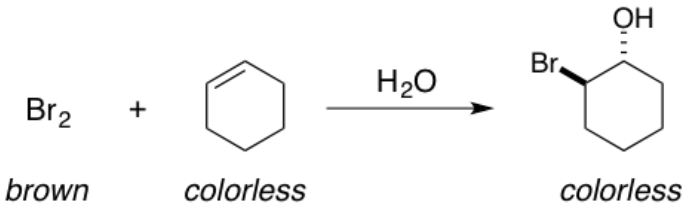
7. Record in your notebook any data needed for your report: spots and solvent front distances, and a sketch of your developed and stained TLC plate. Also, take a picture of your plate so it can be included in your notebook submission at the end of the lab. Once you have recorded your results (and taken a picture), throw the plate into the red solid waste trash. Don't take your TLC plate home.

Note: The vibrant colors of the plate will fade making any interpretation of the plate impossible if not done immediately.

Part 3. Functional Group Test: Bromine Test for the Presence of Alkene

Chemical tests (chemical transformations that are indicative of a particular function group) are sometimes used to verify the presence of a specific functional group in organic compounds. The bromine test is a common test used to confirm the presence of an alkene functional group. Reacting an alkene-containing compound with bromine (Br_2) in water will rapidly and efficiently generate the *trans*-bromohydrin (bromohydrin formation for cyclohexene is shown below). Since bromine is orange-brown in water and the bromohydrin is colorless, the reaction of an organic compound with a Br_2-H_2O mixture resulting in bleaching of the initial orange-brown color indicatives the presence of one (or more) alkene functional groups. If no alkene is present, the molecular bromine will not be consumed, and the brown color will remain.



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Important: Safety Pause

CAUTION – CORROSIVE: Take great care to not come into contact with the bromine. Bromine causes severe skin burns and should be treated with glycerin immediately upon contact with skin. Identify the location of the glycerin in your lab before proceeding. If your skin comes in contact with bromine water, you need to immediately go to the sink and begin rinsing. Ask your TA to bring you glycerin to generously coat onto your skin and then continue to rinse.

Safety Pause

Procedure: Place a small amount (0.5 to 1 mL) of the product into a test tube. Set the test tube into a 125-mL Erlenmeyer flask (see Figure 3). Bring your test tube, nestled in an Erlenmeyer flask, to the bromine testing station and **your instructor will add a few milliliters of aqueous Br_2 solution.** Remove the test tube and carefully swirl the contents to mix. Record your observations about the appearances of your product, Br_2 solution, and the test tube contents after the test is complete.

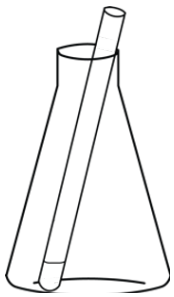

Figure 3. Bromine water test setup

Part 4. Obtaining an IR Spectrum of the Product and Mass

Follow your instructor's directions for acquiring an IR spectrum of your product.

Part 5. Preparation for the Next Lab: Grignard Reaction

It is good practice to always put glassware away clean. Grignard reactions are sensitive to water and so glassware cannot be washed during the next activity as needed. Make sure the following pieces of glassware are cleaned with water **and then acetone (or ethanol) before** you leave today. Check both your drawer and your partner's drawer in case the first Grignard you set up fails to initiate. In that case you will need a second set of clean pieces!

- Condenser
- Claisen adapter
- 250-mL round-bottom flask
- 125-mL separatory funnel/dropping funnel
- Drying tube – If it is filled and the solid is not loose, you will need to rinse it out with warm water and leave it empty to dry until next week. It is almost certain it will not rattle. Check with your instructor if you are unsure.
- Thermometer adapter – removed from your thermometer and cleaned

Clean-Up and Waste Disposal

Activity 6 Specific Cleanup

- **Organic Liquid Waste:**
  - TLC Eluent
  - Acetone or ethanol rinse from TLC chamber
- **Aqueous Waste:**
  - Excess phosphoric acid, sodium carbonate, and sodium chloride solution
    - Note that most phosphoric acid should already be neutralized
  - Aqueous (water) rinses from these chemicals' glassware
  - Contents from the 100 mL RBF after distillation is finished
  - Aqueous layer from the separatory funnel
- **Special Cyclohexene Waste:**
  - Cyclohexene product
  - Excess cyclohexanol starting material
  - Products from bromine test
  - Acetone or ethanol rinses from all of this glassware (the 50 mL RBF, separatory funnel, and the 25 mL Erlenmeyer flask)
- **Solid Waste (Red Can):**
  - Used gloves
  - Used TLC plates
  - Solid sodium sulfate
  - Boiling stones
- Ask your instructor if you are in charge of cleaning up the IR area:
  - No dirty glassware or solids or liquids should be left in the area. Dispose of any waste according to directions above or instructor guidance.
  - No used Kleenex® or plastic pipets- these should be disposed of in IR waste container by the instrument.
  - Make sure that no sample is left on the IR crystal- clean the dirty crystal with Kleenex and isopropyl alcohol.

Activity 6: Procedure

Routine Cleanup

- Clean up your hood space of all trash, spilled chemicals, etc. Don't leave a mess for the people who share this hood at other time slots. Up to 24 other people are sharing this space at various time slots throughout the week. Clean up your mess!
- No dirty or clean glassware should be left in the sink. No used filter paper or wadded up dirty paper towels should be left in the sink.
- **Dirty paper towels go into the REGULAR TRASH,** not the red solid waste trash. This saves the university a lot of waste disposal money!
- Dispose of dirty filter paper in the red solid waste container.
  - Do **NOT** deposit filter paper in the liquid waste eco-funnel as this will cause a clog which will lead to a messy overflow of waste.
  - Do **NOT** leave filter paper in the sink as this is poor lab etiquette and rude.
- Used gloves should be disposed of into the red solid waste.
- **Ask your instructor if you are in charge of cleaning up the balance area** for this week. If you are in charge, do the following:
  - Be sure all reagent bottles are properly capped.
  - Use the small brush to clean off balances.
  - Use small broom and dustpan (located on the wall surrounding the balance area) to remove excess solid from counter. Dispose of excess solids in red solid waste container. Return broom and dustpan to proper location.
  - Wipe down the counter with a moist paper towel.
- **Ask your instructor if you are in charge of making sure the sink area is presentable** for the next lab group.
  - Wash any dirty glassware that was rudely left in the sink. Let clean glassware air dry on rack or window sill area.
  - Dispose of any paper towels, filter paper, or cotton that was rudely left in the sink.
  - **Do not remove broken glass from the drain or the sink**. Rather, tell your instructor and then fill out a "something wrong form" located in the

cabinet above the solid waste containers. Be sure to record room number and the left/right location of the sink.

- All neutralized aqueous solutions can be disposed down the sink with a lot of running water.

Post-Lab Assignment

The Activity 6 Post-Lab Assessment is posted on Labflow and is due before the deadline posted on Labflow.