

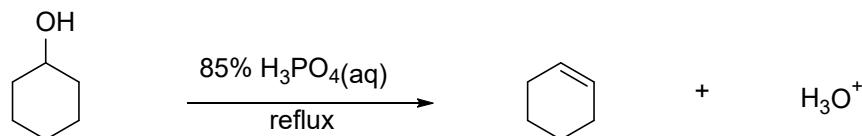
Synthesis of Cyclohexene via Dehydration of Cyclohexanol

Your first formal report will be for this experiment. See the last page of this handout for more information. The general approach towards carrying out an organic reaction:

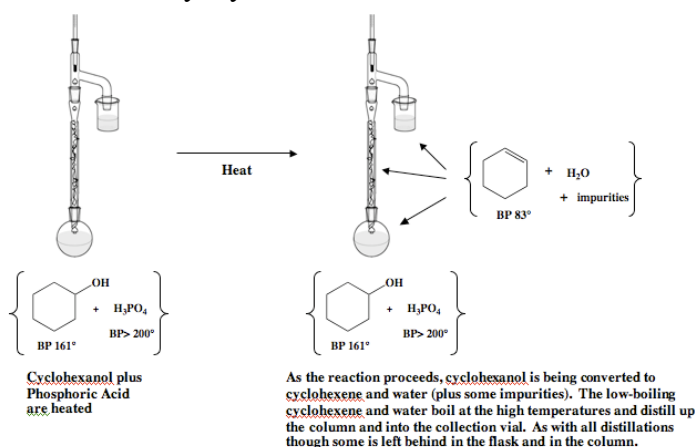
- (1) Write out the balanced reaction, using structural formulas.
- (2) Construct a table of relevant information for reactants and products: e.g., MPs, BPs, MWs, densities, hazardous properties.
- (3) Calculate the correct molar ratios of reactants. Convert moles to grams and milliliters.
- (4) Mix correct amounts of reactants, solvents, catalysts in correct order to give specific concentrations. Possibly heat or cool or irradiate with UV light, allow to react for necessary amount of time, possibly follow reaction progress using chromatography (e.g., TLC, GC) or spectroscopy (e.g., IR, NMR).
- (5) After reaction is complete, the reaction mixture is usually a complex mixture of desired product(s), byproducts, unreacted starting materials, solvents, and catalyst. Product may be light, heat, or air (O₂) sensitive.
- (6) Separation and purification steps (so-called reaction work-up). Some combination of extractions, distillations, recrystallizations, chromatography, etc. are used for the work-up.
- (7) Identify product(s) using spectroscopy (IR, NMR, etc.), chromatography (GC, TLC, etc.), physical properties (MP, BP, etc.), and occasionally chemical tests.

Background Information for the Synthesis of Cyclohexene: In the presence of a strong acid, with the addition of heat, an alcohol can be dehydrated to form an alkene (figure 1). The acid used in this experiment is 85% phosphoric acid and the alcohol is cyclohexanol. The phosphoric acid is a catalyst and as such increases the rate of reaction but does not affect the overall stoichiometry. It can be seen from the balanced reaction that 1 mole of alcohol produces 1 mole of alkene (this information is useful for percent/theoretical yield calculations).

Figure 1. The acid-catalyzed dehydration of cyclohexanol with phosphoric acid.



General Approach: The reaction is carried out in a fractional distillation apparatus. As the alcohol and acid are heated, alkene and water are produced and co-distill into an ice-cooled collection vessel. If the distillation is controlled, slow and steady, cyclohexanol will not co-distill.



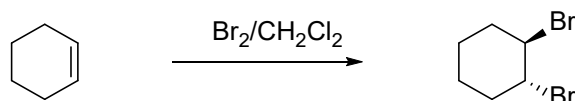
After reaction completion, the collection vial will contain cyclohexene, water, and small amounts of other impurities. This is where the reaction is “worked-up” to obtain the product. This work-up is accomplished by washing the organic species with water, extracting (organic layer) with 1M NaOH, washing (organic layer) with brine (saturated salt water) and drying (organic layer) over calcium chloride (CaCl₂).

Anhydrous CaCl₂ is an inorganic drying agent that binds strongly with water and thus removes any traces of water from the solution. After about five minutes, the solution is separated from the pellets and transferred to a clean, dry tared vial.

You will then analyze the dried product via gas chromatography (GC), infrared red (IR) spectroscopy, perform a chemical analysis to test the presence of an alkene, and calculate a % yield.

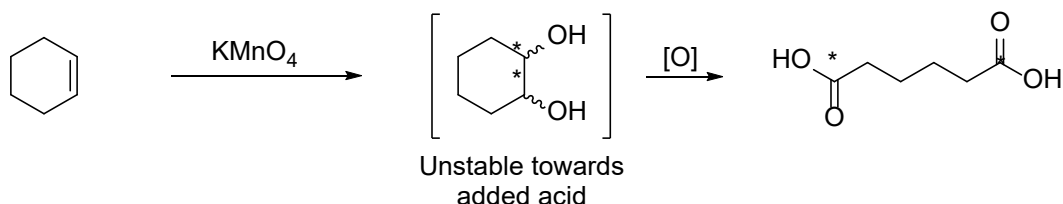
Chemical Tests: The presence of an alkene can be identified by carrying out simple reactions in which a color change can be observed. One such reaction is with bromine (Br₂) in dichloromethane (CH₂Cl₂). The bromine reagent is a reddish-orange color. When it is dripped slowly into a sample of alkene, the bromine reacts with the alkene to form a nearly colorless organic 1,2-dibromide. Because the Br₂ is consumed, the mixture loses the reddish-orange color. If a sample decolorizes bromine under these conditions it can be inferred that an alkene functional group is likely present.

Figure 2. The reaction of an alkene with bromine to yield a trans-1,2-dibrominated product.



A second color test is the reaction with potassium permanganate (KMnO₄). An alkene reacts with the purple-colored KMnO₄ to form a colorless 1,2-diol. Under acidic conditions, the diol reacts further to form a mixture of colorless carboxylic acids, or in the case of a cyclic alkene, a dicarboxylic acid. As the permanganate is consumed, the mixture loses its deep purple color. At the same time, manganese dioxide, a brown precipitate, forms. If a sample decolorizes permanganate and forms a brown precipitate it can be inferred that an alkene functional group is present.

Figure 3. The oxidation of a cyclic alkene to a dicarboxylic acid/



The Prelab:

This is your first synthesis experiment. As such, you now need a reagent table. Your table of reagents (ToR) should always include molar equivalents of any non-solvent or non-catalytic species. Make it look like the table below. A hyphen indicates that data is not needed for that substance (e.g., density of a solid is typically not needed). This table isn't complete. Don't forget to include hazards and any other relevant chemical properties.

Substance	mmol	MW (g*mol ⁻¹)	Density (g*ml ⁻¹)	Mol eq	amount
cyclohexanol					
H ₃ PO ₄	-	-	-	-	

Prelab: You may either print out your prelab and bring it with you to lab, or bring your computer. Your TA will grade it on the spot before you begin the experiment. For the in lab observations, you may use scratch paper and record later in your ELN, or bring your computer and record directly in your ELN.

Postlab Report: Make sure to use the Formal postlab report template on the course website!

Experimental Procedure (rev. 4/2020)

The "Things to Watch Out for In Distillations" listed for the distillation experiment are common to this distillation as well. Review them carefully. As always, use care when inserting the thermometer into the thermometer adaptor. Hold the thermometer close to the adaptor and push and twist gently away from you. Breakage could result in a serious injury. Check for frayed connectors and cracked flasks. Cyclohexene has a disagreeable odor, characteristic of volatile alkenes. Allow the apparatus to cool before disassembling it **in the fume hood**, and dispose of waste in the hood in the ORGANIC LIQUID WASTE CONTAINER. Rinse the apparatus in the waste hood with a SMALL AMOUNT of acetone and dispose of that in the ORGANIC LIQUID WASTE CONTAINER.

CAUTION: cyclohexene is very flammable. Handle phosphoric acid with care. It is corrosive to tissue. If your skin comes into contact with phosphoric acid, wash the contaminated area immediately with water, then soap and water. Clean up acid spills immediately using the sodium bicarbonate in the hood.

Prepare a flow diagram including all steps in the reaction, work-up, and identification. Prepare a table of reagents, products, and byproducts. (Sample of each on Chem 269 website – handouts page.)

Preparation and set-up:

- As always, turn on the hot plate (~225 °C) and be careful as the aluminum block gets hot.
- In this experiment, the phosphoric acid need not be measured very accurately. However, the amount of cyclohexanol determines the theoretical amount of product so it must be measured accurately.
- Place the round-bottomed (rb) flask into a 30 mL beaker to hold it upright
- Set this onto the balance and press zero (this will set the weight of the container to zero – this is called taring)
- Measure in about 2.0 g (± 0.05 g, but weigh it exactly, e.g., 1.964 g or 2.033 g) of cyclohexanol by dropping it in the rb flask with a pipet.
- Add about 0.5 mL of 85% phosphoric acid to the rb flask directly from the buret in the supply hood. Note that the rb flask becomes warm as the addition of acid to alcohol is exothermic.
- Set up a fractional distillation apparatus in the same way as in the distillation experiment. Remember to add boiling chips.
- Use the black plastic connector to connect the flask to the distillation column. This is more resistant to the reactants and heat than the beige connector.
- Be sure that the receiver vial is well immersed in the beaker of ice. If the vial is not cold enough, the product may evaporate and the odor is that of potent gasoline.

Heating and distillation:

- Heat the mixture sufficiently to allow the reaction to take place. The products take some time to form before they begin to distill over into the collection vial. Distill at the usual rate of one drop per 20-30 seconds (if liquid is not collecting in the vial within about 20 minutes, something is wrong; check with your TA).

- b. Do not count the drops like last time, but be sure to note the temperature range over which distillate is collected (what is the BP of cyclohexene?).
- c. Continue collecting until most of the liquid has distilled (about 10% of the initial volume). Lift the apparatus out of its hole in the aluminum block and allow it to cool before cleaning.
- d. There should be two phases (layers) of liquid in the collection vial. Water, one of the products, is insoluble in cyclohexene so forms a second layer. The density of water is greater than that of cyclohexene so the water layer would be expected to form the lower layer. This may not be obvious for two reasons:
 - a. on this small scale of reaction, there is such a small amount of water formed that it may simply cause the liquid to appear cloudy at first and not form a second layer immediately;
 - b. water tends to adhere to glass (polar to polar) so instead of actually forming a second lower layer, it may just appear as small droplets sticking to the side of the vial.

Reaction Work-Up:

- a. Pipet the contents of the vial into a test tube. At this point, water and small amounts of other impurities are mixed in with the cyclohexene product. Water will interfere with IR and GC analysis so it must be removed completely.
- b. Add water (~ 1 mL) to the test tube. Mix the two layers thoroughly by drawing some of the lower up into the pipet and expelling it back through the solution repeatedly for a couple of minutes. This procedure is called washing. Remove the lower aqueous layer and place in a waste beaker.
- c. Add 1 mL of 1 M sodium hydroxide (NaOH) to the tube and mix thoroughly as was done with the water wash. It is important to mix the layers thoroughly (think Italian dressing mixing thoroughness). Remove the lower aqueous layer and place in the beaker you marked for waste.
- d. Add brine (saturated aqueous sodium chloride, ~ 1-2 mL) to the tube and mix thoroughly as was done with the water wash. It is important to mix the layers thoroughly. Washing with brine is a pre-drying step that removes most of the water from the organic phase. Remove the lower aqueous layer and place in the beaker you marked for waste.
- e. Using a clean dry pipet, transfer the organic layer to a clean dry vial. There should be no droplets of water present at this point.
- f. Add several spheres of CaCl₂, cap and gently swirl the contents well. DO NOT STIR or CRUSH the spheres with a utensil. If the spheres lose their shape and clump together, this means they are absorbing water. Add a few more and again gently swirl. Repeat this process until the newly added spheres no longer clump together.
- g. If all the visible droplets of water were not completely removed first, instead of clumping together, the first few spheres of drying agent will break apart and form a cloudy looking mass (layer) at the bottom of the vial. In such a case, carefully pipet the contents to another clean dry vial, leaving behind the cloudy layer. Set the capped vial into a small beaker for safe keeping and allow the solution to dry for at least five minutes. Transfer the dried product to a clean, dry tared vial and obtain/record the mass and calculate a percent yield (review general chemistry if needed).
- h. Sign up for GC/IR analysis, then continue cleaning your equipment until you are called to carry out the GC/IR analysis – do not waste time waiting in line.
- i. Perform the chemical tests as described below.

Calculate the % yield and show your calculations in your ELN. Make sure to include these calculations in your post-lab report.

The results and discussion section of your formal report should include, but is not limited to: a discussion on the purity of your product (GC) and what the IR does, or does not, tell you, and a discussion of the percent yield.

WASTE DISPOSAL: Dispose of all liquid wastes in the organic liquid waste container in the hood. Save the copper wire and sponge, and aluminum foil (if used) for future use.

Chemical Tests to Distinguish Alkenes from Alkanes:

Often, simple chemical reactions can be used to detect the presence of a functional group. Here, you will carry out two such reactions. Run the test reactions on your product and cyclohexane. Do these tests side-by-side to observe the results of a negative test. If you have an insufficient amount of product, scale down quantities by a factor of two, for example.

Bromine in Dichloromethane. Caution: bromine is extremely hazardous to breathe and causes severe burns if it touches the skin.

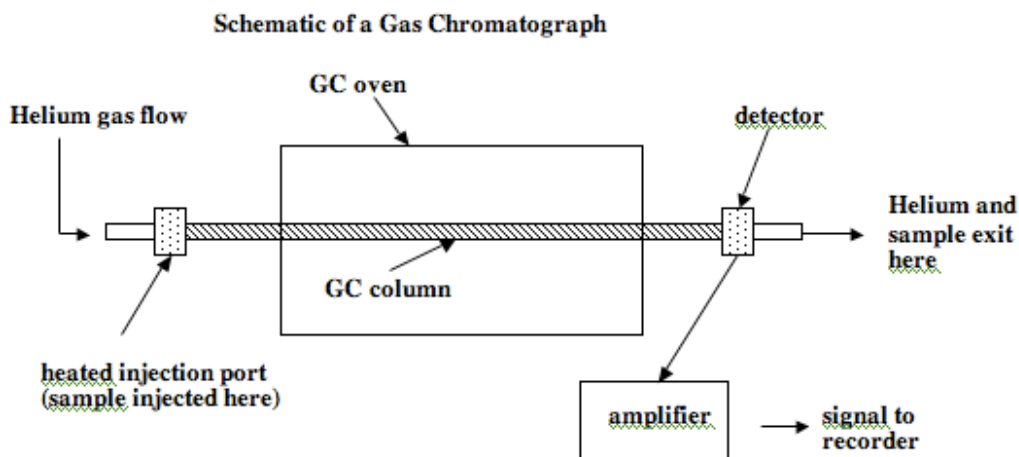
- a. A dilute bromine solution in dichloromethane is used in this test so the hazard potential is much less than if pure bromine were used. The solvent, dichloromethane, is also toxic and must be kept in the hood. If you accidentally allow the bromine solution to touch your skin, immediately rinse the contaminated area with a dilute aqueous sodium thiosulfate solution, which will be stored near the bromine in the hood, then wash with soap and water. Carry out all operations with bromine in the fume hood.
- b. The bromine solution is reddish-orange. Bromine reacts with an alkene to form a colorless dibromide. Thus, if a bromine solution is added dropwise to an alkene, the solution will decolorize until all of the alkene has reacted. Alkanes, on the other hand, do not react with bromine in this way, so the very first drop of bromine solution will cause the reddish-orange color to persist. (Alkanes do react with bromine by a free radical mechanism initiated by light, but this reaction is much slower.)
- c. The test:
 - a. in the hood, add about 0.5 mL of your cyclohexene product to a small test tube and about 0.5 mL of cyclohexane to another small test tube.
 - b. To each, add dropwise, with swirling, 3-4 drops of a 3% solution of bromine in dichloromethane.
 - c. Record any observed color changes after addition of each drop. Dispose of all waste from this test in the Organic Liquid Waste container.

Potassium Permanganate.

- a. Potassium permanganate is purple. It reacts with alkenes to produce a colorless diol and a finely-divided brown precipitate of manganese dioxide. Under acidic conditions, the diol can further react to form a colorless dicarboxylic acid. Thus, when permanganate is added dropwise to an alkene, the purple color disappears and a brownish suspension forms until all of the alkene has reacted. Permanganate does not react with alkanes, so the first drop of permanganate added to an alkane immediately results in a purple solution.
- b. The test:
 - a. add about 0.3 mL of your product cyclohexene to a small test tube and about 0.3 mL of cyclohexane to another small tube.
 - b. To each, add dropwise, with swirling, 2-3 drops of an aqueous solution containing 1% potassium permanganate and 10% sulfuric acid.
 - c. Record any observed changes after addition of each drop. Dispose of waste from this test in the Organic Liquid Waste container in the hood.

BEFORE YOU LEAVE THE LAB: turn off the hot plate, put away your equipment, clean up your work areas, close the fume hood sash completely, and ask your TA for their signature. In general, please try to keep the lab in as good condition as you found it. If you see caps off of bottles, replace the caps. If you see spilled chemicals, clean them up or at least report the spill to your TA.

Gas Chromatography (GC)

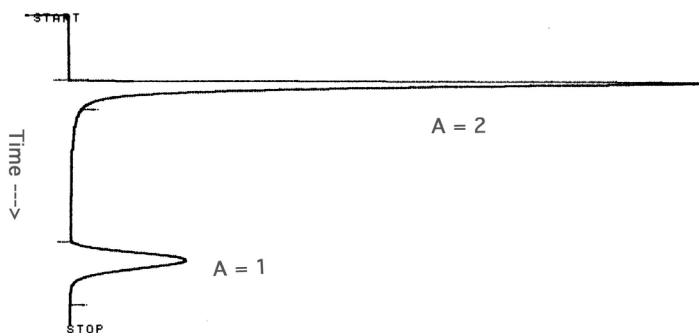


A very small sample ($\sim 0.2 \mu\text{l} = 0.0002 \text{ ml}$) is injected into the hot injector port.

The liquid vaporizes, helium pushes the plug of sample vapor through the thermostated column.

The lower-boiling liquid passes through more quickly than the higher-boiling liquid. As the vapor reaches the detector, a signal is sent to the amplifier and a recorder draws the chromatogram.

GC Example 1. The following GC trace is that of a mixture of a lower-boiling and higher-boiling liquid compound in a ratio of 2:1. You will do only one injection; your sample from the distillation.



The injection point is at the “start” at the top of the chromatogram. The peak labeled “A = 2” is due to the low-boiling liquid which reaches the detector first. The peak labeled “A = 1” is due to the high-boiling liquid which reaches the detector later.

The time between “start” and when the peak appears is known as the retention time.

The area of the peak, not the height, is proportional to the relative amounts of species 1 and species 2. (Area on the chromatogram refers to area)

In our lab, the relative areas are reported by an electronic integrator.

This chromatogram would look similar to the chromatogram of a mixture of 2 parts cyclohexene to 1 part toluene.

Factors affecting separation in GC:

- Column Material: chosen for compounds being separated. Our column in this experiment is called 'Carbowax' and is a polymer of polyethylene glycol.
- Column Length: the longer the column, the longer the compounds take to go through, resulting in a potentially better separation.
- Column Temperature: higher temperature, shorter retention time. Lower temperature, longer retention time. A longer retention time may lead to a better separation.
- Helium Flow Rate: higher flow rate, shorter retention time. Lower flow rate, longer retention time.

In practice, the column material and length are chosen to work with a particular mixture of compounds. Fine tuning of the separation is done by adjusting the temperature and flow rate. For example, if a poor separation is observed (overlapping peaks), the column temperature could be lowered, which would result in a better separation.

Formal Report:

The chemical tests do not need to be included in the experimental procedure formal report. They should simply be mentioned that they were performed as they are common knowledge tests. They should have more of a presence in the table of results and the discussion section.

Your first formal report will be for this experiment. **Make sure to use the formal report template (it is a bit different than the non-formal template), downloadable on the course website.** There are handouts posted on the course website to aide you in writing all aspects of this report, but here is a quick look:

1. With all formal reports, write out a complete *experimental procedure* for the reaction using the example in the aforementioned handout as a template (e.g., “cyclohexanol (x.xx mL, x.xx mmol) was added to . . .” and not “x.xx mL of cyclohexanol was added to . . .”).
2. Be sure to include all aspects of the formal report (see handout).
3. Any calculations should be done in our ELN, and then copied and pasted in your post-lab report. These calculations should be referenced when necessary. Add them as a separate, last page to your report.
4. **Direct conversion to a pdf from a Word file for your formal reports may cause the file size to be too large to submit to Gradescope. If this happens, see the Gradescope tutorial here: <https://www.gradescope.com/help#help-center-item-student-scanning>**

Postlab Questions:

- 1) Draw the structure of only the Zaitsev product that would be obtained from the dehydration of 1-methylcyclohexanol.
- 2) Write out a detailed mechanism of the acid catalyzed dehydration of cyclohexanol. Use only hydronium as your acid source.

- 3) With respect to GC, what effect would raising the column temperature have on the retention time?
- 4) What would happen if you spiked your sample with a small amount of known cyclohexene and re-ran the GC?