

Chem 26Z. Cyclohexene. (revised 7/10).

In this experiment you will synthesize cyclohexene and purify it by distillation. You will check the purity and identity of the product by gas chromatography (GC) and infrared spectroscopy (IR). You will also do some simple chemical tests which distinguish alkenes from alkanes. Review the chapter on distillation and your notes from the distillation experiment. The "Things to Watch Out For in Distillations" listed for the distillation experiment are common to this distillation as well. As always, use care when inserting the thermometer into the thermometer adaptor. Hold the thermometer close to the adaptor and push and twist gently. 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 hood**, and dispose of the wastes in the hood in the PROPER CONTAINERS (see below). Rinse the apparatus with a LITTLE acetone and dispose of that in the Nonhalogenated 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 spills immediately using the sodium bicarbonate in the hood.

Do the Prelab Exercise on p. 334 (a model of a flow sheet is on p. 142). This is something to do for all synthesis experiments. Also always prepare a table of reactants and products such as that shown in the handout, "Sample Notebook and Report".

Preparation of Cyclohexene. As always, if a sand bath is needed, turn it on and set it to about 35 immediately. 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. To measure the reagents do the following: Place the round-bottomed (RB) flask into a 30 mL beaker to hold it upright, tare the beaker and flask, and weigh in about 2.0 g (± 0.05 g, but weigh it exactly, e.g., 1.96 g) of cyclohexanol by dropping it in with a pipet. Using a buret in the hood, add about 0.5 mL of 85% phosphoric acid to the RB flask. Note that the flask becomes warm - addition of acid to alcohol is exothermic. Set up the fractional distillation apparatus exactly as for the distillation experiment, not as that shown in Fig. 19.1 (don't forget a couple of boiling chips). Be sure to use the **distillation** column, **not the longer chromatography** column - the chromatography column does not connect tightly. Use the black plastic connector to connect the flask to the distilling head. This is more resistant to the reactants than is the white connector. Insulate the column by loosely wrapping it with a piece of aluminum foil (not glass wool or cotton). Use an ice-cooled receiver. Otherwise product will evaporate (result: lower yield and increased stench in room).

Heat the mixture sufficiently to distill product over into the collection vial (remember to lower the distilling flask into a slight depression in the sand. This allows for better heating control.) Unlike in a normal distillation this first distillation can and should be done fairly rapidly, not at the usual rate of one drop per 20-30 seconds, but instead at a rate of about one drop per second or two. Note the temperature range over which distillate is collected. Continue distilling until distillation slows dramatically and most of the liquid has distilled (there will be 0.5 - 1 mL of liquid remaining in the flask). Lift the apparatus out of the hot sand and allow it to cool for a couple of minutes. At this point, most of the product mixture has been collected in the collection vial. Note that there are two phases (layers) of liquid in the vial. Water, being one of the products, is insoluble in cyclohexene so forms a second layer. Having a density greater than that of cyclohexene, the water will be the lower layer (on such a small scale however, the water droplets may just stick to the sides of the vial and not form a separate lower layer). If one were to stop at this point, a significant amount of product would be left behind in the distilling apparatus (holdup) and the yield of product would suffer. A method to ensure that all desired product distills is to add a higher boiling liquid (chaser) to the distilling flask and to then continue the distillation. To add chaser, slide the sand bath to one side so that the chaser, if spilled, will not fall into the hot sand. Measure about 2 mL of toluene into a 10 mL graduated cylinder, carefully remove the thermometer and adaptor, and pipet the toluene onto the top of the copper-packed column. The toluene will drip down into the RB flask. Replace the thermometer and continue the distillation. Shortly afterward, after all remaining product has distilled, the temperature will rise. After the temperature has reached about 90° continue distilling until a further 25 drops (about 1

mL) of toluene has been collected, then lift the apparatus up from the hot sand to stop the distillation and allow the flask to cool. Remove the vial and cap it. For safe keeping place it into a small beaker.

Pipet the contents of the vial into a reaction tube. To minimize loss of product rinse the vial with a small amount (< 10 drops) of fresh toluene and pipet this into the reaction tube. Rinsing in this way is a general technique used to minimize loss of product and should be used whenever a material is being transferred from one container to another (call it a transfer rinse). At this point, water, toluene, and small amounts of other impurities are mixed in with the cyclohexene product. Water will interfere with the final distillation so it must be removed completely. To do this first wash (extract) with saturated sodium chloride solution, the volume being about equal to the volume of liquid already in the tube. Mix the two layers thoroughly by drawing liquid up into the pipet and expelling it back through the solution repeatedly for a couple of minutes. Washing with saturated sodium chloride solution is a pre-drying step that removes most of the water from the organic phase. Separate the aqueous layer and temporarily place it into another container. Using a clean dry pipet transfer the organic layer to a clean dry vial leaving behind any water droplets (do a transfer rinse using a few drops of toluene). Add several spheres of calcium chloride drying agent to the vial, cap the vial, and swirl the contents. Continue adding small amounts of calcium chloride until the newly added spheres no longer clump together. The danger of adding too much drying agent is that it absorbs the product and can lead to its loss. Set the capped vial into a small beaker for safe keeping and allow the solution to dry for at least five minutes. During this time the fractional distillation apparatus should be cleaned and dried thoroughly.

Water has been carefully removed from the organic product mixture, so it is important to not reintroduce any water to the mixture. To obtain pure product, the final distillation must be done carefully using clean, dry equipment. Rinse the apparatus first with water, then a little ethanol and then a little acetone to speed up the drying process. Air may be blown gently through and over the apparatus in the hood to evaporate the solvents. The column may be more effectively dried by drawing air through it using an aspirator. It is essential to remove all water and organic solvents before the final distillation. It is however not necessary to FILL the glassware with cleaning solvent. This would be extremely wasteful.

A final fractional distillation must now be done carefully to separate the chaser and any small amounts of other impurities from the product. Pipet the organic product mixture into the 5 mL RB flask, leaving the calcium chloride behind (do another transfer rinse) and distill the mixture carefully through the fractionating column. This fractional distillation is essentially the same as that of cyclohexane and toluene that you did previously. This time however you will collect the cyclohexene as a pure fraction in a clean, dry, tared vial. You need not count drops of distillate. What is most important is changing receiving vials at the right moment.

In a distillation such as this, the idea is to separate lower-boiling and higher-boiling impurities from the desired product. To do this, do not collect distillate as product until the thermometer reaches the BP of the product (\pm about 3° C). That is, first have an "impurities" vial attached to the apparatus to collect low-boiling impurities (if any). To make changing vials easier it is not necessary to cool the "impurities" vial in ice. When the temperature of distillate closely approaches the BP of product, replace the "impurities" receiving vial with a clean, dry, tared "product" vial. Collect distillate as product while the temperature remains at the BP of product (\pm a few ° C) (now you should cool the receiving vial in ice). Once the temperature rises steeply above the BP plateau of the product, replace the vial with the "impurities" vial once again to collect any higher-boiling distillate, then stop the distillation by lifting the apparatus away from the heat. Cap the product vial to prevent evaporation. Note that the temperature may fluctuate by a few degrees during collection of the product - this is okay. As an example look at Fig 5.8. In the fractional distillation, cyclohexane would be collected in vial 1 from 0-1.5 mL (BP 81). Once the temperature rises steeply after 1.5 mL, pure cyclohexane is no longer distilling. Material between 1.5 and 3 mL (BP 81-110) is a mixture of cyclohexane and toluene. Note that once product is collected, unlike in the distillation of cyclohexane and toluene in the previous experiment, it is not necessary to distill and collect toluene. The toluene was simply used to help minimize loss of product.

At this point the product should be clear (clear as opposed to cloudy - clear does not mean colorless). If the product is cloudy, it is still wet with water. If so add more calcium chloride until the product is dry.

Determine and interpret the infrared spectrum and analyze the product by GC. Based on the actual purity of product as shown by GC, calculate the % yield. Demonstrate the presence of the alkene functional group by testing your product with bromine and permanganate as described below.

WASTE DISPOSAL: Dispose of the aqueous, acidic reaction waste (first distillation residue) and sodium chloride wash solution in the hood in the container labeled "Aqueous Acidic Solutions". Please do not place any organic solvents, including acetone and ethanol rinses, into the Acidic Waste container. ALL rinses and other liquid waste from the distillations should be placed in the Nonhalogenated Liquid Waste container. SAVE THE COPPER WIRE, COPPER SPONGE, AND ALUMINUM FOIL 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 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.

(1) Bromine in Dichloromethane. Caution; bromine is extremely hazardous to breathe and causes severe burns if it touches the skin. A dilute bromine solution 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 hood.

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 a reddish-orange color to persist. (Alkanes do react with bromine by a free radical mechanism initiated by light, but this reaction is much slower.)

The test: 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. To each, add dropwise, with swirling, 3 - 4 drops of a 3% solution of bromine in dichloromethane. Record any observed color changes after addition of each drop. Dispose of all wastes from this test in the Halogenated Liquid Waste container.

(2) Potassium Permanganate. 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.

The test: 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. To each, add dropwise, with swirling, 2 - 3 drops of an aqueous solution containing 1% potassium permanganate and 10% sulfuric acid. Record any observed changes after addition of each drop. Place the waste from this test into the "Permanganate Waste" container in the hood.

Postlab Questions

1.) Draw the structures of all possible products that would result from the dehydration of 1,2-dimethyl-1-cyclohexanol. Which would predominate? Which would be found in the least amount?

2.) Mixing cyclohexanol with phosphoric acid is an exothermic process. The overall reaction from cyclohexanol to cyclohexene is endothermic. Using your chemical knowledge and referring to the chemical reactions on p. 335 of Williamson, construct an energy diagram showing the course of the reaction. Label

the diagram with the starting alcohol, the oxonium ion (protonated alcohol), the carbocation, and the product.

3.) In gas chromatography, if two peaks have very similar retention times and thus overlap, without changing the GC column, what two changes could be made to possibly improve the separation?

4.) In the final fractional distillation of cyclohexene and toluene, draw a predicted GC of a sample collected at 84°, just as the temperature begins to rise. Draw a predicted GC of a sample taken at 96° and one taken at 110°, just before the temperature levels off. (For the purposes of this question, you can use the fractional distillation curve in Fig. 5.8.)

5.) Draw the structure of the product from the reaction of cyclohexene plus bromine. Show stereochemistry clearly.

6.) Give two reasons why the Halogenated Waste container is used in the bromine test.