Experiment #4: Preparation and Distillation of Cyclohexene

Pre-Lab Preparation

1. Study the technique sections in your lab manual regarding clamps, boiling, distillation, extraction, drying agents, and infrared spectroscopy.
2. Carry out pre-lab preparations as described in Chapter 11, section 11.6A, or as called for by your instructor.

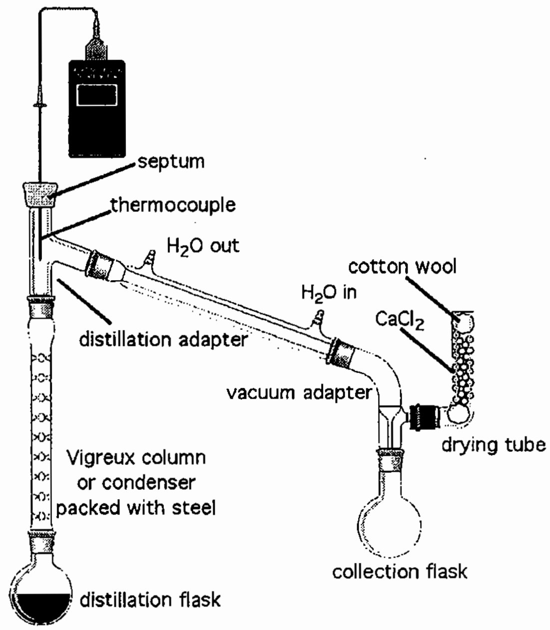
Experimental Procedure

> SAFETY PRECAUTIONS: Phosphoric acid, while safer than sulfuric acid, is corrosive. Avoid contact, and clean up any spills immediately. Cyclohexanol does not appear to present any unusual safety hazards. Cyclohexene is flammable and has a disagreeable odor.

Reaction

1. To a 50 mL round-bottom flask containing a magnetic stir bar (or boiling stone), add 0.074 moles of cyclohexanol and 1.75 mL of 85% H_3PO_4. Use gentle swirling to mix the two layers.
2. Fit the flask with a fractionating column, a distillation adapter, a thermocouple (or thermometer), a condenser, and a vacuum adapter as for fractional distillation (see illustration). A rubber septum should be used to provide a seal between the thermocouple or thermometer and the glassware. Be sure that the seal is good – if it is not, cyclohexene will escape from your glassware, causing your experiment to fail, and those of your classmates who find the odor of cyclohexene objectionable

will complain loudly! A drying tube, as shown in the illustration, can help to control the disagreeable odor of cyclohexene.



Apparatus for dehydration of cyclohexanol

3. Heat the reaction mixture first at a *gentle* reflux for about 5 minutes, then heat the flask more strongly in order to distill the mixture into the collection flask. Keep distilling until the volume remaining in the distillation flask has been reduced to approximately 1 mL.

Workup

4. Transfer the distillate to a separatory funnel and wash with approximately 5 mL of water. Carefully separate the layers and transfer the organic layer into a small, dry Erlenmeyer flask. If any water droplets are visible, remove them before adding the drying agent (sodium sulfate). Add a small amount of anhydrous sodium sulfate to the flask. Let the mixture stand for 5 minutes, occasionally swirling it gently. If the drying agent completely clumps together, its capacity to remove water has been exceeded and a little more sodium sulfate should be added. If you have successfully removed the water, the liquid should be clear, and at least a little of the drying agent should remain free flowing.

5. Decant or pipette the organic liquid away from the drying agent and place it in a clean, dry round-bottom flask. This will be the distillation flask for the next step. The appropriate size depends upon your yield. The flask should be about half full at the beginning of the distillation.

Distillation

6. Fit the flask with a distillation adapter and condenser in preparation for a simple distillation. (The apparatus will look the same as that used for fractional distillation, except that there will be no Vigreux or other fractionating column.
7. Be sure that your thermometer or thermocouple is properly positioned in order to measure the temperature of the distilling liquid accurately (see the illustration above). Carefully distill the organic material, collecting the material that distills in the range of 80 – 90°C. Typically there will be very little material remaining in the distillation flask. Be sure to record the boiling range that you observe.

Characterization

8. Transfer the distilled cyclohexene to a clean, dry, pre-weighed sample vial and determine the mass of the product. If time permits record an infrared spectrum of the distilled product.

Storage

9. You will need the cyclohexene for Experiment 5 – Synthesis of Adipic Acid. Keep it in a well-sealed and suitably labeled sample vial until then.

Post-Lab Questions and Exercises

1. Describe the color and state of your purified product. Report the mass and percent of theoretical yield of the purified product.
2. What boiling point range did you observe during your (a) initial distillation and (b) your final distillation? How do you explain the difference between these, if there was one?

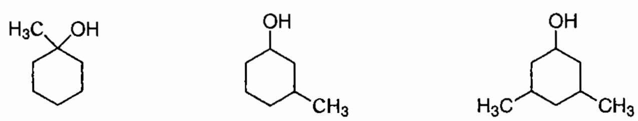
3. What role does phosphoric acid play in this reaction? Use both words and chemical equations to answer this question.

4. Attach your infrared spectrum (if you obtained one) and identify ("assign") the major peaks in the spectrum. If you did not have time to obtain your own spectrum, assign the major peaks in a spectrum obtained from your instructor.

5. Calculate the atom economy for the reaction.

6. Perform an economic analysis for the preparation of cyclohexene via this route.

7. Predict the dehydration product(s) for the following alcohols. Show all anticipated products.



Experiment Development Notes

This experiment is presented in many organic lab texts in various forms. Some use sulfuric acid as a catalyst; others call for the use of phosphoric acid. We use phosphoric acid as a greener reagent. This dehydration chemistry may be readily extended to other alcohols, as hinted at in post-lab exercise 7, and this offers an ideal opportunity for inquiry-driven investigation. (Naturally occurring terpene alcohols are particularly attractive substrates.) In many cases, mixtures of isomers may be anticipated, calling for the use of additional analytical tools to determine the outcome of the reaction. A later edition of this text will include experimental details for the dehydration of α-terpineol and gas chromatographic analysis of the resulting product mixture.