Synthesis and Reactions of Alkenes: Cyclohexene from Cyclohexanol
from K. L. Williamson, Macroscale and Microscale Organic Experiments, 2nd Ed. 1994, Houghton Mifflin, Boston d. p268; revised 10/10/98

Prelab Exercise
Prepare a detailed flow sheet for the preparation of cyclohexene, indicating at each step which layer contains the desired product.

Introduction

Dehydration of cyclohexanol to cyclohexene can be accomplished by pyrolysis of the cyclic secondary alcohol with an acid catalyst at a moderate temperature or by distillation over alumina or silica gel.

The procedure selected for this experiment involves catalysis by sulfuric acid. When a mixture of cyclohexanol and sulfuric acid is heated in a flask equipped with a fractionating column, the formation of water is soon evident. On further heating, the water and the cyclohexene formed distill together by the principle of steam distillation, and any high-boiling cyclohexanol that may volatilize is returned to the flask. However, after dehydration is complete and the bulk of the product has distilled, the column remains saturated with water-cyclohexene that merely refluxes and does not distill. Hence, for recovery of otherwise lost reaction product, a “chaser” solvent is added, and distillation is continued. A suitable chaser solvent is the water-immiscible, aromatic solvent toluene, boiling point 110°C; as it steam-distills, it carries over the more volatile cyclohexene. When the total water-insoluble layer is separated, dried, and redistilled through the dried column, the chaser again drives the cyclohexene from the column; the difference in boiling points is such that a sharp separation is possible. The column holdup (retention of distillate) in the metal sponge-packed column is so great that if a chaser solvent is not used in the procedure, the yield will be much lower.

The mechanism of this reaction involves initial rapid protonation of the hydroxyl group by the sulfuric acid. This is followed by loss of water to give the unstable secondary carbocation, which quickly loses a proton to water or the conjugate acid to give the alkene.

TLC
You are required to run a TLC to monitor the progress of the reaction. Plates should have three spots (or lanes) on the origin: one for the main organic starting material that is being transformed, one for a cospot (starting material and the reaction mixture), and one for the reaction mixture.

Procedure: Preparation of Cyclohexene
Add 0.3 mL of water into a 5-mL round bottomed long neck flask. To this, add 0.4 mL of concentrated sulfuric acid, followed by 2.0 g of cyclohexanol (note, this is 2.0 g not 2.0 mL), and a boiling chip. Add a small piece of stainless steel “ChoreBoy” to the neck of the flask, so that it remains in the neck. Put a cork on the top of the flask, and shake gently to mix the layers. Put your hand around the flask to feel the evolution of heat. Set up the arrangement for fractional distillation as shown in Figure below. Note that the bulb of the thermometer must be completely below the side arm of the distilling head. Wrap the fractionating column and distilling head with glass wool. Be sure to thoroughly insulate the apparatus to help speed up the distillation process. (See the experiment on fractional distillation in Ch 5 of the Lab Guide for details of this technique.)
Heat the mixture gently on the sand bath. Distill, collecting the distillate in a 20 mL vial. Distill until the liquid remaining in the distillation flask has a volume of about 0.5 to 1.0 mL and very little material is distilling; record the boiling temperature range. The reaction mixture will turn black and a small amount of black solid will start to form due to side reactions caused by the conc. H$_2$SO$_4$, but this is normal.

Let the assembly cool a little after removing it from the sand, remove the thermometer briefly, and add 2 mL of toluene (the chaser solvent) into the top of the column using a Pasteur pipette. Note the amount of the organic (upper) layer in the boiling flask and distill again until the volume of this layer has been reduced by about half. Transfer the contents of the vial into a reaction tube, and rinse with a little toluene. Use toluene for rinsing in subsequent operations.

Wash the toluene/product distillate with an equal volume of saturated sodium chloride solution, remove the aqueous layer, and then add sufficient anhydrous calcium chloride to the reaction tube so that it does not clump together. Shake the solution with the drying agent, and let it dry for at least 5 min. While this is taking place, clean the distilling apparatus first with water, then ethanol, and finally a little acetone. It is absolutely essential that the apparatus be completely dry; otherwise, the product will be contaminated with whatever solvent is left in the apparatus, so you should blow the flask out with a stream of nitrogen. Transfer the dry cyclohexene solution to the distilling flask, add a boiling chip, note the atmospheric pressure, and distill the product. At the moment the temperature starts to rise above the plateau at which the product distills (83°C), stop the distillation to avoid contamination of the cyclohexene with toluene. A typical yield of this volatile alkene is about 1 g. Report your yield in grams and your percentage yield. Gas chromatography is especially useful in the analysis of this compound because the expected impurities differ markedly in boiling point from the product.

**Analyses**

In addition to TLC analysis, you may be instructed to analyze your final product by IR, GC, or RI. Analyze your sample according to your Assignment sheet and the instructions on Sample Preparation in Lab Guide.

**Cleaning Up**

The aqueous solutions (pot residues and washes) should be diluted with water and neutralized before flushing down the drain. The ethanol wash and sodium chloride solution also can be flushed down the drain, while the acetone wash and all toluene-containing solutions should be placed in the organic solvents container. Once free of solvent, the sodium sulfate can be placed in the non hazardous solid waste container.

**Post Lab Questions**

1. Assign the peaks of the $^1$H NMR spectrum of cyclohexene below to specific groups of protons on the molecule.

2. What product(s) can be obtained by the dehydration of
   (a) 2-heptanol
   (b) 2-methyl-1-hexanol?

3. Write a detailed mechanism for the dehydration of cyclohexanol to cyclohexene.