Procedure

In the first week of the experiment, the dehydration reaction and the purification by washing with saturated NaCl will be done. The second fractional distillation, spectroscopic and chemical analysis will be done the second week.

Dehydration Reaction
Before beginning, calibrate the thermometer.
Clamp a 100 ml round-bottomed flask to a ring stand and set it over a hot plate/stirrer. Add a magnetic stir bar to the reaction flask and position a 100 ml heating mantle around the flask. Using a glass funnel and 10ml graduated cylinder, dispense 5ml of H_3PO_4 into the reaction flask and mark the level of H_3PO_4 on the outside of the flask using a permanent marker. Marking the level of H_3PO_4 on the flask will allow you to determine when to add toluene to the reaction later on in the experiment. Refer to Figure 2.1 for reference to this set-up.

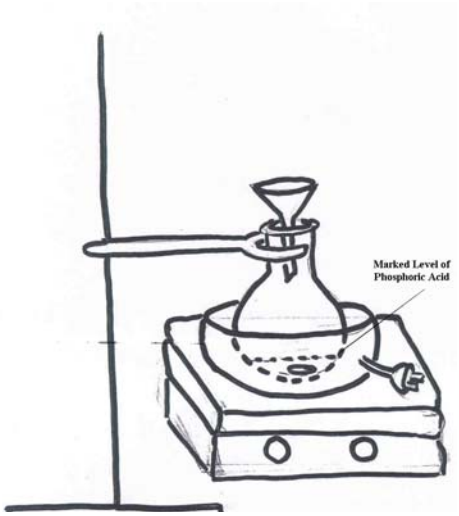

Figure 2.1: Pyrolysis Set-Up

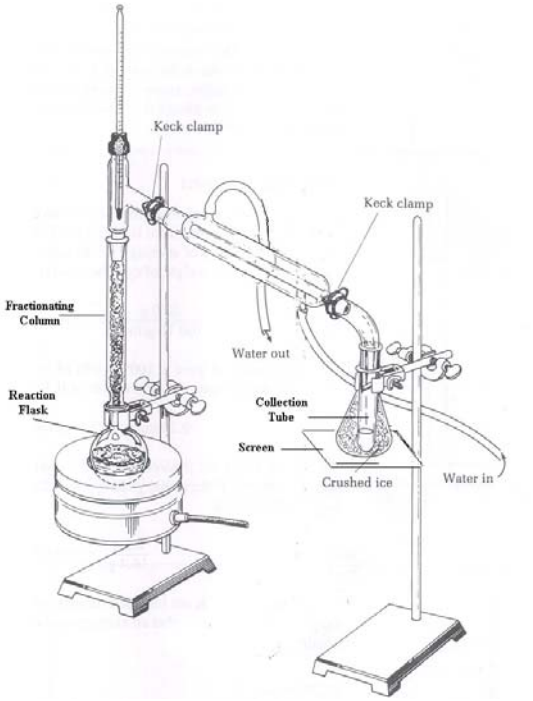

Figure 2.2: Fractional Distillation Set-Up
(adapted from Feiser & Williamson)

Add 20g of cyclohexanol to the reaction flask using a glass pipet and glass funnel. Set up the remaining fractional distillation apparatus as follows, referring to Figure 2.2 as you work. Insert the fractionating column into the reaction flask. Attach the distilling head, thermometer adapter and thermometer. Set up a second ring stand with a ring and ring screen. Attach a condenser to the distilling head and a vacuum adapter to the condenser using Keck clamps. Clamp the vacuum adapter to the ring stand to stabilize the apparatus. Position a collection flask (50ml rb) immersed in an ice bath on the ring screen under the outlet of the vacuum adapter. Connect the heating mantle to the Variac. (Twist plug of heating mantle to ensure contact). Connect water hoses to the condenser inlet and outlet (in at the bottom, out at the top). Fill the ice bath with ice/water to cool the collection flask during distillation. *Have an instructor check your set-up before proceeding.*

Turn on the water. Set the Variac to its highest setting and turn it on. Allow the pyrolysis to proceed until the first few drops of distillate begin to collect in the collection tube. (Be patient! This may take up to 30-45 minutes). Record the temperature reading on the thermometer when the first few drops of distillate begin to collect and monitor the temperature and record it every 5-10 minutes throughout the distillation, making specific note of the maximum temperature. (Distillate should come over at ~70-85°C. This is an *azeotrope* of

cyclohexene and water) When the volume in the reaction flask reaches the mark you made with the permanent marker earlier in the experiment, turn off the Variac and allow the apparatus to cool for 10 minutes. Remove the thermometer adapter with thermometer from the apparatus and insert a clean glass funnel. Add 20 ml of toluene to the reaction flask through the glass funnel and fractionating column. Two layers should be clearly visible in the reaction flask. Using a permanent marker, mark the mid-point of the upper layer in the reaction flask with an "X". (See Figure 2.3). Remove the funnel and re-insert the thermometer adapter and thermometer. Turn on the Variac. Continue the distillation into the same collection tube until the volume in the reaction flask reaches the "X". Turn off the Variac and water. Allow the apparatus to cool for ~10 minutes and disassemble the set-up, taking special care to save the contents of the collection tube. The remaining contents of the reaction flask can be disposed of in the non-halogenated organic waste container *after it is completely cooled to room temperature*.

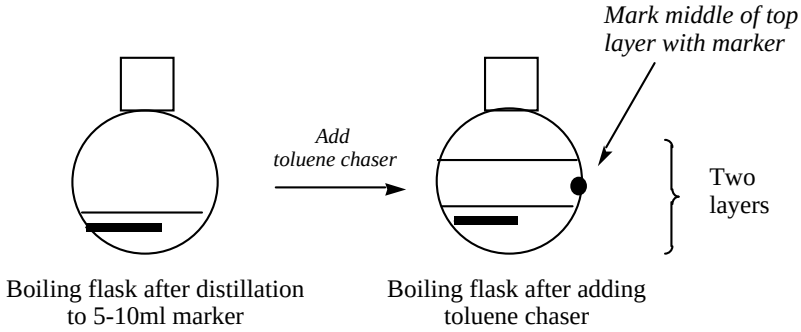

Figure 2.3: Marking the Toluene Layer

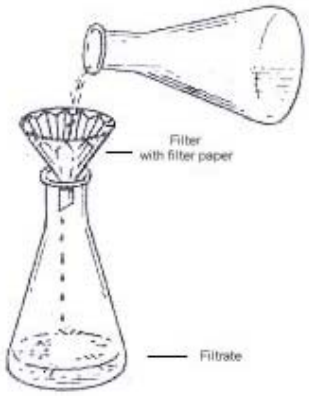

Figure 2.4: Gravity filtration *(adapted from Landgrebe, p. 113)*

Crude Purification with Saturated Sodium Chloride

Clamp a ring to a ring stand and insert a 125ml separatory funnel through the ring. Close the stopcock and transfer the contents of the collection tube to the separatory funnel. Use an additional 5 ml of toluene to rinse the collection tube and pour this into the separatory funnel as well. Add an equal volume of saturated sodium chloride (~20ml) to the separatory funnel. Insert a stopper and shake the separatory funnel to allow the two layers to mix. Set the funnel back into the ring and allow the two layers to separate again. Remove the stopper. Label two 25 or 50ml Erlenmeyer flasks as "water layer" (lower) and "organic layer" (upper). Drain the lower layer into the flask labeled "water layer" and the top layer into the flask labeled "organic layer". Add ~100mg of $MgSO_4$ to the flask labeled organic layer and swirl the contents around for 1-3 minutes. Using gravity filtration (Set up depicted in Figure 2.4), remove the drying agent (solid $MgSO_4$). Transfer the filtrate to a clean, dry vial, labeled with your name and "Crude Cyclohexene". Hand in your product to the instructor who will store it in the refrigerator until next week.

End of Week 1

Calibrate the thermometer. Clamp a 50 ml round-bottomed flask to a ring stand and set it over a hot plate/stirrer. Add a magnetic stir bar to the reaction flask and position a 50 ml heating mantle around the flask. Using a glass funnel plugged with a small wad of cotton, transfer your product from Week 1 to the round bottomed flask. Continue to set up a clean and dry fractional distillation apparatus, using the 50ml rb flask as

the distilling flask. The collection tube must be completely clean and dry. *Have an instructor check your set-up* and begin the distillation. Note the temperature at which the distillate begins to collect in the collection tube. Continue the distillation until there is 2-4 ml of volume (toluene impurities) remaining in the distillation flask and the temperature reading on the thermometer is between 78-85 °C. Record the range over which the entire distillate (pure cyclohexene product) is collected. The boiling point of cyclohexene is ~83 °C. The distillate should be clear, however if it appears cloudy, add ~ 50mg of MgSO4 to the drying tube until the product is dry. Use gravity filtration to remove the drying agent from the product. Transfer the product to a pre-weighed, clean and dry vial, labeled with your name, the boiling point range of the distillate, and "pure cyclohexene".

Boiling Point Determination

Determine the boiling point of the distilled cyclohexene using the capillary boiling point apparatus described in Experiment 1: Boiling Point Determination and Simple Distillation, Organic Chemistry Lab I.

Infrared Spectroscopy

Run IR spectra on cyclohexanol and the cyclohexene product. NaCl plates will be used. Be sure plates are clean and dry. If they are not, clean them before proceeding (See below). Add one drop of the cyclohexanol to the salt plate. Place the second plate on top of the first. Carry the plates in a small beaker to the instrument room for analysis. Clean the plates and repeat the procedure for cyclohexene. Clean the plates and return them to the dessicator. *To clean IR plates, p*lace the plates in a small beaker (25 or 50 ml) and add 15-20 ml methylene chloride. Swirl the plates carefully in the solvent. Remove the plates and dry with Kim Wipes. Do not use paper towels. Plates should never be washed with water.

Chemical Tests

Cyclohexanol and the cyclohexene product will both be analyzed by chemical tests. Procedures for running these tests are provided below.

Br_2 in CCl_4 Test for Alkenes

Set up a test tube rack containing three, small (75mm X 12mm) test tubes. Be sure that the test tubes are clean and dry. Label the test tubes 1-3. In test tube 1, place 2 drops of cyclohexanol, in test tube 2 place two drops of your cyclohexene product, and in test tube 3 place 2 drops of a known alkene, decene. Add one drop of the Br_2 in CCl_4 solution to each test tube. If an alkene is present, the brownish yellow color will dissipate. If an alkene is not present, the brownish yellow color will persist. Use the known compounds (cyclohexanol and decene) for comparison to determine the positive or negative outcome of each test. Set up a table in your notebook to record your procedures, observations and results.

Jones Oxidation Test for Alcohols **Caution: reaction is very exothermic! Test tube will become very hot!**

Set up a test tube rack containing three, small (75mm X 12mm) test tubes. Be sure that the test tubes are clean and dry. Label the test tubes 1-3. In test tube 1, place 2 drops of cyclohexanol, in test tube 2 place two drops of your cyclohexene product, and in test tube 3, place 2 drops of a known alkene, decene. Add one drop of the Jones reagent into each test tube. If an alcohol is present, a blue-green color will appear in about a minute. If an alcohol is not present, the solution will remain orange-yellow. To be able to see the colors fill the test tube approximately half-full with distilled water. Use the known compounds (cyclohexanol and decene) for comparison to determine the positive or negative outcome of each test. Set up a table in your notebook to record your procedures, observations and results.

Proton (1H) NMR Spectra: Identification and Interpretation
Proton NMR spectra for the starting material and the desired product are provided. (See webpage for the experiment). Students are required to identify Spectrum A as cyclohexanol or cyclohexene and Spectrum B as cyclohexanol or cyclohexene as part of the post-lab assignment.

Waste Disposal *(Waste containers located in the back hood.)*
Dispose of all non-halogenated organic compounds/solvents (cyclohexanol, cyclohexene, toluene, acetone) in "non-halogentaed organic waste". Dispose of all halogenated organic compounds/solvents (methylene chloride, Br_2 in CCl_4) in the halogenated organic waste. Dispose of acidic waste (phosphoric acid, Jones reagent) in the aqueous acidic waste. Glass microcapillary pipets and pipets should be disposed of in designated containers. Filter paper is disposed of in the solid waste