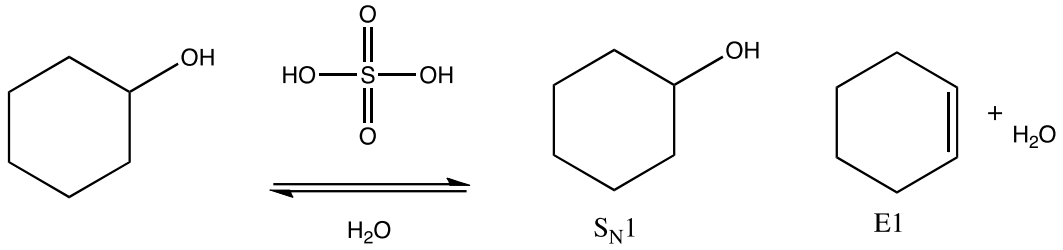
Experiment 1
Dehydration of Cyclohexanol[1]

Chemistry 251
Fall 2012

Background

If we add strong acid and heat to an alcohol in the absence of a good nucleophile, we can promote an $S_N1/E1$ reaction as shown in the reaction scheme below.



This is an excellent method for making alkenes, particularly when other base sensitive chemistry is present!

You may notice that the S_N1 product of this reaction is also the starting material. In order to drive this reaction to the alkene product, we will use fractional distillation as a way to remove product from the reaction vessel and drive the reaction (what 'principle' is this?). Unfortunately in this case, the byproduct of the E1 reaction (water) forms an azeotrope (low boiling mixture) with cyclohexene, meaning that the two cannot be separated by distillation. We will carry out what is know as 'a standard organic work-up' to remove all water from our cyclohexene product.

We will then qualitatively and quantitatively analyze our product using the Br_2 test, and gas chromatography.

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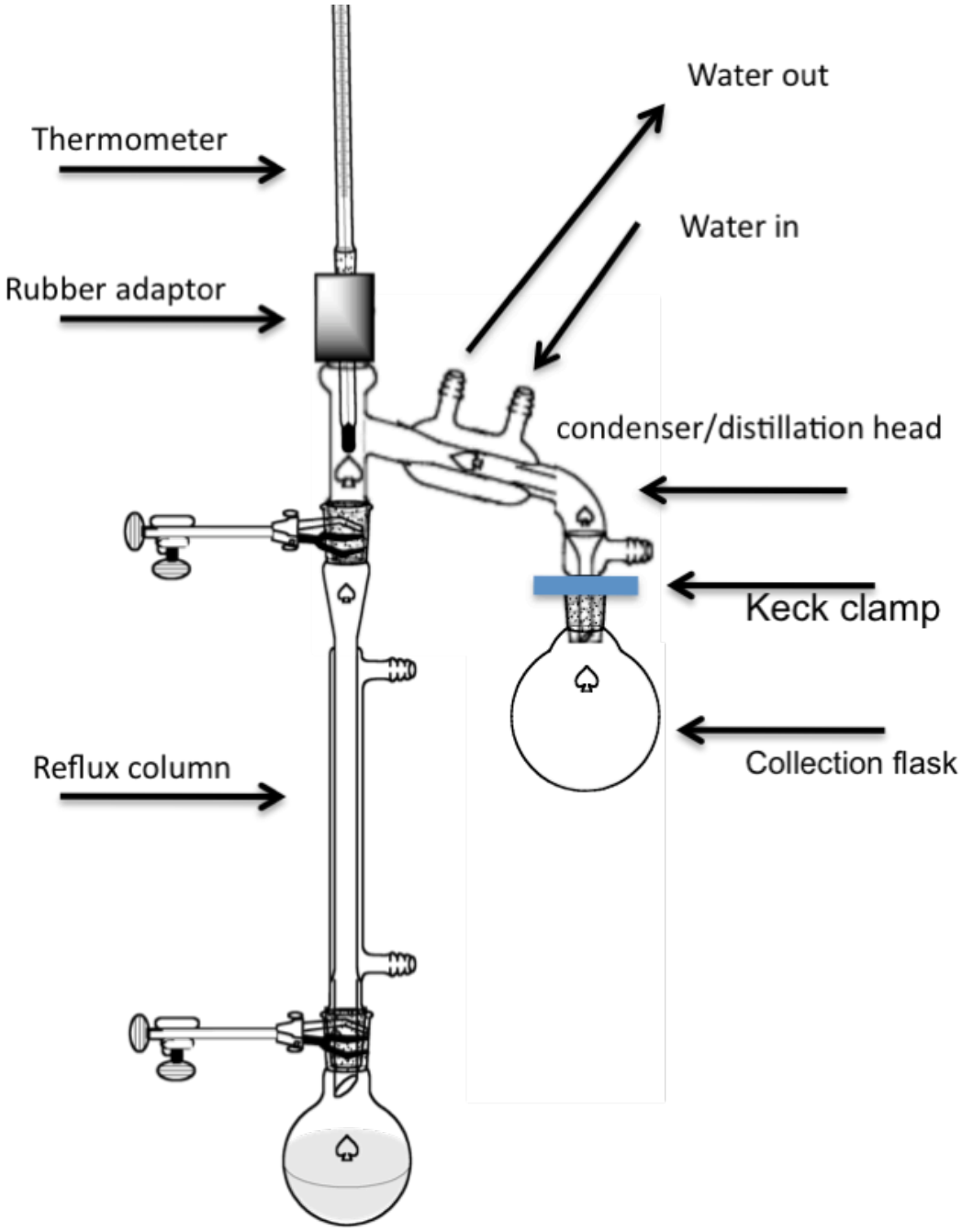
[1] *Experimental Organic Chemistry; A Miniscale and Microscale Approach* 4th ed. Gilbert, J. C.; Martin, S. F., 2006, Thomson/Cole Belmont, Ca. pp. 349-350.

Experimental Procedure

Measure about 5 mL of cyclohexanol in a graduated cylinder and add it to a 25 ml round bottom flask. To this add 2.5 mL of 9 M H_2SO_4 and gently swirl the flask to mix the reagents. (**Caution: 9 M H_2SO_4 is extremely caustic, wear gloves and be careful!)** Add a few boiling chips, and then set up the flask for fractional distillation, using a round bottom flask for collection. (see figure)



Note: We are using the RB flask for collection because cyclohexene has a rather unpleasant odor. We want to minimize our contact with its vapors.

Heat the mixture and watch the condensation line move up the condenser. As the temperature at the thermometer bulb rises, you should not see the temperature rise above 95 °C. When about 2.5 ml of liquid remains in the distillation flask remove the heating element. **! Keep a careful eye on the reaction flask, H_2SO_4 has the potential to react and create H_2S at high concentrations. If the reaction begins to turn black (**not dark or brown, but black**), remove the heat immediately!** (If you think cyclohexene smells bad…)

Work-up:
Pre-weigh a small glass vial, **with a cap**, and write this weight in your notebook.

In your collection flask you should notice two layers. Carefully pour the contents of you flask into a separatory funnel, and remove the aqueous layer. Wash the remaining, cloudy, layer with saturated sodium bicarbonate (5 ml) and then Brine (5 ml). With the cyclohexene still in your separatory funnel (and now significantly less cloudy) bring the funnel to a hood and drain the cyclohexene into a small beaker. Add a few spatula tips of the drying agent Sodium Sulfate (you will know that you have added enough when the liquid is completely clear, and there is un-clumped Na_2SO_4 in the flask), and then carefully decant the solution into your pre-weighed vial. Cap it.

Analysis:

1) You will run a GC on your sample to determine the purity of the sample. Compare your printout to that of cyclohexanol.

2) You will test for the presence of a double bond in your product using the Bromine unsaturation test. (Caution: Bromine can cause severe burns. Wear gloves, be carful, and let your instructor know immediately if there is a spill!) Add 1 ml of the Br_2/CH_2Cl_2 to 2 test tubes. Add 3 drops of cyclohexanol to one, and 3 drops of your product to the other. Record your observations.

Report questions

1) Please write a complete mechanism for this reaction.
2) What was your % yield for this reaction?
3) What is the purpose of each wash in the work-up?
4) Explain why we do not have to worry about the S_N1 product in this reaction.
5) Describe the bromine unsaturation test and how it works, including the mechanism.