

9. E1: Alkenes from alcohols

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and P.F. Schatz:** Chapter 12.2-12.4 for simple and fractional distillation
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online picture of simple distillation

M. Jones: E1, elimination unimolecular reactions, Chapter 8, pgs. 332-335

Vocabulary:

Protonation:	To add a proton (H^+) usually as in an acid base reaction.
Dehydration:	The elimination of H_2O .
Deprotonation:	To remove a proton (H^+) as in an acid/base reaction. In this experiment, water is acting as the base.
Catalyst:	A chemical/compound which promotes/accelerates the reaction but is not consumed by it.

This procedure has been adapted from the microscale procedure described in the third edition of *Macroscale and Microscale Organic Experiments* by Kenneth L. Williamson (Houghton Mifflin, Boston, 1999).

Background

Elimination reactions. In this experiment, cyclohexanol will be dehydrated (loss of H_2O) to form cyclohexene under acidic conditions (see Figure 1).

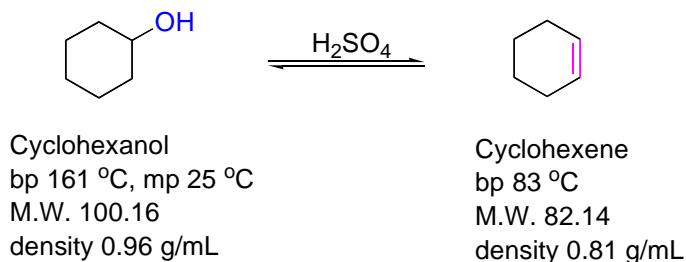


Figure 1. The overall reaction.

The substrate or starting material is cyclohexanol (R-OH). Sulfuric acid is present as a catalyst, which promotes the reaction but is not consumed in it. The hydroxyl group in R-OH is a poor-leaving group because it would have to leave as a hydroxide ion (HO^-). Therefore, an acid is used to protonate the alcohol (**step 1**) and form R-OH_2^+ (see Figure 2). Thus, water (a much better leaving group) is the leaving group in this reaction (**step 2**) and the product is a secondary carbocation. In the following step (**step 3**), a molecule of water deprotonates the carbocation at either of the adjacent carbons. The remaining electrons flow towards the positive charge producing a π -bond between the carbons and forming a double bond.

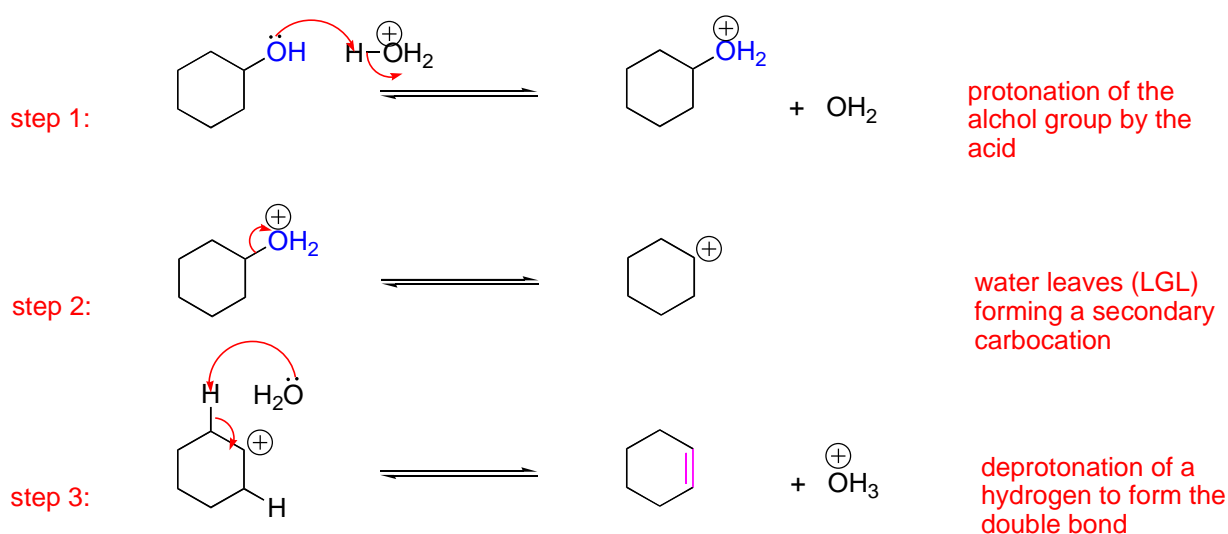


Figure 2. The reaction mechanism for this experiment.

The reaction is reversible as shown in the above scheme (the reverse reaction is acid-catalyzed hydration of alkenes). To drive the reaction forward, the product (cyclohexene) is removed continuously from the reaction mixture by distillation (note that cyclohexene has a lower boiling point than that of the starting compound).

You will perform two alkene tests to determine whether or not you have the alkene product instead of the alkane starting material or some other non-alkene impurity. Alkenes decolorize the iodine and potassium permanganate solutions you will be using. A positive test for the presence of an alkene in the iodine solution will be indicated if the initial purple color becomes clear or light pink. A positive test for the presence of an alkene in the potassium permanganate solution will be indicated if the initial purple color disappears and a dark brown suspension (manganese dioxide) forms in a clear to light brown solution.

For your lab report, you will record the temperature range of your final distillate, the theoretical yield, and the % yield. There may be time to run an IR on your product.

Tips:

- Make sure the thermometer is below the side arm of the distillation apparatus
- Control heat to distill only a few drops per minute.
- Make sure to note the approximate volume before starting the second distillation.
- While the solution is sitting with the drying pellets, clean the distillation apparatus to save time using water, ethanol, and a little acetone.

Experiment

Measure and record the volume of about 10 mL of cyclohexanol using a graduated cylinder. Transfer the cyclohexanol sample quickly to a 50 mL round-bottomed flask to prevent solidification in your graduated cylinder. Add a boiling chip and 1.0 mL of concentrated sulfuric acid to the flask. Swirl the solution to mix the different layers to ensure they are mixed. Your sample should turn a dark brown/greenish color after it is mixed. If this color change does not occur, add up to an additional 0.5 mL of concentrated sulfuric acid to the flask. Set up the equipment for simple distillation. Gently heat the solution; as you do, the color of your sample should get darker. Distill off the liquid until 1-2 mL is left in the flask; do not let the residue burn in the flask! Do not let the vapor exceed 90-95°C. Record the temperature range at which the solution was distilled (temperature at which the first drop was distilled until the temperature when the last drop distilled off). Also, record the volume of the distillate that was collected in your lab notebook. Remove the heat source and let the apparatus cool down.

Clean the entire distillation apparatus with water and then rinse with a small amount of ethanol, followed by a small amount of acetone. Make sure it is completely dry before beginning the second distillation!

Wash the distillate with an equal volume of saturated sodium chloride (NaCl) solution. Swirl the solution to thoroughly mix. Allow the layers to separate and then remove the sodium chloride (aqueous) layer with a pipette. Neutralize the organic layer by adding saturated sodium bicarbonate dropwise with a pipette (and mixing after each drop) and checking with pH paper. Dry the organic layer by adding anhydrous sodium sulfate and shaking the reaction tube. While you are waiting for the sample to dry, reassemble the distillation apparatus. Transfer the dry organic layer to a clean 10 mL round-bottomed flask, add a boiling chip, and collect the distillate at temperatures between 79-84 °C. Make sure to record the temperature range of the distillate. Record the final volume of distillate that was collected in your post-lab report.

Testing for your Alkene Product. Your TA will supply you with two small test or reaction tubes. You will be performing these tests in a hood! To the first tube, add 1 mL of the aqueous potassium permanganate solution. Add a few drops of your product. Record your observations and conclusions.

To the second tube, add 1 mL of the iodine solution. Add a few drops of your product, and let sit for 5 minutes. Record your observations and conclusions.