9. E2 Reaction: Formation of cyclohexene from bromocyclohexane

M. Jones: E2 Reaction, 7.9, pgs 301-311, Figures 7.74, 7.75, 7.78, 7.79, 7.80, 7.81, 7.82

This procedure has been adapted from the macroscale procedure described in the online procedure by Dr. Liz Atkinson, Dr. Bob Wolcott, and Kay Johnson for CHE 321 Organic Chemistry in the Department of Chemistry at the McMinnville Campus of Linfield College

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Background

In this experiment, you will perform an E2 (elimination bimolecular) reaction using bromocyclohexane as your substrate (R-L) using hydroxide as the Nu/base.

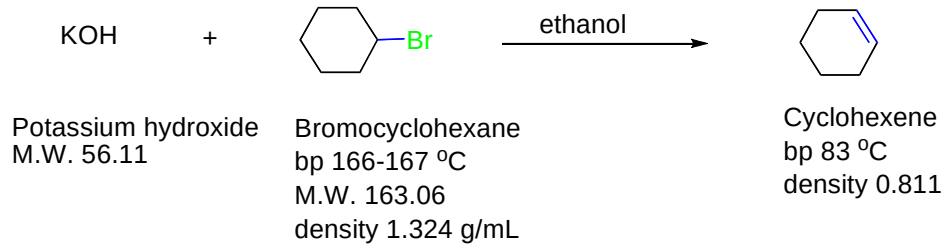

Figure 1. The general reaction for the formation of cyclohexene starting from bromocyclohexane using potassium hydroxide as a catalyst.

In E2 reactions, we first identify the R-L and whether or not the carbon of the C-L is methyl, primary (1^o), secondary (2^o), or tertiary (3^o). Then, we identify the Nu, which acts as a base in this reaction. In this case, the R-L is bromocyclohexane, the C is secondary, and the Nu is hydroxide, which is charged. Remember, there is a competition between substitution and elimination.

The mechanism is a one-step reaction where both the substrate and nucleophile are involved. An *anti* elimination is favored due to the flow of electrons. That means that the hydrogen, which is picked off by the base, has a 180 ^{o} dihedral angle with the leaving group (bromide). For this to happen, the bromide has to be in the axial position in a chair conformation. Even though the chair conformation where an equatorial bromide is favored, there is population of the other chair conformation. The mechanism for this reaction is depicted in Figure 2.

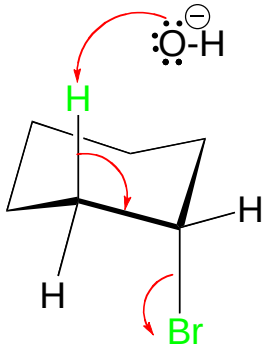

Figure 2. The *anti* elimination of the reaction.

Tips:
-Record all volumes and weights.
-Record the temperature range of your distillate.
-Be careful when handling potassium hydroxide and bromocyclohexane.

Experiment

Experimental procedure. Add 5 g potassium hydroxide, 5 mL bromocyclohexane, 10 mL of 95% ethanol, and a boiling chip to a 50 mL round bottom flask. Swirl the flask until almost all of the potassium hydroxide has dissolved. Place a reflux condenser on top of the flask. Heat the mixture to reflux for 45 minutes. While you are waiting, fill a large reaction tube with 12 mL of water.

Reaction workup. After the 45 minutes, cool the flask to room temperature. Then, pipette the contents of your flask into the reaction tube containing the water. Cap the reaction tube and shake the contents. Let the reaction tube sit for at least five minutes.

Wash your round bottom flask and condenser with water, ethanol and a small amount of acetone. Leave them to dry.

Slowly remove the lid from your reaction tube. Pipette the product (organic layer) from the water layer into another reaction tube. Add 10 mL of water to the organic layer. Cap the reaction tube and shake. Allow the layers to separate for five minutes. Remove the cap and extract the water layer into a waste container (do not discard!). This process is called washing. Wash the organic layer again with 10 mL of water. Cap the reaction tube and shake. Allow the layers to separate for at least five minutes. Remove the cap and extract the water layer into the waste container. Wash the organic layer one final time using 10 mL of water. Cap the reaction tube and shake. Allow the layers to separate for five minutes. Remove the cap and again extract the water layer into the waste container. Make sure to identify the organic and aqueous layers correctly! Dry the organic layer using anhydrous sodium sulfate. Remove the sodium sulfate by gravity filtering the organic layer through a piece of filter paper into a clean dry reaction tube. Measure your volume before proceeding.

Make sure your round bottom flask and condenser are completely dry before proceeding.

Purification. Then, return the organic layer to the clean, dry 50 mL round bottom flask, add a boiling chip, and purify the product using simple distillation as performed previously for the E1 reaction. Distill off the product between 79-84 ^{o}C, and record the temperature range at which the product distills. Remove the flask from heat after the liquid stops distilling or when there is around a milliliter remaining in the flask. Cool the flask and then record the final volume of the product you collected.

IR Spectrum. Record an IR spectrum of your product. Your TA will assist you. Identify, if present, any OH, CO, or C=C stretches to determine if your product is cyclohexene, cyclohexanol, or a mixture of the two compounds.