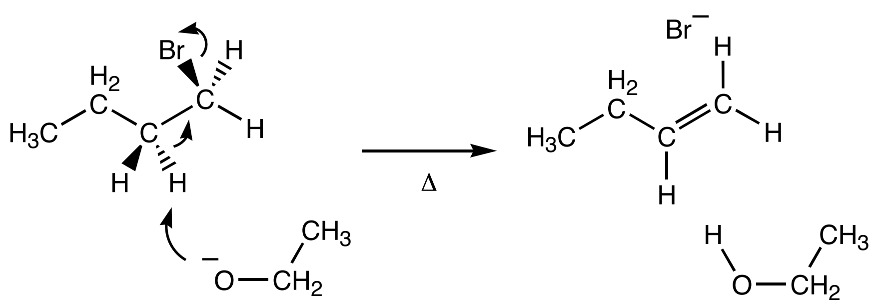
Dehydrohalogenation

Objective

To perform a bimolecular elimination (E2) reaction and use gas chromatography to determine the product distribution.

Background

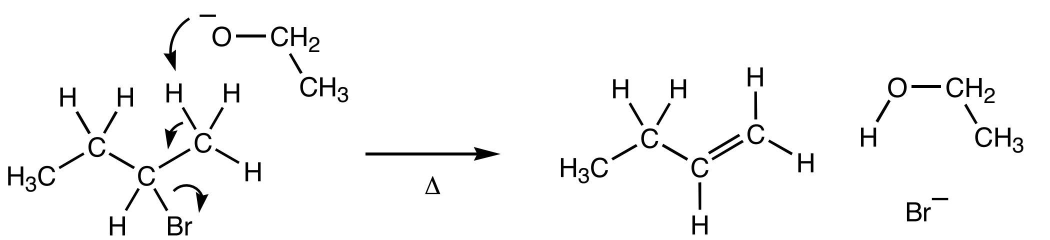
Bromide is a good leaving group and in the presence of a good nucleophile, the nucleophile can push off the leaving group. However, if the nucleophile is also a strong base, an alternate reaction can occur. Instead of pushing the leaving group off, the base can abstract a proton. The electrons that once held the proton in place, can in turn push the leaving group off. As seen in equation 1, the result is an alkene.



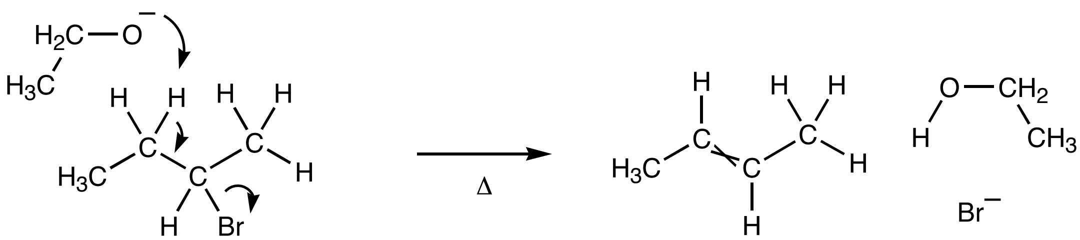
eq 1

The reaction becomes more interesting when the leaving group is not on a primary carbon. Note in equation 1, that the proton bring removed is β to the leaving group (one carbon away from the leaving group). In equation 1, one can see that there are two so-called β-hydrogens. Removing either β-hydrogen produces 1-butene.

A secondary alkyl halide like 2-bromobutane, on the other hand, has five β-hydrogens that can be removed. Removing a proton (a β-hydrogen) from the primary carbon produces 1-butene (see equation 2). However, removing a proton (a β-hydrogen) from the secondary carbon produces 2-butene (see equation 3). Since 2-butene exists as two stereoisomers, three products are possible from the reaction of potassium ethoxide with 2-bromobutane. The products are, of course, 1-butene, *Z*-2-butene, and *E*-2-butene.



eq 2



eq 3

Since the boiling points of 1-butene, *E*-2-butene, and *Z*-2-butene are different, the relative yields of each of the products can be determined by analyzing the gaseous mixture of products with a gas chromatograph (GC). When injected into the stream of helium gas inside a gas chromatograph, the products of the reaction are carried along until they interact with the waxy surface inside the GC column. Materials with higher boiling points spend more time interacting with the waxy surface as compared to materials with lower boiling points. Thus, materials with higher boiling points move through the column more slowly than materials with lower boiling points, and the faster moving, low-boiling materials are separated from the slower moving, high-boiling materials.

As the materials exit the instrument, they pass over a heated filament that detects their presence. This signal is recorded on an integrating chart recorder. At the end of the GC experiment, the integrating chart recorder reports the relative areas under the peaks that appear on the chromatogram due to the signal sent by the detector. Assuming that detector is equally sensitive towards all of the materials—an assumption that is reasonable for this experiment, but is often not true in other experiments—the relative areas under the peaks correspond to the relative concentrations of the materials in the mixture.

Procedure[1]

Dehydrobromination of 1-Bromobutane
Add 3.0 mL of ethanolic sodium hydroxide to a 5-mL conical vial. Add a spin vane and 0.32 mL of 1-bromobutane to the vial. Grease the ground-glass joint and connect the S-shaped gas collection tube to the vial. Stir the solution and heat the reaction slowly (to a maximum of 90 °C).[2] After collecting 2 mL of gas in an inverted test tube (gas that is mostly air), replace the test tube with a plastic tube capped at one end with a rubber septum. Continue collecting gas until you have collected approximately 4 mL. Analyze the sample using a gas chromatograph.

Remove the S-shaped gas collection tube from the water bath before you cool the reaction. If the temperature inside the vial drops before the gas collection tube is removed from the water, water will be drawn into the reaction vessel as the pressure drops.

Dehydrobromination of 2-Bromobutane

Add 2.0 mL of ethanolic sodium hydroxide to a 3-mL conical vial. Add a spin vane and 0.16 mL of 2-bromobutane to the vial. Grease the ground-glass joint and connect the S-shaped gas collection tube to the vial. Stir the solution and heat the reaction slowly (to a maximum of 80 °C).[2] After collecting 2 mL of gas in an inverted test tube (gas that is mostly air), replace the test tube with a plastic tube capped at one end with a rubber septum. Continue collecting gas until you have collected approximately 4 mL of gas. Analyze the sample using a gas chromatograph.

Remove the gas collection tube from the water bath before you cool the reaction. If the temperature inside the vial drops before the gas collection tube is removed from the water, water will be drawn into the reaction vessel as the pressure drops.

GC Analysis of the Product Mixtures

Look up the boiling points of 1-butene, *E*-2-butene (*trans*-2-butene), and *Z*-2-butene (*cis*-butene). Withdraw 0.5 mL of the gaseous product mixture for the gas collection tube. Without delay analyze the mixture on a 20% DC 200 column. Record the retention times and relative areas for each of the peaks in the chromatogram.

Experimental Report

Tabulate your data (reaction performed, structure of the products produced in the reactions for each of the products, and relative yields of the products). Results from this experiment and the dehydration of 1- and 2-butanol will be combined for a report that compares and contrasts two types of elimination reactions.

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[1] Adapted from Pavia, Lampman, Kiz, and Engel, "Dehydrobromination of 1-Bromobutane and 2-Bromobutane.", *Introduction to Organic Laboratory Techniques: A Microscale Approach.* Saunders College Publishing, 1999.

[2] It is important that the reaction not be heated beyond the specified reaction temperature and cooled back to the correct temperature. If the reaction is heated too strongly and then cooled to the correct temperature it is likely that water will rush back into the reaction vessel and quench the reaction.