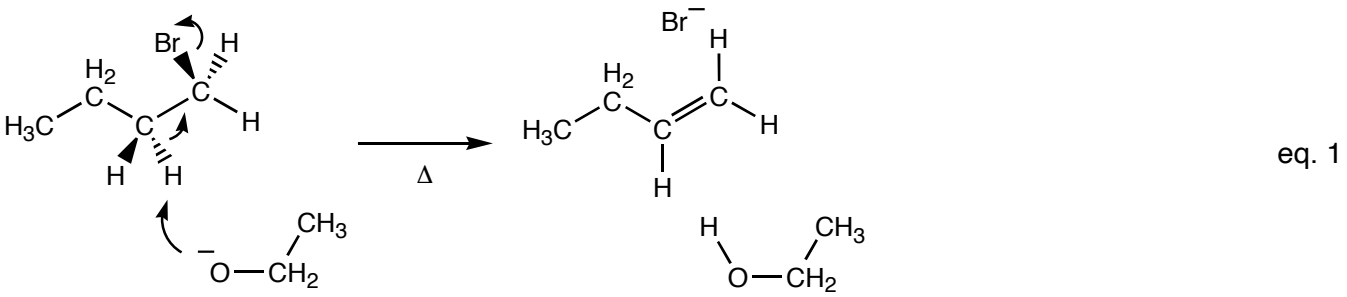
Alkene Formation: Dehydrohalogenation of 1- and 2-bromobutane and dehydration of 1- and 2-butanol

Objective

To perform elimination (E1 & E2) reactions and use gas chromatography to determine the product distribution.

Background

Bromide is a good leaving group. When an alkyl bromide is combined with a strong base, the base can abstract a proton, and the electrons that once held the proton in place, can in turn push the leaving group, the bromide, off. As seen in equation 1 the result is an alkene. This reaction is referred to as an E2 reaction.

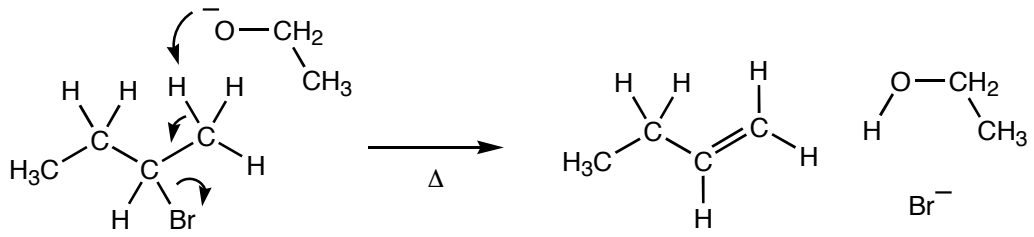


eq. 1

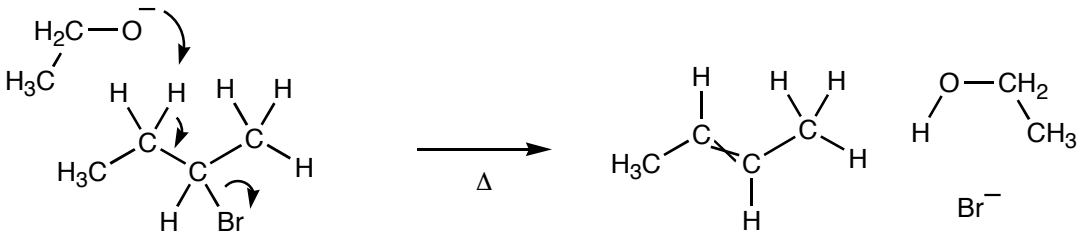
When the leaving group is a secondary alkyl halide, the reaction becomes more interesting. Note in equation 1, that the proton bring removed is β to the leaving group (one carbon away from the leaving group). In equation 1, you can see that there are two so-called β-hydrogens. Removing either β-hydrogen produces 1-butene.

When the leaving group is a secondary alkyl halide, the reaction becomes more interesting. 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, you 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.

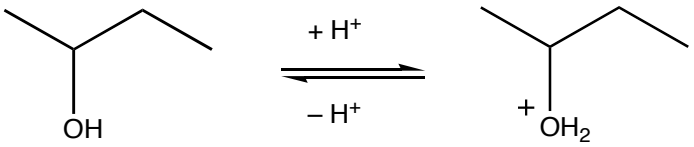


eq. 2



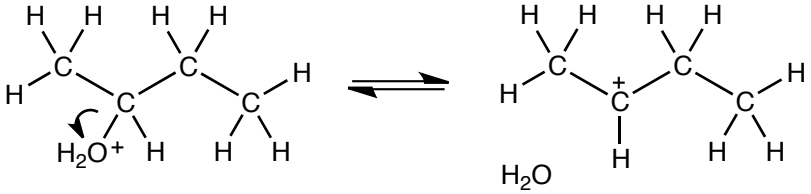
eq. 3

Alcohols are not good leaving groups, but the addition of acid to an alcohol converts the bad hydroxyl leaving group to a good leaving group, water (eq. 4).

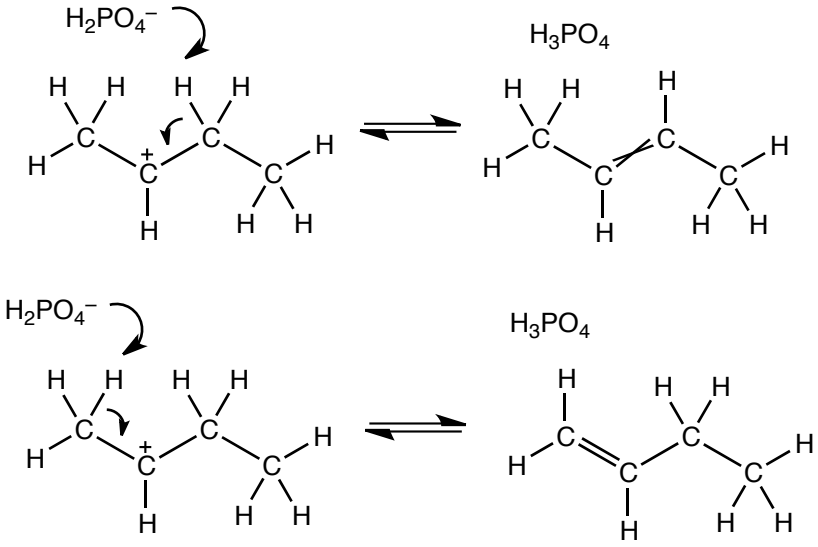


eq. 4

After the alcohol is converted to a good leaving group, the molecule can participate in a variety of reactions. One such reaction is, an elimination reaction. Since the alcohol has been converted to a good leaving group by an acid, by necessity, a strong base cannot be present, thus the elimination reaction, when possible, proceeds by an E1 mechanism. That is, a carbocation forms, and then a weak base, like the conjugate base formed when the acid protonated the alcohol, can abstract a proton.



E1 Reaction Step 1

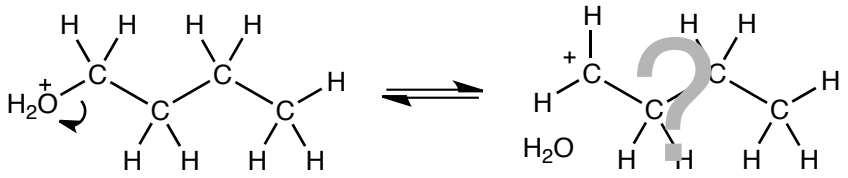


E1 Reaction Three Possible Step 2

Scheme I

As depicted in Scheme 1, E1 reactions produce a variety of products. Wherever there is a β-hydrogen that can be removed, it will be removed, and an alkene will result. Thus, the reaction of phosphoric acid with 2-butanol can form 1-butene and 2-butene. If a chemist desires to form only

1-butene, the chemist my be tempted to consider the reaction of 1-butanol with phosphoric acid. After all, reactions of 1-bromobutane with ethoxide produce only 1-butene. A more thoughtful analysis of the proposed reaction, however, reveals a problem. The formation of a carbocation is a hallmark of an E1 reaction. When a reasonably stable carbocation forms, for example a secondary or tertiary carbocation, an E1 reaction proceeds as expected. However, if the leaving group is attached to a primary carbon atom (see eq 2), as it would be with 1-butanol, one is left wondering, what will happen? After all, primary carbocations are too unstable to form under typical refluxing conditions.



eq. 5

Since the boiling points of 1-butene, *E*-2-butene, and *Z*-2-butene are different, the relative yields of each of the products of the dehydrohalogenation and dehydration reactions 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, lower-boiling point materials are separated from the slower- moving, higher-boiling point 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.

In this experiment, you will attempt E2 reactions on 1- and 2-bromobutane and E1 reactions on 1- and 2-butanol. You will analyze the results by gas chromatography and determine the relative yields of the butenes for each of the reactions.

Procedure[1]

Consult with your instructor to determine which reactions you will run.

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 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 a 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.

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 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 a 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 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.

Dehydration of 2-butanol
Adjust the temperature of an aluminum block to 80 °C.[2] Add 0.20 mL of 2-butanol and a spin vane to a 3-mL conical vial. Add 0.30 mL of the sulfuric acid–phosphoric acid solution to the vial. **This mixture is extremely corrosive and it should be handled very carefully.** After stirring the solution briefly, grease the ground-glass joint and connect the S-shaped gas collection tube to the vial. Place the vial in the aluminum block and position an inverted test tube over the end of the S-shaped gas collection tube that has been submerged in a water bath. While stirring and heating the solution, collect the gas that is produced by displacing water from the inverted test tube. After collecting 4 mL of gas in the test tube (gas which is mostly air), replace the test tube with a plastic tube capped at one end with a rubber septum. Continue collecting gas by displacing water from the plastic tube until you have collected approximately 4 mL of gas. If necessary, slowly increase the temperature of the reaction to a maximum of 100 °C. Analyze the products (0.5 mL) 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.

Dehydration of 1-butanol
Adjust the temperature of an aluminum block to 140 °C.[2] Add 0.20 mL of 1-butanol and a spin vane to a 3-mL conical vial. Add 0.30 mL of the sulfuric acid–phosphoric acid solution to the vial. **This mixture is extremely corrosive and it should be handled very carefully.** After stirring the solution briefly, grease the ground-glass joint and connect the S-shaped gas collection tube to the vial. Place the vial in the aluminum block and position an inverted test tube over the end of the S-shaped gas collection tube that has been submerged in a water bath. While stirring and heating the solution, collect the gas that is produced by displacing water from the inverted test tube. After collecting 4 mL of gas in a test tube (gas which 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. If necessary, slowly increase the temperature of the reaction to a maximum of 170 °C. Analyze the products (0.5 mL) 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.

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 OPN-RESL-C 80/100 column. Remember to record the retention times and relative areas for each of the peaks in the chromatogram in your notebook.

Experimental Report

Tabulate your data for this experiment and for the dehydrohalogenation of 1- and 2-bromobutane (reaction performed, structure of the products produced in the reactions for each of the products, and relative yields of the products).

1. (6 pts.) Draw a mechanism for the dehydrohalogenation of 1-bromobutane.

2. a. (6 pts.) Explain why the dehydrohalogenation of 1-bromobutane produces one product whereas the dehydrohalogenation of 2-bromobutane produces three products.

   b. (6 pts.) Explain why the products of the dehydrohalogenation of 2-bromobutane are formed in the relative yields that you observed. Remember to identify the compounds.

3. (6 pts.) Draw a mechanism for the dehydration of 2-butanol.

4. (6 pts.) Explain why the product distribution in the dehydrohalogenation of 2-bromobutane is similar to the product distribution for the dehydration of 2-butanol.

5. (6 pts.) Explain why the product distribution for the dehydration of 1-butanol more closely resembles the product distribution for the elimination reactions involving 2-bromobutane and 2-butanol than it does the dehydrohalogenation of 1-bromobutane. (Include a mechanism for the dehydration of 1-butanol in your explanation.)

[1] Adapted from Pavia, Lampman, Kiz, and Engel, "Dehydration of 1-butanol and 2-butanol.", *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.