Elimination Reactions:

Acid-Catalyzed Dehydration of an Alcohol

Purpose

The goal of this experiment is to synthesize an alkene from an alcohol using acid catalyzed dehydration. Purity of the alkene product will be analyzed using gas chromatography. The product will be analyzed with IR spectroscopy and NMR spectroscopy.

Learning Objectives

Synthesize an alkene from an alcohol by acid catalyzed dehydration.

Characterize the alkene product using infrared spectroscopy.

Identify the role of an acid in the dehydration of an alcohol.

Analyze the results of the reaction using gas chromatography.

Identify a product of a reaction using IR spectroscopy.

Identify the product of a reaction from ^{1}H NMR spectroscopy.

Laboratory Skills

Set up a reaction.

Perform a distillation.

Calculate a percent yield of reaction.

Analyze a gas chromatogram.

Analyze an IR spectrum of the product of the reaction.

Analyze a ^{1}H NMR spectrum of the product.

Equipment

- Macroscale distillation set-up
- Gas chromatography instrument, vials, and syringes
- FTIR instrument and IR sample preparation materials
- NMR instrument and NMR tubes

Chemicals

- 85% Phosphoric acid
- Cyclohexanol
- Concentrated sulfuric acid
- Anhydrous calcium chloride (or other drying agent)
- Dichloromethane
- $CDCl_3$

Background

Elimination Reactions

An elimination reaction is a type of organic reaction in which two substituents are removed resulting in the formation of a pi-bond. In most organic eliminations, a proton (H^+) and a leaving group (LG) are removed to make the alkene. The leaving group is a usually a weak base such as a halide or tosylate ion.

E1 and E2 Mechanisms

An elimination reaction can proceed through two possible mechanism pathways: E1 or E2 as shown in Figure DO.1. The E2 reaction is concerted reaction where the H^+ removal, C=C bond formation, and loss of the LG all occur in on simultaneous step. The E1 reaction occurs stepwise. The LG leaves the structure forming a carbocation. In the second step, then H^+ is removed by a weak base (often a protic solvent such as water) leading to the formation of C=C bond.

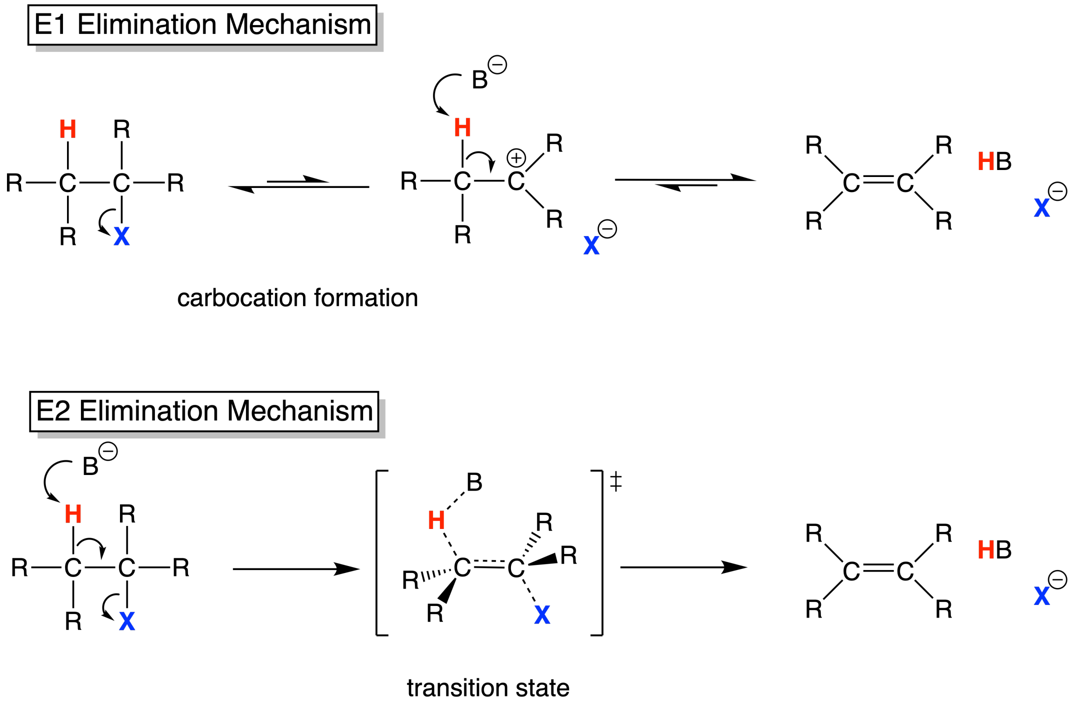

Figure DO.1: E1 and E2 Elimination Mechanisms

Regiochemistry of E1 Reactions

In many cases, the elimination reaction may proceed to alkenes that are constitutional isomers, with one formed in excess of the other. This is described as regioselectivity.

The major product of an E1 elimination is usually the more substituted alkene (Zaitsev), while the minor product is the less substituted alkene (Hofmann). As an alkene becomes more substituted (more carbons attached to the carbons involved in the pi-bond), the structure becomes more thermodynamically stable. This observation comes from measuring the enthalpy of hydrogenation for various alkenes.

Because E1 reactions proceed through a carbocation, there is a possibility of carbocation rearrangements. A rearrangement will typically occur when an unstable carbocation can be transformed into a more stable carbocation.

One rearrangement pathway where an unstable carbocation can be transformed into a more stable carbocation is called a hydride shift (Figure DO.2). In a hydride shift, a hydrogen moves from one carbon to another adjacent carbon in order to reach a more substituted and more stable carbocation. Similarly, eliminations often favor the more stable trans product over the cis product (stereoselectivity).

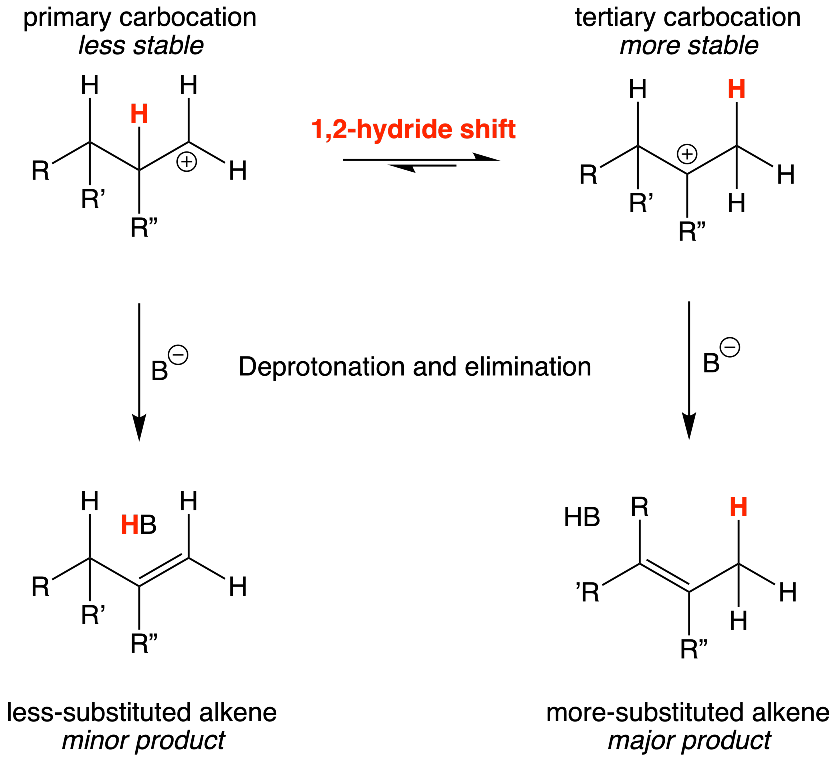

Figure DO.2: Rearrangements of carbocations during an elimination

In this experiment, you will perform the dehydration of cyclohexanol. In this reaction, there is only one possible product, cyclohexene, because the starting material is symmetric.

Dehydration of an Alcohol

The dehydration of an alcohol is the loss of water from the alcohol, resulting in an alkene. Alcohols do not easily undergo base-catalyzed eliminations because the hydroxyl group (–OH) is a poor leaving group (strong base). However, under acidic conditions, the hydroxyl group can be protonated to form a better leaving group. The general mechanism is an E1 elimination mechanism that involves the hydroxyl leaving group picking up a proton and leaving as a water molecule. Then, a proton is removed, moving electrons to create a new double bond, as illustrated in Figure DO.3.

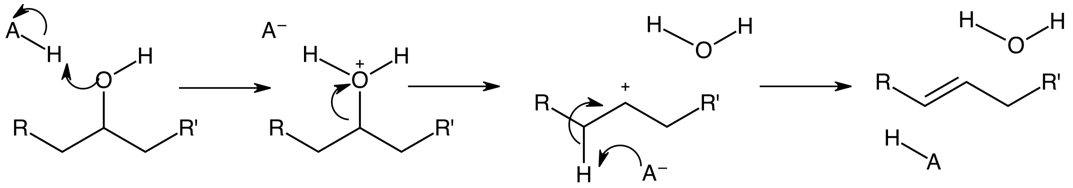

Figure DO.3: General mechanism of acid-catalyzed dehydration of an alcohol

As seen in Figure DO.3, E1 elimination reactions involve the formation of a carbocation intermediate. Dehydration reactions work best with secondary and tertiary alcohols due to the increased stability of the carbocation intermediate. The observed trend in reactivity of alcohols to acid-catalyzed dehydration is thus:

methanol < primary alcohol < secondary alcohol < tertiary alcohol

Role of the Acid Catalyst

The dehydration of an alcohol requires a catalyst, usually an acid, for the reaction to occur. The acid plays two roles in the mechanism. First, the acid protonates the hydroxyl group, making a good leaving group of water. Then, the conjugate base of the acid removes a hydrogen cation (proton) from a carbon adjacent to the cation in the intermediate. Therefore, the acid is regenerated throughout the reaction, as is required to be a catalyst.

The most common acid catalysts for the alcohol dehydration are sulfuric or phosphoric acid. Other acids, such as hydrochloric or hydrobromic acid, are not used because the small conjugate base ions (halide ions) could participate in a competing nucleophilic attack on the carbocation intermediate.

Improving a Reversible Reaction Yield

Alcohol dehydration is a reversible process, as the presence of water could recreate the alcohol from the alkene. To optimize the yield of the alkene, the reversibility can be addressed by distilling off the product as it is made. The removal of the alkene from the reaction mixture has two benefits. First, decreasing the alkene concentration pushes the equilibrium toward the product side. Second, the alkene is removed from the water in the reaction flask to reduce the reverse reaction.

In the dehydration of cyclohexanol performed in this lab, distillation during the reaction works well as there is a large difference in the boiling points of the reactant (cyclohexanol bp = 161 °C) and the product (cyclohexene bp = 83 °C). Thus, the cyclohexanol mostly remains in the reaction flask during the distillation to continue reacting with the acid. If any of the acid happens to distill over with the cyclohexene, it can easily be neutralized with aqueous sodium bicarbonate. Traces of water can also be removed by using a drying agent, such as anhydrous magnesium sulfate or calcium chloride.

Gas Chromatography

Gas chromatography (GC) is an analytical technique used to separate the chemical components of a sample mixture and then detect them to determine their presence or absence and/or relative quantities.

In gas chromatography, the organic molecules are vaporized and then carried through a column with an inert carrier gas such as helium or nitrogen (mobile phase). The gas chromatography column (stationary phase) is a glass or metal tube containing a microscopic layer of a polymer. The molecules will move through this column at different speeds based on polarity and boiling point.

As the compounds emerge from the end of this column, a detector will “detect” the presence and amount of an organic molecule. *Retention time* is the amount of time it takes for a molecule to move through the column.

The chromatographic data is presented as a graph of detector response (y-axis) against retention time (x-axis). This gas chromatogram is a visual representation of each organic sample eluting from the column. The retention times can be used to identify the compound when compared to the retention time of the known compound run under the same conditions.

Calculation of Percent Composition from a GC Chromatogram

The peaks displayed in a gas chromatogram represent the detector response to that compound. The area under a peak is proportional to the amount of compound present in the solution. By integrating the area under the peak, the relative concentration of each component can be calculated:

$$\text{Percent composition} = \frac{\text{area of peak 1}}{\text{area of peak 1 and peak 2}} \times 100 \qquad \text{(Equation DO.1)}$$

Procedure

Safety Precautions

Safety goggles are required!

All work should be performed in the fume hood.

Cyclohexanol is a flammable, hygroscopic irritant.

Cyclohexene is a flammable irritant.

Anhydrous calcium chloride is a hygroscopic irritant.

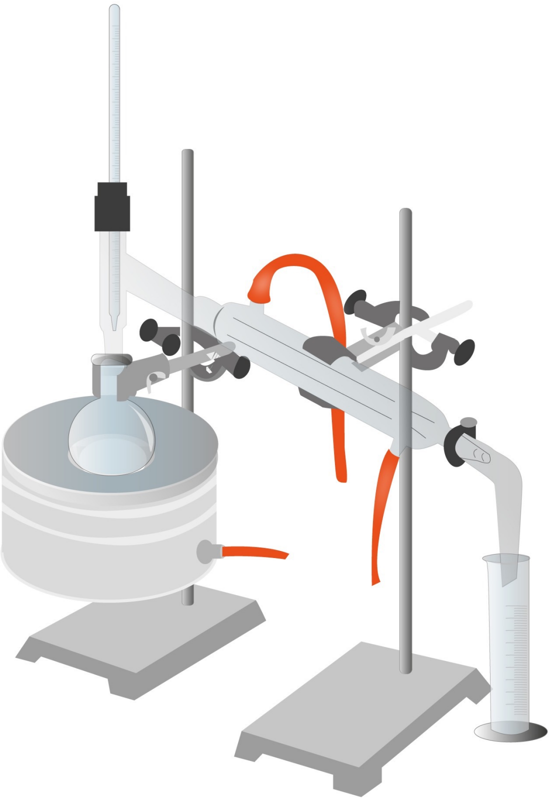

Figure DO.4: Macroscale distillation set-up

1. Place 5.0 mL of 85% phosphoric acid and 15 mL of cyclohexanol (density 0.96 g/mL) into a 100 mL round bottom flask. Add a few boiling stones or a stir bar.

2. Assemble the distillation apparatus (Figure DO.4) ensuring that the thermometer bulb should be aligned at or slightly below the opening in the side arm of the distillation head. Each ground joint is greased by putting three or four stripes of grease lengthwise around the male joint and pressing the joint firmly into the other without twisting.

3. Attach a water condenser to the round-bottom flask.

4. Remember, water goes in the bottom and out the top. Attach a clamp holder to the end of the drain tube to keep it weighted in the drain. Turn water to a trickle. If it is slowly draining, it is high enough. Begin a low flow of water through the condenser.

5. Use a cooled large test tube as a receiver. Cool the test-tube by standing it in a beaker of ice water.

6. Place the set up on a heating/stir plate.

7. Turn on the hot plate to start heating the solution. Monitor the temperature and the boiling of the solution throughout the distillation process. Control the rate of distillation as a high rate of distillation will lead to incomplete reaction.

8. Continue heating and stirring while the product is distilling into a receiving flask or vial.

9. Watch the temperature of the vapor and stop the distillation when the vapor temperature rises above 85 °C and you have collected about 10–15 mL of distillate.

10. Turn off the hot plate, water flow, and stirrer, allowing the distillation apparatus to cool.
11. Place the contents of the receiving flask into a separatory funnel. Place the funnel in a ring stand.
12. Allow two layers to form in the separatory funnel. Cyclohexene (density 0.81 g/mL) will separate out from the water. Drain off the bottom aqueous layer.
13. Add 10 mL water to the liquid in the separatory funnel, stopper the funnel and shake to allow thorough mixing of the liquids.
14. Return the funnel to the ring stand, loosen the stopper and allow the layers to separate. Drain out the aqueous layer again.
15. Wash the cyclohexene with 10 mL of 10% sodium carbonate solution. Mix well. Allow the layers to separate and drain off the aqueous layer.
16. Repeat the washing with another 10 mL of water.
17. Transfer the cyclohexene into a clean dry beaker and add a spatula full of anhydrous calcium chloride (or other drying agent). Allow to stand for a few minutes. If the mixture is cloudy, you will need to add another spatula full of drying agent.
18. Measure and record the mass of a dry, empty vial.
19. Filter or decant the cyclohexene away from the drying agent into a clean, dry pre-weighed vial.
20. Dispose of the aqueous layer in the appropriate waste.
21. Measure and record the mass of your product.
22. Dispose of all solvents and drying agents into the appropriate waste container. Wash glassware with soap and water.

Characterization

1. Most GC columns are sensitive to water. Make sure your distillate has been dried with anhydrous sodium sulfate.

2. Place 1 or 2 drops of your distilled toluene into a small labeled vial and add 1 mL of dichloromethane.

3. 1.0 µL of each this solution will be injected into the GC.

4. Ask your instructor for directions for your GC instrument.

5. Obtain an IR spectrum of the product.

6. Dissolve a small amount (~10 mg) of the product in 700 µL of $CDCl_3$, place the solution in an NMR tube, and obtain a proton NMR spectrum.

7. Dispose of all solvents into the appropriate waste container. Wash glassware with soap and water.

Calculations and Analysis

Write the balanced chemical equation for the reaction.

Complete the table below by entering the relevant literature values and completing the calculations.

Report Table DO.1: Reactants and Products Table

	Molar Mass (g/mol)	Density (g/mL)	Volume used (mL)	Mass used or produced (g)	Moles used or produced (mol)
Cyclohexanol	________	________	________	________	________
Cyclohexene	________	—	—	________	________

GC Analysis

Standards

Standard retention time of dichloromethane solvent (min) ______________

Standard retention time of cyclohexanol (min) ______________

Standard retention time of cyclohexene (min) ______________

Reaction Mixture

Retention time of your product (min) ______________

Area for your product peak ______________

Retention time of any remaining starting alcohol (min) ______________

Area for remaining starting alcohol ______________

IR Analysis

See *(Click here)* for more help on interpreting IR spectroscopy.

Online, in the Labflow report, complete the table with 3 Major IR peaks

Report Table DO.2: IR Analysis

IR Peak, cm^{-1}	**Bond Type**

If available, compare your spectrum to reference spectra. *(Click here)* to access the SDBS database of spectra, where you may find reference spectra for the starting material(s) and/or product.

^{1}H NMR Analysis

See *(Click here)* for more help on interpreting ^{1}H NMR spectroscopy.

Online, in the Labflow report, complete the following table to analyze the NMR signals in ppm.

Report Table DO.3: Proton NMR Analysis

Chemical shift, ppm	**Integration**	**Multiplicity**	**Partial structure**

If available, compare your spectrum to reference spectra. *(Click here)* to access the SDBS database of spectra, where you may find reference spectra for the starting material(s) and/or product.