Dehydration of an Alcohol

Objectives

- Synthesize cyclohexene from cyclohexanol by dehydration.
- Characterize the alkene product using infrared spectroscopy.
- Identify the role of an acid in the dehydration of an alcohol

Background

Dehydration of an Alcohol

The dehydration of an alcohol is the loss of water from the alcohol, resulting in an alkene. The reaction is one method to prepare alkenes. The general mechanism involves the hydroxyl group leaving. Then, a hydrogen cation is removed, moving electrons to create a new double bond, as illustrated in Figure 1. The reaction involves the formation of a carbocation, so secondary and tertiary alcohols are more reactive toward dehydration due to the increased stability of the carbocation intermediate. Primary alcohols tend to follow a different mechanism for dehydration if it does occur.

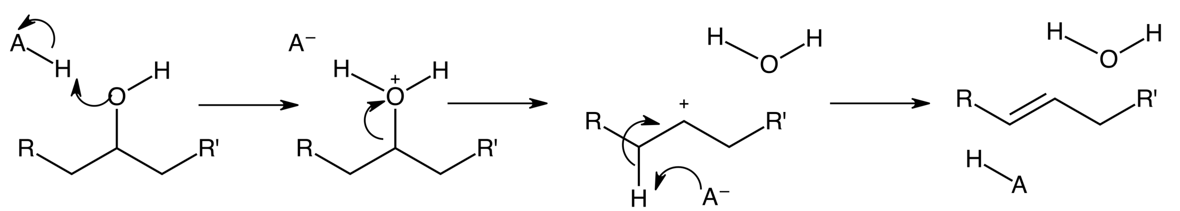

Figure 1 General mechanism of acid-catalyzed dehydration of an alcohol

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 from a carbon adjacent to the cation in the intermediate. Therefore, the acid is regenerated throughout the reaction as 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 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 ºC) and the product (cyclohexene bp=83 ºC). Thus, the cyclohexanol 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.

Materials

- 85% phosphoric acid
- Cyclohexanol
- Concentrated sulfuric acid
- Anhydrous calcium chloride
- Microscale glassware kit
- Pasteur pipette
- FTIR

Safety goggles are required!

All work should be performed in the fume hood.

Cyclohexanol is a flammable, hygroscopic irritant. Cyclohexene is a flammable irritant. Phosphoric acid is corrosive. Sulfuric acid is a toxic, corrosive oxidizer. Anhydrous calcium chloride is a hygroscopic irritant.

Procedure

Dehydration of an Alcohol

1. Place 1.50 mL of 85 % phosphoric acid and 1.50 mL (1.422 g) of cyclohexanol into a long neck 5 mL round bottom flask.
2. Add three drops of concentrated sulfuric acid and a magnetic stir bar to the round bottom flask.
3. Assemble the distillation apparatus with the round bottom flask in the heating block.
4. Turn on the stirrer and the hot plate to start the heating process.
5. Continue heating and stirring while the product is distilling into a receiving flask or vial.
6. Watch the temperature of the vapor and stop the distillation when the vapor temperature rises above 85 ^{o}C.
7. Turn off the hot plate and stirrer, allowing the distillation apparatus to cool for tear down and clean up.
8. Place the contents of the receiving flask into a small test tube and allow it to cool. You should see two layers form in the tube. Determine which is the organic layer and which is the aqueous layer.
9. Dispose of the aqueous layer in the non-halogenated waste.
10. Add 0.25 g of anhydrous calcium chloride to the organic layer and swirl.
11. Allow the calcium chloride to stand for 5 minutes.
12. Measure and record the mass of an empty vial.
13. Use a Pasteur pipette to transfer the product from the tube to the dry, massed vial, leaving the calcium chloride behind.
14. Measure and record the mass of your product.

Pre-Lab Questions

Prepare for lab by completing and understanding the answers to these questions. Refer to the Background or another resource, such as your textbook, if necessary.

1. What precautions should one use when working with H_2SO_4 and H_3PO_4?

2. Calculate the theoretical yield for the dehydration of 3.0 mL cyclohexanol. The molar mass and density of cyclohexanol is 100.16 g/mol and 0.948 g/mL and the molar mass and density of cyclohexene is 82.15 g/mol and 0.811 g/mL.

3. When 2-butanol undergoes an E1 dehydration, three alkenes are possible. Draw the structures for the alkenes and name most abundant one.

Lab 10: Dehydration of an Alcohol Report Sheet

Name ______________________ Section ______________________

Date ______________________ Instructor ______________________

Dehydration of an Alcohol

Amount of reactant used (grams) ______________________

Amount of reactant used (moles) ______________________

Space for calculations:

Product obtained (grams) ______________________

Product obtained (moles) ______________________

Space for calculations:

Product theoretical yield ______________________

Space for calculations:

Product percent yield ______________________

Space for calculations:

Write the equation for the reaction.

Post-lab Questions

1. Is your percent yield within reason of what you would expect? Explain your answer.

2. Compare your IR data to that which you would expect for cyclohexanol. Do you have cyclohexene or cyclohexanol? Explain your answer.

3. Are there other tests that could be used to determine if cyclohexanol is present in your product? Give at least one test with some detail of the expected result for the presence of cyclohexanol.