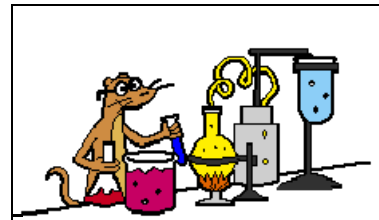


EXPERIMENT 9 – Alkene Synthesis From Alcohol

Preparation of Cyclohexene From Cyclohexanol



Purpose:

- Preparation of an alkene by dehydration (elimination of water) of an alcohol in the presence of an acid catalyst.
- Calculation of percentage recovery of product.
- Test for purity and identification of alkenes

Equipment:

10-mL graduated cylinder
condenser
glass adaptor (2)

round bottom flask (25mL, 50- mL)
thermometer
grease

heating mantle
thermometer adaptor
rubber tubing (2)

Chemicals:

cyclohexanol
 $\text{Br}_2 / \text{CCl}_4$

phosphoric acid (85%)
0.5 % KMnO_4

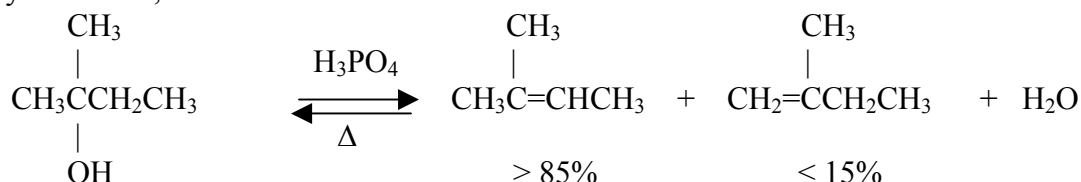
10 % Na_2CO_3
drying agent (CaCl_2)

Discussion:

Dehydration is an elimination reaction of an alcohol: The elimination reaction involves the loss of an OH from one carbon and an H from an adjacent carbon. Overall, this amounts to the elimination of a molecule of water, resulting in a pi-bond formation of an alkene or alkyne. The loss of water from a molecule is called dehydration. In many cases alcohol dehydration require an acid catalyst and heat. Phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) are the most commonly used acid catalysts.

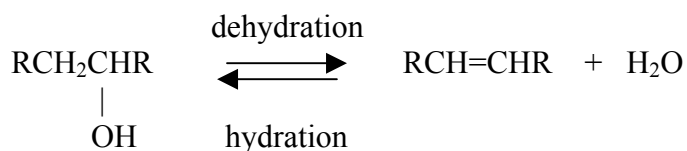
When more than one elimination product can be formed, the major product is the more substituted alkene-the one obtained by removing a proton from the adjacent carbon that has fewer hydrogens (Recall Zaitsev's rule). The more substituted alkene is the major product because it is the more stable alkene, so it has the more stable transition state leading to its formation.

Dehydration of 2-methyl-2-butanol produces primarily 2-methyl-2-butene, a tri-substituted alkene, rather than 2-methyl-1-butene, a di-substituted alkene:



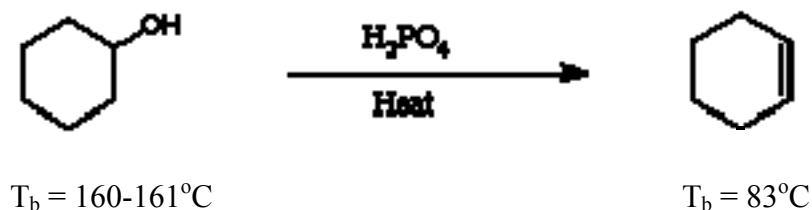
Alkenes can be hydrated (adds water) in the presence of an acid catalyst:

The hydration of an alkene is the reverse of the acid catalyzed dehydration of an alcohol:



To prevent the alkene formed in the dehydration reaction from reforming back the alcohol, the alkene can be removed by distillation as it is formed, because it has a much lower boiling point than the alcohol. Removing a product displaces the reaction to the right. (Recall Le Chatelier's principle).

In this experiment, Cyclohexanol is dehydrated to cyclohexene according to the following reaction:



Because the OH group is a very poor leaving group, an alcohol is able to undergo dehydration only if its OH group is converted into a better leaving group.

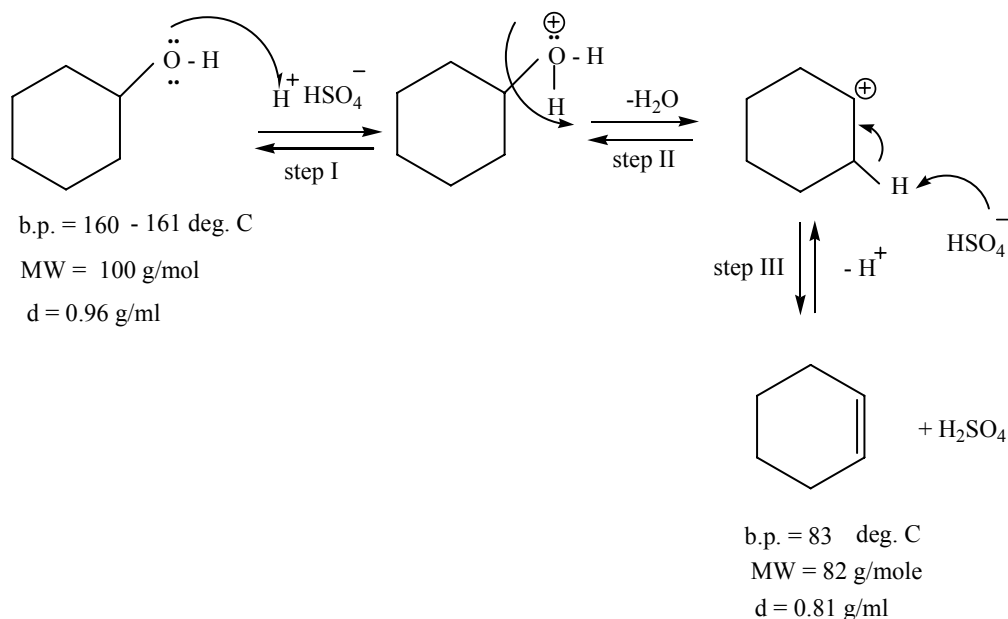
One way to convert an OH group into a good group is to protonate it. Thus, in the first step of dehydration reaction, protonation changes the very poor leaving group -OH into a good leaving group -OH_2^+ .

In the second step, water departs, leaving behind a carbocation.

In step three, the base HSO_4^- removes a proton from the carbon adjacent to the positively charged carbon, forming an alkene and regenerating the acid catalyst H_2SO_4 .

Because the cyclohexene has lower boiling point than the cyclohexanol, the cyclohexene can be distilled as it forms.

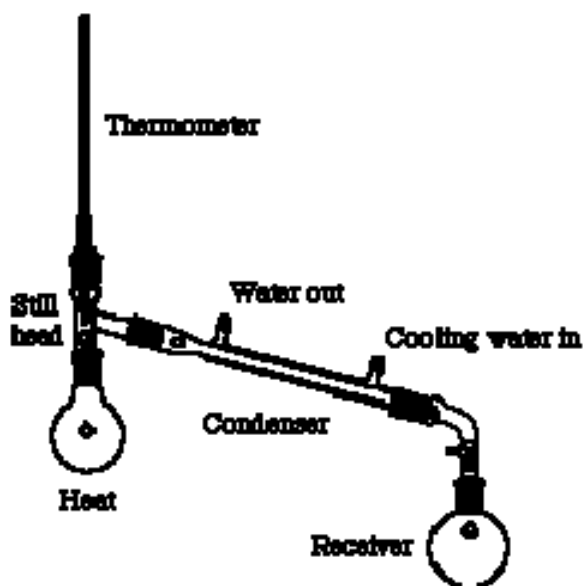
Mechanism:



The reaction is conducted in a distillation apparatus. As the reaction mixture is heated, the lower boiling products (cyclohexene, b.p. 83°C , and water, b.p. $= 100^{\circ}\text{C}$) distill out and are collected in the receiving flask. Any unreacted cyclohexanol (the starting material) and Phosphoric acid (the catalyst) are left in the distilling flask because of their high boiling points (161°C and 213°C , respectively). However, since a small amount of phosphoric acid still appears in the receiving flask, the product is washed with aqueous sodium carbonate to neutralize the acid. Cyclohexene is insoluble in water and thus is not lost during the washing with aqueous sodium carbonate solution. The last traces of water are removed from the crude cyclohexene using anhydrous sodium sulfate (a salt which forms a hydrate).

Experimental Procedure

Step I - Measure 10 mL of cyclohexanol into 50.0 mL round-bottom flask. Carefully add 3 mL of 85% phosphoric acid; H_3PO_4 , the boiling chips, and mount the flask for simple distillation (see Fig. Below: either use column packing or low hold-up packing). Slowly heat the mixture until it comes to a gentle boil. After 10 minutes of gentle boiling, increase the heat sufficiently to cause distillation (the temperature of the distilling vapor should not exceed 100°C) and collect the distillate in a cooled 25 mL round bottom flask as a receiver.



Distillation set- up

To the distillate, add 1 mL of 10% sodium carbonate solution, Na_2CO_3 , to neutralize any traces of acid, which have been carried over. Transfer the liquid to a separatory funnel, add 5 mL of cold water, swirl the mixture gently, and drain off the lower aqueous layer.

Pour the upper organic layer into a small, dry 50 mL Erlenmeyer flask, and dry it over anhydrous calcium chloride (add about one tea spoon) for 5 to 10 minutes with a cover.

Step II (ask instructor if necessary) - Decant the dried cyclohexene into a small distilling flask, add a boiling stone, attach the flask to a simple distillation assembly, and distill carefully. Collect the material distilling at 80 to 85°C . Determine the weight of the product and calculate the percentage yield.

Step III – Use 5-10 drops of product in two small test tubes and test with drop-wise bromine (decoloration) and drop-wise potassium permanganate (dark brown precipitate) for purity and identification of alkene.

EXPERIMENT 9 – Alkene Synthesis From Alcohol

Data and Results**REPORT FORM**

Name _____

Instructor _____

Date _____

1. Reaction Equation

2. Amount of reactant (cyclohexanol) used _____ g _____ ml

3. Theoretical number of moles cyclohexanol
(calculation) _____ mole4. Theoretical number of moles cyclohexene
(calculation) _____ mole5. Amount of product theoretically obtainable
(calculation) _____ g

6. Actual yield _____ g

5. Percentage yield
(calculation) _____ %

Pre-Laboratory Questions–EXP 9 Name:

Due before lab begins. Answer in space provided.

1. Define the following terms.

Dehydration –

Catalysis –

Chaser solvent -

2. What is the function of each of the following reagents in this experiment: phosphoric acid; anhydrous sodium sulfate; sodium carbonate solution, and saturated sodium chloride solution.

3. Outline mechanism for the dehydration of 2-methylcyclohexanol

4. Name or draw the structure, whichever is appropriate, of each of the following compounds.

a. cyclohexene

b. $\text{CH}_3\text{-CH}_2\text{-CH=CH}_2$

c. 2-methyl-1-pentene

d. $\text{CH}_3\text{-CH}_2\text{-OH}$

e. cyclopentanol

Post-Laboratory Questions–EXP 9 Name:

Due after completing the lab.

1. Outline mechanism for the dehydration of 1-methyl-1-cyclohexanol.
2. What is the major disadvantage of using concentrated sulfuric acid (or hydrochloric acid) rather than 85% phosphoric acid for the dehydration of alcohols?
3. Why is the receiving flask supposed to be kept on ice during the preparation of cyclohexene?
3. If 0.138g of cyclohexene (C_6H_{10}) was obtained from 0.240g of cyclohexanol ($C_6H_{12}O$), what is the percentage yield of cyclohexene?
4. Complete each of the following reactions by drawing the structures of the organic products.

