Cerritos Community College

Organic Chemistry 211 Laboratory

Synthesis of Alkenes

(Dehydration of Alcohols)

Objective: To synthesize two isomeric types of methylcyclohexene via acid-catalyzed dehydration of 2-methylcyclohexanol.

General Equation:

$$\underset{\text{Alcohol}}{R_2CH\text{-}CR_2\text{-}OH} \xrightarrow{H^+} \underset{\text{Alkene}}{R_2C{=}CR_2} + H_2O$$

Experiment Overview: This is a microscale approach to the synthesis of alkenes (olefins) via the acid-catalyzed dehydration of alcohols. As shown in the general equation form above, the loss of water occurs through the loss of a hydroxide ion (the functional group of the alcohol) and a hydrogen ion. The hydroxide ion, being a poor leaving group, is first protonated by the acid catalyst to become a good leaving group (H_2O). As the protonated hydroxide leaves in the form of neutral water, it leaves a carbocation behind, which could rearrange to a more stable carbocation, *if the molecular geometry permits*. The elimination of the hydrogen ion takes place from a carbon (called ß carbon) adjacent to the carbon holding the positive charge. As seen below, there are two possible isomeric types of methylcyclohexene forming. The purity of these products could be determined via TLC and IR testing.

Safety notes:

(1) The dehydration products formed in these reactions are highly flammable. Hot plate should be used instead of a burner.
(2) Handle phosphoric acid with care. Should the acid be spilled on your skin, wash it off with copious amounts of water.

Procedure:

Day 1: dehydration reaction & collection of product (Simple distillation apparatus)

1. In a 5 mL conical vial, place 1 mL of 2-methylcyclohexanol, 2 mL of 85% phosphoric acid, and a spin vane.
2. Have the conical vial stand on a hot plate and mount it in a simple distillation apparatus form (remember to grease the vial), with a centrifuge tube as the receiving flask. It is extremely important to have the vial directly touching the hot plate.
3. Slowly heat the contents to a gentle boil. After 10 minutes of gentle boiling, increase the heat sufficiently to cause distillation.
4. Distill out 0.5-0.7 mL of the product *while keeping the temperature of the distilling vapor below 96^oC by regulating the rate of heating.*
5. After collecting enough distillate, discontinue the heat, and wait until the apparatus is cooled before taking it apart.

Day 2: TLC & IR

1. Dry the collected product with anhydrous sodium sulfate for 10 minutes and then transfer the dried content into a tared test tube (using the pipette cotton plug technique, using a VERY SMALL amount of cotton to minimize the loss of the product through the plug) and cork it.
2. Determine the weight of the product and calculate the percent yield. Show the product in an appropriately labeled container to your instructor.
3. The purity of the product will be examined via TLC (Solvent system: 70% of heptane and 30% of ethylacetate) and IR testing. Explain your results.

For your Report:

Calculation & results:

(1) Based on the theoretical yield and actual yield of the alkene, calculate the percent yield for the reaction. (Hint: How would you know the mass of the reactant given its volume?) Note: trace amount of acid may have been carried over in distillation, but we would omit it here.
(2) Calculate the Rf value for each isomeric form of the alkene.
(3) Analyze IR.
(4) Predict ^{1}H NMR of each isomeric form of the alkene.

Discussion:

(1) Draw a mechanism for each possible product of the reaction and explain. For example, are the mechanisms E1 or E2? Why is an acid catalyst required? Predict how many products are possible and explain why.
(2) Compare your prediction with your experimental data.
(3) Discuss on the purpose of TLC in this experiment. Are you able to tell the relative amounts of each isomer (major / minor products) or identify each isomer? Look up literature data on the relative amounts of each isomer.
(4) Others.

Needed (per student):

2-methylcyclohexanol (1 mL)----------→ 15 mL per laboratory
85% phosphoric acid (2 mL)----------→ 30 mL per laboratory
Anhydrous sodium sulfate----------1 jar per laboratory