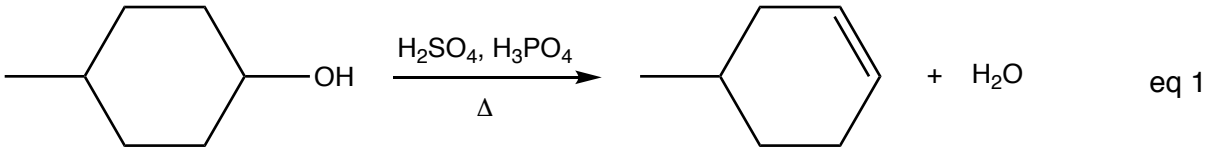
4-Methylcyclohexene Synthesis

Objective

To develop organic laboratory techniques, to synthesize 4-methylcyclohexene, and to gain experience using Fourier Transform Infrared (FTIR) Spectroscopy to characterize the product of a reaction.

Background

As we have previously noted, hydroxyl groups are not good leaving groups. However, the addition of an acid to an alcohol can convert a bad leaving group, hydroxide, to an effective leaving group, water. In the absence of a nucleophile, a protonated alcohol can undergo an elimination reaction. The synthesis of 4-methylcyclohexene can be accomplished in this way.



eq 1

Although the synthesis of 4-methylcyclohexene is straight forward, isolation of the product is complicated by the formation of many byproducts. Since the boiling point of the product is lower than the boiling point of the starting material and many of the byproducts, the 4-methylcyclohexene is isolated from the reaction mixture by distillation. Of course, one byproduct of the reaction, water, has a boiling point similar to the boiling point of 4-methylcyclohexene. Thus, the distillate will contain both water and 4-methylcyclohexene.

Procedure[1]

> **Warning: concentrated sulfuric acid is corrosive and it will cause burns on contact with skin. Wear protective gloves.**

Synthesis of 4-methylcyclohexene
Place 1.5 mL of 4-methylcyclohexanol in a tared 5-mL conical vial. After determining the mass of the 4-methylcyclohexanol in the vial, add 0.40 mL of 85% phosphoric acid and six drops of concentrated sulfuric acid. Add a spin vane to the vial. Attach a Hickman distillation head equipped with a water-cooled condenser to the vial. Cap the apparatus with a drying tube filled with calcium chloride (see figure 1).

Turn on the cooling water and stirrer and slowly heat the reaction to 160 to 180 °C. Periodically transfer the distillate that collects in the well of the Hickman head to a clean 3-mL conical vial. Continue collecting the distillate until the reaction mixture stops boiling.

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[1] Adapted from Pavia, Lampman, Kiz, and Engel, "4-methylcyclohexene", *Introduction to Organic Laboratory Techniques: A Microscale Approach.* Saunders College Publishing, 1999.

Approximately 0.5 mL will remain in the reaction vial. Transfer all of the distillate to the 3-mL conical vial. Using a Pasteur pipet with a bent tip, rinse the material clinging to the walls of the condenser into the well of the Hickman head with 1 mL of a saturated, aqueous sodium chloride solution. Transfer the rinse from the well of the Hickman head to the vial that contains the product.

Figure 1

Apparatus for the synthesis of 4-methylcyclohexene.

Isolation of 4-methylcyclohexene

Allow the distillate to separate into layers. Remove the aqueous layer, and after confirming its identity, discard it. Transfer the organic layer to a small, clean, dry test tube. Add 3–4 microspatulas of anhydrous sodium sulfate to the test tube and allow the drying agent 15 minutes to dry the product. Carefully transfer the dry 4-methylcyclohexene to a tared, clean, dry vial. Determine the mass of the 4-methylcyclohexene collected.

Analysis of the 4-methylcyclohexene

IR Spectrum

Obtain an IR spectrum of your product and of the starting material, 4-methylcyclohexanol, using the Attenuated Total Reflectance FTIR Spectrometer. After collecting your spectrum, clean the instrument with a wipe wetted with acetone. Compare the IR spectrum of the product to the IR spectrum of the starting material, 4-methylcyclohexanol.

Boiling Point Determination

Place approximately 5 μL of 4-methylcyclohexene into a melting point capillary tube. Use a 10 μL syringe to add the 4-methylcyclohexene to the capillary tube. Insert the syringe into the capillary tube and slowly withdraw it as the plunger is depressed. The capillary tube may need to be bounced or spun in a centrifuge to get the liquid to the bottom. Add a microcap "bell", open-end down, to the melting point capillary. Heat the assembly gently in a Mel-Temp until a rapid stream of bubbles appears at the bottom of the bell; record this temperature. Turn off the heater, and observe the sample. When the temperature drops below the boiling point of the liquid, the pressure of the vapor inside the bell will drop and the sample will be drawn into the bell. Record the temperature at which the 4-methylcyclohexene is drawn into the bell. The boiling point range is the two temperature that were just recoded. If determining the temperature that the stream of bubbles appeared was difficulty, the capillary tube containing the now filled bell can be heated again, and when the liquid leave the bell, the boiling point of the liquid has been reached.

Chemical Test for Unsaturation

Place 2 drops of 4-methylcyclohexene into a small test tube. Add 5 drops of a methylene chloride solution of bromine to the 4-methylcyclohexene drop-wise. Make observations

about any colors or color changes observed. Repeat the chemical test for unsaturation using 2 drops of 4-methylcyclohexanol.

Experimental Report

Do not write a formal "experimental" describing the synthesis of 4-methylcyclohexene. Instead, in a typed report, using skeletal structures draw a balanced chemical equations for the reaction that was performed, report the yield (mass, moles, and percent) of the product, the physical appearance, the boiling point, and the results of the chemical tests for unsaturation. Please attach your IR spectra to the report. In addition, respond to the following prompts.

The lefthand side of the IR spectrum of the 4-methylcyclohexanol contains a peak at approximately 3340 cm^{-1}, whereas the IR spectrum of the 4-methylcyclohexene does not have a prominent peak at that position. Explain this difference.

The IR spectrum of the 4-methylcyclohexene contains new peaks at approximately 3025 and 1650 cm^{-1}. Explain the appearance of these new peaks; that is, explain what functional groups account for the appearance of the aforementioned peaks.

Explain why both IR spectra contain similar peaks between approximately 2950 and 2840 cm^{-1}.

The product, 4-methylcyclohexene, is forming in the presence of protic acids, and alkenes can react with acids. Based on the hypothesis that the 4-methylcyclohexene can react with the protons present in the solution draw the structures of other alkenes that could be produced.