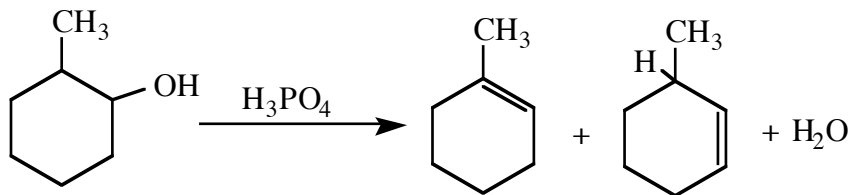


EXPERIMENT 9

DEHYDRATION OF 2-METHYLCYCLOHEXANOL



In this experiment, a microscale distillation apparatus will be used to perform an acid-catalyzed dehydration reaction of 2-methylcyclohexanol (mixed cis- and trans- isomers) to produce a mixture of methylcyclohexenes. The product mixture will be analyzed by qualitative tests for the presence of alkenes. The identity and relative amount of each product will be determined using gas chromatography. The experiment is derived from “Dehydration of Cyclohexanol” in C.F. Most, p. 335.

A. PRELAB ASSIGNMENT

1. Prepare a Table of Physical Constants for the following compounds: cis-2-methylcyclohexanol, trans-2-methylcyclohexanol, o-xylene, 1-methylcyclohexene, 3-methylcyclohexene, methylenecyclohexane, phosphoric acid. As usual, include structures, formulae, molecular weights, and other relevant properties.
2. Write the equation for the dehydration of 2-methylcyclohexanol in your notebook.

A. PROCEDURE FOR DEHYDRATION OF 2-METHYLCYCLOHEXANOL

Reaction

1. Set up the microscale distillation apparatus and sand bath according to the lab demonstration. (See diagram of Fractional Distillation, on the back page of this manual, but do not use packing in the column for the first distillation.) Pay attention to the correct position of the thermometer in the still head. Be sure that the thermometer fits tightly in the adapter.

2. Put 0.5 mL of 85% phosphoric acid (caution: phosphoric acid can cause severe burns) into a 5 mL round-bottom long-necked flask and add a magnetic stir bar. Mark the liquid level in the flask for future reference. Add 2.5 mL of 2-methylcyclohexanol (mixed isomers), measured accurately with a syringe.
3. Heat the mixture gently on the sand bath. (The part of the flask containing the liquid should be completely covered with sand.) Carefully distill the reaction mixture (start with a Variac setting of 70) until the residue in the flask (called the pot residue) has a volume of about 0.5 mL **or** until the boiling point (head temperature) rises above 111°C. Lower the heat if there is excessive foaming or if the temperature rises rapidly after distillation has started. Note the appearance and boiling range of the distillate.
4. Lower the sand bath to let the flask cool a little. Remove the thermometer briefly, and add about 2 mL of o-xylene (the chaser solvent) into the top of the column, using a disposable pipette. Mark the level of the upper layer in the boiling flask and distill again until the volume of the layer has been reduced by about half or the temperature drops below 112 °C.

Work-up and Isolation of Product

1. Wash the mixture with about 2 mL of saturated sodium chloride solution. (Cap and invert the tube a few times.) Remove the aqueous layer with a Pasteur pipette, and dry the organic layer over anhydrous potassium carbonate. Shake the mixture occasionally, and let it dry for at least 5 minutes. Meanwhile, clean the distilling apparatus first with water, then with ethanol, and finally with a little acetone. Evaporate the residual acetone with a dry pipette attached to the vacuum line. It is absolutely essential that the apparatus be **COMPLETELY DRY**.
2. Record the tare weight of a clean, dry vial with the cap. Be sure that the vial has a tight-fitting cap. Transfer the dry methylcyclohexene solution to the distilling flask, add a magnetic stir bar, and pack the neck of the flask **loosely** with stainless steel sponge. Distill the mixture slowly and carefully until the

head temperature starts to rise above 111°C or until the temperature drops below about 90°C. (The upper limit of 111°C is an approximation of a typical distillation.) To avoid contamination of the products with o-xylene, stop your distillation whenever the temperature rises more than one degree above the top of the range observed for distillation of the major bulk of your product mixture.

3. Determine the weight of the distillate. Keep the vial capped tightly at all times after weighing, since the alkenes evaporate rapidly.

Tests for Alkenes

Perform the following tests on your distillate to confirm the presence of alkenes.

1. Bromine Test for Unsaturation

Put 0.5 mL of tetrahydrofuran (THF) in a test tube. Add 2 drops of the liquid to be tested and stir the mixture. Add 2 drops of Bromine in Carbon Tetrachloride reagent, and mix. A positive test is disappearance (decolorization) of the orange-yellow color of the bromine solution.

Test the product mixture, 2-methylcyclohexanol, cyclohexene, cyclohexane, and o-xylene. Record your observations and results in tabular form.

Include a balanced equation showing stereochemistry for each positive test result.

2. Baeyer Test for Unsaturation

Put 0.5 mL of THF in a test tube. Add 2 drops of the liquid to be tested. Then add a 1% aqueous alkaline solution of KMnO_4 dropwise. Initial disappearance of the purple color (decolorization) is a positive test.

Test the product mixture, cyclohexene, 2-methylcyclohexanol, cyclohexane, and o-xylene. Record your observations and results in tabular form.

Include a balanced equation showing stereochemistry for each positive test result.

ANALYSIS AND CALCULATIONS

1. Calculate the yield and percent yield, assuming that the distillate is 100 percent mixed methylcyclohexenes.
2. From the gas chromatography trace of distributed to you, identify each product (and solvent, if any) by retention times. Be sure to note the conditions used to produce and record your chromatography trace. Attach the chromatograph to a right-hand page of your notebook with tape.

If the product is found to contain more than 2% xylene, the yield calculation must be corrected. Use the following formula:

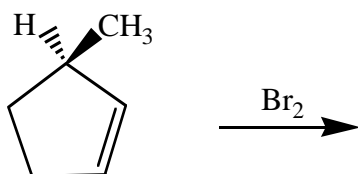
$$\% \text{ true product} = \frac{(\text{total weight}) - [(\% \text{ xylene}/100) \times \text{total weight}]}{\text{theoretical weight}} \times 100$$

B. QUESTIONS

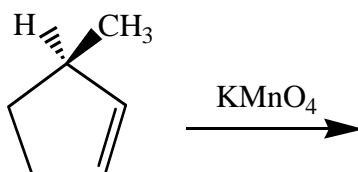
1. Based on the results obtained in your experiment, formulate a mechanism that will account for all observed products.
2. Instead of rapidly distilling her products, a student refluxed her reaction mixture. After drying and distilling, she obtained nearly 100% 1-methylcyclohexene. Explain, by means of a mechanism, what happened to her reaction mixture.
3. Define the following terms (1 to 2 sentences):
 - a. chaser solvent
 - b. catalyst
4. Predict the more stable chair conformation of both cis- and trans-2-methylcyclohexanol. Identify each substituent as being axial or equatorial. (Draw the structures.)

5. With careful attention to stereochemistry, determine all products for the following test reactions:

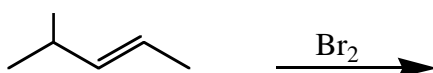
a.



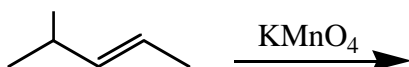
b.



c.



d.



C. DISCUSSION AND CONCLUSION

Include the following points in your discussion: Do the physical properties of the product, test observations and analysis results tell you anything? Is this reaction a good synthetic method? Explain your answer.

IMPORTANT FAMILIES OF ORGANIC COMPOUNDS

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