

Dehydration of 2-Methylcyclohexanol

Dehydration is the process of removing water. When fruit is dehydrated or dried, the removed water is not covalently bound to the substrate and the water is removed relatively easily. When chemical dehydrations occur, a covalent bond is broken to a hydroxyl group “-OH” and a covalent chemical bond is broken to a hydrogen on an adjacent atom. This process costs more energy. A new covalent bond forms between the two atoms on which the -OH and -H were bound. Therefore a chemical dehydration forms a new water molecule and a new double bond.

Dehydration is a commonly used industrial chemical process to form carbon-carbon double bonds. More details about this can be found in the on-line notes.

Phosphoric acid catalyzes the dehydration you will carry out. Drierite® is a desiccant which is added to the reaction flask. The Drierite® adsorbs both the water that forms and that is already present in 85% H₃PO₄. This helps shift the reaction equilibrium toward product. The reaction is being carried out in the bottom of a Hickman still. As the more volatile alkene product forms it vaporizes and collects in the ring. This further shifts the equilibrium. The product that condenses and runs down into the collection ring of the Hickman still should be dry and ready for yield determination.

Often more than one isomer can form during a dehydration reaction. Reaction conditions can have large effects on the relative amounts of the isomeric products. In this week's experiment, 2-methylcyclohexanol will be dehydrated, and three products may form. The three products are 1-methylcyclohexene, 3-methylcyclohexene and methylene cyclohexane.

The formation of product may be validated by IR or a Bayer test. The product composition may be determined by GC analysis.

Almost everything in the procedure is done in a particular way, so it is a good idea to follow it to achieve a good yield of the product. A reasonable yield of the alkene product is 40-70 %. Learn about different parts of a Hickman still before using and handle it with care. Each Hickman still has to be custom made and replacements are costly and not readily available.

PRE-EXPERIMENT ASSIGNMENT

Read and study this chapter of the manual and the on-line notes on the Organic Chemistry web site. You may also find it helpful to reread your organic text and lecture notes on acid catalyzed dehydration.

A student who has prepared for the Dehydration of 2-methylcyclohexanol experiment should be able to:

- 1) Draw the overall reaction, with all starting materials and all products.
- 2) Be able to draw and name all of the chemicals used and produced in this experiment.
- 3) Explain the main safety concerns associated with this experiment.
- 4) Explain the role of the Drierite® (Calcium Sulfate)
- 5) Give a drawing of, and identify the components from a drawing of, the Hickman still apparatus used for distillation. Explain the function of each part of the apparatus and compare them to the parts of a regular distillation setup that you used for fractional distillation.
- 6) Take an IR of the product. Interpret IR spectra of 2-methylcyclohexanol and the products. List and assign peaks that are present in the spectrum of product and not in the spectrum of 2-methylcyclohexanol, and vice versa.
- 7) Analyze the product using a GC. Interpret a GC Chromatogram including peak identification and percentage of each component.
- 8) Perform the day's experiment safely and successfully.

Quizzes given after the experiment has been performed may include:

- 8). Calculate the theoretical yield and the percent yield for this and similar experiments given the necessary data, and perform any of the intermediate calculations required by this process.
- 9) Predict the products of dehydration reactions, including those that involve rearrangement. For more details see your CHEM 2210 lecture materials.

The Reaction

It will save time if you turn on your sand bath in the hood as soon as you come to lab. Start with a setting of about 30. Check the temperature of your sand bath by carefully inserting only the bulb of a mercury thermometer into sand. Do not jam the end of the thermometer against the bottom of the sand bath. It is much hotter along the bottom and the liquid in the thermometer will boil and break the thermometer. Make sure that the temperature is about 140-150°C by adjusting the setting. Do not let the temperature go above 160°C. If the still is a little dirty in the bottom, it is fine and will not compromise the product yield or integrity. Do not use a still which contains water droplets. Using a short piece of a straw, load the bottom part of a Hickman still apparatus with granulated Drierite so that you have a little more than a half of the bottom volume filled. Make sure that all of the granules are on the bottom, and none of them are in the collection ring of the Hickman still. If some Drierite® gets in the ring, dump out the still and start again.

Place about 1 mL of 85 % H_3PO_4 in the bottom of the still with a Pasteur pipette, but once again do not contaminate the collection ring. A good idea is to wipe the pipette containing H_3PO_4 from the outside with a piece of a Kim-Wipe, quickly insert it into the Drierite layer in the bottom part of the Hickman still, and add the acid. After you mix the Drierite with the acid there will be no visible liquid.

Measure 0.75mL of 2-methylcyclohexanol either by pipetting into your reaction tube or by using your small syringe. Add the 2-methylcyclohexanol to the bottom of the Hickman still being careful not to contaminate the collection ring.

Place only the bottom part of the still into a preheated sand bath (it is important that temperature is 140-150°C and **not above 160°C**). Some of the Drierite should not be heated, so do not cover entire bottom of the apparatus with sand. Heat the apparatus and observe product condensation in the collection ring. The distillation should be completed in about 20 minutes. If no distillate is collected after 10 minutes of heating, consult with your instructor.

When you see no more distillate condensing in the collection ring, unplug the sand bath, raise the clamp on the ring stand, lifting the Hickman still from the sand, and let the apparatus cool to room temperature. Transfer your product from the collection ring into a pre-weighed small shell vial with a slant Pasteur pipette, cap it (don't forget to include the weight of the cap), and determine the yield.

The Infrared Analysis

Take an IR spectrum of a neat sample of your product by placing a small drop of it between two NaCl plates. Your instructor will provide you with an IR spectrum of your starting cyclohexanol.

The Gas Chromatography Analysis

Your instructor may want you to analyze your sample using Gas Chromatography (GC). Take a GC by injecting a small volume (~4 μl) into the designated GC machine. Record all of the machine parameters including column type and length, injection amount, oven temperature, injector temperature and detector temperature. Compare chromatogram to chromatogram of known materials. Determine amounts of each product present.

CLEANUP

Used Pasteur pipettes are placed in the broken glass box after use. Your product and all used reaction mixtures are poured into the non-halogenated organic liquid waste bottle in the hood if your instructor does not collect it.

Small amounts of left over phosphoric acid may be slowly added to a beaker of water (always add acid to water, never the other way around). Slowly pour this diluted acid down the sink with plenty of water running.

POST-EXPERIMENT ASSIGNMENT

Write the lab report and have it ready to turn in by the beginning of the next lab. Include your IR spectrum in your Data section and calculate the theoretical and percent yields. In your Conclusions section, interpret the IR spectrum and compare it to the spectrum of the starting 2-methylcyclohexanol provided by your instructor. Discuss the IR of the reactant. What IR is expected from a pure product. Compare this to the IR from the product obtained. Draw a conclusion about the purity of your product based on this comparison. Can the different alkenes be detected using the IR?

A GC may be run during the same class time or possibly one week later. Using the chromatogram state the amounts of each component present in the product mixture. Explain how each peak was assigned. Explain the product composition. Was the product predicted to be present in the largest amount, actually present in the largest amount? Prepare for the dehydration portion of the next quiz.