

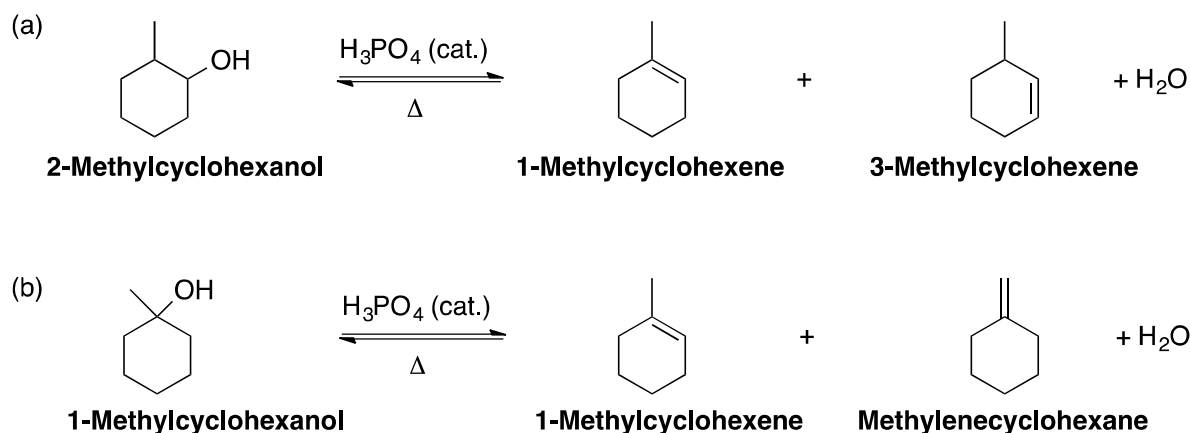
## Experiment 5 – Dehydration of Methylcyclohexanols

### Recommended Background Reading (McMurry's Organic Chemistry)

- Elimination Reactions: Chapter 11.7 – 11.10
- Reactions of Alcohols (Dehydration): Chapter 17.6
- Oxidative Cleavage of Alkenes: Chapter 7.9

As the name suggests, dehydration reactions involve the loss of water. In organic synthesis, a dehydration reaction is synonymous with an elimination reaction with an alkene product. The *regiospecificity* of the reaction is dependent on Zaitsev's rule, where the major product tends to be the more substituted alkene. When two different products are possible, these products are constitutional isomers of each other or in this case can be referred to as *regioisomers*. The type of *elimination mechanism* (E1 or E2) can depend on the type of reagent used as well as the substitution pattern of the starting material. In the case of the elimination of alcohols, reactions are performed under acidic conditions and therefore the E1 mechanism is favored. The exception would be for the dehydration of primary alcohols, which takes place *via* an E2 mechanism. Furthermore, when *isomerizable alkenes* are produced, the *stereochemistry* of the product (*cis* or *trans*) would be dictated by the type of mechanism taking place and the chirality of the starting material.

In this experiment, students will perform the acid-catalyzed dehydration of either **1-** or **2-Methylcyclohexanol** (**Figure 1**). The elimination reactions have two theoretically possible regioisomeric products. According to Zaitsev's rule, students should be able to predict the major and minor products. Students will use gas chromatography (GC) to analyze the reaction mixture and compare to the retention times of commercially available standards to confirm their hypotheses. In addition, students will confirm the presence of an alkene in their product with a potassium permanganate (KMnO<sub>4</sub>) chemical test. KMnO<sub>4</sub> is used in what we call the "Barney reaction." It starts off dark purple and will turn brown with the formation of a precipitate (MnO). Refer to the McMurry text for a further discussion of the permanganate-mediated oxidative cleavage reaction.



**Figure 1.** Dehydration of methylcyclohexanols.

Students will be assigned an alcohol starting material when entering lab. The lab notebook and pre-lab questions should address both reactions to be prepared for either.

### **Notebook Preparation** – students work individually

- *Purpose:* Draw both reaction schemes from **Figure 1**. Circle your assigned reaction in lab.
- *Reagent Table:* Make a table with amounts physical properties of each alcohol and alkene in **Figure 1** as well as for  $\text{H}_3\text{PO}_4$ . This includes amount (mg or mL), mmol, MW, bp or mp, density, and a one-word hazard if applicable (irritant, corrosive, etc.)
- *Procedure:* Step-wise written procedure in your own words. Include a sketch of the microscale distillation apparatus and filter pipet as described in lecture.
- *Cleanup & Safety:* Copy **Table 1** into your notebook.

### **PROCEDURE**

Prepare a sand bath to reach a target temp of 150 – 170 °C on a hotplate at your station. Check the temperature periodically but *do not leave the thermometer in the sand bath*. Recall that hot plates should never be set higher than ½ of the maximum heat setting (med-low to medium is ideal). Keep an eye on temperature and adjust accordingly. It may be appropriate to turn off the hot plate for a little while. Do not touch the sand bath or container while it is hot!

The dehydration reaction will be run “neat” meaning no additional solvent is used. The alcohol acts as both the starting material and the solvent. Obtain 750  $\mu\text{L}$  of the assigned alcohol using the provided pluringe (1- or 2-Methylcyclohexanol; the 2-methyl compound is a *cis/trans* mixture) and dispense into a pre-weighed 5-mL round-bottom flask, then obtain the mass of starting material by difference. 1-Methylcyclohexanol is a solid at room temperature (mp ~24 °C) and may be in a warm water bath. Carefully add 225  $\mu\text{L}$  of concentrated phosphoric acid ( $\text{H}_3\text{PO}_4$ ) using the pluringe provided. Note that conc.  $\text{H}_3\text{PO}_4$  is an 85% w/w solution in water (85 g of  $\text{H}_3\text{PO}_4$  per 100 g of solution; density = 1.685 g/mL). Add a boiling chip and clamp a Hickman still to set up the microscale distillation apparatus using a small amount of grease (include a sketch of this apparatus in the notebook, given in lecture). Use a plastic Keck clip to connect the flask to the still. Attach a water-cooled condenser on top of the Hickmann still to prevent product from evaporating. Immerse the vial or flask a little more than half-way into the sand bath. It is okay to put the reaction in the sand bath before it reaches the target temperature.

As the reaction occurs, any alkene products that form will distill and collect into the Hickman still, driving the equilibrium to the right to make even more product! Keep a careful eye on the amount of liquid remaining in the flask. Turn off the heat once approximately half of the volume has been collect in the Hickman still (or when half the volume in the flask is gone). Do not move the apparatus to cool as the distillate could drop right back into the reaction flask and the product must be distilled again. Using a pipet, carefully transfer the distillate to a screw-cap vial. Add small microspatula-fulls of  $\text{Na}_2\text{SO}_4$  at a time until the drying agent runs free in suspension (snow globe-style). Cap the vial and let the system sit for 5 minutes. Filter through a pipet with a loose cotton plug as instructed by the TA and collect the filtrate into a pre-weighed dry screw-cap vial. Include a sketch of the filter pipet in the notebook as given in lecture. Record the mass. Recalculate the theoretical yield based on the mass of alcohol and use this value to calculate % yield (see in-lab #2).

### **Analysis: IR, GC, and $\text{KMnO}_4$ Test** – perform in any order

**GC:** Inject 0.2  $\mu\text{L}$  of the product only. Compare with the retention times on the provided chromatograms to identify the peaks in your product. Do not remove the chromatograms from the wall! Integrate the peaks of the product mixture and calculate percent composition. Refer to the pages in your notebook for performing and analyzing GCs. You must analyze the chromatograms for retention time and percent composition before leaving the lab. Record your data in your notebook in table format.

**IR:** Obtain the IR spectrum of your product. Refer to the pages in your notebook for performing IR. Your TA will provide the IR of the starting material. Analyze both of these IRs in table format before leaving the lab. It is highly recommended, but not required, that you make an IR table for an alcohol and alkene before coming to lab (same format as in the IR exercise). At minimum, include in your notebook the expected stretches in alcohols and alkenes. The literature IR spectra for the alkenes are provided in a separate document online. Literature IR spectra for the alcohols are not provided and can be omitted from the table. Water can interfere with the IR spectrum of the product. If you observe an O-H stretch in the IR, it could either be from the presence of water or starting material. Analysis of the GC will be your definitive answer on that point.

**Permanganate Test:** Add 0.5 mL of the provided 0.5%  $\text{KMnO}_4$  solution to four separate, 10 x 75 mm test tubes. Label the test tubes as follows:

1. Product      2. Cyclohexane      3. Cyclohexene      4. Alcohol (starting material)

Add 2-3 drops of product to tube #1. Carefully agitate the contents of the tube and record your observations (color change and/or formation of a precipitate). The formation of a black-brown precipitate is considered a positive test. Repeat the test adding cyclohexane to #2, cyclohexene to #3, and the starting alcohol to #4.

**Table 1.** Clean-up and Safety – copy into your lab notebook.

| Clean-up                                                                                                                                                                                                                                               | Safety                                                                                                                            |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|
| <i>Liquid methylcyclohexanols waste:</i><br>*Remaining contents of the reaction flask (transfer by pipet)<br>* Product after analysis                                                                                                                  | $\text{H}_3\text{PO}_4$ is corrosive. Handle with care.                                                                           |
|                                                                                                                                                                                                                                                        | 2-Methylcyclohexanol & $\text{Na}_2\text{SO}_4$ are irritants.                                                                    |
|                                                                                                                                                                                                                                                        | $\text{KMnO}_4$ is a strong oxidizer.                                                                                             |
|                                                                                                                                                                                                                                                        | 1-Methylcyclohexanol, cyclohexane, and cyclohexene are flammable.                                                                 |
| <i>Alkene tests waste:</i><br>*Use a pipet to transfer from test tube into waste.                                                                                                                                                                      | Allow the sand bath to cool before breaking down. Handle warm/hot equipment with hot mitts provided in the lab, NOT paper towels. |
| <i>IR:</i> Carefully wipe salt plates with salted acetone and return to the desiccator.<br><i>GC:</i> Rinse GC needles 3x with acetone (regular, not salted) before and after injections.<br><b>DO NOT INJECT ALCOHOL</b> as it will clog the syringe. |                                                                                                                                   |
| Generally make the room look just as good as it did in the beginning of lab!                                                                                                                                                                           |                                                                                                                                   |

Adapted from Palleros, D. "The Dehydration of Methylcyclohexanols" in *Experimental Organic Chemistry*. Wiley: New York, **2000**, p. 268 - 272.

## Pre-lab Questions

1. (5 points) Do you expect the dehydration of 1-methylcyclohexanol to proceed by an E1 or E2 mechanism? Calculate the theoretical yield of product (in mg and mmol) if 750  $\mu\text{L}$  of alcohol were used. Show your work. Review your general chemistry text/notes before asking for help!
2. (5 points) Do you expect the dehydration of 2-methylcyclohexanol to proceed by an E1 or E2 mechanism? Calculate the theoretical yield of product (in mg and mmol) if 750  $\mu\text{L}$  of alcohol were used. You do not need to show your work (you already did in #1).
3. (4 points) Draw the organic products for the reaction of 1-methylcyclohexene with  $\text{KMnO}_4$  (McMurry Chapter 7.9). Indicate the by-product that forms the brown precipitate.
4. (4 points) What compound(s) do you expect to be in the distillate when the dehydration reaction is complete?
5. (4 points) What is the advantage of setting up this reaction with a distillation head in between the round-bottom flask and condenser, as opposed to using a water-cooled condenser for refluxing the reaction?
6. (4 points) What is the purpose of  $\text{Na}_2\text{SO}_4$  in this experiment?
7. (4 points) Could you distinguish between 3-methylcyclohexene and methylenecyclohexane based only on their GC retention times? Base your answer on their boiling points.

## In-lab Questions

1. (4 points) Report the mass (in mg) and millimoles (mmol) of product obtained (actual yield).
2. (4 points) Calculate the percent yield (% yield) of the synthesis. Show your work.  
$$\% \text{ yield} = [(\text{actual yield}) / (\text{theoretical yield})] \times 100\%$$
3. (5 points) Report the GC experimental conditions from the bulletin board above the instrument. In table format, report the GC retention times and integration for products. Report the retention times for the standards and identify the peaks in the chromatogram of the product. Present your data in table format.
4. (4 points) Report the percent composition of the product. Discuss the distribution of products in terms of the relative stability of the products.
5. (4 points) Report and briefly discuss the results of the permanganate test.
6. (4 points) Interpret the IR results. Briefly discuss the main identifying peaks. Include two typed tables for the detailed analysis of the IR spectrum of the starting material and product.
7. (5 points) Report the instrument limit of error (ILE) for each measuring device used for the reaction (numbers & units). Refer to the Error Analysis Activity for a refresher on determining ILE's. How did these sources of intrinsic error affect your result (reported yield)?

For example: "*Bromine (0.30 mL  $\pm$  0.05 mL, 17% I.E.) was measured with a 1-mL plunger, which has an uncertainty (ILE) of  $\pm$  0.05 mL.*" Your numbers may be different!

**Exp 5 – Dehydration of  
Methylcyclohexanols**

Name \_\_\_\_\_

Section Day \_\_\_\_\_ Time \_\_\_\_\_

TA Name \_\_\_\_\_

CHEM 8L GRADING RUBRIC - Use as cover page for report

| SECTION                                                                                                                                                      | INSTRUCTOR COMMENTS | POINTS ASSIGNED |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|-----------------|
| IN-LAB QUIZ                                                                                                                                                  |                     | / 5             |
| <b>LAB REPORT</b>                                                                                                                                            |                     |                 |
| <b>ABSTRACT</b><br>One paragraph, four-six sentences:<br>Purpose, procedure, main result(s), and<br>conclusion(s). Refer to technical writing<br>guidelines. |                     | / 25            |
| <b>INTRODUCTION</b><br>Original responses to pre-lab questions<br>with TA initials                                                                           |                     | / 30            |
| <b>RESULTS</b><br>The main results are stated, as outlined in<br>the in-lab questions, using complete<br>sentences.                                          |                     | / 30            |
| <b>NOTEBOOK PAGES</b><br>Proper format: reaction scheme, chemical<br>info table, experimental procedure, waste<br>and clean-up procedure.                    |                     | / 15            |
| <b>NEATNESS AND ORGANIZATION</b><br>Proper order and format, spelling and<br>grammar (see syllabus for full descriptions<br>of each section).                |                     | / 10            |
| <b>LAB TECHNIQUE &amp; CLEAN UP</b><br>Lab space left clean, proper technique,<br>instructions followed, checked in with TA<br>before leaving.               |                     | / 10            |
| <b>LAB REPORT TOTAL</b>                                                                                                                                      |                     | <b>/ 125</b>    |