Experiment 5 – Dehydration of Methylcyclohexanols

Learning Objectives

- Observe microscale distillation apparatus to collect products of a dehydration reaction
- Use gas chromatography to determine percent composition of products, exemplifying Zaitsev's rule
- Apply IR Spectroscopy to determine reaction success
- Interpret chemical tests to determine the presence or absence of alkene

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* Please find "How to Prepare & Assignments" after the procedure

As the name suggests, dehydration reactions involve the loss of water. A dehydration reaction is a type of elimination reaction with an alkene product (C=C double bond). 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*) may be dictated by the type of mechanism taking place and the chirality of the starting material.

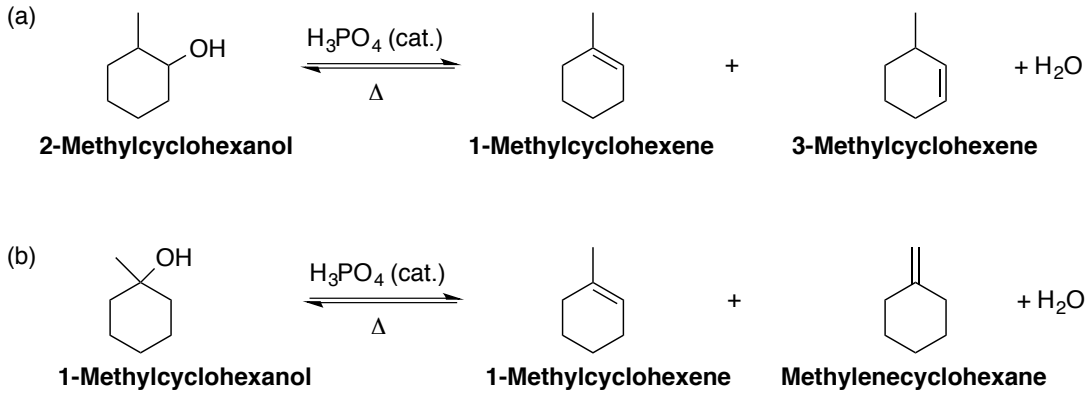


Figure 1. Dehydration of methylcyclohexanols

In this experiment, students will perform the acid-catalyzed dehydration of either **1-** or **2-methylcyclohexanol** (**Figure 1**). Students are assigned an alcohol starting material at the beginning of lab. The pre-lab questions should address both reactions to be prepared for either. The elimination reactions have two possible regioisomeric products. The major and minor products can be predicted according to Zaitsev's rule, which states that a more highly substituted alkene is more stable and favored. Students 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 confirm the presence of an alkene in the product with the potassium permanganate ($KMnO_4$) chemical test. $KMnO_4$ is lovingly called the "Barney reaction." It starts off dark purple and turns brown with the formation of a precipitate (MnO_2). Refer to the McMurry or Klein text for further discussion of the permanganate-mediated oxidative cleavage reactions.

PROCEDURE

Reaction Setup

Prepare a sand bath to reach a target temp of 150 °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 μL of the assigned alcohol using the provided pluringe 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 μL of concentrated phosphoric acid (H_3PO_4) using the pluringe provided. Note that conc. H_3PO_4 is an 85% w/w solution in water (85 g of H_3PO_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). Use a plastic Keck clip to connect the flask to the still. Connect water hoses with clamps to a microscale condenser so that the water enters on the bottom and exits through the top. Attach the condenser on top of the Hickmann still to prevent product from evaporating. Immerse the 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.

Reaction Workup

As the reaction occurs, any alkene products that form will boil 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 collected 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-fuls of Na_2SO_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. Record the mass. Recalculate the theoretical yield based on the mass of alcohol provided in lab and use this value to calculate % yield.

Analysis: IR, GC, and $KMnO_4$ Test – *perform in any order*

GC: Inject 0.2 μL of the product only. Compare with the retention times on the provided chromatograms to identify the peaks in your product. 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 and 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% $KMnO_4$ 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 to be 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.

<table>
<tr><th>Clean-up</th><th>Safety</th></tr>
<tr><td rowspan="4">Liquid methylcyclohexanols waste:
*Remaining contents of the reaction flask (transfer by pipet)
* Product after analysis</td><td>H_3PO_4 is corrosive. Handle with care.</td></tr>
<tr><td>2-Methylcyclohexanol & Na_2SO_4 are irritants.</td></tr>
<tr><td>$KMnO_4$ is a strong oxidizer.</td></tr>
<tr><td>1-Methylcyclohexanol, cyclohexane, and cyclohexene are flammable.</td></tr>
<tr><td>Alkene tests waste:
*Use a pipet to transfer from test tube into waste.</td><td>Allow the sand bath to cool before breaking down. Handle warm/hot equipment with hot mitts provided in the lab, NOT paper towels.</td></tr>
<tr><td colspan="2">IR: Carefully wipe salt plates with salted acetone and return to the desiccator.
GC: Rinse GC needles 3x with acetone (regular, not salted) before and after injections.
DO NOT INJECT ALCOHOL as it will clog the syringe.</td></tr>
</table>

Experiment adapted from Palleros, D. “The Dehydration of Methylcyclohexanols” in *Experimental Organic Chemistry*. Wiley: New York, **2000**, p. 268 - 272.

How to Prepare & Assignments - Follow Exp 5 Canvas Module…

Before Lab

- Read this PDF and/or listen to podcast
- Attend and/or watch **lab lecture,** taking notes on **lecture templates,** and the **pre-lab videos**
- Practice the lab online, including common mistakes, on the **Slugs@home platform**
- **Pre-lab questions** incorporated into **Pre-lab Quiz** – check Canvas for due date

Lab Notebook Preparation – *Required before lab;* Use the **worksheet** to prepare your **lab notebook** …

- **Purpose:** brief summary of the main lab goals and dehydration reaction schemes
- **Reagent Table** – add chemical properties; Wikipedia is a reliable source for chemical info
- **Procedure with Diagrams** – hand-drawn using procedure in this PDF, Slugs@home, & class notes
  - Instructions, sketches, & labels for all **equipment, chemical names** with **amounts**, & **transfers**
  - Format: Break it up with flow charts, bullet-points, comic strip, and/or whatever works for you!

During Lab

- Check the **safety rules** to dress for lab and arrive a few minutes early to **Thimann Labs**
- **Pre-lab talk:** tips for success and open Q&A; Show your **lab notebook pages** to your TA
- Perform the experiment with a partner, fill out data & observations in **lab notebook**

After Lab

- Individual: Upload **Notebook Pages** to Canvas by midnight on lab day – completeness / participation
- Work with your partner to complete the **Lab Report** – due date on Canvas
  - One student uploads the complete report to GradeScope (GS)
  - "**Select Pages**" then "**Add Group Members**" to include your partner's name

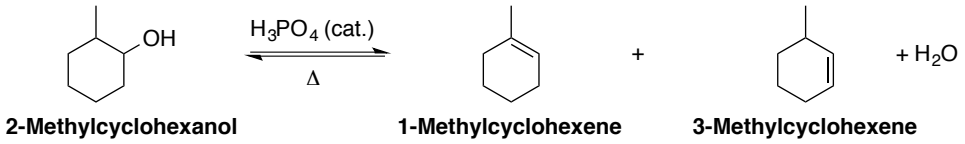
Additional Background Reading on Reactions

Reaction	**Sections in McMurry Organic Chemistry, 8th ed.**	**Sections in Klein Organic Chemistry, 3rd ed.**
Elimination Reactions	11.7-11.10	7.1, 7.6 – 7.7, 7.9, 7.11
Dehydration	17.6	12.9
Oxidative Cleavage of Alkenes – permanganate test	7.9	8.12

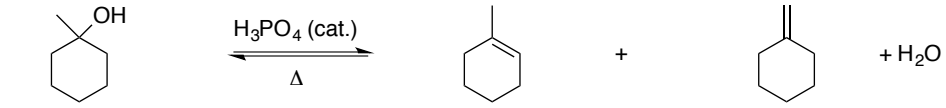
Pre-lab Questions

Incorporated into individual Canvas pre-lab quiz due the day before lab.

The acid-catalyzed dehydration of alcohols affords a mixture of two alkene isomers, along with water. Students carry out this reaction using with 750 μL of 1-methylcyclohexanol (density = 0.919 g/mL) or 2-methylcyclohexanol (density = 0.93 g/mL) and 225 μL of a concentrated solution of phosphoric acid (85% w/w, sol'n density = 1.685 g/mL). *Note: "w/w" = weight per weight, in this case 85 g of pure H_3PO_4 per 100 g of H_3PO_4 concentrated solution.*



2-Methylcyclohexanol **1-Methylcyclohexene** **3-Methylcyclohexene**



1-Methylcyclohexanol **1-Methylcyclohexene** **Methylenecyclohexane**

For 1-3: Show your work with units on every value using dimensional analysis – how units cancel.

1. **Convert the amounts of 1-methylcyclohexanol, 2-methylcyclohexanol, and phosphoric acid into mmols.** With the exception of molecular weights, all conversion factors are provided in the paragraph above. Calculate molecular weights (g/mol) using the structures above.

2. 1-Methylcycohexanol is the limiting reagent in the reaction (catalysts are regenerated, cannot be limiting). What is the **theoretical yield (in mg) of 1-methylcyclohexene** in this reaction? Both alkene products have the same molar mass. For simplicity, assume a 1:1 ratio of alcohol to 1-methylcyclohexene in the calculation.

3. 2-Methylcycohexanol is the limiting reagent in the reaction (catalysts are regenerated, cannot be limiting). **What is the theoretical yield (in mg) of 1-methylcyclohexene in this reaction?** Use the same assumption as in #2.

4. Do you expect the dehydration of 1-methylcyclohexanol and 2-methylcyclohexanol to proceed by an **E1 or E2 mechanism**? List **two factors** about these reactions to support your answer.

5. Draw the **products** for the reaction of **1-methylcyclohexene with $KMnO_4$** (McMurry Chapter 7.9 or see lecture notes – Klein text doesn't specifically cover oxidative cleavage with $KMnO_4$). Indicate the **by-product** that forms the **brown precipitate**.

6. What **compounds** do you expect to be in the **distillate** when the dehydration reaction is complete?

7. What is the **purpose of Na_2SO_4** in this experiment?

8. Look up the boiling points of **3-methylcyclohexene** and **methylenecyclohexane**. **Explain** why only one of these compounds is injected as a **standard for GC retention time**.

LAB REPORT

Complete the report with your lab partner – one student uploads to GradeScope

Abstract

Consult the writing guidelines to write a draft of the abstract after completing the in-lab questions and before leaving lab, time permitting. Either way, plan ahead to get help with the abstract by going to TA office hours or submitting a draft with the worksheet on Canvas.

- **Purpose** – read the introduction to this document to devise a one-sentence purpose
- **Methods** – include all chemical names, specialized glassware, and methods used for analysis
  - *Note:* this is NOT the procedure!
- **Results** – mass recovery (mg), percent yield, one main result for each method for analysis of product
  - GC: report percent composition only, not retention times & areas
- **Conclusion** – are the results consistent with predictions / purpose of the experiment? Restate the predicted major product and whether this was observed.

In-lab Questions

1. Report the **mass (in mg)** and **millimoles (mmol) of product** obtained (actual yield). Show your work for the mole calculation.

2. Calculate the **percent yield (% yield)** of the synthesis using the 'actual yield' from #1 and 'theoretical yield' from the pre-lab. Show your work.

% yield = [(actual yield) / (theoretical yield)] x 100%

3. Report the **retention times for the standards** in table format. Show your work for each calculation. Consider which reaction you were assigned (1-methyl or 2-methylcyclohexanol) to be sure you have retention times for both potential products. *Hint: refer to pre-lab questions for reminder on product retention times.*

4. Report the **GC retention times and integration for products. Identify each peak** in the chromatogram of the product.

5. Report the **percent composition of the products**. **Discuss** the distribution (ratio) of products in terms of the relative stability of the products.

6. Report and briefly discuss the results of the **permanganate test**.

7. Interpret the **IR results**. Include two typed tables for the detailed analysis of the IR spectrum of the starting material and product. Briefly discuss the **main identifying peaks** – how can IR be used to determine whether the reaction was complete?

8. The questions above were about individual forms of analysis. Now it's time to put it all together! Briefly discuss the **success of your dehydration reaction using chemical test results, IR, and GC data** combined. What is the **main product**? Are any other compounds present in your product mixture? If so, identify the impurities or by-products to the best of your ability.

9. What would be the substitution product of the reaction of **1-methylcyclohexanol** with a nucleophilic acid like **HCl** instead of H_3PO_4? Draw the full chemical reaction.