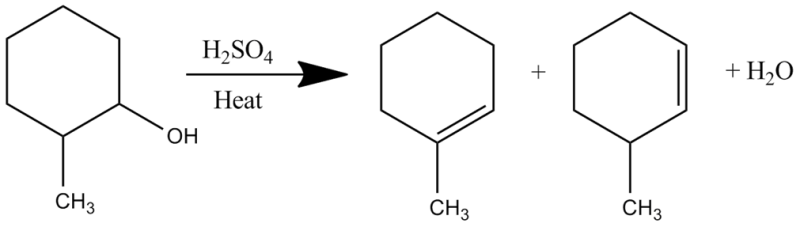
Experiment 3

Dehydration of 2-Methyl-cyclohexanol

In this experiment, you will perform an acid-catalyzed dehydration of *cis*- and *trans*-2-methyl-cyclohexanol to form a mixture of 1-methyl and 3-methyl-cyclohexene. This reaction happens via an E1 mechanism. You will collect samples of these products and test them for unsaturation. You will also test the same products using gas chromatography with the Go Direct Mini GC. Your analysis by gas chromatography will help determine the percent yield of each product. You will use this analysis to determine the major product and, from that, infer the more stable carbocation formed during the intermediate step.



cis- and *trans*-2-methyl-cyclohexanol → 1-methyl-cyclohexene + 3-methyl-cyclohexene + H_2O

OBJECTIVES

- Perform the acid-catalyzed dehydration of *cis*- and *trans*-2-methyl-cyclohexanol.
- Test the products for unsaturation.
- Determine the major product of the dehydration using gas chromatography.

MATERIALS

One of the following
- Chromebook, computer, or mobile device with Vernier Instrumental Analysis app[1]
- LabQuest 2 (software is pre-installed; v2.9.0 or newer required)[2]
- LabQuest 3 (software is pre-installed; v3.0.7 or newer required)[2]

Go Direct Mini GC
Go Direct Wide-Range Temperature and Graphical Analysis 4 app[3]
1 µL Hamilton syringe
goggles and gloves
paper towel or lint-free wipe
n-hexane
cis- and *trans*-2-methyl-cyclohexanol
magnetic stir bar
25 mL round-bottomed flask
9 M sulfuric acid
fractional distillation apparatus

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[1] Instrumental Analysis v1.3 or newer required; download the most recent version for free at **www.vernier.com/ia**

[2] Download the most recent version of LabQuest software for free at **www.vernier.com/downloads**

[3] Any temperature probe or thermometer that can measure temperature in the fractional distillation apparatus will work.

heating mantle
stir plate
10 mL graduated cylinder
ice-water bath
pipettes
small separatory funnel
3 M sodium hydroxide solution
10 mL saturated sodium chloride solution
25 mL Erlenmeyer flask
anhydrous calcium chloride
test tubes
0.1 M bromine in dichloromethane
potassium permanganate solution
scale

PRE-LAB ACTIVITY

Complete Table 1. This information is a common starting point for understanding the behavior of a set of substances that may be found in a mixture being tested by gas chromatography.

Table 1

Compound	Boiling temperature (°C)	Molar mass (g/mol)	Chemical structure
2-methyl-cyclohexanol			
1-methyl-cyclohexene			
3-methyl-cyclohexene			

PROCEDURE

Part I Distillation

1. Put on safety goggles and gloves.

2. Place a small magnetic stir bar and 5 mL of the mixture of *cis*- and *trans*-2-methyl-cyclohexanol in a 25 mL round bottomed flask, and add 3 mL of 9 M sulfuric acid. Gently swirl the flask to thoroughly mix the liquids.

3. Set up the fractional distillation apparatus as shown in Figure 1. Attach the flask prepared in Step 2. Use a 10 mL graduated cylinder, cooled in an ice-water bath, as the receiver.

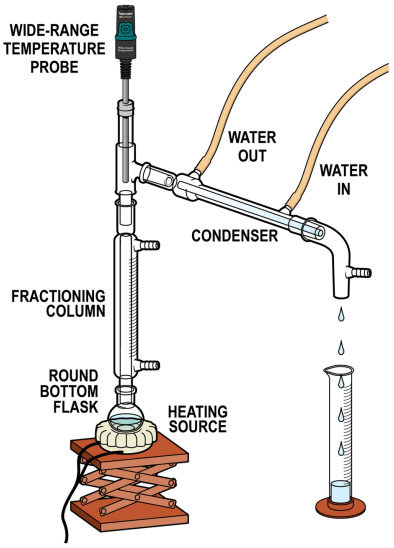

Figure 1

4. Heat and stir the reaction mixture using a heating mantle and magnetic stirrer. Adjust the settings to get a steady distillation rate.

5. Maintain the distillation temperature between 95°C and 100°C, and collect the distillate at a rate of about one drop, every one to two seconds, until ~3 mL of the organic olefin mixture has been collected. If the distillation rate becomes very slow, add 3 mL of water to the reaction flask and resume the distillation.

6. Transfer the distillate to a small separatory funnel and wash the organic product successively with 10 mL of water, 10 mL of 3 M aqueous sodium hydroxide solution, and 10 mL of saturated sodium chloride solution.

7. Drain the organic layer into a 25 mL Erlenmeyer flask and add a small amount of anhydrous calcium chloride. After swirling for a few minutes, if the solution is not clear, add more of the drying agent, swirl, and wait until it clears. Decant the organic solution away from the $CaCl_2$ using a Pasteur pipet, and transfer the solution to a tared vial.

8. Weigh the products and calculate the percentage yield.

Part II Test for unsaturation

9. Conduct a bromine test for unsaturation.
   a. Obtain two test tubes.
   b. Place ~1 mL of 0.1 M bromine in dichloromethane in each test tube.
   c. Add ~1 drop of the starting material to the first test tube.
   d. Add ~1 drop of the products to the second test tube.
   e. The rapid disappearance of the orange bromine color to give a colorless solution is indicative of unsaturation. Record the result for each test in the data table.

10. Conduct the Baeyer test with potassium permanganate for unsaturation.
   a. Obtain two test tubes.
   b. Place 0.5 mL of the starting material into a clean test tube.
   c. Add ~2 drops of potassium permanganate solution. The formation of a heavy brown precipitate (MnO_2) is indicative of unsaturation.
   d. Repeat Steps b and c for the products. Record the result for each test in your data table.

Part III Gas chromatography

11. Set up the Go Direct Mini GC by following the directions for your equipment:

Instrumental Analysis

   a. Launch Instrumental Analysis.
   b. Connect the Mini GC to your Chromebook, computer, or mobile device via USB or Bluetooth wireless technology. If using Bluetooth, click or tap Connect an Instrument, connect to your Mini GC, and click or tap Done.
   c. Click or tap Gas Chromatography.
   d. Set the temperature and pressure profile to the parameters listed in Table 2. Then, click or tap Apply to initiate the profile.

LabQuest

   a. Connect the Go Direct Mini GC to your device via USB or Bluetooth wireless technology. If using Bluetooth, tap the Sensors menu and choose Wireless Device Setup►Go Direct. Select your instrument and tap OK.
   b. Start data collection.
   c. Set the GC Profile settings to the values in Table 2.

Table 2

Start temperature (°C)	45
Hold time (min)	2
Ramp rate (°C/min)	5
Final temperature (°C)	95
Final hold time (min)	8
Pressure (kPa)	11

12. While the Mini GC is warming up, follow the procedure in this step to clean and flush the syringe with n-hexane. **Important**: The glass syringe is fragile. Be careful not to bend the needle or bend the plunger. Never pull the plunger back more than 50% of its total volume.
    a. Depress the plunger fully.
    b. Submerge the tip of the syringe needle into the vial of n-hexane. **DANGER**: *n-Hexane,* C_6H_{14}: *Keep away from heat, sparks, open flames, and hot surfaces—highly flammable liquid and vapor. Do not eat or drink when using this product. Avoid breathing mist, vapors, or spray. May be fatal if swallowed and enters airways. May cause damage to organs. Causes skin and eye irritation. May cause drowsiness or dizziness. Suspected of damaging fertility or the unborn child. Do not handle until all safety precautions have been understood*.
    c. Pull back the plunger to fill the barrel with 0.4 µL of n-hexane.
    d. Expel the liquid onto a lint-free wipe or a paper towel.
    e. Repeat Steps a–d at least two times, or until you are comfortable pulling up a liquid into the syringe and measuring the volume in the syringe barrel.

13. Follow the process in Step 12 to clean and flush the syringe with a 10:1 hexane:2-methyl-cyclohexanol dilution of your starting material, the first sample to be injected into the Mini GC.

14. Once the Mini GC has reached the correct start temperature and pressure, the software will indicate that the GC is ready for injection and the check LED will turn green. Collect a 0.2 µL volume of the 10:1 hexane:2-methyl-cyclohexanol dilution of your starting material for injection. Insert the needle into the injection port of the Mini GC. Depress the syringe plunger; immediately following, press the button on the Mini GC to initiate data collection. Be careful not to bend the plunger as you press it down. Pull the needle out of the injection port immediately. Data collection will automatically stop after 20 minutes, or you can choose to end it early if you are satisfied that your species has eluted completely.

15. Name your sample appropriately.
    - Instrumental Analysis: Click or tap the y-axis label. Click or tap the pencil icon next to the data set you wish to rename. Name your sample set and then click or tap Rename.
    - LabQuest: From the Table screen, tap the Run 1 label. Name your sample set and tap Done.

16. Analyze the chromatogram.
    - Instrumental Analysis: Drag across the peak to select it, then click or tap Add Peak Integral, . Record the retention times in Table 3.
    - LabQuest: From the Analyze menu, choose Advanced, then Peak Integration. Select the signal you wish to analyze. Once the Peak Integration screen appears, highlight the peak you wish to analyze and tap Add. Record the retention times in Table 3.

17. Test the products.
    a. Click or tap Initiate Data Collection (Instrumental Analysis) or Collect (LabQuest). Then, click or tap Apply; you will use the same parameters as before.
    b. While waiting for the instrument to warm up, follow the process in Step 12 to clean and flush the syringe with the product you want to test.
    c. Repeat Steps 14–16.
    d. Repeat this process to test the remaining products.

18. Save the file as directed by your instructor. Keep your test results open; you will need to refer to the various chromatograms to answer the Data Analysis questions.

19. When you are done with data collection, make sure to turn the Mini GC power switch to the off position and disconnect the Mini GC from AC power.

DATA TABLE

Table 3			
Compound	Bromine test result	Baeyer test result	Retention time (min)
2-methyl-cyclohexanol			
1-methyl-cyclohexene (from product)			
3-methyl-cyclohexene (from product)			

DATA ANALYSIS

1. What was your reaction percentage yield?

2. Identify the major product. Justify your answer.

3. Draw the E1 reaction scheme for the formation of 1-methyl-cyclohexene.

4. Draw the E1 reaction scheme for the formation of 3-methyl-cyclohexene.

5. Between the two reaction schemes, which is the more stable carbocation? Justify your answer.