

Experiment #5, Alkenes: Preparation, Reactions, and Properties

Experimental Organic Chemistry: A Miniscale and Microscale  
approach by Gilbert and Martin, Section 10.1-10.3

8-7-06

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INTRODUCTION:

Alkenes are very important reagents in the production of the Diels-Alder reaction and in the dehydration of alcohols. Using a strong acid as a catalyst, one can dehydrate an alcohol to produce an alkene. However, several alkenes can be produced depending of the thermodynamic stability of the products. The thermodynamic stability can be calculated experimentally using Gibbs-free energy and can be compared to the energy calculated in Chem3D. In this experiment, we will convert 2-methylcyclohexanol to a mixture of 1-methyl- and 3-methylcyclohexene. The double bond is more selective to one product than another and will be proven with the Gas-Liquid chromatograph. The purpose of this lab is to verify that the more substituted carbon will receive the double bond at a greater percentage in this experiment. A fractional distillation will be used to eliminate the hydroxide and drive the reaction towards the products, incorporating LaChatlier's principle.

PROCEDURE

- Place a small magnetic stirbar and 5-mL of the mixture, cis & trans 2-methylcyclohexanol in a 25-mL round bottom flask, add to this 3-mL of 9M sulfuric acid.
- Adjust for even stirring rate and distill the mixture through a fractional distillation setup. Use thermowell heater as the heat source. Use your 10-mL graduated cylinder in an ice-water bath as your receiver. Make a record of the volumes and temperatures.
- Collect distillate at a rate of one drop every one or 2 seconds.
- If, at the end of the distillation, the rate of distillate becomes very slow and if you don't have 3-4-mL of the organic olefin mixture in your distillate, add 3-mL of water to the flask and resume the distillation.

- Transfer the distillate to a small separatory funnel and wash the organic product successively with 10-mL of water, 10-mL of 3 N aqueous sodium hydroxide solution, and 10-mL of saturated sodium chloride solution.
- Drain the organic layer into a 25-mL Erlenmeyer flask and dry it over a small amount of anhydrous calcium chloride.
- After swirling for a few minutes, decant the solution away from the  $\text{CaCl}_2$  using a Pasteur pipet to transfer the solution to a tared vial. (The solution should be clear) Weigh and calculate the % yield for the reaction. Do not distill.
- Test the product mixture for unsaturation with the Bromine & Baeyer Test. Carry out the two control tests. One on cyclohexane (which should be negative) and one on cyclohexene (which will be positive). Use test tubes for the tests. The Baeyer test will form brown precipitate for a positive test.
- Analyze your product by chromatography. The GC should give % composition of the product. The shorter retention time is the compound, 3-methylcyclohexene, and the longer retention time is the compound, 1-methylcyclohexene.

REACTION AND MECHANISM

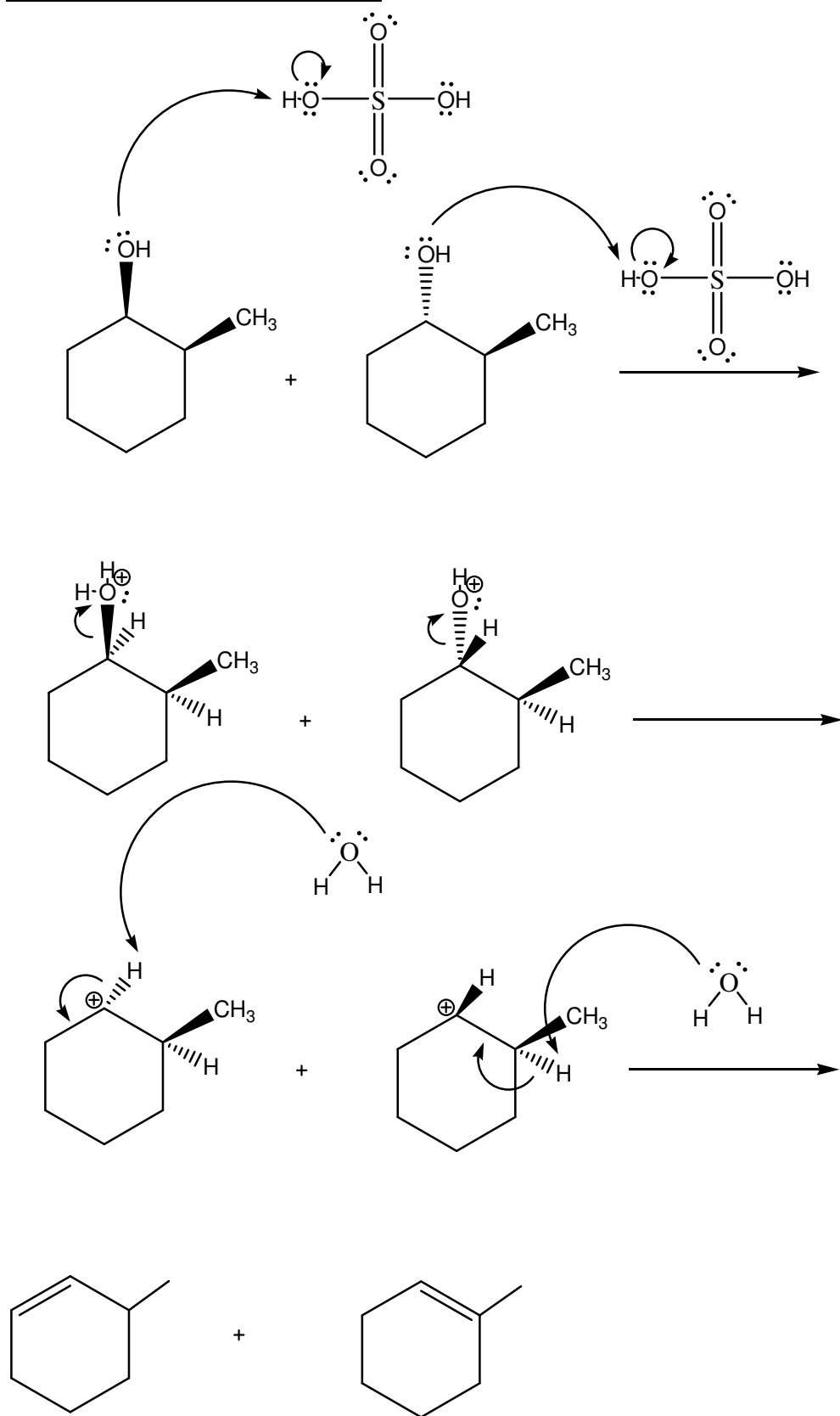


TABLE 1: REAGENTS

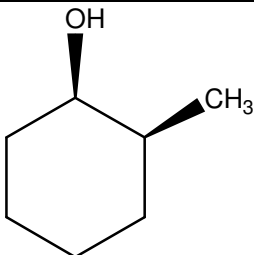
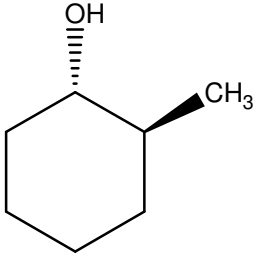
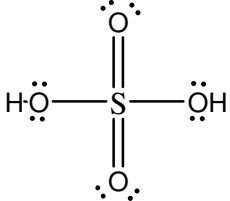
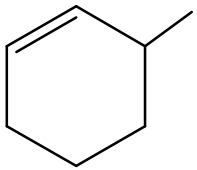
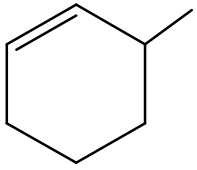

<u>Compound Number</u>	<u>Compound</u>	<u>Density</u>	<u>Molecular Weight (g/mol)</u>	<u>Physical Properties</u>
<b>1</b>	 cis-2-cyclohexanol	Density = 0.92 g/mL	114.19	Liquid, b.p. 155-180°C
<b>2</b>	 trans-2-cyclohexanol	Density = 0.92 g/mL	114.19	Liquid, b.p. 155-180°C
<b>3</b>	 Sulfuric Acid	Density = 1.84 g/mL,	98.08	clear, colorless, odorless oil, b.p. 337°C, corrosive, toxic

TABLE 2: PRODUCTS

<u>Compound Number</u>	<u>Compound</u>	<u>Theoretical Yield (g)</u>	<u>Molecular Weight (g/mol)</u>	<u>Physical Properties</u>
<b>4</b>	 1-methylcyclohexene	1.94	96.17	b.p. = 110 °C Insoluble in water, clear, colorless
<b>5</b>	 3-methylcyclohexene	1.94	96.17	b.p. = 110 °C Insoluble in water, clear, colorless

<b>6</b>	 water		18.0	Clear, b.p. 100°C
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### YIELD DATA

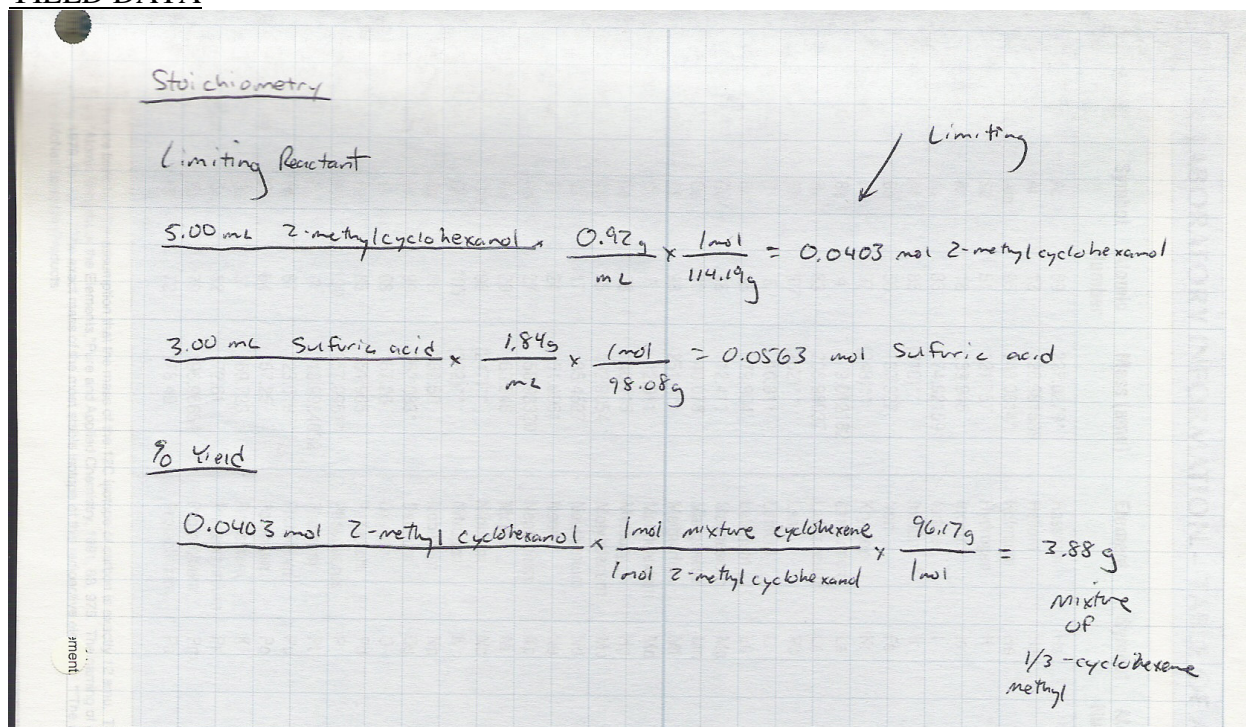


TABLE 3: % Yield of 1-methyl-3-methylcyclohexene

Compound	Theoretical	Observed	% Yield
Mixture of 1-methyl, 3-methylcyclohexene	2.29 g	3.88 g	59.0 %

The % Yield from the initial reaction was 59.0%. This yield was fairly good considering a few factors limited collection of the product. During heating, the cyclohexanol decomposed, which was indicated by black tar-like substance. In addition, product was also stuck in the separatory funnel upon the final wash of saturated NaCl.

TABLE 4: Weight Results from Reaction

	Weight (g)
Vial and Product	14.31
Vial	12.02
Product	2.29

Table 4 shows the weight recovered. The percent yield is located above in Table 3.

TABLE 5: Unsaturated Test Results from Reaction

Cyclohexane	Cyclohexene	Mixture of Cyclo
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	(control)	(control)	hexene
Bromine Test	Negative	Positive	Positive
Baeyer Test	Negative	Positive	Positive

Table 5 shows that all tests for unsaturation of the product were positive. The bromine test yielded a clear liquid, then an orange liquid, and then a clear liquid. The Baeyer test yielded a oily brown precipitate. The two control tests had results as expected. It was good to test the controls because of the unique nature of the Baeyer test on the cyclohexene, which was an oily brown precipitate. I could then expect a similar result when the product was tested for unsaturation using the Baeyer test.

#### SYNOPSIS OF AND NOTES ON EXPERIMENTAL PROCEDURE-RESULTS

During this experiment the mixture of cis/trans 2-methyl-cyclohexanol was heated in a fractional distillation. The variable temperature control was started at 50 volts. The temperature was gradually increased till 80 volts until the drops of distillate were consistent at 1-2 drops per second. 10 minutes after the round bottom was heated, black residue formed from the decomposition of the product. The milky distillate was formed slower than desired (about 50 minutes). The distillate was slightly cloudy and a total of 5.80 mL was collected after retrieving remaining distillate from the condensing column.

TABLE 1: TEMPERATURE AND VOLUME OF DISTILLATIONS

<i>Fractional Distillation</i>	
<b>Initial Temperature: 78.8°C</b>	
<b>Initial Volume: 0.00mL</b>	
Temp (°C)	Volume (mL)
78.8	0.00
79.0	0.50
79.6	1.00
78.3	1.50
72.1	2.00
81.9	2.50
80.9	3.00
95.0	3.50
94.8	4.00
98.9	4.50
98.3	5.00
<b>TOTAL</b>	<b>5.80</b>
<b>Volume</b>	

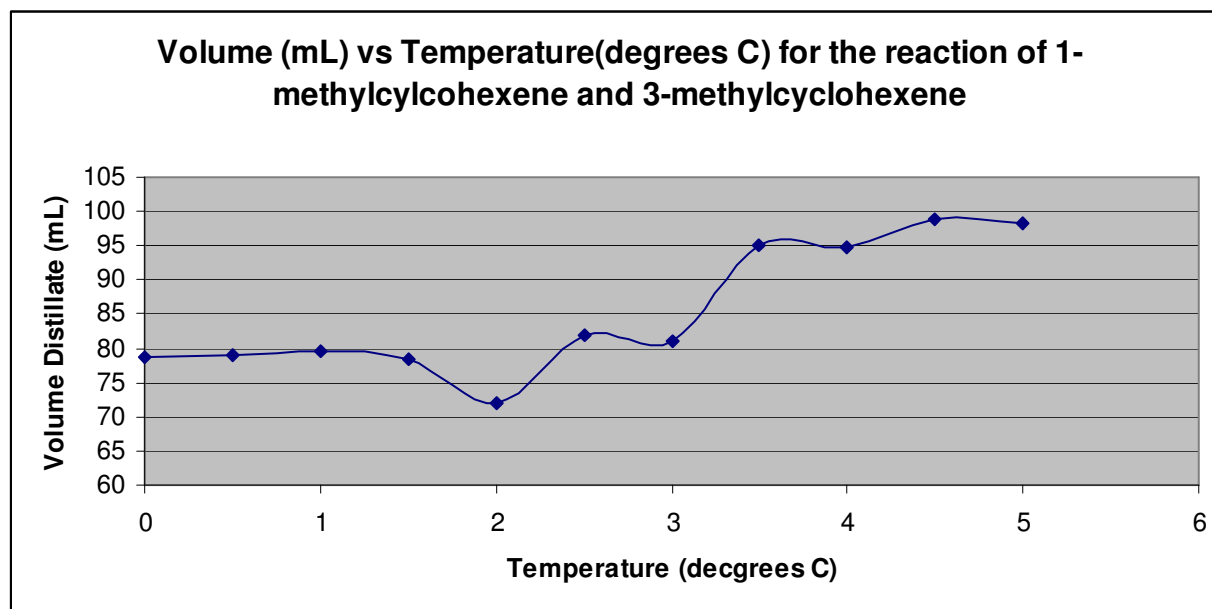
- GC #6
- Column A
- 2.5  $\mu$ L
- Polarity (-)
- Current: 100 mA
- Column T = 79  $^{\circ}$ C
- Detector = 125  $^{\circ}$ C
- Injector = 124  $^{\circ}$ C

TABLE 2: Gas Chromatograph % Composition

<i>% Composition</i>	<i>Unknown Mixture Y (%)</i>
<i>1-methylcyclohexene</i>	67.853
<i>3-methylcyclohexene</i>	32.147

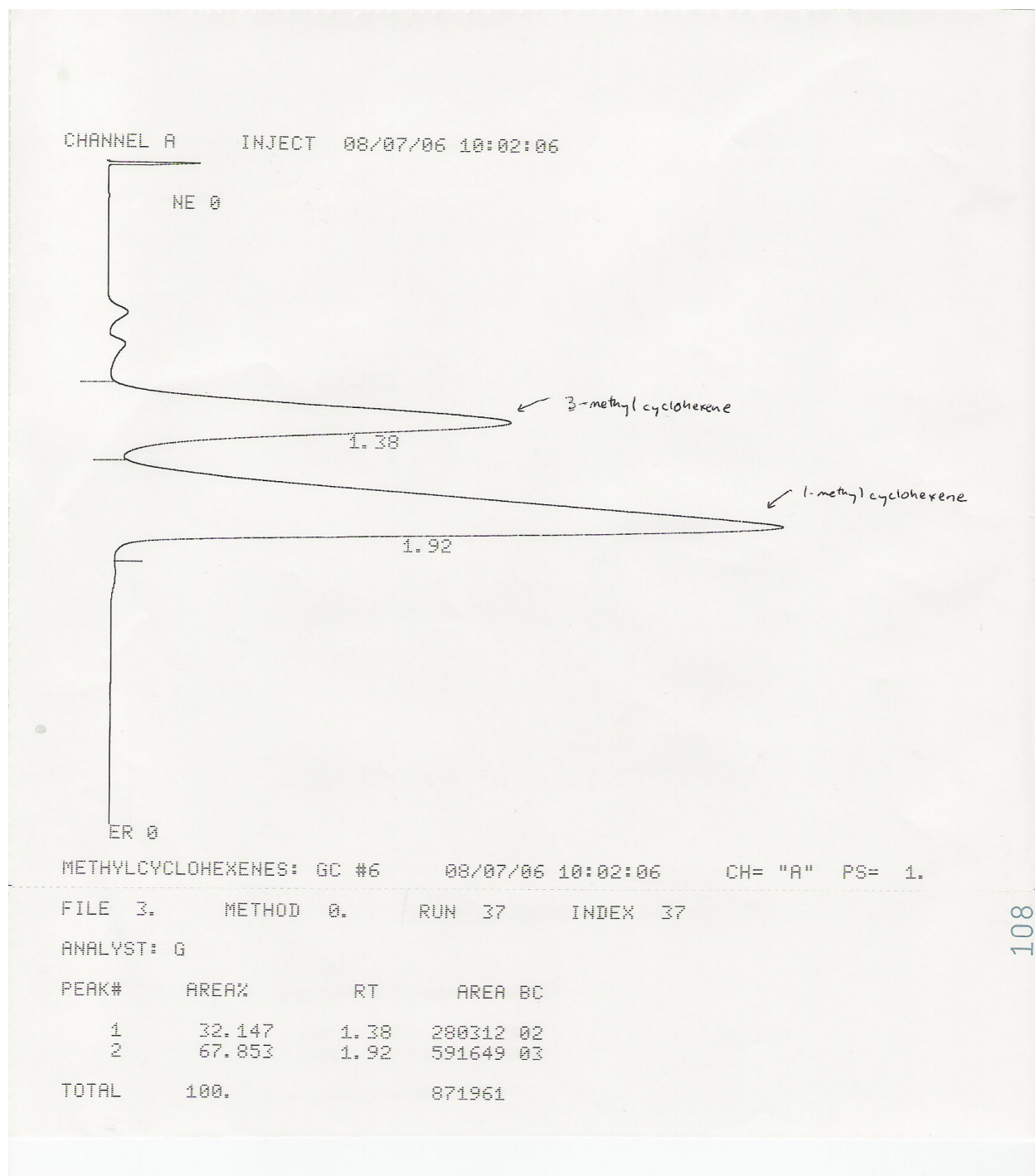
According to the data the 1-methylcyclohexene had a yield of 67.853% and the 3-methylcyclohexene had a yield of 32.147%. This data is consistent with what theoretically should happen. The 1-methylcyclohexanol will rather form a stable carbocation on the 1<sup>st</sup> position rather than the less-substituted 3<sup>rd</sup> position. Therefore, the 1-methylcyclohexene is a more substituted double bond and a more stable double bond.

CHART 1: Fractional Distillation



In Chart 1 the volume of distillate vs. temperature is graphed. The temperature decreased as the distillate reached 2 mL and the concentration of the sulfuric acid increased. 3 mL of water was added, which increased the temperature to approximately 85 $^{\circ}$ C. Finally the reaction was pushed to completion after the temperature was increased using the variable thermowell.

CHART 3: Gas Chromatography Analysis of Mixture of Products



### OBSERVED PHYSICAL PROPERTIES OF THE PRODUCTS OBTAINED

After several washes the product was clear liquid that had a peculiar odor. There was about 5.8 mL of product obtained.

### INTERPRETATION OF INSTRUMENTAL DATA

The % composition was obtained by the GC analysis, which found that the 3-methylcyclohexene had a shorter retention time and a lower % yield, while the 1-



methylcyclohexene had a longer retention time and a higher % yield. The % composition of the mixture was not a surprise and was expected.

Below is the work shown to determine experimentally the relative amounts of the two methylcyclohexenes. Assuming the acid-catalyzed dehydration reaction produces products under thermodynamic control, one can calculate the relative amounts of each isomer based on their stability. From the GC traces, we can obtain a  $K_{eq}$  for the relative amounts, which was 2.1107. This value represents that there is 2.1107 times 1-methylcyclohexene than 3-methylcyclohexene in our product, as determined by the GC. The  $K_{eq}$  value can be plugged in to the Gibbs free energy equation (at 100°C),  $\Delta G = -RT \ln K_{eq}$ . The Gibbs free energy change between the two structures is 0.55471 kcal/mol.

The experimental value is then compared to the computational value (using Chem 3D) of the Gibbs free energy. As shown below the Gibbs free energy is 1,061.1 kcal/mol. We have assumed that the entropy between the two isomers is close to zero. After determining the computational value, the  $K_{eq}$  can be determined. Computationally,  $K_{eq} = 4.17$ . the ratio of products predicted by Chem3D is 4.44 to 1 (1-methylcyclohexene:3-methylcyclohexene). Therefore there is a two-fold difference between the experimental and computational values of the products predicted. The possible reason is experimental error. There was a possibility of polymerization and loss of product in the separatory funnel. All work is shown below.

Experimental  
GC Percentages

1-methylcyclohexene 67.853%

3-methylcyclohexene 32.147%

$$K_{eq} = \frac{[1\text{-methylcyclohexene}]}{[3\text{-methylcyclohexene}]} = \frac{[67.853]}{[32.147]} = 2.1107$$

$$\begin{aligned}\Delta G &= -RT \ln K_{eq} \\ &= -(8.199 \text{ cal/kmol})(373.15 \text{ K})(\ln 2.1107) \\ &= 554.71 \text{ cal/mol} \\ &= 0.55471 \text{ kcal/mol}\end{aligned}$$

$$100^\circ\text{C} + 273.15 = 373.15 \text{ K}$$

Computational

Using Chem 3D

1-methylcyclohexene

Total E  
4.4127 kcal/mol

3-methylcyclohexene

5.4738 kcal/mol

Difference

1,061.1

$$\text{kcal/mol} = \Delta H = \Delta G \quad (\text{Assume Entropy} = 0)$$

$$\Delta G = -RT \ln K_{eq}$$

1,061.1

$$= -(1.99 \text{ cal/kmol})(373.15 \text{ K})(\ln K_{eq})$$

$$K_{eq} = 4.17$$

Ratio:

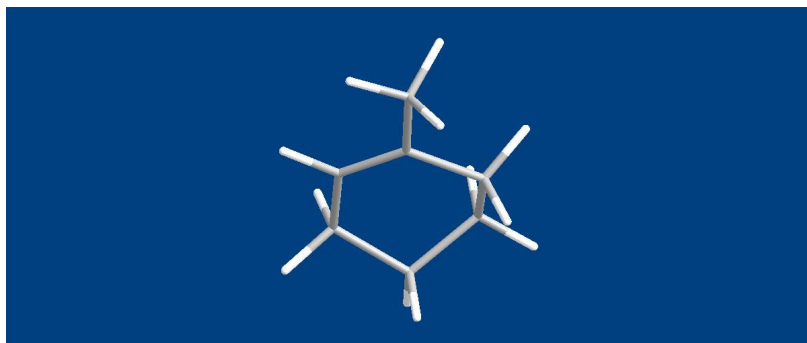
Experimentally  
Computationally

1-methylcyclohexene : 3-methylcyclohexene

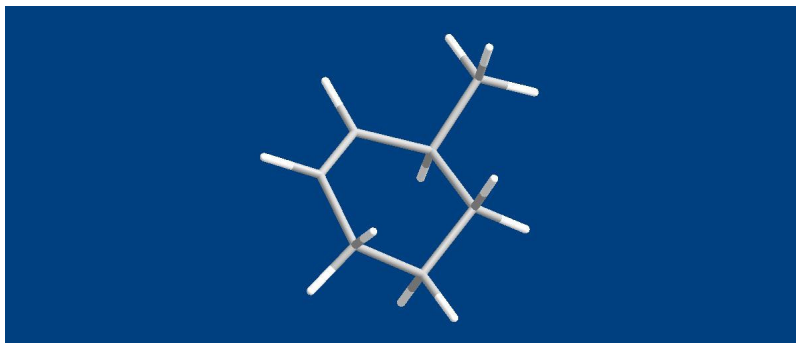
2.1107 : 1

4.17 : 1

1-methylcyclohexene



3-methylcyclohexene

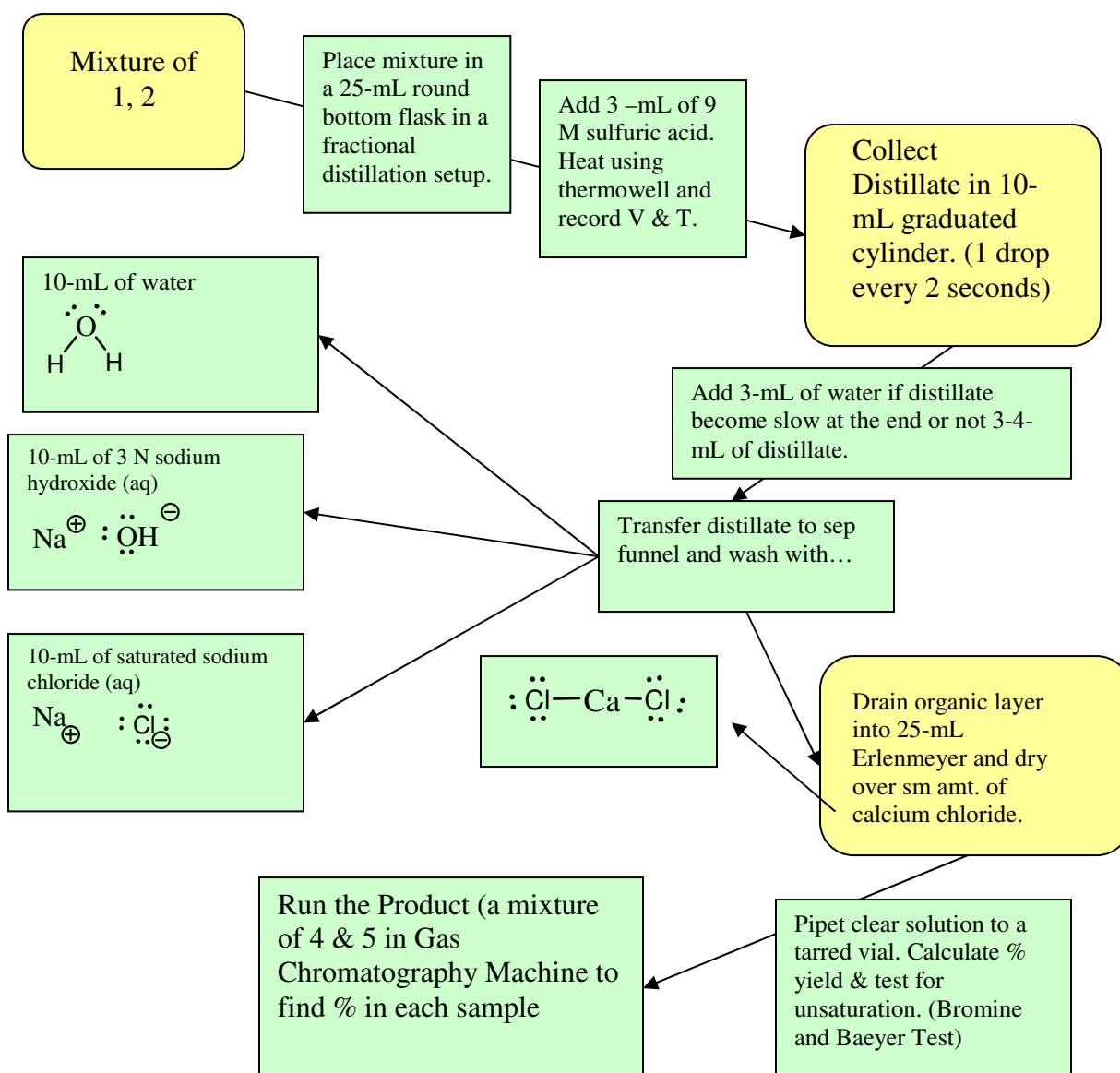


## SIGNIFICANT SIDE REACTIONS

- N/A

## METHOD OF PURIFICATION

*Flow Chart of Lab* (The numbers in the following flow chart are derived from Table 1: Reagents and Table 2: Products)



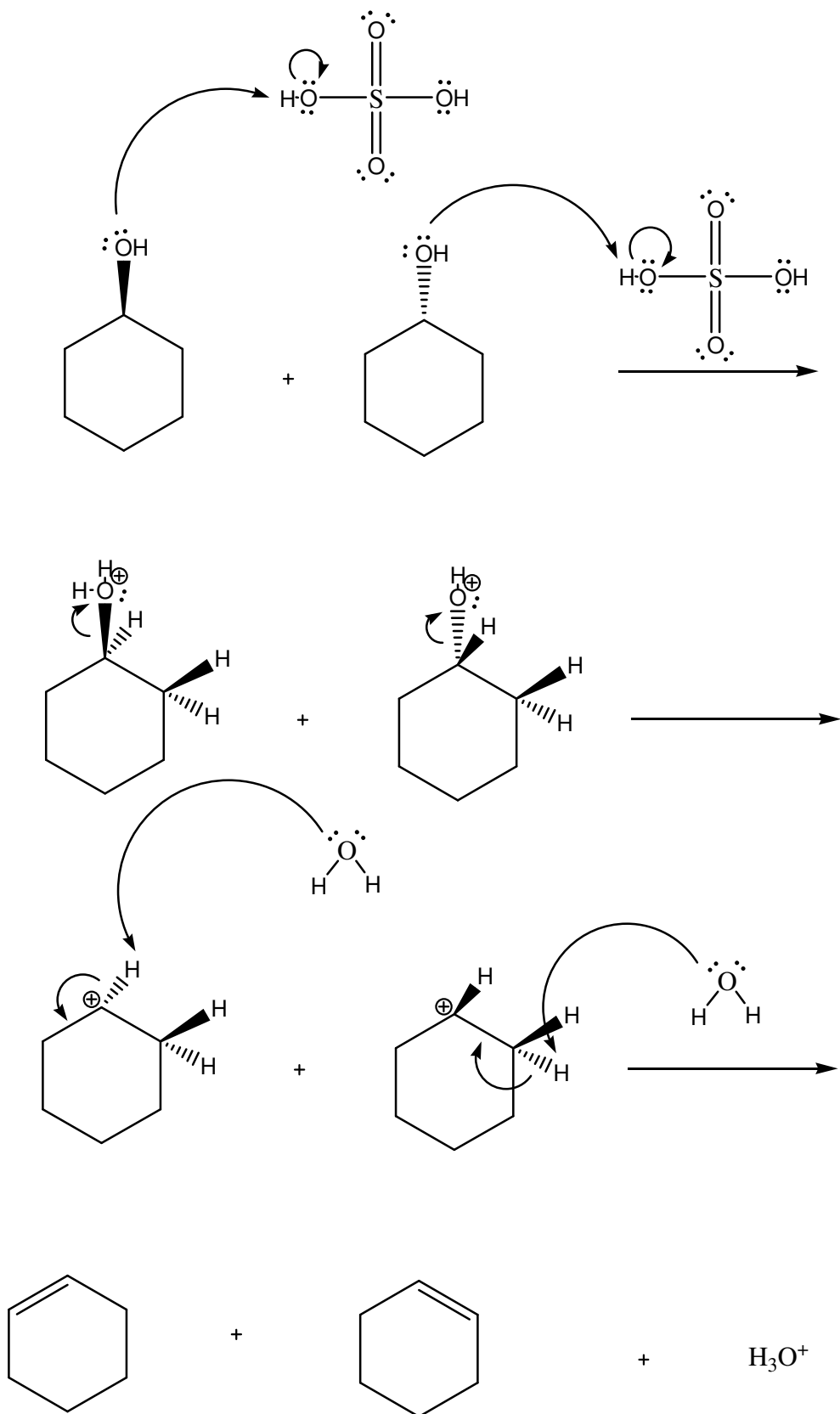
## CONCLUSIONS

In this experiment, alkenes were produced from the dehydration of a cyclic alcohol. After using a strong acid as a catalyst, the alcohol was protonated and then removed using fractional distillation. The thermodynamic stability of the carbo-cation determines which double-bonded product will be formed in the most abundance. Because the double bond is more substituted in the 1-methylcyclohexene, it is the most abundant product. This result was verified experimentally and computationally. Also, using the Gibbs-free energy equation and the ratios of products produced, one can calculate the energy between the mixture of products. In addition, the Gibbs-free energy can be calculated computationally using Chem3D. The lab and Chem3D verified that the more substituted carbon will receive the double bond at a greater percentage.

## ANSWERS TO ASSIGNED QUESTIONS

1. *Why is the boiling point of the parent alcohol higher than that of the product alkene?*
  - The boiling point of the parent alcohol, 2-cyclohexanol, is higher than the product alkene (110°C) because of the greater intermolecular forces in the alcohol. As the intermolecular forces increase, the boiling point increases. The boiling point of the alcohol has hydrogen bonding while the alkene does not. Hydrogen bonding contributes significantly to the higher boiling point of the reactant (155-180°C).

21. Provide a detailed mechanism for the acid-catalyzed dehydration of cyclohexanol. Use curved arrows to symbolize the flow of electrons.



(both products are the same but are both shown)