EXPERIMENT #5 7/30/07 ALKENE FORMATION: ACID-CATALYZED DEHYDRATION OF AN ALCOHOL

2. INTRODUCTION AND PURPOSE

2-methylcyclohexanol was converted to a mixture of 1-methyl and 3-methylcyclohexene by an acidcatalyzed dehydration. The product mixture was tested for unsaturation and analyzed via gas chromatography (GC). The ratio of the two hexenes in the product mixture was compared to that predicted by molecular mechanics (MM2) calculations.

3. MAIN REACTION & MECHANISMS



4. TABLE OF REACTANTS & PRODUCTS **Table of Reagents**

| | Structure | MW | Amounts used | | Moles theoretically | | |
|--|-----------|----------|-----------------|-------|------------------------|----------|---------------------------------|
| Compound | # | (g/ mol) | mL | grams | used | required | Physical properties |
| 2-methylcyclohexanol, | 1 | 114.187 | 5 | 4.43 | 0.0388 | 0.0388 | Density = 0.914 g/ mL |
| $C_7H_{14}O$ (cis and trans) | | | | | | | $b.p. = 163^{\circ}C$ |
| 9M Sulfuric acid, H ₂ SO ₄ | - | - | 3 | - | 0.027 | - | Catalyst, dehydrating |
| | | | | | | | agent |

Table of Products

| | | Structure | MW | Theoretical yield | | |
|---------------------|--------------------------------|-----------|----------|-------------------|--------|-----------------------|
| Compound | | # | (g/ mol) | grams moles | | Physical properties |
| 1-methylcyclohexene | C ₇ H ₁₂ | 2 | 06 1719 | 2 72 | 0.0288 | $b.p. = 110^{\circ}C$ |
| 3-methylcyclohexene | | 3 | 90.1718 | 5.75 | 0.0388 | $b.p. = 104^{\circ}C$ |
| Water | H_2O | - | 18.0 | 0.70 | 0.0388 | $b.p. = 100^{\circ}C$ |

5. YIELD DATA

THEORETICAL CALCULATIONS:

| | H2 C ₇ H ₁₃ OH → | $\sim C_7 H_{12}$ + | - H ₂ O | |
|--------|---|---------------------|--------------------|--|
| Before | 0.0388 mol | 0 | 0 | |
| Change | -0.0388 mol | +0.0388 mol | +0.0388 mol | |
| After | 0 | 0.0388 mol (3.73 g) | 0.0388 mol | |

| OBSERVED YIELD: | |
|--------------------------------------|--------------------|
| Mass of product (alkene) mixture (%) | 2.31 g (62% yield) |

6. EXPERIMENTAL PROCEDURE AND RESULTS

- 1. **FRACTIONAL DISTLLATION:** A fractional distillation apparatus was setup as shown in Gilbert and Martin, p 53. 5-mL 1-methylcyclohexanol and 3-mL 9M H₂SO₄ was placed in the reaction flask and the products distilled and the distillate collected in a 10-mL graduate cylinder cooled in an ice-water bath. The distillate volume and stillhead temperature were recorded.
- 2. **EXTRACTION:** The (organic) distillate was washed successively with 1) 10-mL H₂O 2) 10-mL 3 N NaOH, 3) 10-mL brine and then drained and dehydrated with anhydrous CaCl₂. The product mixture was analyzed via gas liquid chromatography.
- 3. **SATURATION TESTS:** Bromine and Baeyer tests were performed on the product mixture to determine saturation, as described in Gilbert and Martin, pp.652-654.

| Mass, empty rxn. flask + stopper | 37.31 g | | | | | |
|----------------------------------|--------------|------------------------------|--|--|--|--|
| Mass, rxn. flask + ~5 mL alcohol | | 41.74 g | | | | |
| Mass, empty vial | | 13.75 g | | | | |
| Mass, vial + alkene mixture | | 16.06 g | | | | |
| Bromine test | cyclohexane: | magenta colored (-) | | | | |
| | cyclohexene: | brown ppt formed (+) | | | | |
| | product mix: | brown ppt formed (+) | | | | |
| Baeyer test | cyclohexane: | orangish color persisted (-) | | | | |
| | cyclohexene: | solution became clear (+) | | | | |
| | product mix: | solution became clear (+) | | | | |



Gas Chromatography—3-methylcyclohexene has a shorter retention time than 1-methylcyclohexene.



| GC data: |
|----------|
|----------|

| Substance | Peak Area % | | | | |
|---------------------|-------------|--|--|--|--|
| 3-methylcylohexene | 30.748% | | | | |
| 1-methylcyclohexene | 69.252% | | | | |

7. OBSERVED PHYSICAL PROPERTIES OF PRODUCTS OBTAINED. See data table

8. SIGNIFICANT SIDE REACTIONS

The most significant side reaction was the formation of a black polymer in the reaction flask as the alkene product reacted with the carbocation formed to create a larger carbocation, which would continue to react with more alkene product. This side reaction could be minimized by more efficient distillation (i.e. removal) of the alkene produced. A sample mechanism is shown:



9. METHOD OF PURIFICATION (extraction flowchart, H₂O, NaOH, NaCl, remove unreacted alcohol, water)



10. CONCLUSIONS

The dehydration reaction produced alkenes, as shown by the positive result for the bromine and Baeyer tests for unsaturation.

The product yield was only 62% because of the polymer forming side reaction and the unavoidable loss of some product during the extraction process.

11. ANSWERS TO ASSIGNED QUESTIONS

1. The boiling point of the parent alcohol is higher than that of the product alkene because the alcohol molecules can form hydrogen bonds, increasing the intermolecular forces of attraction. Because the molecules are more highly attracted to each other, it takes more energy to separate them, thereby increasing the boiling point.

21. Acid-catalyzed dehydration of cyclohexanol



EXTRA QUESTION. MM2 prediction vs. GC data. See data table by GC and conclusions for comparison.

| GC data: | |
|--|--------------------|
| Substance | Peak Area % |
| 3-methylcylohexene | 30.748% |
| 1-methylcyclohexene | 69.252% |
| Ratio (K _{eq experimental}) | 2.2522 |
| $\Delta G (at \sim 100^{\circ} C)^{*}$ | -0.60265 kcal/ mol |
| for conversion of | |
| 3-methylcyclohexene | |
| to 1-methylcyclohexene | |

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

| M | olecu | lar N | 1ecl | hani | ics (| M | M 2 | l) (| lata | : |
|---|-------|-------|------|------|-------|---|------------|------|------|---|
| - | - | | | | | | | | | |

| Substance | Steric Energy | | | |
|---|---------------|--|--|--|
| | (kcal/ mol) | | | |
| 3-methylcylohexene | 5.0288 | | | |
| 1-methylcyclohexene | 3.9935 | | | |
| Difference ($\Delta H = \sim \Delta G$) | -1.0353 | | | |
| for conversion of | | | | |
| 3-methylcyclohexene | | | | |
| to 1-methylcyclohexene | | | | |
| Ratio predicted by | 4.0341 | | | |
| MM2 calc. (K _{eq theoretical}) | (80% to 20%) | | | |

When comparing the ratio of products from the GC analysis of the distillate against the ratio predicted by Molecular Mechanics (MM2), the MM2 calculations predicted a greater ratio of the more stable one (1-methlycyclohexene) to the less stable hexane (3-methylcyclohexene).

The reason for the disparity between the experimental ratio (from the GC) and the predicted ratio (from MM2) may be attributed to 1) some fractionation during the collection of the distillate, and to a lesser extent, 2) the actual temperature of the stillpot (where equilibrium occurred) being higher than 100° C. Fractionation would cause a lower experimental ratio than predicted by molecular mechanics because while the product formed in the stillpot may have had the ratio predicted by mechanics, the process of distillation would enrich the percentage of the higher energy hexane because it has a lower boiling point.

12. BIBLIOGRAPHY

Dailey, William. Chemistry 502: Laboratory Manual, Summer 2007. UPenn.

Gilbert and Martin, Experimental Organic Chemistry: A Miniscale and Microscale Approach, Saunders College, 1998.