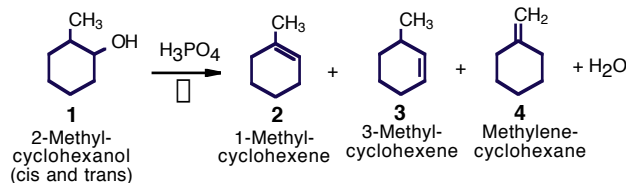


## Dehydration of 2-Methylcyclohexanol

Adapted by R. Minard and D. Dorisio (Penn State Univ.) from a microscale procedure used by the University of California, Irvine, in its undergraduate labs. The procedure is based on a paper titled *Dehydration of 2-Methyl-cyclohexanol* by R. L. Taber and W. C. Champion, *J. Chem. Ed.*, **44**, 620 (1967). Revised 2/24/02

### Introduction:

The purpose of this experiment is to analyze and to interpret mechanistically the results of acid-catalyzed dehydration of 2-methylcyclohexanol.



Dehydration of 2-methylcyclohexanol, **1** (B.P. = 163-166°C) with 85% phosphoric acid yields a mixture of three products: the main product overall (75-80%) is 1-methyl-1-cyclohexene, **2** (B.P. = 110-111 °C); also present are 3-methyl-1-cyclohexene, **3** (B.P.=104 °C) and methylenecyclohexane, **4**. The relative amounts of each product can be determined by gas chromatographic analysis of the mixture.

Interestingly, distillation of the product mixture gives fractions of varying composition, where the lower boiling product distills later. If all of the products were formed instantaneously, then obviously the lower boiling component would be expected to distill earlier; that it does not implies that there is either more than one kind of reaction taking place or else there is more than one component in the starting material; here, it is both! The phenomenon is called the "Evelyn Effect" and is briefly discussed in a recent article by David Todd of Juniata College in the *Journal of Chemical Education*, **71** (1994) 440.

Apparently, the alkenes distill nearly as fast as they are formed; therefore, 1-methylcyclohexene forms faster than 3-methylcyclohexene. The reagent supplied by Aldrich is a mixture of approximately 50-50 *cis*- and *trans*- 2-methylcyclohexanol. (In a separate experiment, it has been shown that the *cis* isomer dehydrates about 30 times faster than the *trans* isomer under identical reaction conditions.) The 1-methylcyclohexene predominates in all fractions collected, but the early fraction is over 90%, the fifth fraction as low as 55%.

The reaction appears to proceed mainly by a *trans* mechanism (E2 mechanism), the *cis* isomer reacting more rapidly. However, the presence of methylenecyclohexane (about 8% of the total alkene product) gives evidence that a E1 mechanism is possible, as well.

### Prelaboratory Exercises:

In your chemical data table give the theoretical yield of total methylcyclohexene isomers.

(1) Why is it important to surround the receiving flask with an ice-water bath?

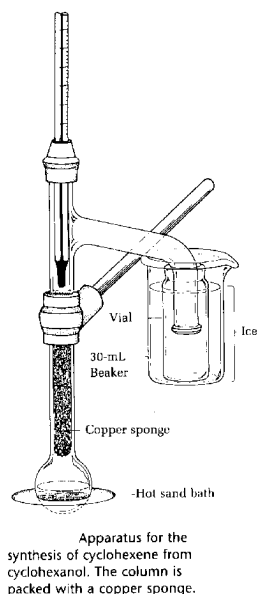
(2) In gas chromatography, components in a mixture can be separated from one another because these components have different solubilities in the non-volatile stationary phase. Compound **X** and Compound **Y** have identical boiling points. Compound **X** has a greater affinity for the non-volatile liquid phase, **Z**, than does Compound **Y**. When a mixture of **X** and **Y** is separated, which component should be the first component off the column?

### Cautions:

85% phosphoric acid is corrosive to skin and clothing. Neutralize any spills with sodium bicarbonate and quickly wash the affected areas of skin with lots of soap and water.

### Synthesis, Isolation, and Purification:

Place 2.0 g of 2-methylcyclohexanol, 0.5 mL of 85% phosphoric acid (HANDLE WITH CARE!), a boiling chip, and a 1/2" stirring bar into a 5-mL round-bottom-long-neck flask. Lightly pack the neck with a stainless steel sponge ("ChoreBoy"), and carefully mix the reactants thoroughly by swirling gently. The reaction should be carried out by a modified version of the Microscale fractional distillation apparatus as shown in the figure below (see also the figures in Chapter 5 of the Lab Guide). Attach the round bottom flask to the curved distilling side arm. Place the thermometer in the top of the side arm so that the thermometer bulb is below the sidearm opening. Distill out the products by heating the mixture gently on the sand bath. Do not allow the temperature of the distillate to rise above 96°C. Continue distilling until approximately 1.6 mL of liquid have been collected.



**DO NOT ALLOW THE DISTILLING FLASK TO BECOME DRY!** Transfer the distillate to a reaction tube, slowly add solid sodium chloride ( $\text{NaCl}$ ) until the distillate is saturated with sodium chloride, and then, cautiously, with gentle shaking, add enough sat'd  $\text{NaHCO}_3$  (10% sodium bicarbonate) solution to make the distillate neutral to litmus. After allowing the organic and aqueous layers to separate, transfer the organic layer (using a Pasteur pipet) to a clean, dry reaction tube. Dry the product over anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), and transfer the dried product to a clean, dry, and labeled "shorty" vial. Screw the lid on tightly as the cyclohexene can evaporate otherwise.

#### Gas Chromatographic Analysis:

Analyze a dichloromethane solution of your product mixture by gas chromatography on a gas chromatograph in Rm 206 Whitmore which has been set up for this purpose. Add one drop of your product to ~2 mL of dichloromethane and inject only 1 microliter. Use the GC instrument and chromatographic conditions defined in the "*Compendium of GC Conditions*" in Room 206.

#### Cleaning Up:

The small amount of phosphoric acid and 2-methylcyclohexanol remaining in the distillation flask and the aqueous layer remaining in the reaction tube can be flushed down the drain with lots of water.

#### Final Report:

Attach your gas chromatogram, including the GC analysis parameters sheet, to your final report. By analyzing your gas chromatogram, establish the identity of the peaks and the relative % composition of the peaks which represent the products of the dehydration reaction. Use the method of triangulation or an electronic integrator to determine the relative amounts of each alkene present in the product mixture. Be sure to label each significant peak and to show how you determine % composition. By referring to your experimental results and the accepted mechanism of reaction for the acid catalyzed dehydration of alcohols, offer a simple explanation for the presence of the two products and their relative abundance.

#### **Answer the following questions at the end of your report.**

- (1) The method of "spiking" is frequently used to positively identify a component in a mixture. When this method is used, 2 chromatograms are run: (1) a chromatogram of the mixture and (2) a chromatogram of the mixture to which has been added a small amount, or "spike" of a known standard compound. For example, a mixture is known to contain 50% compound **A** and 50% compound **B**. The first gas chromatogram, #1, of this mixture reveals 2 peaks of about the same size, but it is not clear which is **A** and which is **B**. Therefore, the experimentalist adds a small amount of authentic compound **B**, available as a pure standard from another source, to a small portion of the original 50/50 mixture and injects this "spiked" mixture to obtain a second gas chromatogram #2. On the basis of an increase in the size of one of the peaks in chromatogram #2, the experimentalist is able to state which chromatographic peak, the first or second, is compound **B**. Draw hypothetical chromatograms #1 and #2, showing how the experimentalist is able to establish the identity of the peaks.
- (2) Review the E1 and the E2 mechanism for acid-catalyzed dehydration of alcohols in your textbook. What geometric requirement of the E2 mechanism causes the cis isomer to dehydrate faster? If the trans isomer undergoes E2 elimination, what product is formed?
- (3) How does Zaitsev's Rule (also spelled Zaitzev, Saytseff, or Saytzev, depending on which book you refer to) apply to this experiment?
- (4) The presence of methylenecyclohexane in the product mixture is said to be evidence of at least some E1 mechanism operating; draw a mechanism that accounts for this product.

# Synthetic Experiment PreLab Grading Sheet

Name(s): \_\_\_\_\_

TA: \_\_\_\_\_

Date: \_\_\_\_\_

## PreLab For Exp't # 73

### Dehydration of 2-Methylcyclohexanol

	Possible Points	Missed Points
Date, Name, Desk #, Experiment # & Title(abbreviated after 1 <sup>st</sup> pg), Section & TA Name	4	
Summary	8	
Goals	8	
Reactions, structures, conditions, diagrams	14	
Completeness of Chemical Data Table(s)	14	
PreLab Exercise	16	
Chromatographic Behavior Comparison	12	
Spectral Features Comparison	12	
Work-up - Explanation of the product isolation and purification process	12	
<b><i>TOTAL FOR PRELAB</i></b>	<b>100</b>	

Date Handed in: \_\_\_\_\_

General Comments:

**Total Points:** \_\_\_\_\_

# Synthetic Experiment Final Report Grading Sheet

Name: \_\_\_\_\_

TA: \_\_\_\_\_

Date: \_\_\_\_\_

## Final Report For Exp't #: 73

### Dehydration of 2-Methylcyclohexanol

	Possible Points	Missed Points
Name, Date, Experiment Title (abbreviated after 1st page) and every page numbered	4	
<i>OBSERVATION and DATA</i> - Overall organization, readability, completeness	8	
Data: Weighing data, molecular weights, moles, density, volumes, distillation temperatures, analysis conditions. (GC analysis conditions sheet)	12	
Yield: Show % yield calculations with limiting reagent clearly stated. Purity: Give boiling point, color, or other indicators of purity.	12	
<i>RESULTS AND DISCUSSION</i> - Overall organization, readability, completeness	8	
Results; Achievement of goals	16	
Product Analysis Data: Quality and Interpretation – All peaks assigned and structures drawn on chromatogram for each  Calculation of the relative amounts of 3 isomers. Is starting material seen in the chromatogram and noted?  Discussion of product ratios in terms of isomer stability – kinetic versus thermodynamic control.	20	
<i>POSTLAB QUESTIONS</i>	20	
<i>TOTAL POINTS</i>	100	

Date Handed in: \_\_\_\_\_

General Comments:

**Total Points:** \_\_\_\_\_