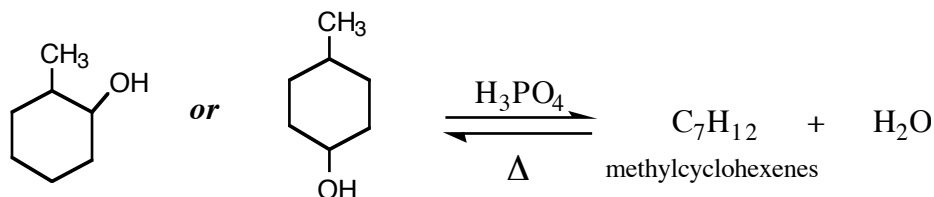


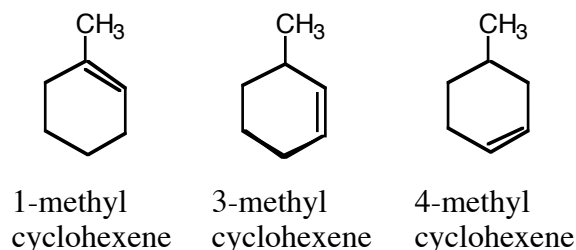
Experiment 9: Dehydration of Methylcyclohexanols

You will carry out the dehydration of either 2-methylcyclohexanol or 4-methylcyclohexanol by heating the alcohol in the presence of phosphoric acid:



The yield of this reaction will be increased if the alkenes are removed as they are produced, thus shifting the equilibrium to the right. For this reason, the reaction will be carried out in such a way that the alkene products distill out of the reaction mixture as they are formed.

The products of this elimination reaction can include the following isomers:



Elimination reactions such as this can proceed by different mechanisms. Direct elimination of water from 4-methylcyclohexanol would produce 4-methylcyclohexene, while direct elimination of water from 2-methylcyclohexanol would produce 1- and 3-methylcyclohexene. In the latter instance, the product that is favored by the reaction might be determined by Zaitsev's rule, which states: when HZ is removed from a species to form an alkene, hydrogen is lost preferentially from the carbon atom, of those adjacent to the carbon atom bonded to Z, that has fewer hydrogens. Thus, if Zaitsev's rule is followed for the dehydration of 2-methylcyclohexanol, then 1-methylcyclohexene would be the favored product. Alternatively, elimination reactions can occur via the formation of a carbocation and subsequently, rearrangements can take place. This sort of mechanism would result in the formation of 1- and 3-methylcyclohexene, in addition to 4-methylcyclohexene, from the dehydration of 4-methylcyclohexanol.

Physical Properties

Compound	Mol. Wt.	boiling pt.	density
2-methylcyclohexanol	114.2	166	0.930
4-methylcyclohexanol	114.2	173	0.914
1-methylcyclohexene	96.2	110	0.813
3-methylcyclohexene	96.2	104	0.801
4-methylcyclohexene	96.2	102	0.799

After you have carried out the reaction and purified the alkenes by distillation, you will analyze the products by gas chromatography. In order to identify the peaks in the

chromatogram, your TA will spike some samples with pure 1-methylcyclohexene. Read about *Peak Enhancement* on pp 269-270 of *TOC*.

Note: The peaks for 3- and 4-methylcyclohexene will not be well separated on your gas chromatogram; however, the presence of a peak due to 1-methylcyclohexene will indicate whether or not a rearrangement has occurred in the case where 4-methylcyclohexanol is used as starting material.

Pre-lab assignment

- Outline the following experimental procedure.
- Calculate the mass and volume of 150 mmol of methylcyclohexanol.
- Calculate the theoretical yield of methylcyclohexenes.
- Estimate the maximum volume of alkene that should be in the distillate when the reaction is completed. Use 0.80 g/mL as the density of the alkene mixture.

Procedure

Measure 150 mmol of either 2-methylcyclohexanol or 4-methylcyclohexanol (as assigned by your TA) in a graduated cylinder. Tare an empty 100 mL round-bottomed flask (supported in a beaker), then add the 150 mmol of methylcyclohexanol and record the weight of the liquid. Add 5 mL of 85% phosphoric acid, drop in a few boiling chips and swirl the flask to mix the reactants. Set up a *fractional* distillation apparatus using the reaction flask as the distilling flask. Your fractionating column should not contain any packing material. Use a 25 mL graduated cylinder as the receiver and place the cylinder in a beaker full of ice.

Boil the reactants gently so that vapors ascend slowly up the column and begin to condense into the receiver. When the vapors reach the still head and the temperature has stabilized, record the still head temperature. Observe it at intervals throughout the reaction. Control the rate of heating so that the distillation rate is 1-2 drops per second or less and the temperature stays below 120°C. Estimate the volume of the alkene (top) layer in the distillate, and as it nears the value you calculated for your theoretical yield, monitor the still head temperature constantly. Lower the thermowell and turn it off when you observe a marked temperature change at the still head or foaming and dense white fumes in the reaction flask. Carefully discard the residue in the reaction flask as directed by your TA. Measure and record the volumes of the alkene layer and the water layer.

Wash the distillate in a separatory funnel with two 10-mL portions of saturated sodium bicarbonate solution. Vent frequently! Dry the alkene layer over anhydrous calcium chloride. Filter off the drying agent through a cotton plug in a funnel, and collect the product in a round-bottomed flask. Dispose of the calcium chloride in the **Laboratory Byproducts** jar.

Rinse out your condenser with acetone to remove any water, then purify the product by simple distillation. Collect all the liquid that distills above 100°C and below 115°C. Collect the distillate in a tared vial which is kept on ice. Weigh the product.

Your TA will inject your product onto the gas chromatograph. Record the chart speed. Measure the area and retention time of each peak. To estimate the area of a peak, multiply the width at half-height by the height of the peak (see pp 270-271 in *TOC*).

Identify the peaks by comparison with a chromatogram provided by your TA where a sample has been spiked with an authentic sample of 1-methylcyclohexene. Dispose of the remaining product in the appropriate **Laboratory Byproducts** jar.

Name _____ Date _____

T. A. _____ Lab period _____

Results and Calculations (to be handed in at the next lab period)

Calculate the theoretical volume of water in the distillate. Compare this value and the estimated volume of alkenes which you calculated in the pre-lab assignment with the values that you actually observed.

Calculate your percent yield of alkenes based on the *weight* of methylcyclohexanol used. [You must do a mole/mass calculation to calculate the percent *yield*. You are not calculating a percent *recovery*.]

Attach your GC trace. Report the retention times and areas of each peak that corresponds to a product.

Calculate the mole percent of the product mixture which is 1-methylcyclohexene and the percent which is 3- and/or 4-methylcyclohexene. Calculate the mass of 1-methylcyclohexene and the mass of 3- and/or 4-methylcyclohexene present in the product mixture.

Compare your results with someone who used a different starting material. If 2-methylcyclohexanol is used as starting material, does the formation of products follow Zaitzev's rule? If 4-methylcyclohexanol is used as starting material, is there evidence for the occurrence of carbocation rearrangements?