## Molecule to Organism Fall 2002 ORGANIC LAB for Week 8 Dehydration of 2-Methylcyclohexanol.

**Reading:** Solomons: Dehydration of alcohols (sec. 7.7); the E1 reaction (sec. 6.18), lab techniques on fractional distillation.

#### **Objectives:**

- To carry out an elimination reaction (E1).
- To test Zaitsev's rule
- To learn the technique of fractional distillation
- To see some characteristic properties of alkenes

#### **Introduction:**

The dehydration of alcohols with acids is a general laboratory method for preparing alkenes. Strong mineral acids, such as sulfuric or phosphoric acids, usually are used as catalysts.

Phosphoric acid rather than sulfuric acid is the preferred catalyst mainly for safety reasons. The cyclohexanol and sulfuric acid mixture can give off irritating and toxic sulfur dioxide fumes during heating. However, remember that concentrated phosphoric acid is very irritating to the skin and gloves should be worn when handling it.

You will dehydrate 2-methylcyclohexanol, and using Zaitsev's rule to predict the products, more than one alkene should be formed, with the most stable being the major product. You should draw the mechanism out and predict your products and the one that will predominate. Remember this is an E1 mechanism, and carbocations can and do undergo rearrangements.

The alcohol starting material is normally a 50:50 mixture of *cis* and *trans* isomers:



This mixture of isomers can lead to variations in product ratios because the two isomers undergo dehydration and rearrangement at different rates (the *cis* isomer is known to be about 30 times more reactive toward dehydration), but ratio variations can be minimized if we use conditions that ensure complete dehydration of both alcohol isomers.

The alkene products can react with water (in the presence of acid) to return to the starting material, so an equilibrium between alcohol and alkenes is established. Formation of the alkenes can be favored by

removing them by distillation from the reaction mixture as they form (Le Chatalier's principle). Make sure you check the boiling points of all of possible alkene products and 2-methylcyclohexanol. Unavoidably, a small amount of phosphoric acid co-distills with the product. It is removed by washing the distillate mixture with aqueous sodium carbonate. The final alkene mixture will be separated and the individual products identified and quantified using gas chromatography.

Alkenes will react with  $Br_2$  and decolorize it, and will also react with a cold solution of potassium permanganate (purple) to discharge its color, and produce a brown precipitate,  $MnO_2$ . (See Solomons sections 8.6 and 8.10). We will carry out these tests, and you should draw the structures of the organic products you would expect by reacting these compounds with your alkene products.

#### **Experimental Procedure:** ALL WORK MUST BE CARRIED OUT IN THE HOOD

Set-up a fractional distillation apparatus. Using a funnel, pour 20 mL of 2-methylcyclohexanol into a 100 mL reaction flask. **Take care in this step:** Add the  $H_3PO_4$  (4 mL) directly from the dispensing bottle into the reaction flask containing the methylcyclohexanol. Add a boiling chip and immediately attach the flask to the distillation apparatus. You will need to insulate the reaction flask and adapter. Use a 25 mL graduated cylinder as the receiver. Now turn on the heating mantle.

As the dehydration reaction occurs, the alkenes and the water will slowly rise in the flask. The first drops of distillate will appear within approx. thirty minutes. Distill the products until the production of distillate is negligible. Some residue will remain in the reaction flask; do not boil it dry. Remove the heating mantle and the stir bar and then pour the distillate into a 125-mL separatory funnel.

Drain the aqueous layer. Extract the organic layer with 5 mL of a saturated solution of sodium carbonate. Watch out for gas production! Drain the aqueous layer through the stopcock and then wash the remaining organic layer with 10 mL of a saturated solution of sodium chloride. (Washing with a saturated solution of NaCl improves the separation of the two phases by making the aqueous layer more ionic. Washing with water alone might not give a clean separation.) Drain the aqueous layer and then drain the remaining organic layer into a dry Erlenmeyer flask. Add a teaspoon of anhydrous sodium sulfate, swirl and then stopper. After 15 minutes, pour the **dry** alkene mixture through fluted filter paper into a **dry** pre-weighed scintillation vial.

# Clean-up: Clean the reaction flask and adapter with acetone and put the washings in the waste bottle in the hood. DO NOT wash the flask in the sink.

#### **Gas Chromatography:**

- Although the alkene products have very similar boiling points, we will attempt to separate them using GC: use the nonpolar column heated to 50-55°C.
- You should also run the standard alkenes to compare to your products.

**Identification tests:** you should carry out the following to confirm the presence of alkenes. For both, we have samples of cyclohexane and cyclohexene to provide both positive and negative controls.

- Reaction with a dilute solution of bromine: Place a counted number of drops of your control or product alkene in a small flask or beaker with a ml or so of dichloromethane. All a 2 % solution of bromine in dichloromethane dropwise until the bromine color persists. How many drops are required for each sample? Bromine must be handled in the hood!
- Reaction with a cold potassium permanganate solution. Add a counted number of drops of your sample or control sample to several drops of potassium permanganate in water. What is observed?

If you have time, you could run an IR of your product mixture. What peaks would you expect for an alkene? How would this be different than that of the starting alcohol?

### Prelab Questions: Answer these before coming to lab!

- 1. What type of reaction will you carry out in this experiment?
- 2. What are the potential alkene products and what are their boiling points? A nomenclature note: the compound with a double bond as a branch off of the ring (cyclohexane=CH<sub>2</sub> is named methylenecylohexane.)
- 3. Clearly draw the mechanism for the acid-catalyzed dehydration of 2-methylcyclohexanol.
- 4. Why do we not use hydrochloric or hydrobromic acids to catalyze this reaction? Explain and draw out what you think might happen in the presence of either of these acids.

**Post-Lab:** Include the following data:

- weight of combined alkene product
- per cent yield
- boiling range of products.
- GC data (number, identification, and relative amounts of products) Does the ratio of product alkenes fit the theoretical prediction?
- Structures of products formed in the chemical identification tests.
- Draw the product that would result from the addition of conc. permanganate solution to your major alkene product and prolonged heating. (Sec. 8.11)