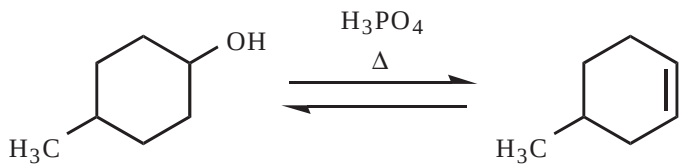
EXPERIMENT 25

DEHYDRATION OF 4-METHYLCYCLOHEXANOL



MW = 114.2

b.p. = 171-173
(cis/trans mixture)

MW = 96.2

b.p. = 101-102

ISSUES

1. Nature of the acid used as catalyst
2. Reversibility of the reaction and driving equilibrium towards the desired product
3. Relative boiling points of starting materials and products if a distillation is desired
4. Would a cis or a trans starting material be more efffective as an elimination substrate?

FORMATION OF AZEOTROPES IN DISTILLATION

Page 724 - 725 of textbook: When distilling mixtures of liquids, azeotropes can form. An azeotrope is a mixture of liquids with fixed composition that distills as if it was a single compound. That is, azeotropic mixtures cannot be separated by simple distillation. Examples of azeotropic mixtures are given in table 15.2 (p. 726).

In this experiment, the reaction mixture contains several liquids, namely the alkene product (b.p.= 101-102°), the alcohol starting material (b.p.= 171-173°), and water (b.p.= 100°) from the reaction and from phosphoric acid (which is sold as an 85% solution in water). Sulfuric acid is also a liquid, but its b.p. is very high. The boiling point of the product is very close to that of water, so they can codistill. Some of the alcohol can also codistill, even though its b.p. is substantially different from the others. Finally, some of the acid might codistill with the water due to formation of hydrogen bonding. A complete separation of liquids by simple distillation is almost never possible.

DRIVING EQUILIBRIUM REACTIONS BY LeCHATELIER'S PRINCIPLE

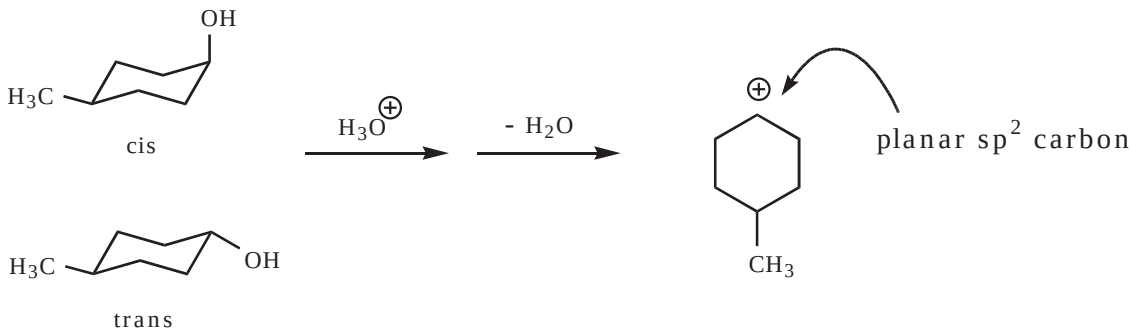
In this reaction, we drive the equilibrium towards formation of the product by removing the alkene as soon as it forms. We accomplish this by distillation. Removal of the product from the reaction mixture will result in formation of more product, according to LeChatelier's principle.

The crude distillate will contain mostly product, but will also contain some alcohol, water, and acid.

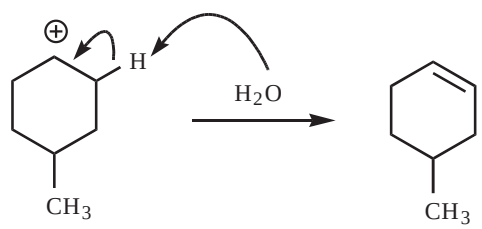
EFFECT OF GEOMETRIC ISOMERISM ON E1REACTIONS

The starting material used in this experiment is actually a mixture of cis and trans isomers. The question is, does that have any effect on the effectiveness of the dehydration, which we know to be an E1 reaction?

The answer is no, for both cis and trans isomers will first have to form the same flat carbocation, which then undergoes the elimination step.



The carbocation then undergoes elimination to form the product, regardless of whether the initial alcohol was cis or trans.



If this was an E2 reaction, then the structure of the starting material could make a difference because of the anticoplanar requirement for E2 reactions

YIELD CALCULATIONS USING CONVERSION FACTORS

From the balanced equation we know this to be a 1:1 reaction, meaning that one mole of starting material should yield one mole of product. It is frequently easier to calculate actual yield using moles (or millimoles) rather than grams. Practically any kind of conversion is most easily handled by using conversion factors. In this reaction we start with 1.5 mL of alcohol. In millimoles, this would be

$$1.5\ \text{mL} \times \frac{0.914\ \text{g}}{1\ \text{mL}} \times \frac{1\ \text{mmol}}{.114\ \text{g}} = 12.03\ \text{mmol of alcohol}$$

density mass per mmol

Likewise, once the alkene product has been weighed, the weight can be easily transformed into mmoles to calulate the percent yield of the reaction.

$$\frac{x\ \text{mmoles alkene obtained}}{12.03\ \text{mmol (theoretical yield)}} \times 100 = \%\ \text{yield}$$

SOME IMPORTANT EXPERIMENTAL NOTES

1. Do not use boiling stones to boil a system containing strong acids. The acid will destroy the stones. Always use your magnetic spin vane to stir.

2. ALKENES HAVE A STRONG, NOXIOUS, RANCID ODOR. STAY IN THE HOOD AT ALL TIMES! If you must handle the product from this reaction outside the hood, always use a capped vial or closed container.

3. Do not rinse any items containing alkene or reaction products in the regular troughs or sinks. Rinse your vials with acetone in the hood into the sink or into the organic waste container, then rinse outside the hood if more cleaning is needed.

4. If you experience nausea or dizziness from smelling alkene vapors, step outside the lab and get some fresh air. You should feel better after a while. If you don't feel better, advise your instructor immediately.

5. Remember to use an O-ring and an aluminum foil shield during the distillation step.

6. The book says to do two unsaturation tests (p. 211): one with bromine and one with $KMnO_4$. DO NOT DO THE BROMINE TEST. DO ONLY THE $KMnO_4$ TEST.

7. Ignore the unsaturation test description paragraph on p. 216 and refer to the picture on the next page instead. No 1,2-dimethoxyethane is needed, nor will it be available in the lab.

8. DO NOT DETERMINE THE BOILING POINT OF THE ALKENE, as instructed on p. 214 of the textbook. The smell in the lab will become unbearable. Take the IR spectrum instead, applying your sample on the IR card and quickly taking it to the instrument room for spectral recording.

9. Please clean up all sand spills from the distillation step. Leave the lab as you would like to find it.

UNSATURATION TEST

Alkenes change the color of potassium permanganate from purple to brown.