

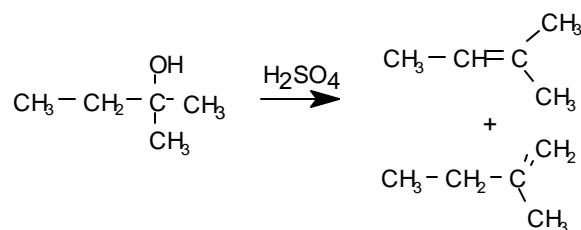
Exp't 70

Alkenes from Alcohols: Analysis of a Mixture by Gas Chromatography

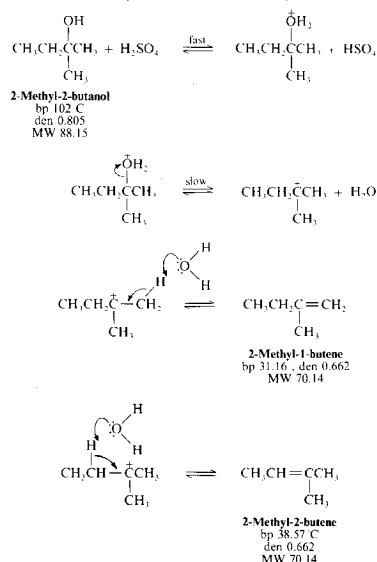
from K. L. Williamson, *Macroscale and Microscale Organic Experiments*, 2nd Ed. 1994, Houghton Mifflin, Boston. p268; revise 10/9/00

Prelab Exercise: In your chemical data table give the theoretical yield of total butene isomers. If the dehydration of 2-methyl-2-butanol occurred on a purely statistical basis with no selectivity, what would be the relative proportions of 2-methyl-1-butene and 2-methyl-2-butene?

Introduction



The sulfuric acid catalyzed dehydration of 2-methyl-2-butanol (*t*-amyl alcohol) proceeds readily to give a mixture of alkenes that can be analyzed by gas chromatography. The mechanism of this reaction involves the intermediate formation of the relatively stable tertiary carbocation followed by loss of a proton either from a primary carbon atom to give the terminal olefin, 2-methyl-1-butene, or from a secondary carbon to give 2-methyl-2-butene.



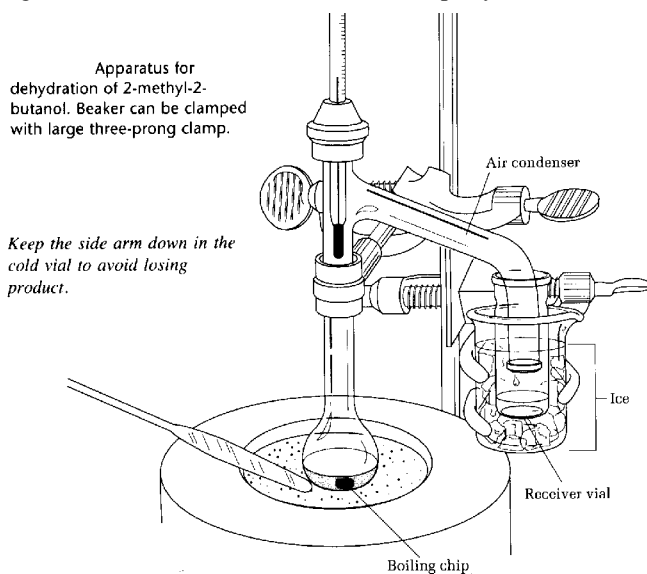
Each step of this E1 elimination is reversible and thus the reaction is driven to completion by removing one of its products, the alkene. In these reactions several alkene isomers can be produced. The Saytzeff rule states that the more substituted alkene is the more stable and therefore the one formed in larger amount. And the *trans* (*E*) isomer is more stable than the *cis* (*Z*) isomer. With this information it should be possible to deduce which peaks on the gas chromatogram correspond to a given alkene structure and to predict the ratios of the products.

Procedure: Dehydration of 2-methyl-2-butanol

- Into a 5 mL long-necked round-bottomed flask place 1 mL of water and then add dropwise with thorough mixing 0.5 mL of concentrated sulfuric acid. Cool the hot solution in an ice bath, and add to the cold solution 1.00 mL (0.80 g) of 2-methyl-2-butanol. Mix the reactants thoroughly, add a boiling stone, and set up the apparatus for simple distillation as shown in the diagram below. Hold the flask in a towel while connecting the apparatus to guard against spills or flask breakage. Cool the receiver (a vial) in ice to avoid losing the *very volatile products*.

Warm the flask on the sand bath to start the reaction, and distill the products over the temperature range 30-43° C. After all the products have distilled, the rate of distillation will decrease markedly. Cease distillation at this point.

After this, the temperature registered on the thermometer will rise rapidly as water and sulfuric acid begin to distill.



- IT IS IMPERATIVE THAT YOUR SYSTEM IS FREE OF LEAKS AND THAT THE ICE BATH IS KEPT COLD THROUGHOUT THE DISTILLATION. KEEP ALL DISTILLED LIQUIDS COLD AND CAPPED AS MUCH AS POSSIBLE TO AVOID LOSS OF ALL YOUR PRODUCT.
- To the distillate add 0.3 mL **cold** 3 M sodium hydroxide solution to neutralize sulfurous acid, mix well, draw off the aqueous layer, and dry the ORGANIC product over anhydrous calcium chloride pellets, adding the drying agent in small quantities until it no longer clumps together. **Keep the vial cold in an ice bath and capped when not purifying or drying it.** The yield reported in the literature is 84 % when the reaction is carried out on a much larger scale. Weigh the product, calculate the yield, and analyze it by gas chromatography. The average yield on a small scale is 50%. 2-Methyl-1-butene boils at 31.2°C, and 2-methyl-2-butene boils at 38.6°C so if you cannot analyze the product immediately, store the labeled shorty vial in freezer of a frig.

Analysis: Analyze your sample according to your Assignment Sheet and instructions on Sample Preparation in Lab Guide. DO NOT ADD DICHLOROMETHANE, but instead analyze the pure liquid as a “neat” sample on the gas chromatograph. (Check the GC compendium in 206 W for GC conditions). In analyzing your results, consider that the carbocation can lose any of 6 primary hydrogen atoms, but only 2 secondary hydrogen atoms to give the final product olefins.

Cleaning Up: The residue in the reaction tube should be diluted with water, neutralized with sodium carbonate, and then flushed down the drain.

Post Lab Questions

1. Write the structure of the three olefins produced by the dehydration of 3-methyl-3-pentanol.
2. Give a detailed mechanism for the dehydration reaction of 3-methyl-3-pentanol
3. From your knowledge of the dehydration of tertiary alcohols, which olefin should predominate in the product of the dehydration of 2-methyl-2-butanol and why?

Notes on Gas Chromatography: A Carbowax column works best, although any other nonpolar phase such as silicone rubber should work as well. With a nonpolar column packing, the products are expected to come out in the order of their boiling points. A typical set of operating conditions could be obtained in the GC compendium in the instrument room. The molar amounts of each compound present in the reaction mixture are proportional to the areas under the peaks in the chromatogram. Gas chromatography is especially useful in the analysis of this compound because the expected impurities differ markedly in boiling point from the product.