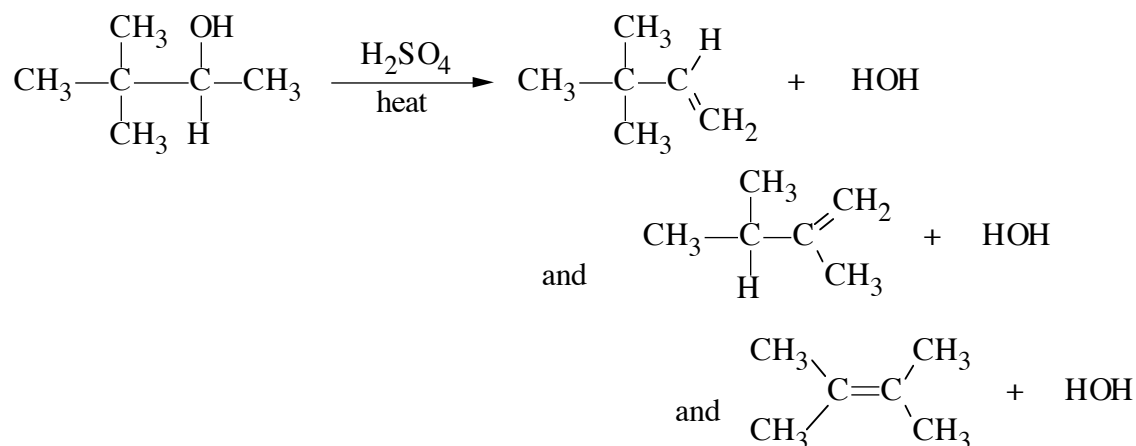


Acid-Catalyzed Dehydration of an Alcohol with Rearrangement

Source: AEM adaptation of journal article: Sayed, Y.; Ahlmark, C. A.; Martin, N. H. *J. Chem. Ed.* **1989**, *66*, 174-175.

Alkenes are an important organic functional group present in a variety of natural products and useful for preparing other functional groups. Alcohols can be dehydrated to alkenes when they are heated with an acid catalyst. The reaction mechanism for this dehydration includes the formation of carbocations, which can easily rearrange. This experiment demonstrates such a rearrangement and shows that under acid-catalyzed conditions, where an equilibrium can exist, the primary product is the most stable alkene (the thermodynamic product). The reaction that we will carry out is shown below.



Note that all three of these alkenes are produced in the reaction and are present in the volatile product mixture. This product mixture can be analyzed by gas chromatography (GC). Read Pavia's chapter 22, which discusses GC theory and practice: pages 333-354.

The experiment that you will use has been adapted from an article in the *Journal of Chemical Education*. Follow the procedure written below, including the usual information in your pre-lab notebook preparations, in your in-lab notes on procedure, and in the post-lab finalization of the experiment. (Note: be sure to include in your physical properties table the molecular masses and the boiling points of the organic starting material and each of the products in this lab. These physical properties may not be listed in the Merck, but can be found in the CRC.)

Experimental Procedure:

1. Place a known amount of 3,3-dimethyl-2-butanol into a 10 mL roundbottom flask; usually the TA will dispense exactly 1.000 mL from a pipetman into your flask. You can use its density to calculate the mass of this starting material.
2. VERY Carefully add 3 to 5 drops of concentrated H₂SO₄ and a couple of boiling chips.
3. In your hood, set up a simple distillation apparatus, similar to the one shown in Figure 14.1 on page 201 of Pavia's text. You will need your 10 mL round-bottom flask, a microscale distillation head (not a Hickman distillation head!), your thermometer and its adapter, a water-cooled condenser, and an adapter to direct the distillate into your TARED receiving flask (a conical vial). Don't forget to be sure that you still have an "open" system!
4. Slowly and gently begin heating the reaction mixture, giving it time (~20-30 minutes) to attain equilibrium before collecting distillate. Increase the heat under your solution until it boils, making sure to keep the condensing vapor temperature under 110°C. Note: even though the vapor temperature should not exceed 110°C during the distillation, the sand bath temperature WILL exceed this temperature! Typically, a sand bath temperature will rise to about 130°C or higher while the distillate is collected at a reasonable rate.
5. Collect the distillate in a tared conical vial. Keep this vial cooled in a small ice bath while you are collecting, so that the product vapors do not evaporate. Stop the reaction when you have collected only about 0.3 mL of the product mixture, and be sure to measure the mass of the product (at RT). Calculate the theoretical yield and overall % yield for the reaction. This % yield will be low since we stopped collecting product before we got it all. Please keep these alkene mixtures in the hood or tightly capped as much as possible; they have very strong unpleasant aromas.
6. Analyze the product by gas chromatography. Be sure to record which GC you used, which column you used on that GC, and all of the exact settings on the GC (including column temperature and sample size). Obtain at least two good GC printouts.
*** Be sure that the helium tank is turned off at the end of the day!
7. **Xerox** the two printouts and **attach the originals** to your write-up to be turned in. You will be given GC data for each alkene separately and for an equimolar mixture of the alkenes. Using your GC data and this additional data calculate the relative % abundance of each alkene in each of your chromatograms of the product mixture separately. Compare the two chromatograms.
8. In your conclusion, be sure to ID each component that you can on the GC trace and relate the product ratio to the mechanism!

Cleanup. Dilute the materials from the still pot with water, neutralize with aqueous saturated NaHCO₃ solution, and flush down the drain. Place your product mixture (after GC analysis!) in the used organic materials bottle.