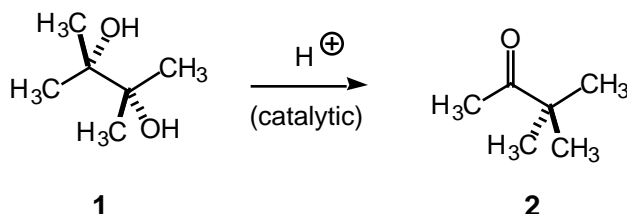


Problem Set #11

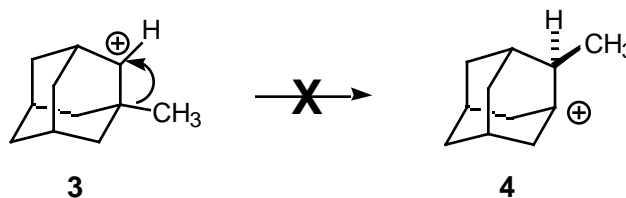
Chemistry 3230

April 6, 2001

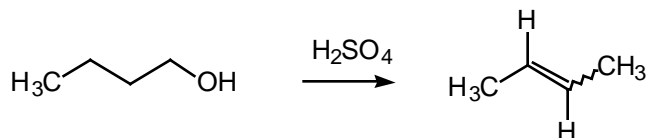
1. The rearrangement of pinacol (**1**) to pinacolone (**2**) in acid solution was first reported in 1860. Write a mechanism for this process. Related rearrangements of compounds bearing hydroxyl groups on adjacent carbons (1,2-diols) are now generally known as *pinacol rearrangements*.



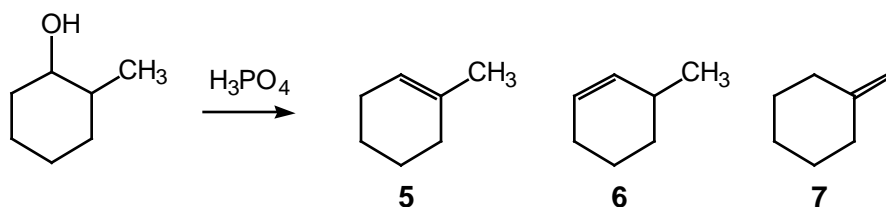
2. The adamantyl cation **3** does not undergo Wagner-Meerwein rearrangement by 1,2-methyl migration. One reason for this might be that the carbocation left behind in such a process would be a relatively unfavorable bridgehead cation. Perhaps more important is a stereoelectronic effect. By considering the orbitals that would be involved in the shift shown below, explain why the process cannot occur.



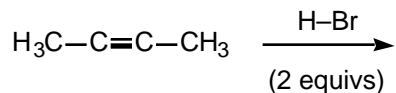
3. Dehydration of 1-butanol under acidic conditions leads to a mixture of *cis*- and *trans*-2-butenes. Write a careful mechanism for this conversion, being careful not to invoke a primary carbocation as an intermediate.



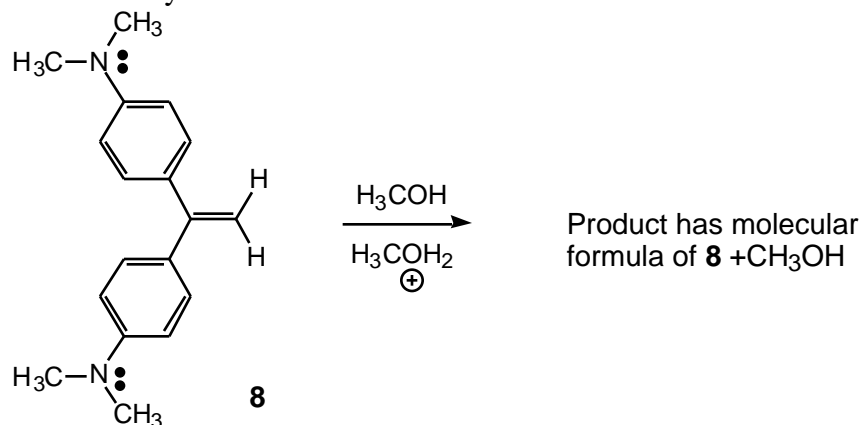
4. Provide a mechanism for the formation of the following products (**5**, **6**, and **7**) from acid catalyzed dehydration of 2-methylcyclohexanol.



5. We haven't said anything yet about the chemistry of alkynes (carbon-carbon triple bond-containing compounds). Nevertheless, reasoning by analogy to addition of H-X to double bonds, you should be able to predict the product formed when two units of HBr add to 2-butyne.



6. Alkene **8** adds methanol under conditions of acid catalysis.
- Write the product of the reaction
 - The intermediate carbocation is so stable that it actually builds up to detectable concentrations during the course of the reaction. Give the structure of the carbocation, and draw resonance structures to show why it is so stable.



7. Write a mechanism for the formation of **10** and **11** from isoprene (2-methyl-1,3-butadiene) and methyl methoxymethyl sulfate (**9**) in the so-called Lebedev Methoxymethylation. A C=C unit will be the nucleophile (you have to decide which one) and the electrophile is formed by initial ionization of **9** to a resonance-stabilized carbocation. Note that an equivalent of sulfur trioxide is formed in the reaction.

