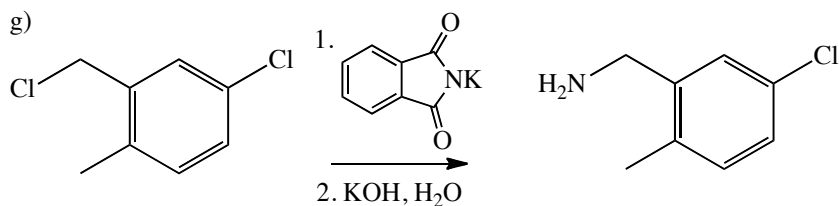
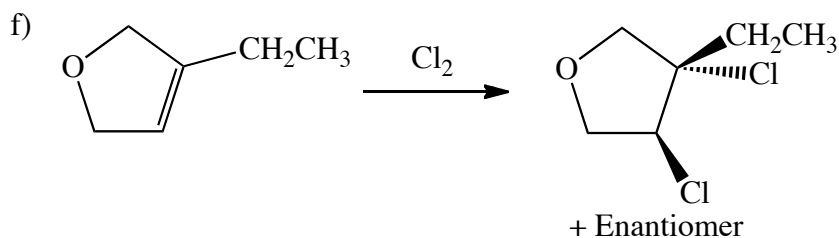
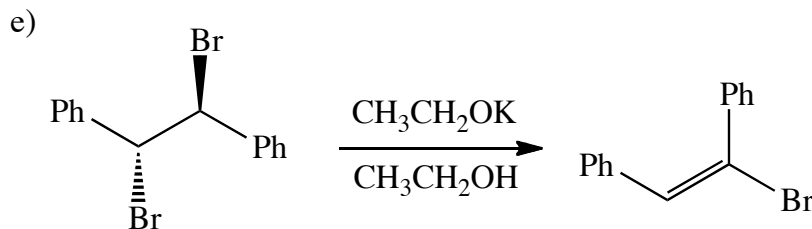
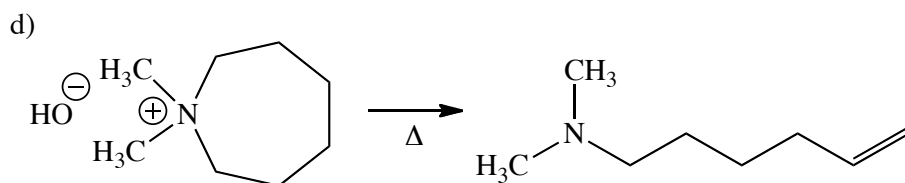
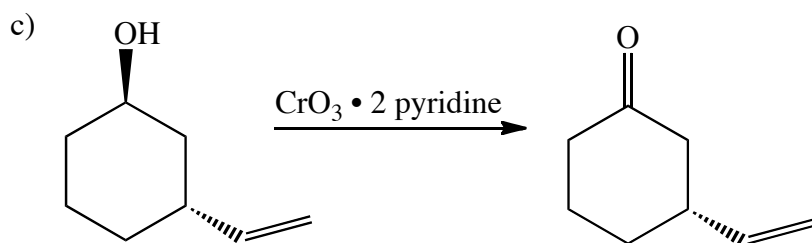
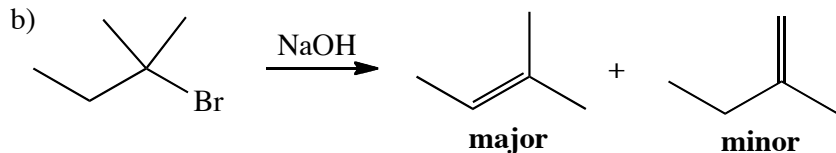
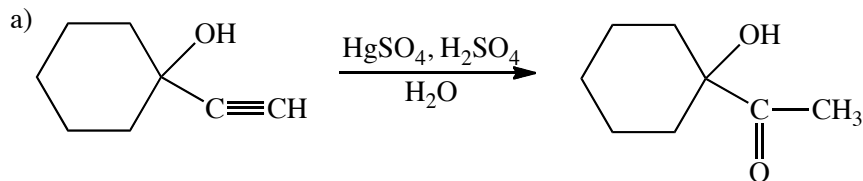


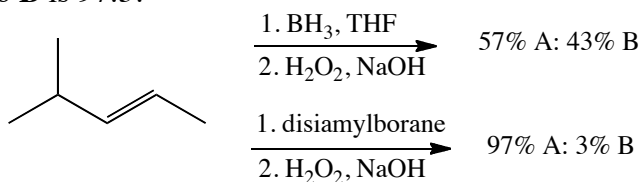
**Chemistry 250A -- Exam #3 Answer Key -- November 13, 2009**

Show non-zero formal charges for all structures. There are 5 pages.

1. (21 pts) Complete the following reactions. (Hint: They all react!) Clearly show the stereochemistry of the products where appropriate. Label major and minor products where appropriate.



2. (14 pts) When the alkene shown below is treated with borane in THF, followed by  $\text{H}_2\text{O}_2$  and  $\text{NaOH}$ , two products, **A** and **B** are formed in at 57:43 ratio. When disiamylborane is used instead, the ratio of **A** to **B** is 97:3.

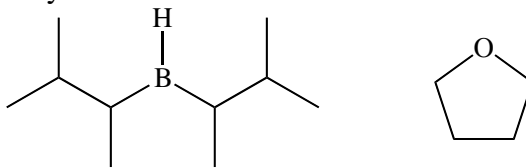


a) Provide names for both the alkene shown above and for  $\text{H}_2\text{O}_2$ .

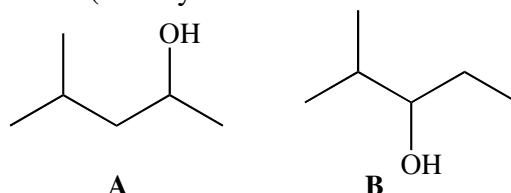
***Trans-(or E)-4-methyl-2-pentene***

**Hydrogen peroxide**

b) Draw the structure of disiamylborane and THF.



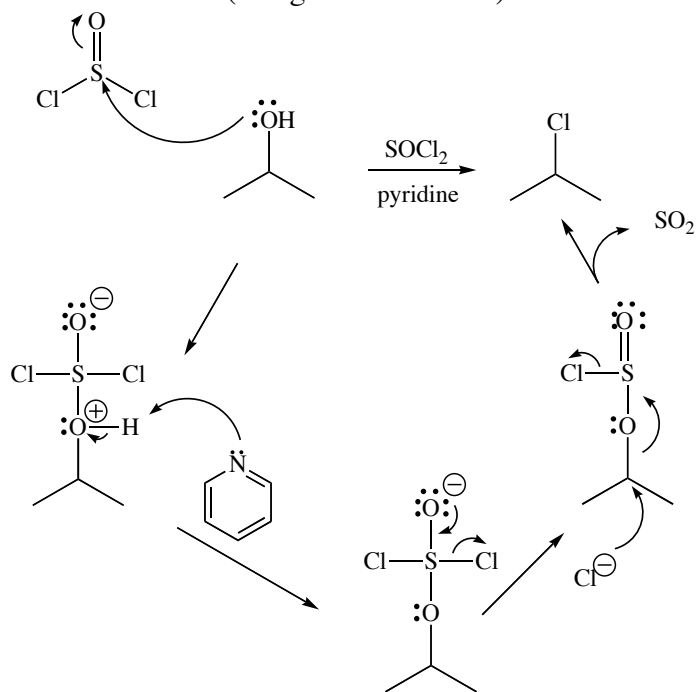
c) Draw the structures of **A** and **B**. (Clearly indicate which is which.)



d) Clearly explain the reason for the differences in the percentages.

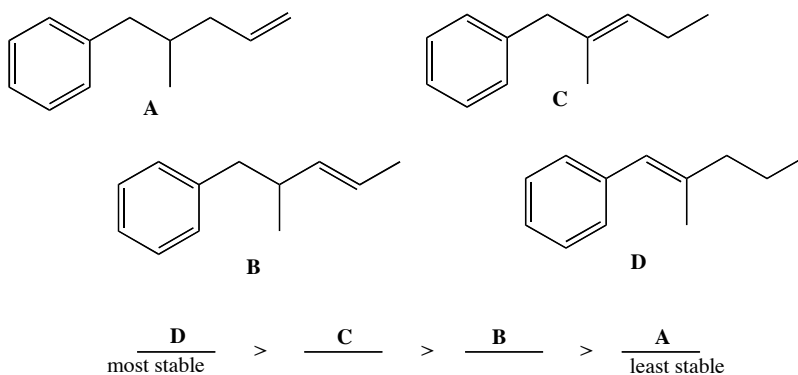
**Boron and hydrogen add across the double bond simultaneously. Since the boron is larger (and hence more sterically demanding) than a hydrogen, it prefers to add to the least hindered side. But since the boron in  $\text{BH}_3$  is attached to small groups (hydrogens), this steric preference isn't to dramatic. However, when two of the hydrogens on the boron are replaced with bulky disiamyl groups, the boron end of the B-H bond has a much stronger preference for the least hindered position. Essentially, when the boron adds to the left hand side of the double bond the disiamyl groups run into the isopropyl group attached there, whereas there is much less steric hindrance with the methyl group on the other side. (In the second step of the reaction the boron is replaced with an OH, so the major product has the OH on the least hindered side.)**

3. (9 pts) Write a detailed mechanism (using curved arrows) for the following reaction.

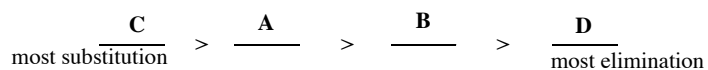
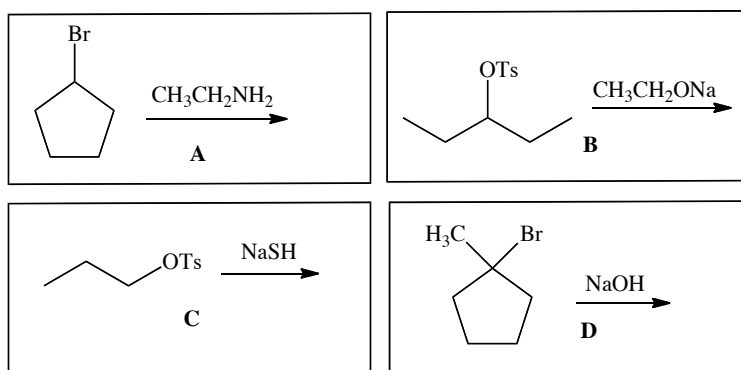


4. (10 pts) Rank the following compounds according to the indicated property:

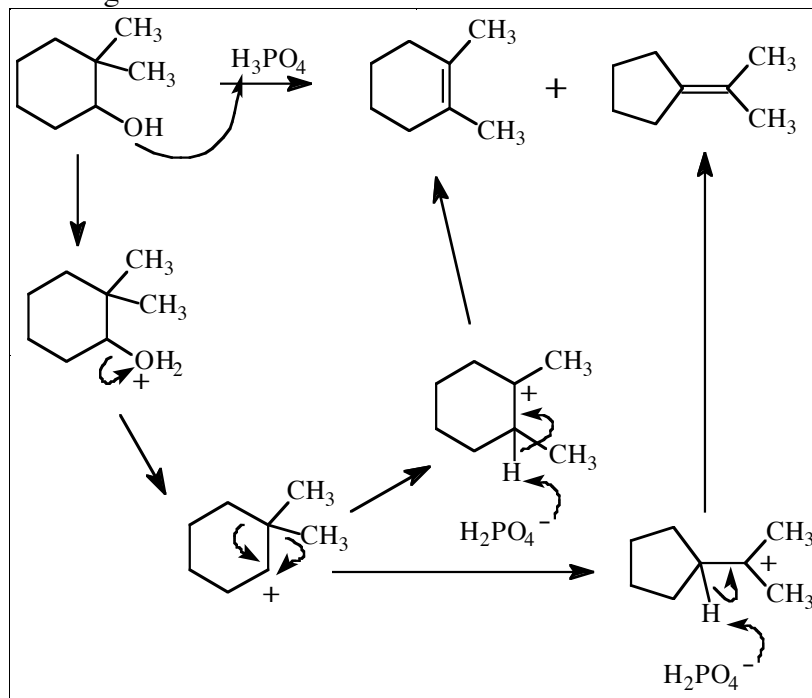
a) stability



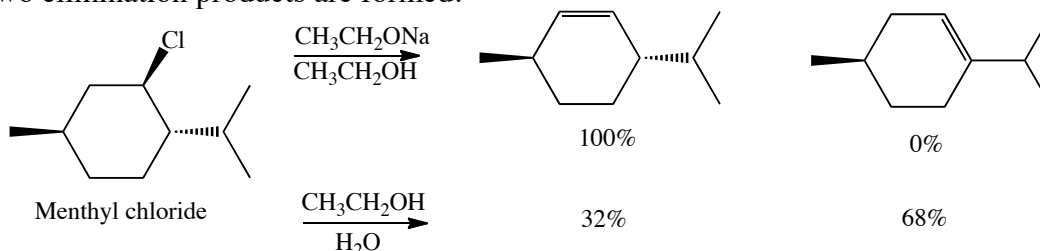
b) Ratio of substitution/elimination



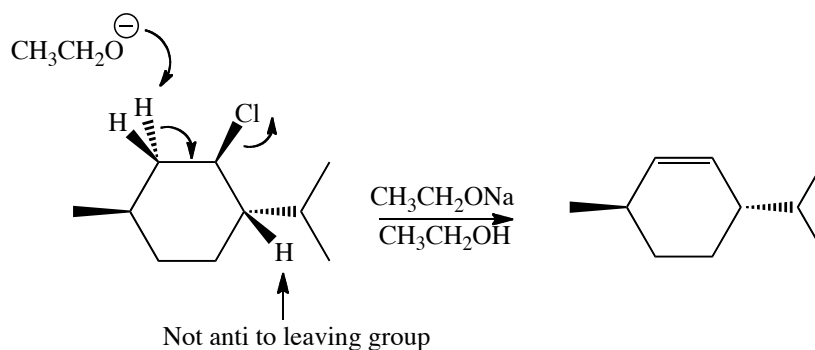
5. (10 pts) Write a detailed mechanism (using curved arrows) to account for the products observed in the following reaction.



6. (16 pts) When menthyl chloride is treated with sodium ethoxide in ethanol, only one elimination product is produced. However when menthyl chloride is treated with ethanol in water two elimination products are formed.

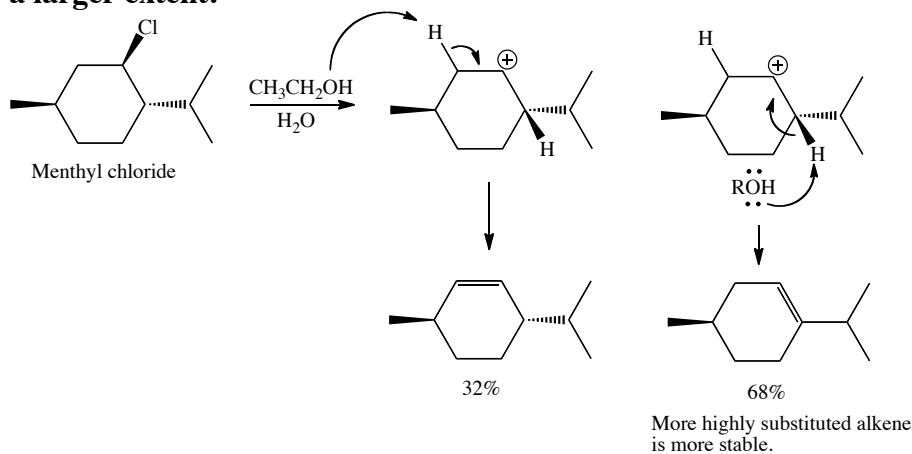


a) Draw detailed mechanisms (using curved arrows) for both of these reactions showing the formation of the products. Then clearly explain why only one product is obtained under the first set of conditions, and why a mixture favoring the other product is obtained under the second set of conditions.



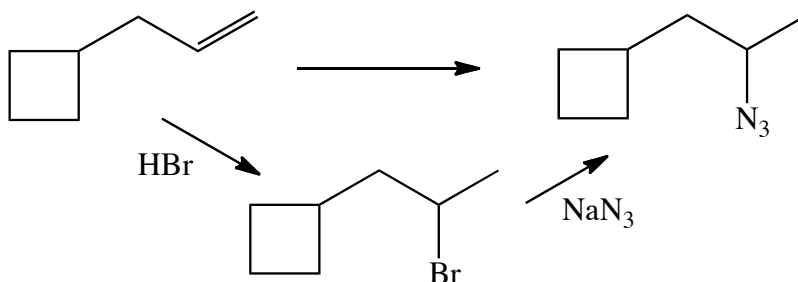
In the presence of a strong base, the first reaction proceeds via an E2 mechanism as shown above. The E2 reaction proceeds fastest when the bonds to the hydrogen being abstracted and the leaving group are periplanar to each other, which in a six-membered ring requires that they be in a trans-diaxial conformation. In menthyl chloride there is only one beta hydrogen in this orientation and therefore elimination proceeds to give only the product shown.

By contrast, the second reaction proceeds via an E1 mechanism as shown below. (The absence of a strong base makes the E2 mechanism unfavorable.) In the E1 mechanism the leaving group leaves first, producing a carbocation. The hydrogen is removed in a second step, but since the leaving group has already left, there is no requirement for the hydrogen to be anti to the leaving group. Thus, unlike the E2 case, both isomeric products can be efficiently produced. The second product, with the isopropyl group on the double bond, contains a more highly substituted double bond and thus is more stable than the first product and, to the extent that the transition state also has double bond character, is produced to a larger extent.

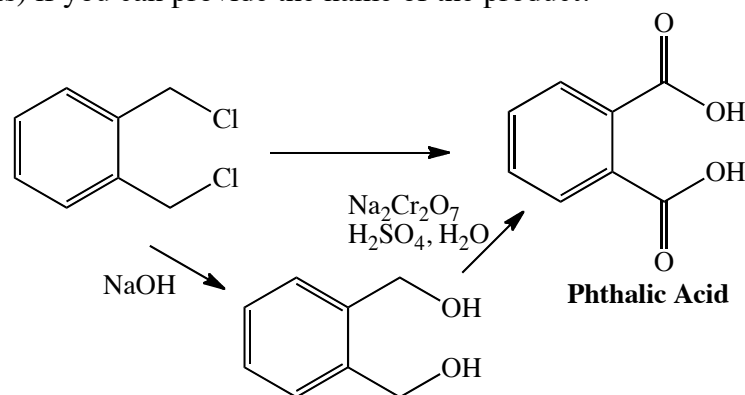


7. (20 pts) List the reagents necessary to accomplish the following transformations. In addition to the indicated starting material, you may use any molecules of 3 carbons or less as well as any standard reagents. (For multistep transformations show the major organic product for each step. You do **not** need to show the mechanisms.)

a)



b) Extra credit (2 pts) if you can provide the name of the product.



c)

