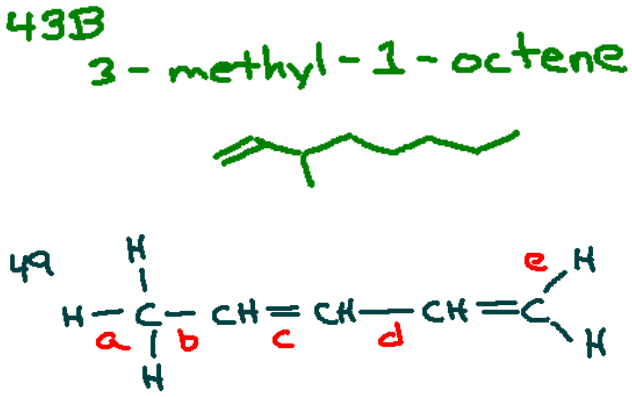
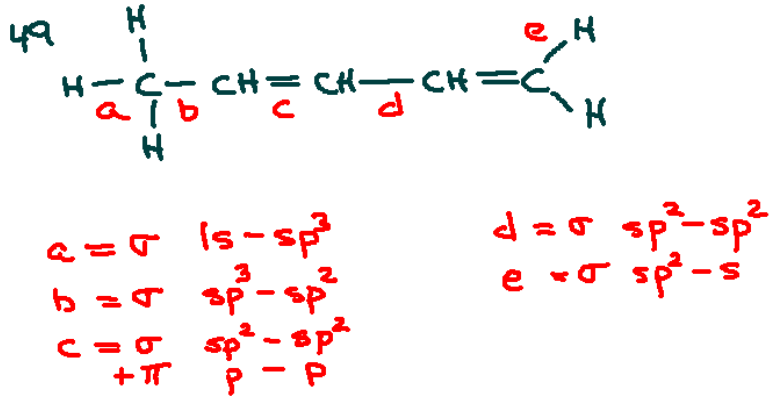
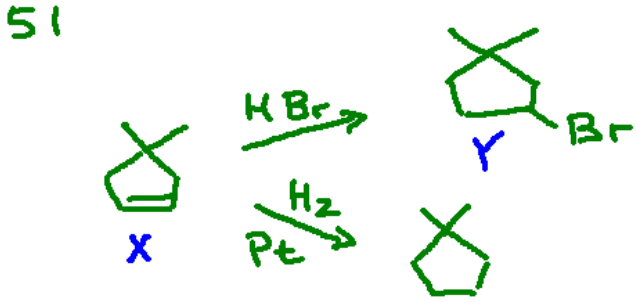
Chem 201, 2009
HW #3, due Th, Oct 1, 12 PM

ANSWERS

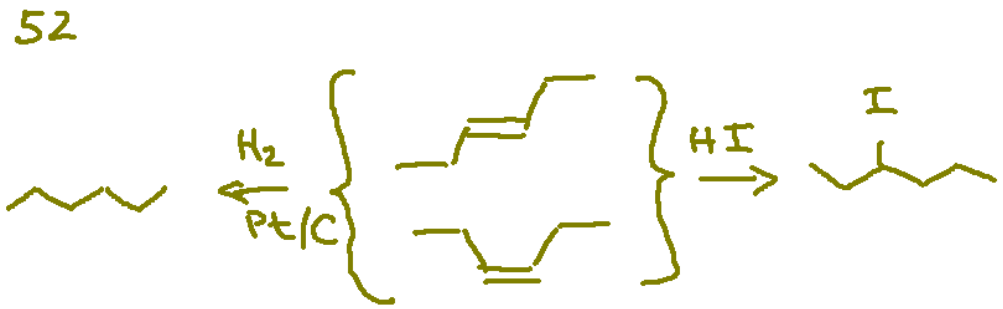
#1. Loudon problems from chapter 4: 43B, 49, 51, 52







If the double bond in X were positioned differently, e.g., 3,3-dimethylcyclopentene, *two* products would be produced from the HBr addition.



If the double bonds in the alkenes were positioned differently, e.g., *(E)*- and *(Z)*-2-hexene, *two* products would be produced from the HBr addition.

#2. The rate of reaction of HBr with 2-methyl-1-butene (**A**) differs substantially from the rate of reaction of HBr with 1-butene (**B**).

a. Which reaction is faster? Explain.

The reaction with **A** is faster. The rate-determining step in HBr + **A** produces a tertiary carbocation, while the comparable step in HBr + **B** produces a secondary carbocation. The Hammond postulate tells us that the transition state leading to the tertiary carbocation will be more stable and the barrier for the rate-determining step will be smaller.

b. Draw a reaction energy diagram for each "HBr + alkene" reaction that is consistent with your prediction. Identify the rate-determining step on your diagrams and make sure your diagram includes formulas for the species found at each energy *minimum*.

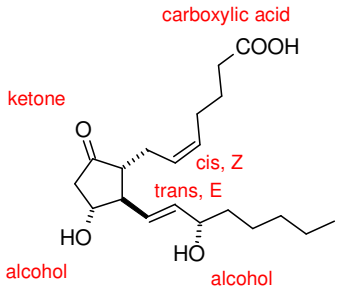
c. Which acid should react faster with **B**, HBr or HCl? Justify your answer with a reaction energy diagram.

HBr should react faster with **B** because it is a stronger acid than HCl. ΔG^{o} (and by the Hammond postulate, $\Delta G^{\ddagger}$) for the reaction of **B** + HBr → carbocation + Br^- is smaller than the comparable reaction with HCl.

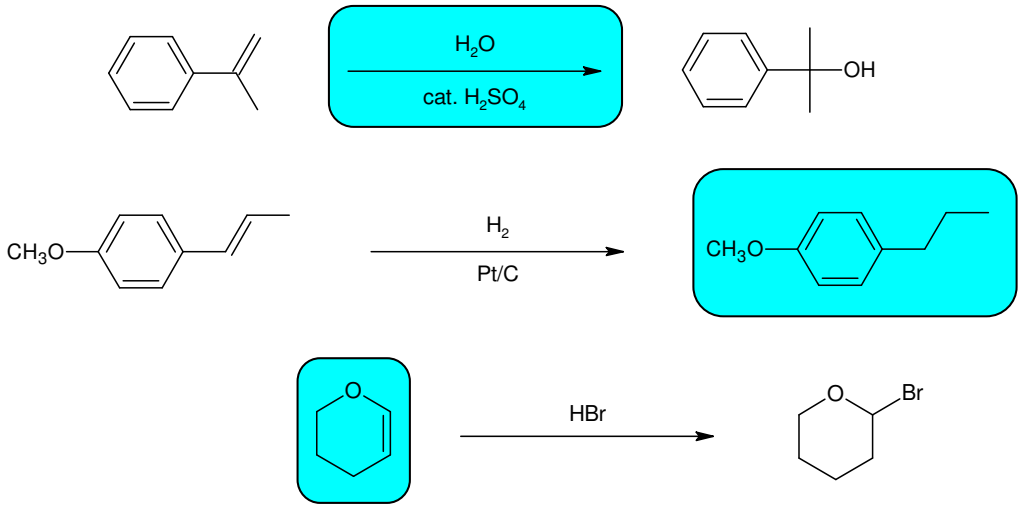
#3.

a. Prostaglandins are a family of highly active biological molecules found in all animal tissues and responsible for a range of physiological effects. One member of the family is shown below. Label all of its functional groups.

b. Based on the positions of the alkene hydrogens, label each alkene as *cis* or *trans*. Next, using the Cahn-Ingold-Prelog (CIP) rules, label each alkene as *Z* or *E*.

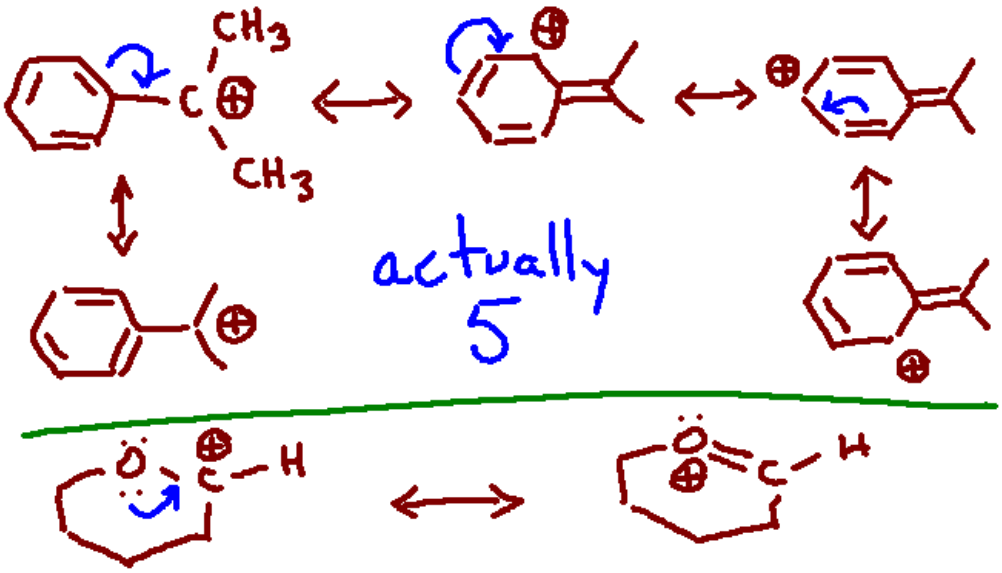


#4. Draw the missing item (reagent, starting material, or product).

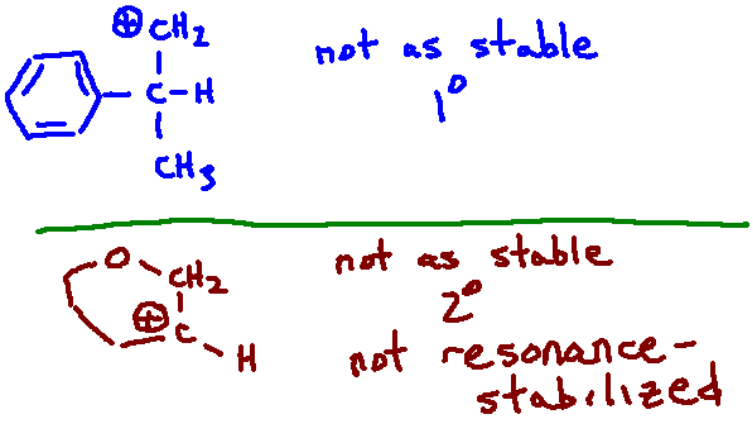


#5. Two of the reactions in #4 are regioselective and involve carbocation intermediates.

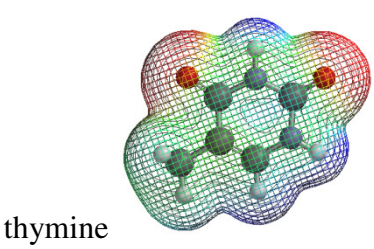
c. These intermediates are resonance hybrids. Draw all of the important resonance structures for each (four structures for one, two for the other)

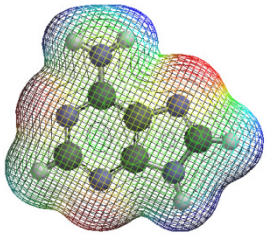


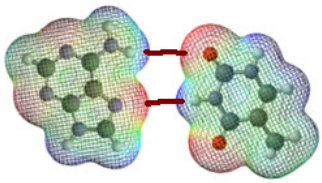
d. Draw the carbocations that lead to the unobserved regioisomers[2]. Briefly explain why these reactions are regioselective.

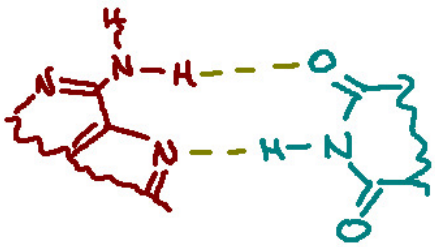


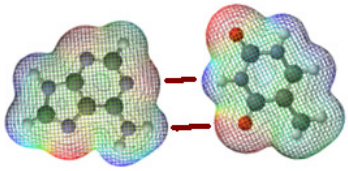
#6. Biochemists have found that thymine and adenine can hydrogen bond to each other by simultaneously forming *two* hydrogen bonds. Based on the potential maps (-200 to +200), draw at least *two* different structures showing this kind of hydrogen bonding.

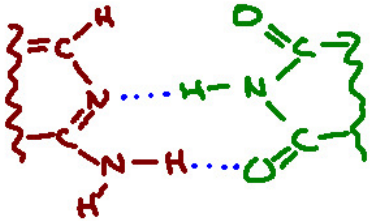

thymine


adenine

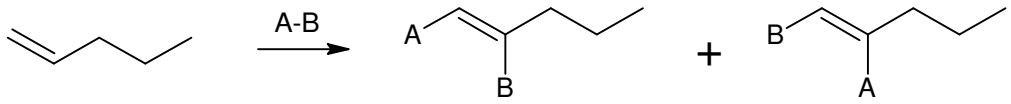








[2] A **regioselective** reaction (p. 148) is any *addition* reaction in which addition of A-B actually occurs more in one direction than the other.



The two products that might form in a reaction of this type are called **regioisomers**.