

Exam #1

Chemistry 334

Principles of Organic Chemistry II

Thursday October 5, 2006

Name: KEY .

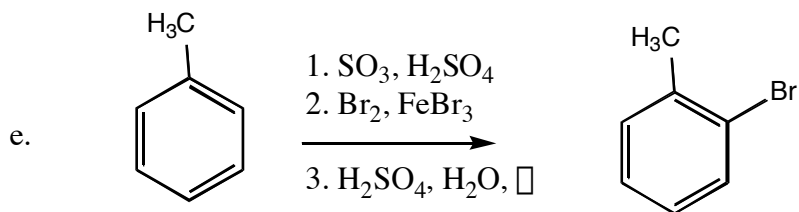
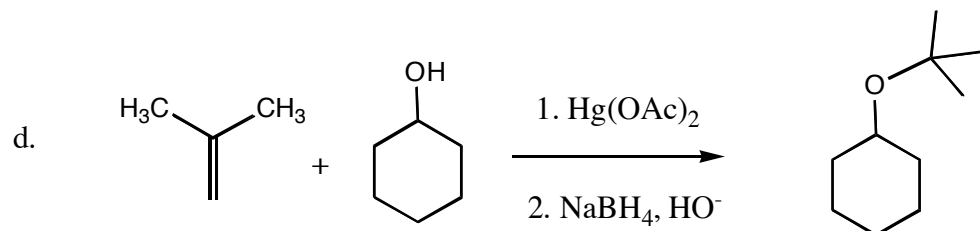
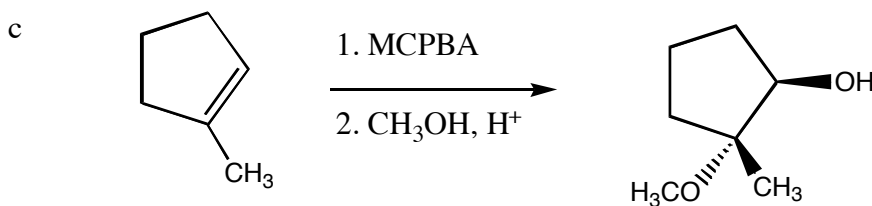
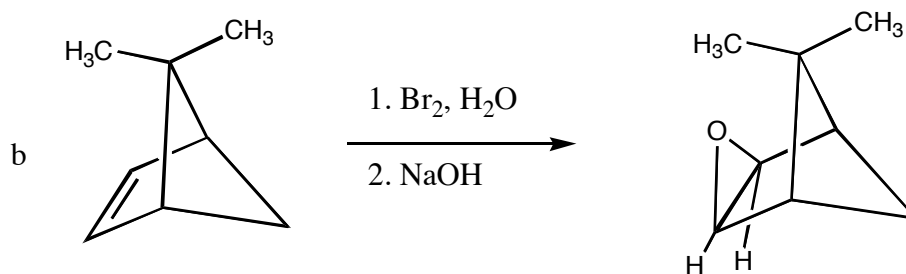
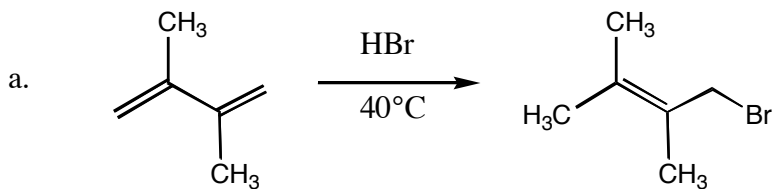
The exam is worth a total of 100 points; there are six questions. Please show all work to receive full credit for an answer.

By putting your name on this exam, you agree to abide by California State University, Northridge policies of academic honesty and integrity

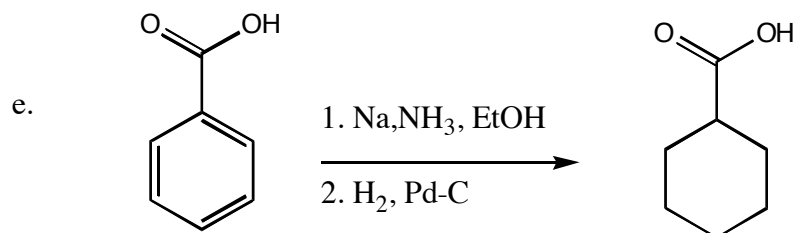
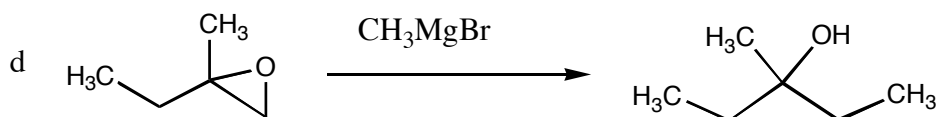
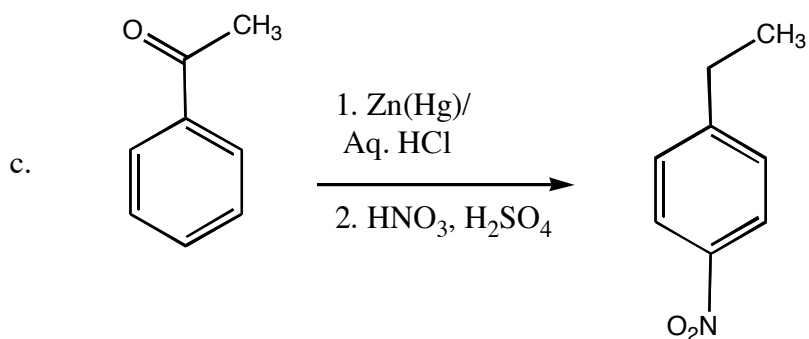
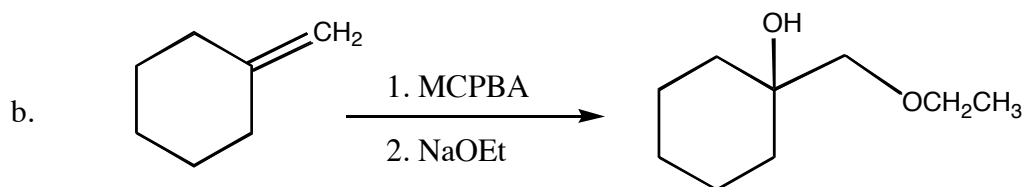
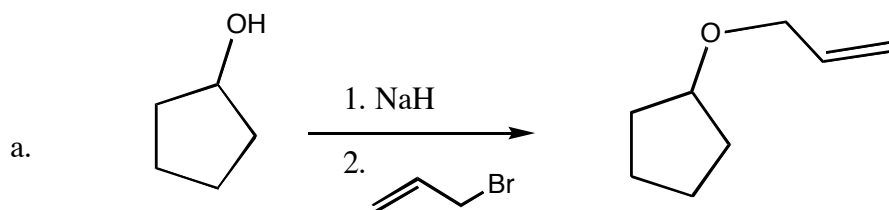
Molecular models are allowed for this exam. Calculators are not needed.

Good Luck!

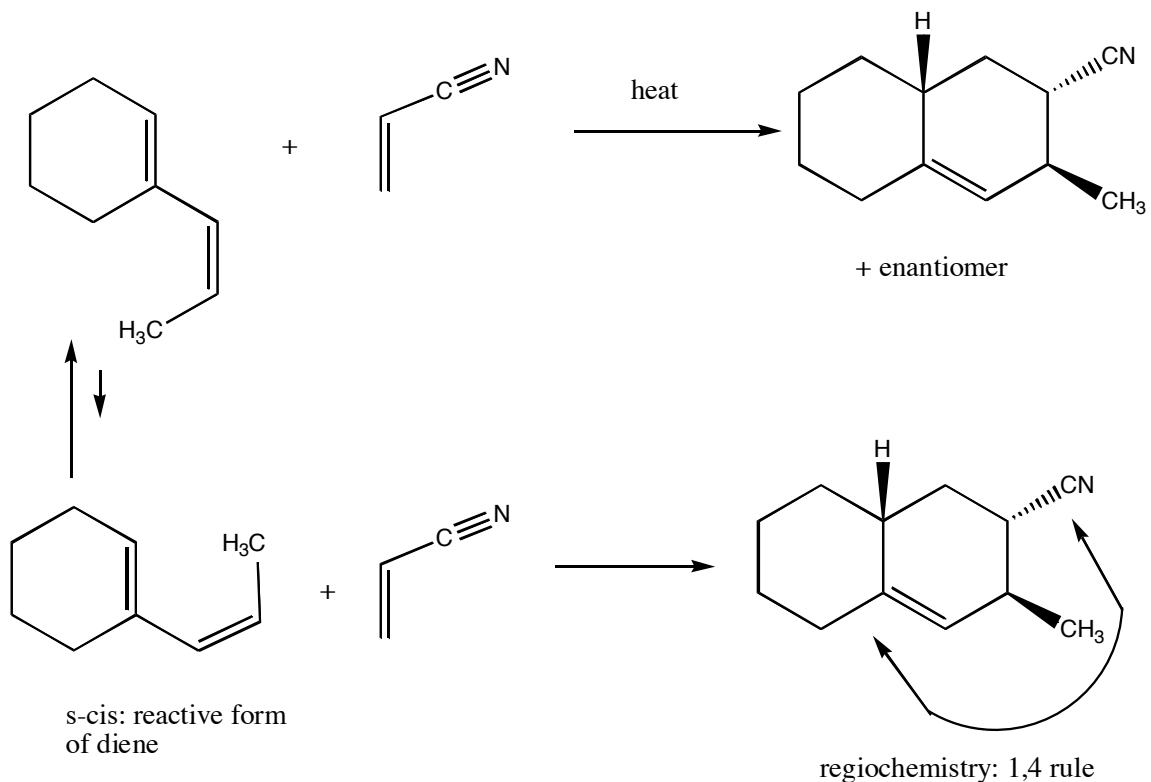
1. Predict the products of the following reactions. **Remember to indicate stereochemistry where relevant.** (20 pts)



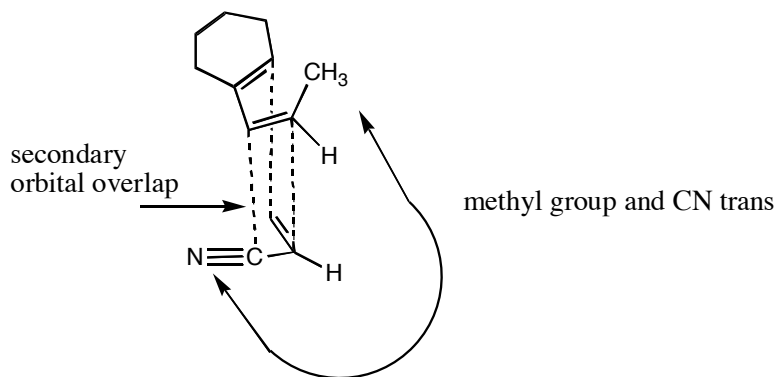
2. Indicate reagents to accomplish the following transformations. More than one step may be required. (20 pts)



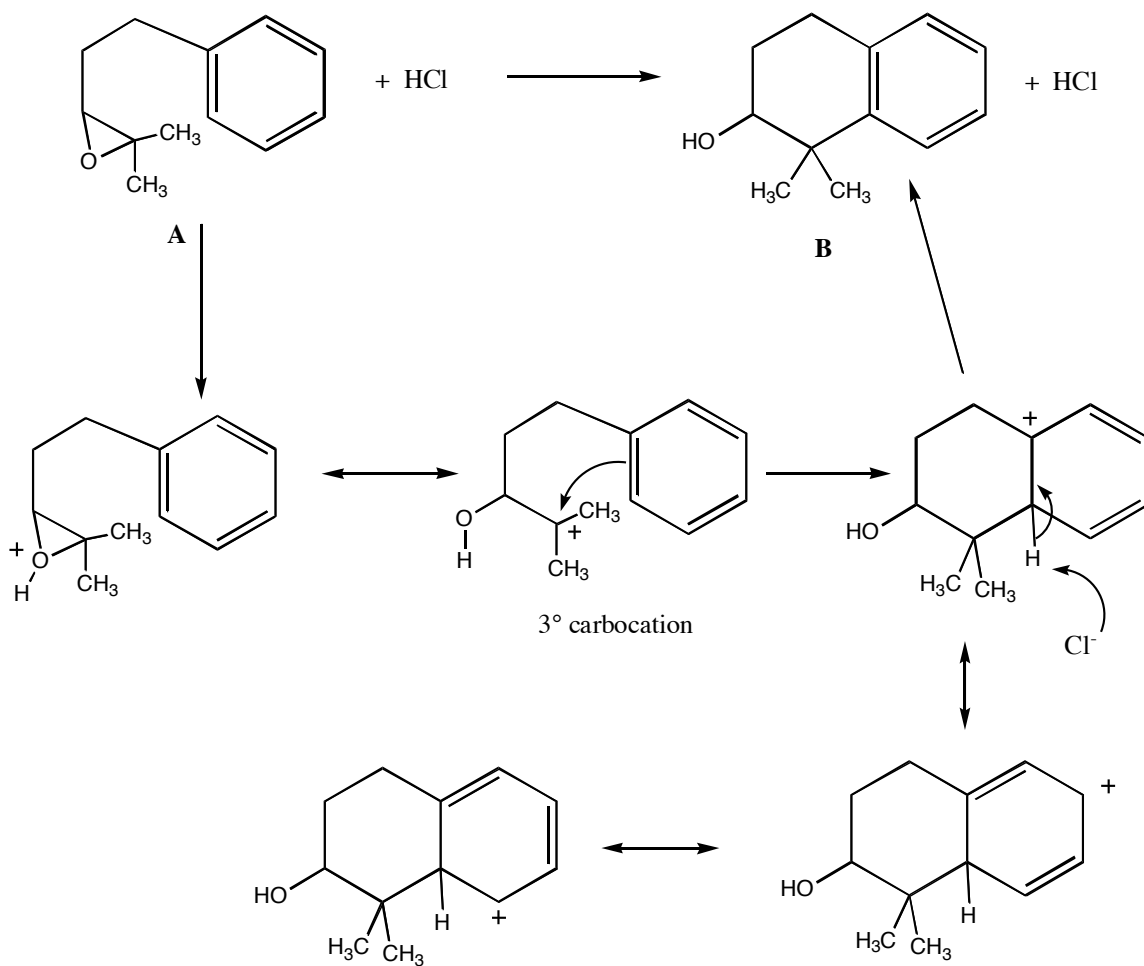
3. Draw the structure of the product of the following reaction, being sure to indicate both regiochemistry and stereochemistry. Provide a brief rationalization for your regiochemical and stereochemical assignments (15 pts).



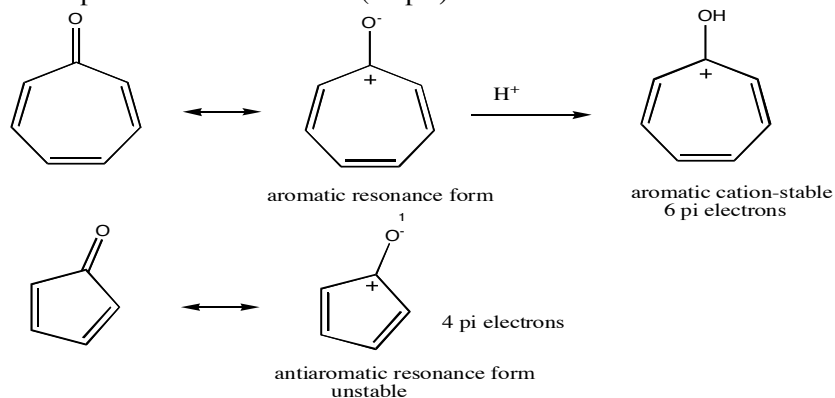
stereochemistry: endo approach of dienophile:



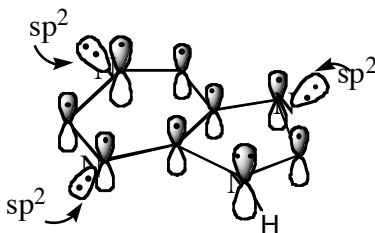
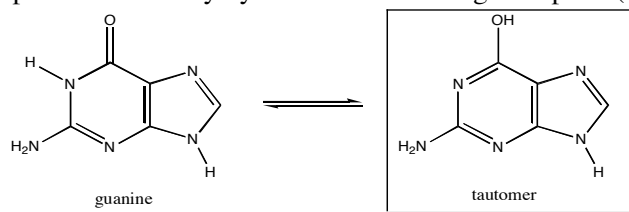
4. Treatment of epoxide **A** with a catalytic amount of HCl in diethyl ether leads to the formation of alcohol **B**. Show a detailed, step-by step mechanism for the transformation of **A** to **B** using the curved arrow notation. Be sure to include all intermediates and resonance forms where appropriate. (15 pts)



5. a. Drawing (resonance) structures to support your answer, explain why an unusually **stable cation** is formed when cycloheptatrienone is treated with acid (H^+), and why cyclopentadienone is so **unstable** that it undergoes spontaneous Diels-Alder reaction with itself at low temperatures when formed. (10 pts)

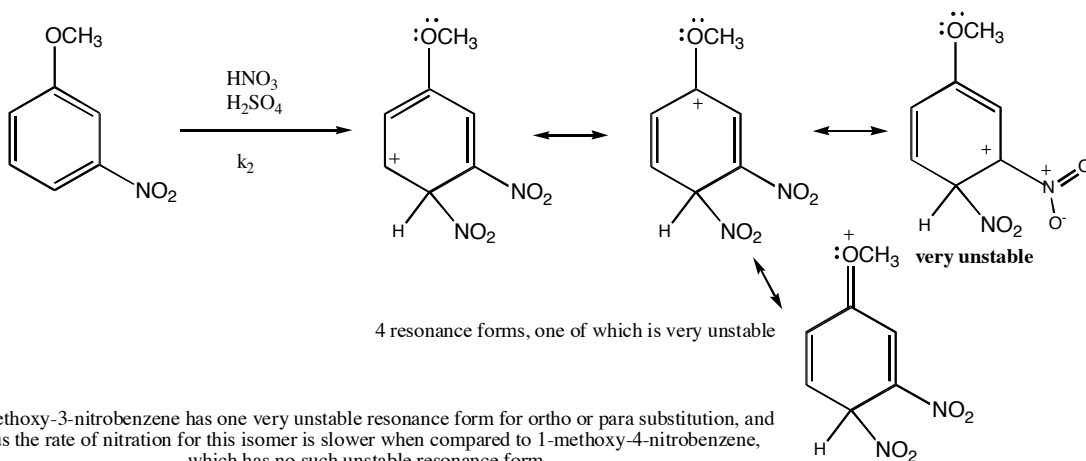
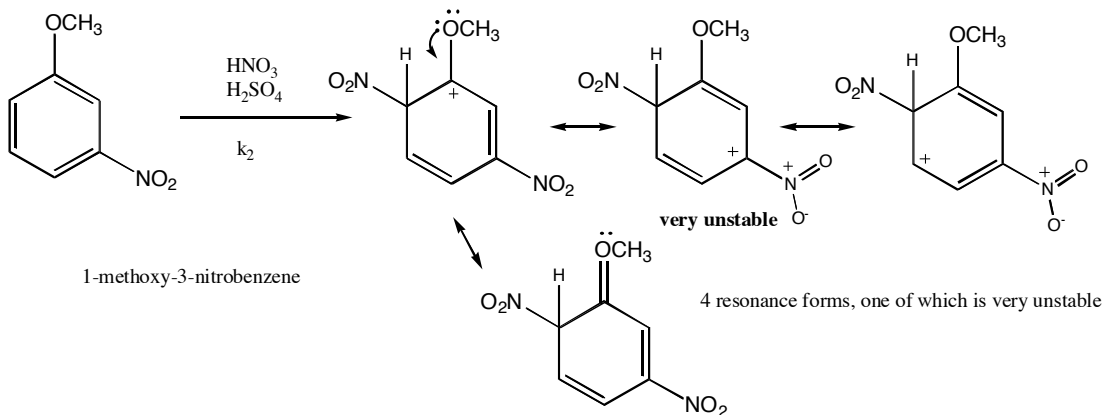
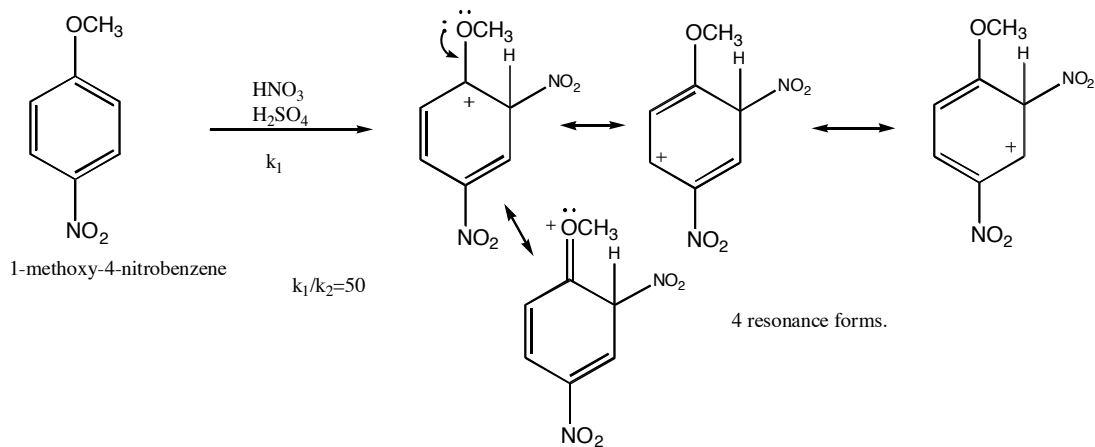


- b. Consider the heterocyclic base guanine, found in DNA. It has an easily formed tautomeric (isomeric) form as shown below. Is the tautomer aromatic? Draw out all lone pairs on heteroatoms, and then diagram the three-dimensional orbital structure of the tautomer to explain your answer. Include all p orbitals and any hybrid orbitals bearing lone pairs (10 pts).



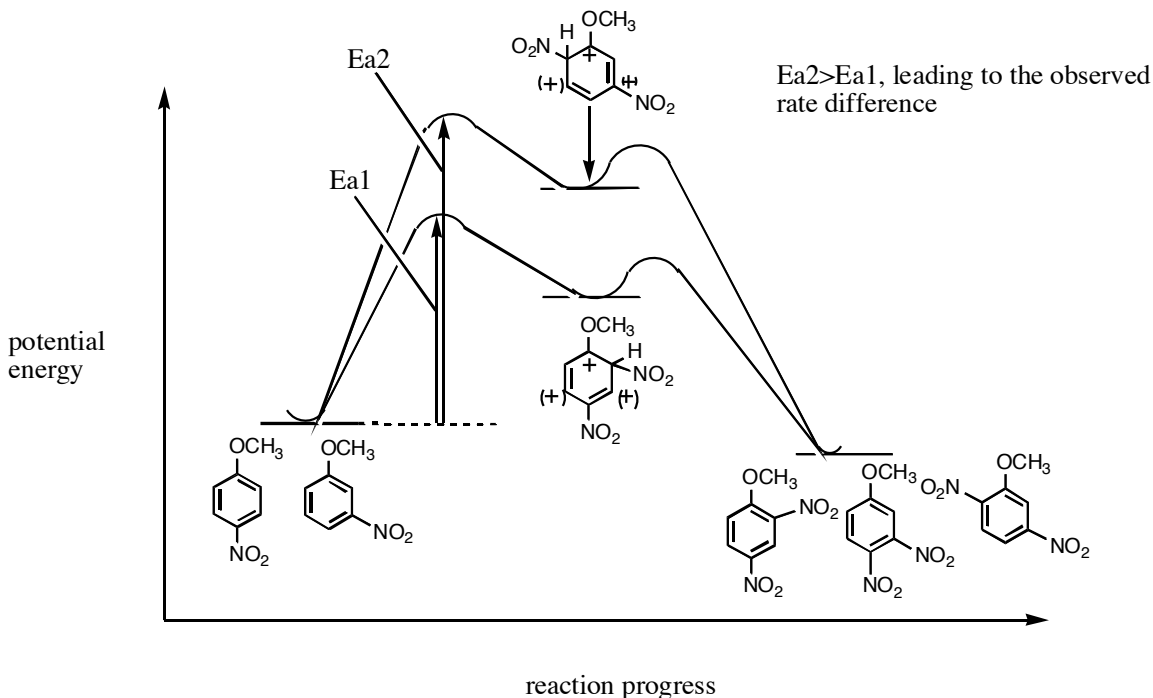
aromatic: 10 pi electrons

6. The rate of nitration of 1-methoxy-4-nitrobenzene is 50 times that of 1-methoxy-3-nitrobenzene. By showing resonance forms for the respective nitration intermediate(s), explain this rate difference. (10 pts)



Bonus (10 pts)

Draw a reaction energy profile diagram for problem 6. Be sure to include both reactions on the same graph, and indicate the relative energy levels of the intermediates. For simplicity, assume that the potential energy levels of both reactants are the same, and that the potential energy levels of all the products are the same.



For electrophilic aromatic substitution, the rate-determining step is the first step, formation of the arenium ion intermediate; this means that the first step has the highest activation barrier. Reactions that have lower activation barriers for the rate-determining step proceed faster. Since the rate-determining step is endothermic, the transition state will resemble the intermediate both in structure and in energy (the Hammond postulate). Thus, more stable intermediates will have more stable transition states leading to them, and to a first approximation we can say that the reaction with the more stable intermediate will proceed faster. As can be seen from the diagram above, the arenium ion intermediate formed from nitration of 1-methoxy-4-nitrobenzene is more stable than that formed from 1-methoxy-3-nitrobenzene (as discussed in the resonance form analysis for problem 6), and thus we expect the activation barrier leading to the more stable intermediate to be lower. As a result, at a fixed temperature, 1-methoxy-4-nitrobenzene undergoes nitration faster than 1-methoxy-3-nitrobenzene, and the energy difference $E_{a2} - E_{a1}$ is approximately proportional (neglecting differences in the Arrhenius factor A for reactions of *different* isomers) to the natural logarithm of the ratio of the rate constants k_1 and k_2 ($\ln 50$).

Congratulations!

Score:

1. _____ /20

2. _____ /20

3. _____ /15

4. _____ /15

5. _____ /20

6. _____ /10

Bonus: _____ /10

Total: _____ /100