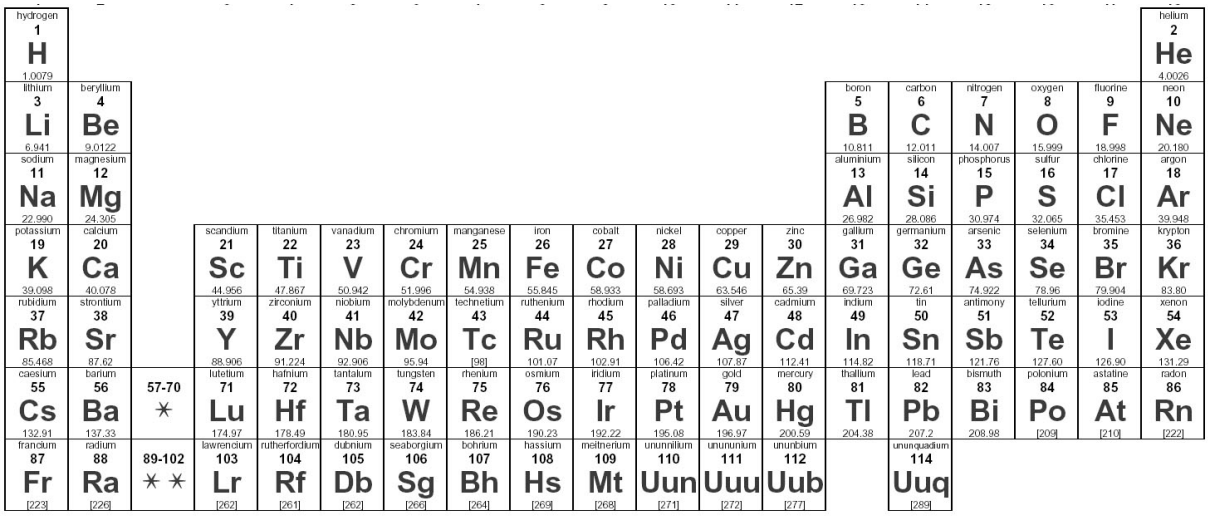
Organic Chemistry 2 Name:_____
First Examination
February 15/17, 2012
Prof. Malachowski

The examination has eight questions on five pages. The point values for each question are found with the question. Partial credit will be given where appropriate.

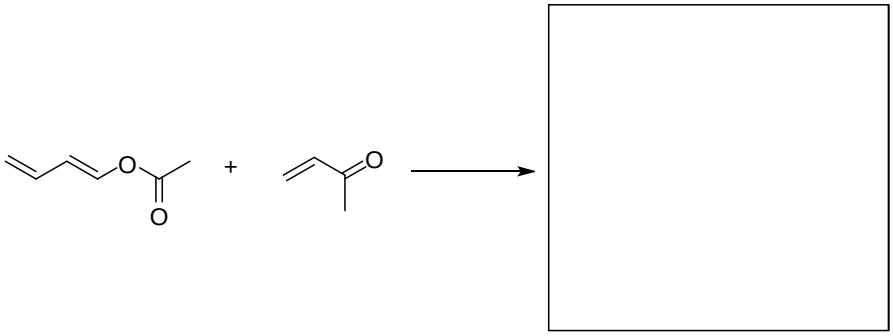
Read each question carefully before answering. Be certain you understand everything the question is requesting. Do the easy questions first. If questions appear confusing or exceedingly complex , then you may need to rethink the question. Keep in mind the intended examination topics.

In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Don't forget to include lone pairs of electrons and formal charges when appropriate.

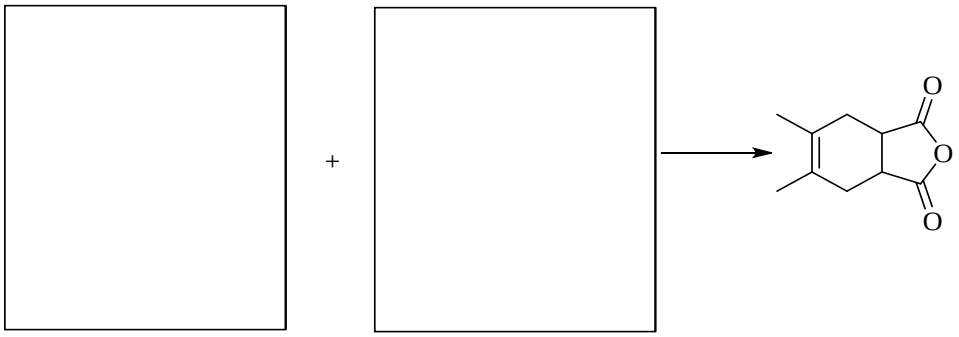


1. Provide the necessary information, product(s) or starting materials, to complete the following reactions. (5 pts. each)

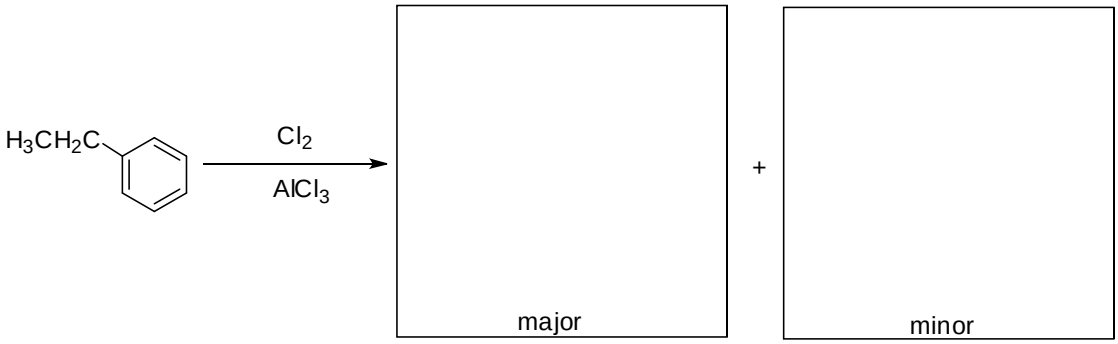
a)



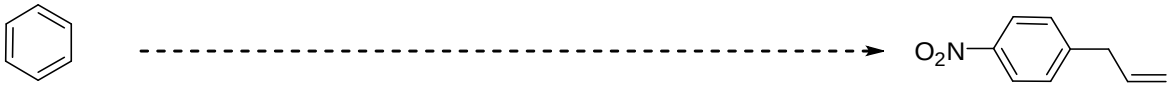
b)



c)

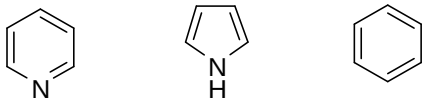


2. Suggest a series of reactions to take the starting material on the left to the product on the right. This will require two or three steps. You may use any inorganic reagent and any organic reagent of seven carbons or less. (6 pts.)



3. Rank the following structures in order of their reactivity in electrophilic aromatic substitition reactions. (3 pts. each)

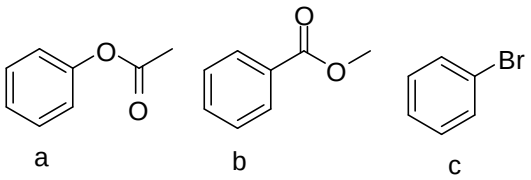
a)



a b c

most reactive _____>_____>_____ least reactive

b)

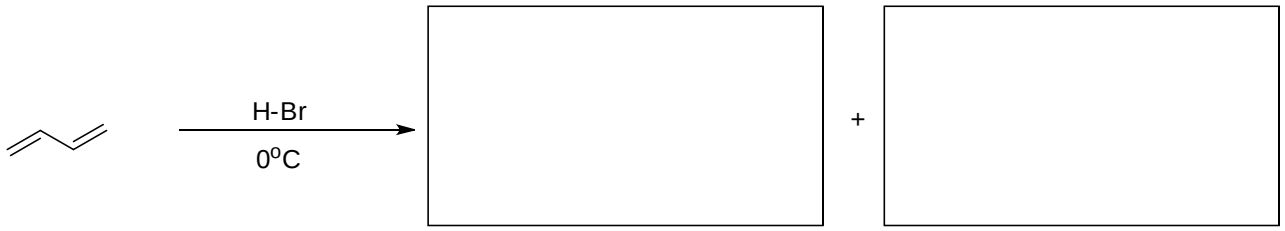


a b c

most reactive _____>_____>_____ least reactive

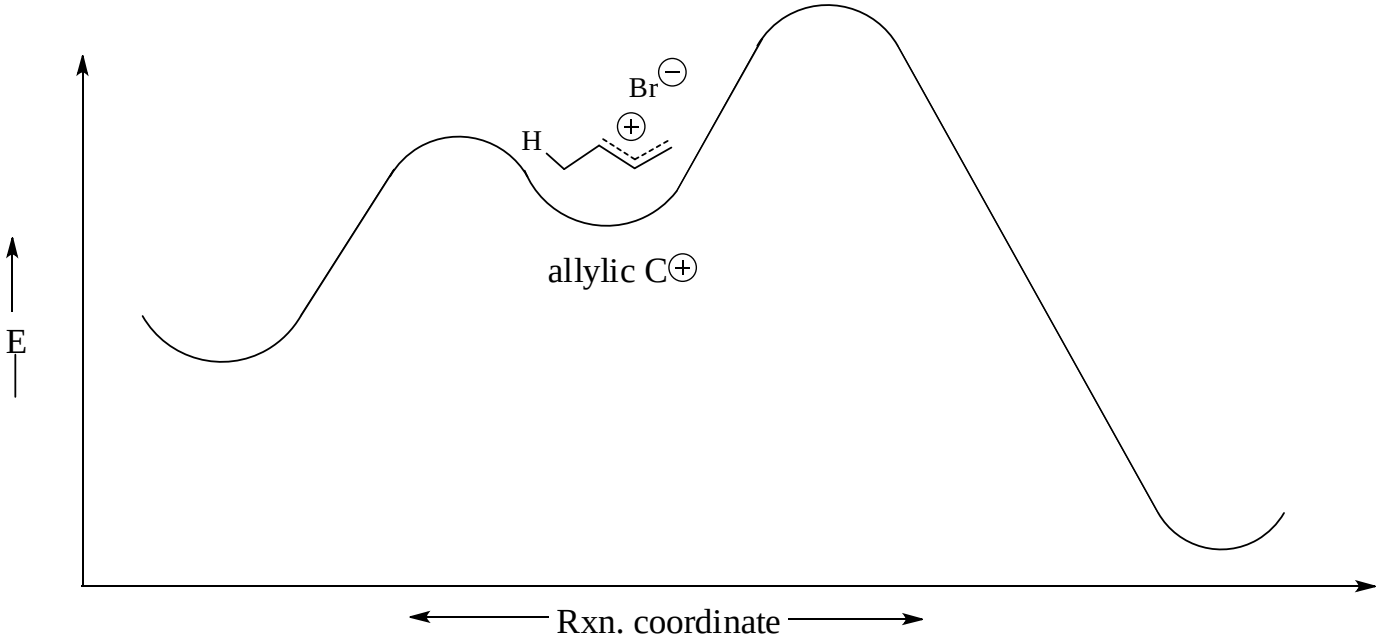
4. Answer the following questions about the reaction of 1,3-butadiene with HBr.

a) Draw the products of the reaction in the boxes below. (6 pts.)



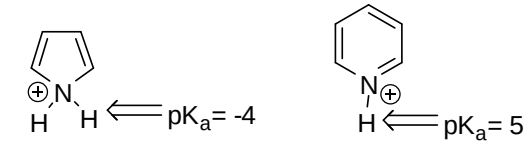
71% 29%

b) The energy diagram for the second step in the reaction is shown below. Label or place the following items on the diagram: energy of activation (E_a) for the 1,2 product; E_a for the 1,4-product; structure and location of the kinetic product; structure and location of the thermodynamic product. (9 pts.)



5. Multiple choice questions. (5 pts. each)

a. Which answer best explains the difference in pK_a for the designated proton in pyrrolium and pyridiniumcation?

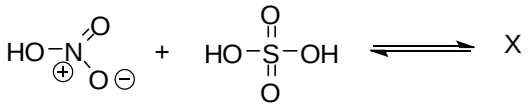


pyrrolium cation pyridinium cation

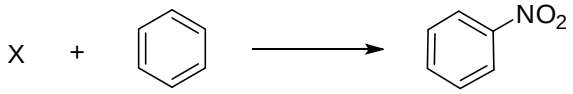
i) Pyrrole is a stronger conjugate acid than pyridine.
ii) Pyrrole loses aromaticity when it protonates to form the pyrrolium cation.
iii) Pyrrole is a more electron rich aromatic ring than pyridine.
iv) Pyridiniumcation distributes the cation charge around the ring better.
v) Pyridine has more stable molecular orbitals and a smaller HOMO-LUMO energy gap.

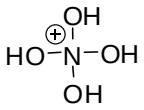
b. Circle the structure of the intermediate X that forms in the following reaction sequence.

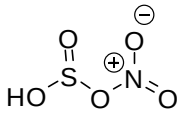
1st step:



2nd step:



i) 

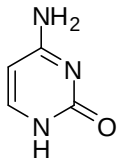
ii) 

iii) 

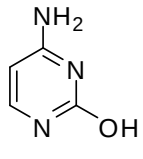
iv) 

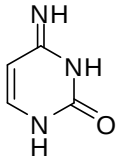
v) 

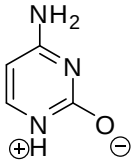
c. Which structure represents an aromatic tautomer or structural isomer of cytosine?

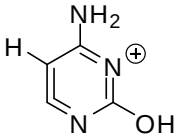


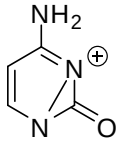
cytosine(C)

i) 

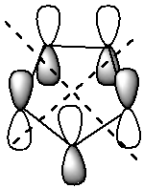
ii) 

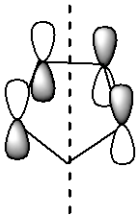
iii) 

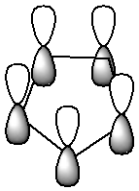
iv) 

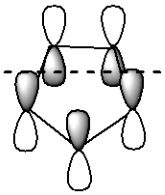
v) 

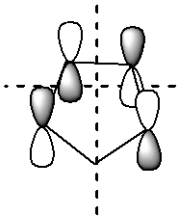
d. Circle the *two* molecular orbital representations of cyclopentadienyl anion shown below that represent HOMO orbitals.

i) 

ii) 

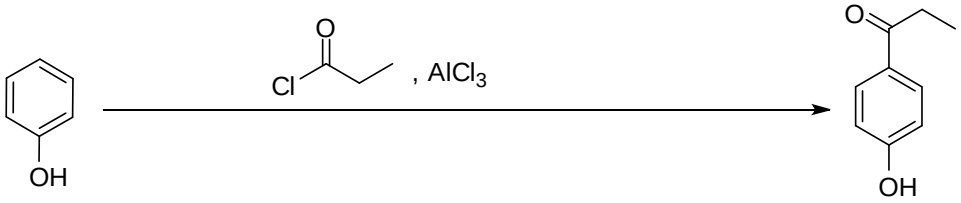
iii) 

iv) 

v) 

6. Provide the necessary information about the reaction shown below.

a) Draw the mechanism of the reaction. You do NOT need to include resonance structures. You should include all formal charges and curved electron flow arrows. (9 pts.)



b) Show all the important resonance contributors of the key ring intermediate in the reaction. Be sure to include formal charges and curved electron flow arrows to indicate all electron movement. (6 pts.)

7. a) Draw the molecular orbital diagram for 1,3-butadiene in the space below. Include orbital phase and node information. Label the bonding and antibonding orbitals. Identify the HOMO and LUMO orbitals. (10 pts.)
b) To the right of your diagram, show the effect of UV absorption at 217 nm. Draw the energy diagram for the excited state of 1,3-butadiene that results from this absorption. Assume the absorption is a π to π^* transition. You do not need to redraw the molecular orbital pictures with the phases. (3 pts.)

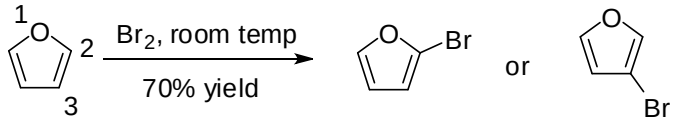
MO diagram for 1,3-butadiene

MO diagram for excited state of 1,3-butadiene

energy

UV absorption
(λ_{max}=217 nm)

8. As shown below, the bromination of furan can in theory afford two possible products, the C-2 or the C-3 isomer. (10 pts.)



C-2 product C-3 product

a) Draw the carbocation intermediate for the reaction of both possible products. Draw all the important resonance forms for each carbocation intermediate. Be sure to include electron flow arrows, lone pairs and formal charges where appropriate.

b) Which product is favored, the C-2 or C-3? Briefly explain why.

c) The bromination with furan occurs at room temperature, while that for benzene needs a Lewis acid catalyst and considerable heating. Circle the answer that best explains this reactivity difference.

i) Five member rings are always more electron rich than six member rings.
ii) Benzene has special stability from its aromatic system and furan is non-aromatic which is a more reactive state.
iii) Furan has six π electrons controlled by 5 nuclei, while benzene has the same number of π electrons and one more nucleus.
iv) The HOMO-LUMO gap for benzene is smaller which makes the pi electrons of benzene less stable.
v) Furan comes from the Latin word furfur which means bran and so it has the same explosive reactivity that too much bran in your diet can have.