Organic Chemistry 2 Name:__Lindsey Vonn_____
First Examination
February 17/19, 2010
Prof. Malachowski

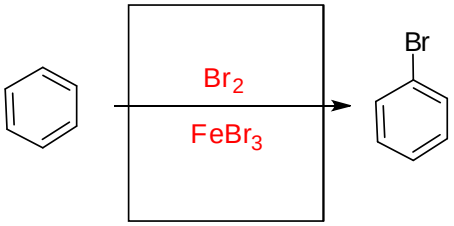
The examination has nine questions on five pages. The point values for each question are found with the question. Partial credit will be given where appropriate.

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.

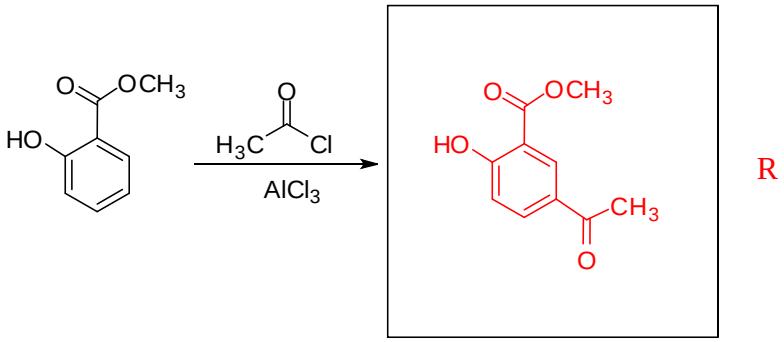
In organic chemistry, hand-drawn pictures convey specific information. Be sure the drawing you have made conveys the essential information required to answer the question. Make certain that three-dimensional pictures display the correct atom arrangements. Don't forget to include lone pairs of electrons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

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

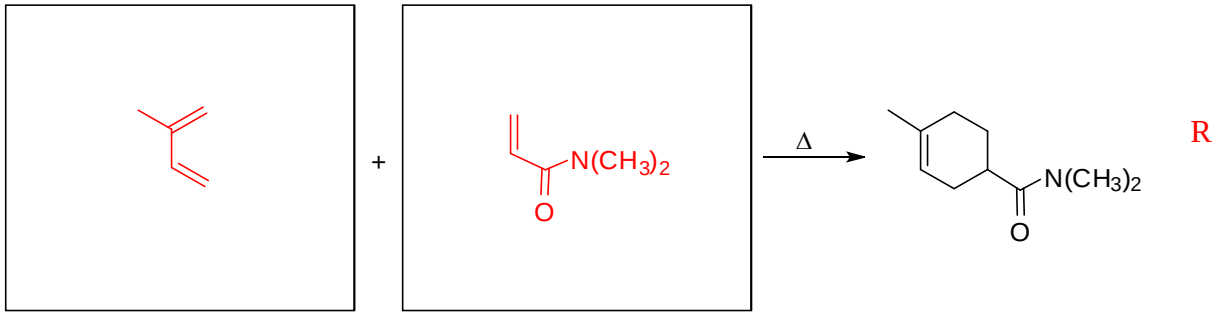
a)



b)

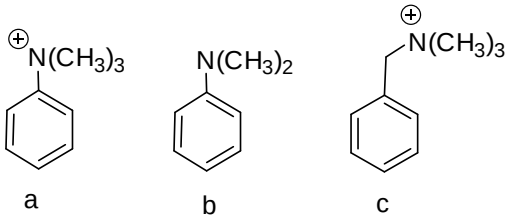


c)



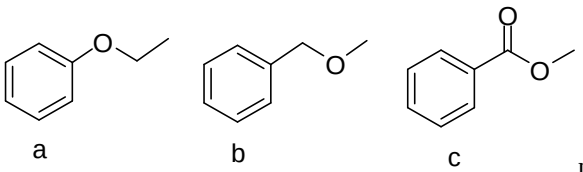
2. In question 1, write an 'R' to the right of reactions that demonstrate regioselectivity and write an 'S' next to reactions that illustrate stereoselectivity. (2 pts.)

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



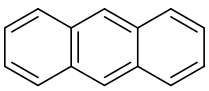
most reactive __b__ > __c__ > __a__ least reactive

Loudon 16.43



most reactive __a__ > __b__ > __c__ least reactive

4. Identify the following structures as aromatic, non-aromatic or anti-aromatic. For your evaluation you should consider the structure as drawn. Fused ring molecules should be considered as one whole structure. (4 pts.)

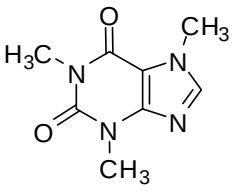


anthracene

__aromatic__

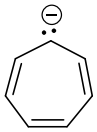
furan

__aromatic__



caffeine

__non-aromatic__

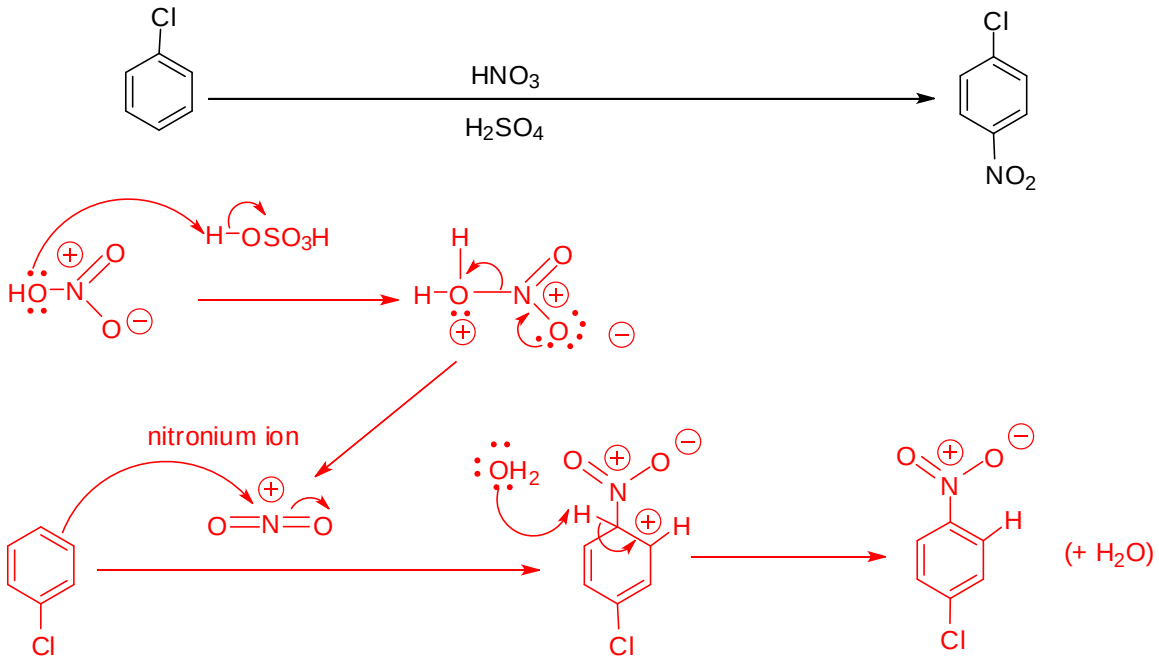


cycloheptatrienyl anion

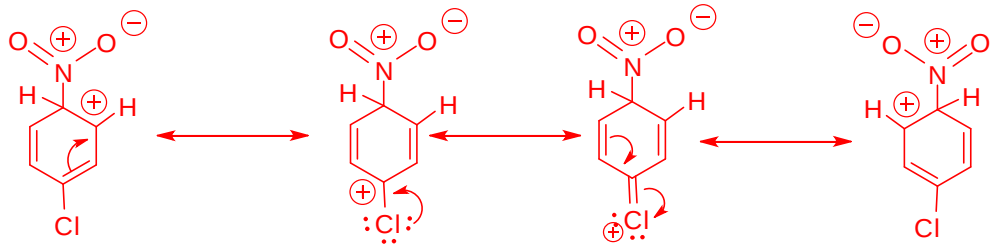
__anti-aromatic__

/27 pts.

5. 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. (10 pts.)



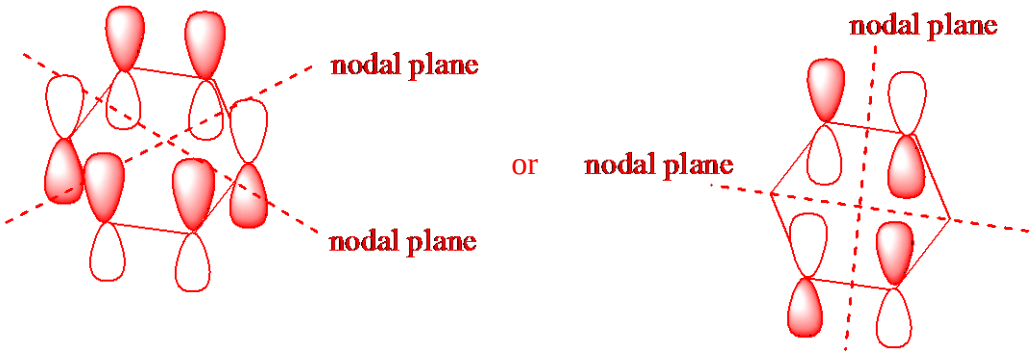
b) Show all the important resonance contributors of the key ring intermediate in the reaction. Be sure to include formal charges and curved electron flow arrows to indicate all electron movement. (7 pts.)



6. Draw <u>one</u> of the lowest unoccupied molecular orbitals (LUMO) and <u>one</u> of the highest occupied molecular orbitals (HOMO) for benzene. Be sure to include nodes. (6 pts. each)

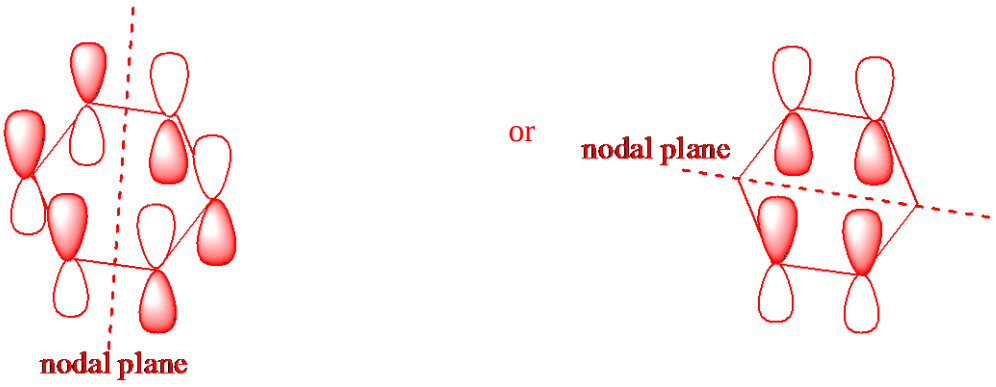
benzene

LUMO:



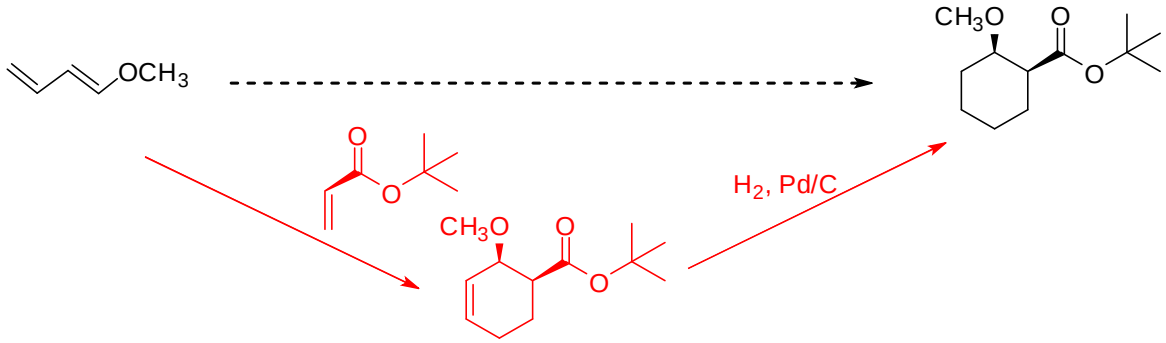
/23 pts.

HOMO:

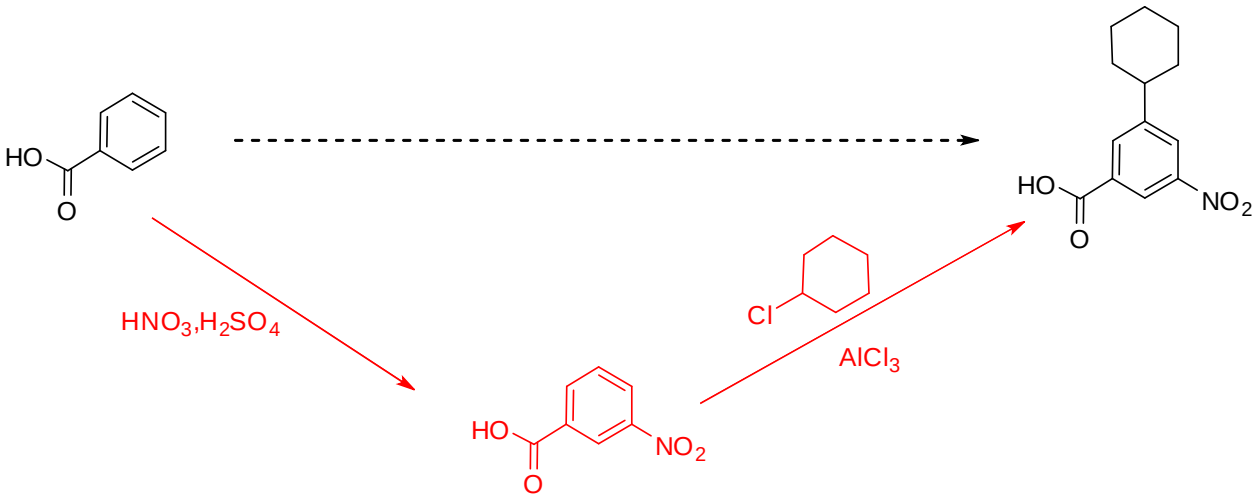


7. Suggest a series of reactions to take the starting material on the left to the product on the right. This will require two or three steps. You may use any inorganic reagent and any organic reagent of seven carbons or less. (7 pts. each)

a)



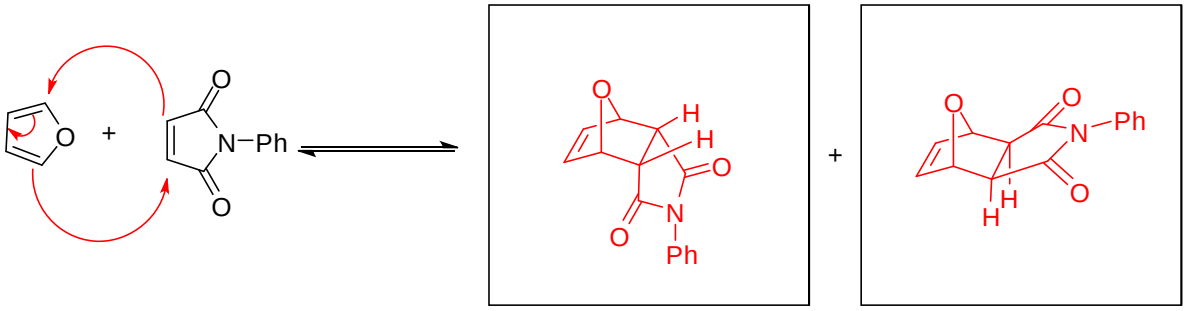
b)



/20 pts.

8. Answer the following questions about the reaction shown below which was discussed in class.

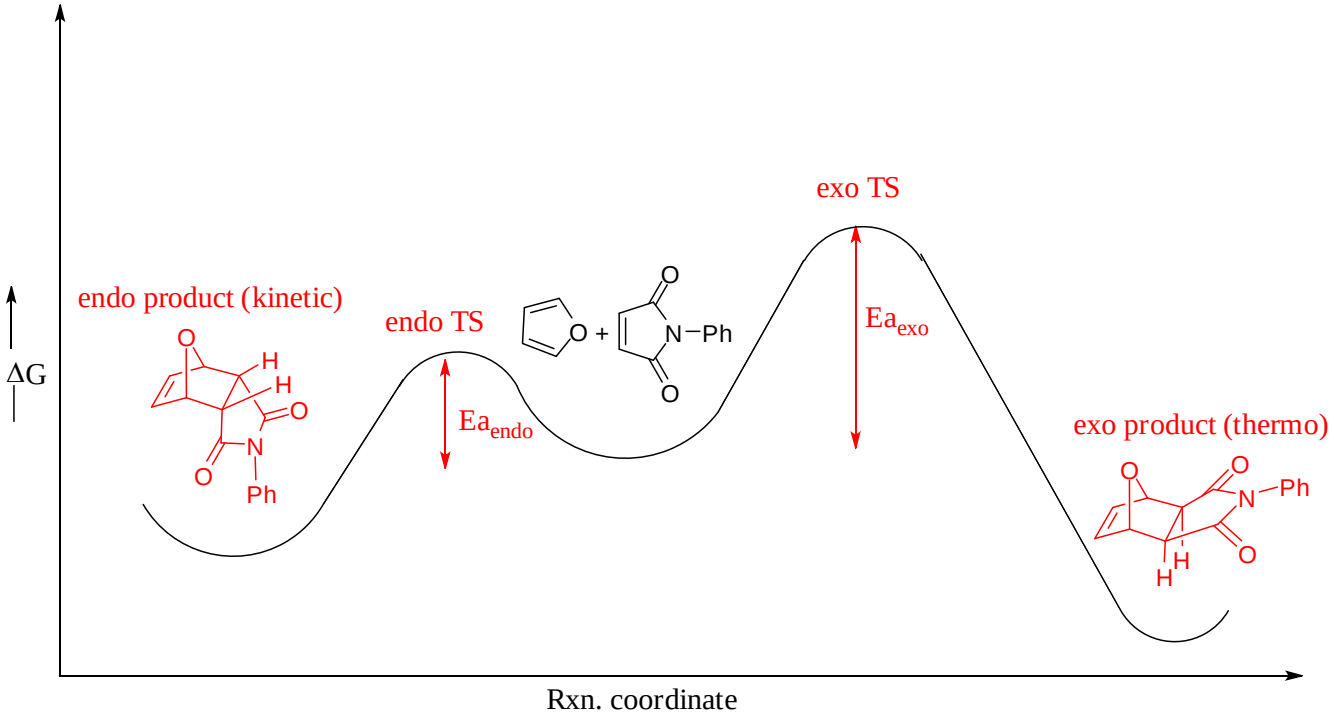
a) The following reaction provides two possible stereoisomeric products. Draw the two possible products in the appropriate box below. (6 pts.)



endo product exo product

b) Draw the mechanism of the reaction using the conventional curved electron flow arrows on the structures shown in part a. (4 pts.)

c) As described in class, the endo product forms first at lower temperatures, but upon prolonged reaction times and warmer temperatures, the exo product becomes the major product. Based on these facts, label the energy diagram below with the following items: endo product, exo product, endo transition state (TS), exo TS, endo energy of activation (Ea_{endo}) and exo energy of activation (Ea_{exo}). You do NOT need to draw any structures, but you do need to place the items in the correct location on the diagram. (6 pts.)



9. Indole structures are very important in nature and consequently have been the focus of a considerable amount of synthetic chemistry research. They undergo electrophilic aromatic substitution reactions similar to benzene and pyrrole. Answer the following questions based on our discussions of the reactions of these structures.

a) As shown below, the electrophile, CH_3-I, reacts exclusively in the five member pyrrole ring of indole. Circle the answer that best explains why the pyrrole ring reacts before the benzene ring. (2 pts.)

(i) The pyrrole is a more electron rich ring than benzene due to the nitrogen's lone pair of electrons.

(ii) Five member rings always react in preference to six member rings.

(iii) If benzene were to react, it would lose aromaticity.

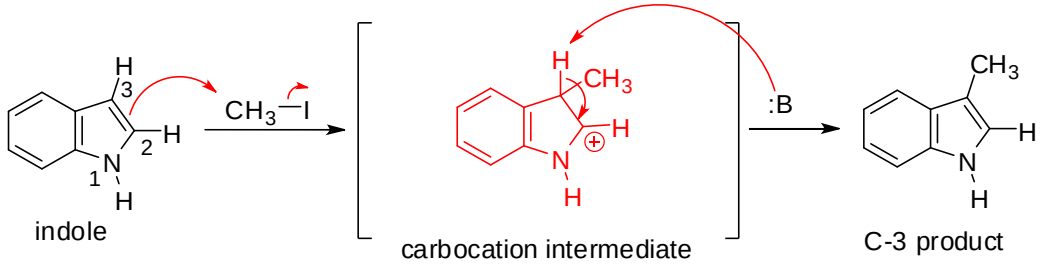
(iv) The alkene of the five member ring is not part of an aromatic system, so it can react more readily.

(v) Nitrogen is electronegative making the pyrrole ring more electron poor.

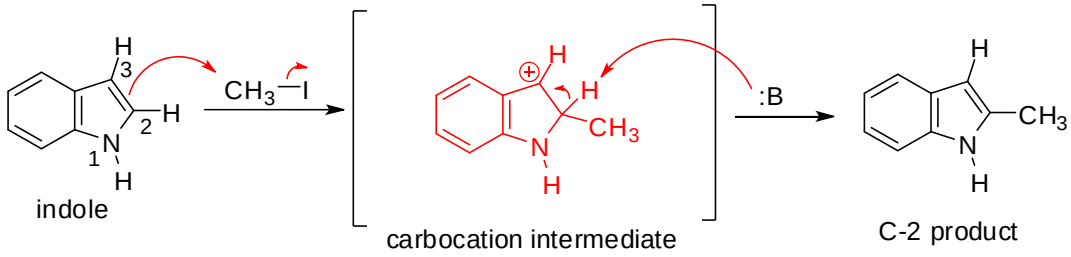
/18 pts.

The electrophilic aromatic substitution with indole can occur at two different positions, C-2 or C-3, but it reacts almost exclusively at C-3. Analyze the reaction mechanism in the questions below to understand the regioselectivity of the reaction.

b) Draw the curved electron flow arrows for the electrophilic aromatic substitution of the C-3 position of indole and draw the carbocation intermediate that results. Note that indole is so reactive, a Lewis acid catalyst is not necessary. Finish the process by drawing the electron flow arrows that eliminate a proton and return the structure to aromaticity. (4 pts.)

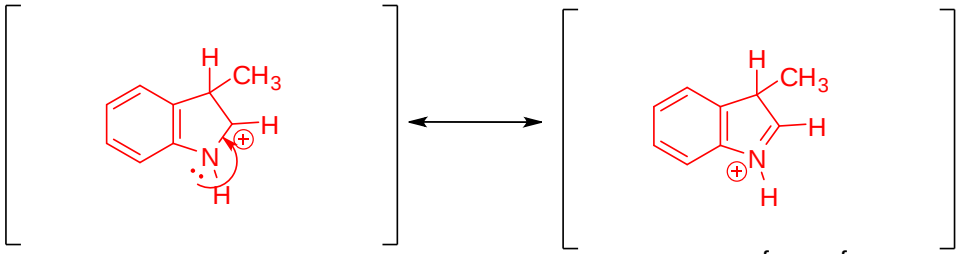


c) Do the same for the C-2 product. (2 pts.)

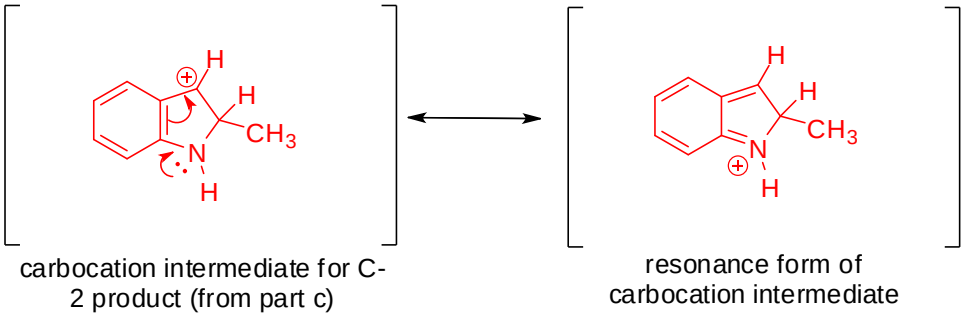


A comparison of the stability of the carbocation intermediates for both reaction paths reveals the basis of the regioselectivity.

d) Redraw the carbocation intermediate for the C-3 product (part b above) and then provide an important resonance form that involves the nitrogen lone pair of electrons. Use curved arrows to indicate electron flow. (2 pts.)



e) Redraw the carbocation intermediate for the C-2 product (part c above) and then provide an important resonance form that involves the nitrogen lone pair of electrons. Use curved arrows to indicate electron flow. (2 pts.)



f) Compare the resonances forms in part d and e. Why is the resonance form in part d more stable than the resonance form in part e? (2 pts.)

The resonance form in part d retains an aromatic benzene ring while the resonance form in part e does not have an aromatic ring.

/12 pts.