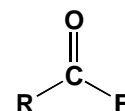
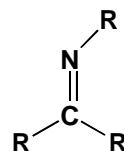
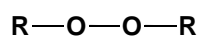
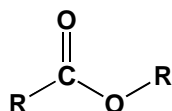
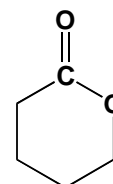
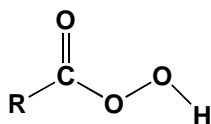
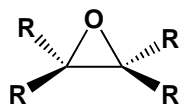
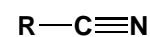
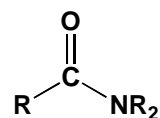
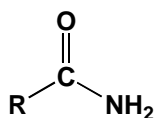
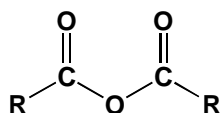
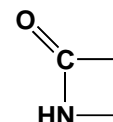
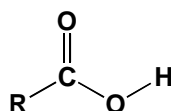
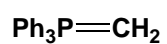
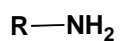


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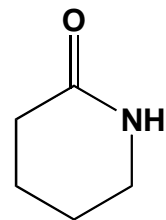
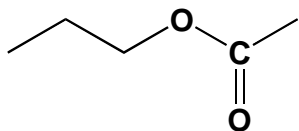
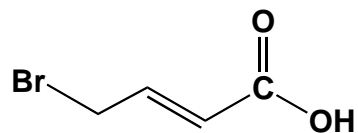
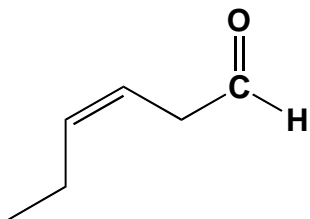
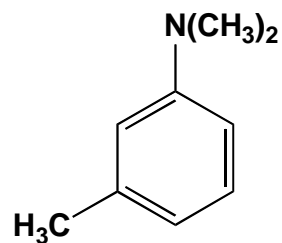
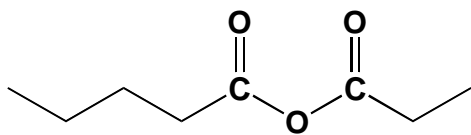
C section *These questions carry no points toward the final total in this exam, but they must be answered correctly for you to receive a grade of C or better in the course.*

Identify the class of compounds each of the following molecules belong to (0 pts).

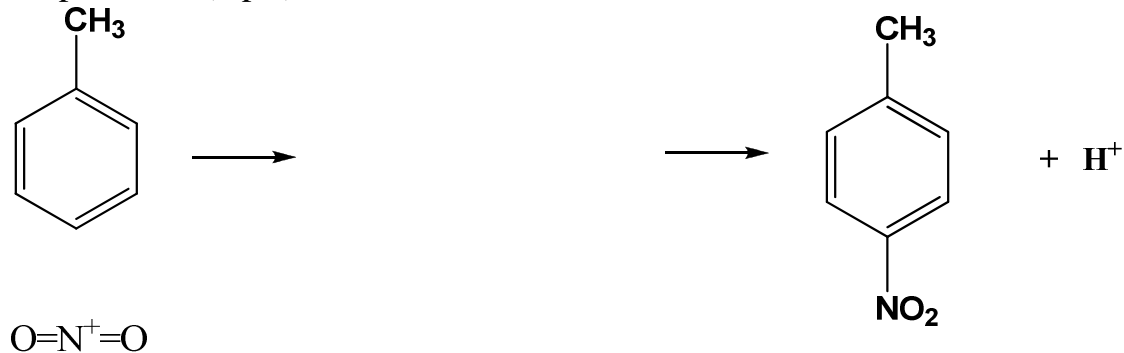


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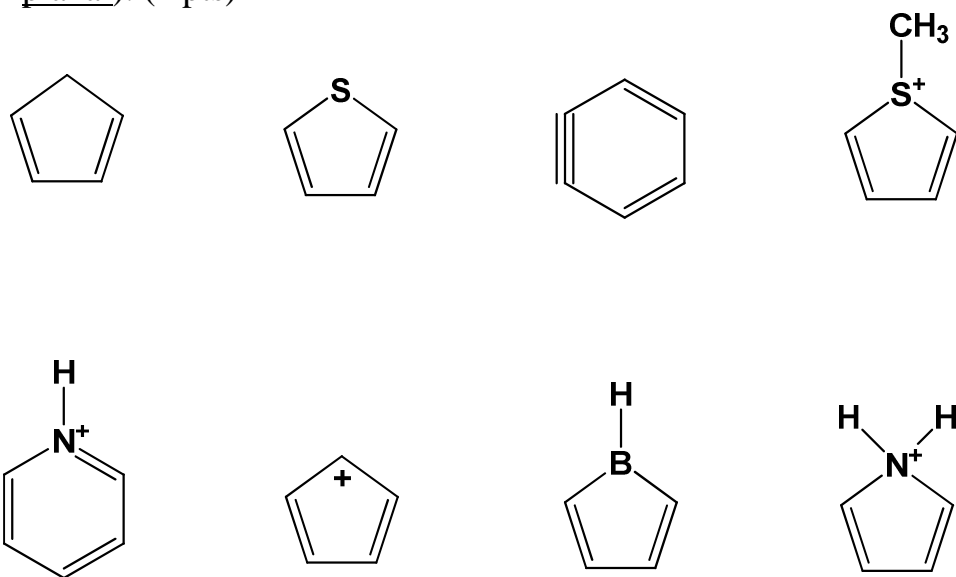
2) Name the following compounds in IUPAC acceptable terms. (0 pts)



- 3) Demonstrate the mechanism for the following **electrophilic aromatic substitution** by supplying curly arrows on the reactants leading to the intermediate and drawing the intermediate with curly arrows leading to the products. (0 pts)



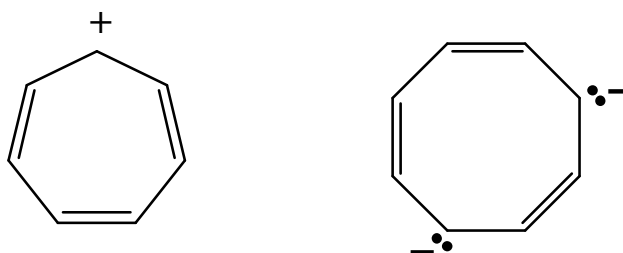
- Part A** Indicate which of the following molecules are aromatic (**A**), non-aromatic (**NA**) or anti-aromatic (**AA**). (Assume all the molecules are planar). (4 pts)



1. Briefly explain your choice of one of the **anti**-aromatic compounds. Use an algebraic formula.(1pts)

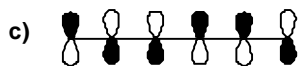
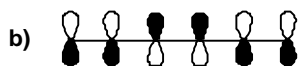
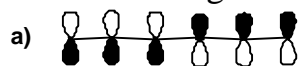
2. What is an orbital?(2pts)

3. Choose one of the two molecular ions and using the polygon rule, draw out and decide whether it is aromatic or anti-aromatic. (2pts)



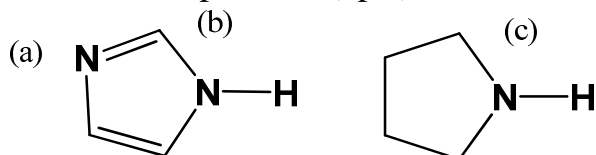
4. The following diagrams are for some of the π MOs in a conjugated system. What is the total number of π MOs in this conjugated system?

Identify the following molecular orbitals as bonding, antibonding, or nonbonding. Identify which number π MO each is. (3 pt.)



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5. Rank the three indicated N atoms in order of basicity and explain your ranking with as few words as possible (3pts).



Most basic: _____

least basic: _____

(15pts)

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6. The addition of (1 equivalent of) DBr to cyclopentadiene generates a mixture of products. (D is an isotope of hydrogen, ^2H)

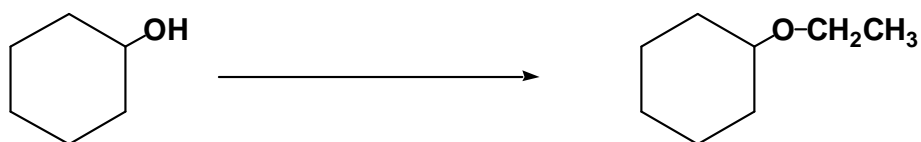
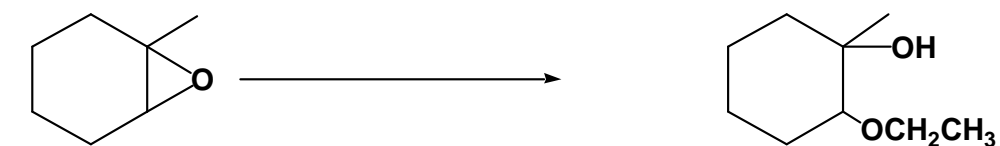
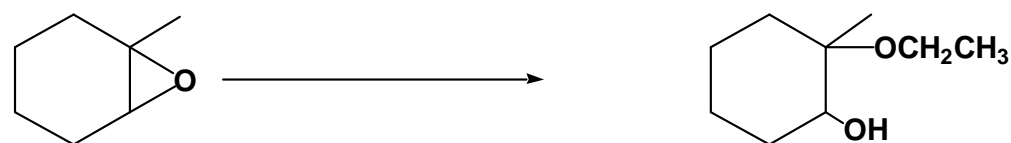
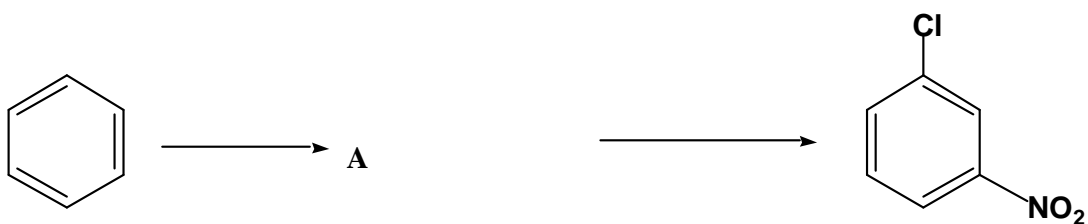
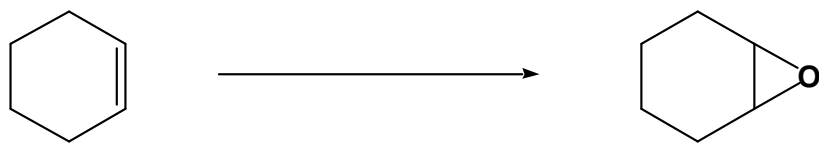


Draw the products, and mechanistically account for the mixture of products.

Which product would you expect to dominate as the temperature of the reaction is raised? (3 pts)

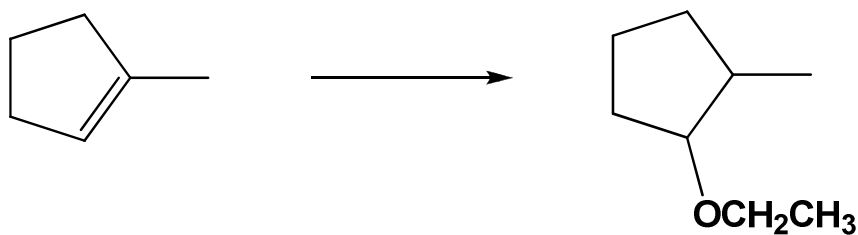
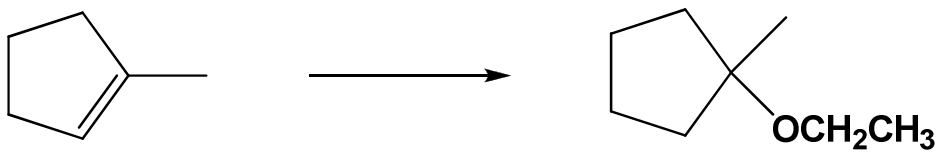
(18pts)

6. Give reagents and conditions to accomplish the following transformations. (8 pts)



(continued on next page)

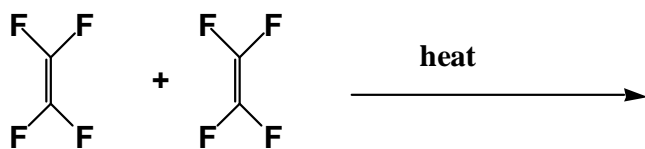
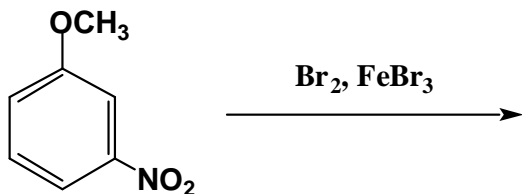
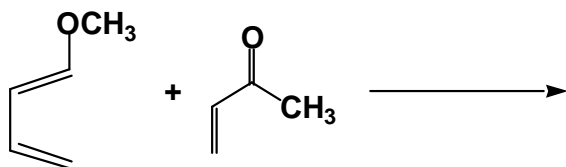
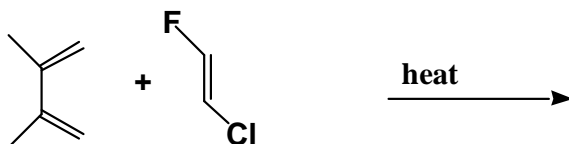
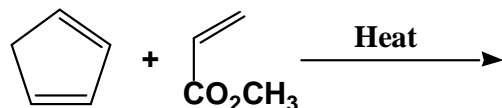
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7. Show how you would synthesize butyl isopropyl sulfide using 1-butanol, 2-propanol, and any solvents and reagents you need. (2 pts)

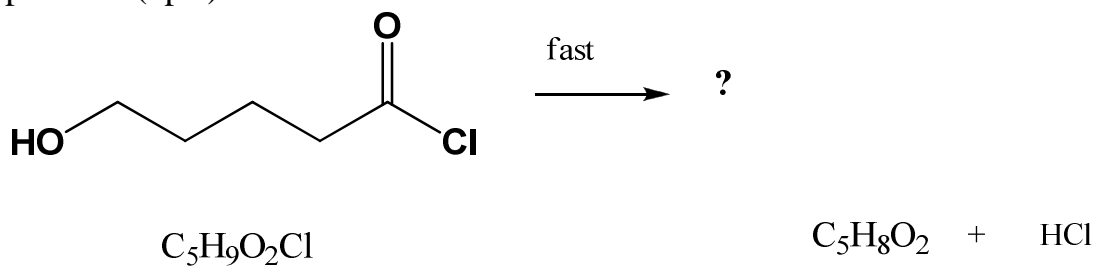
(28pts)

8. Predict the products in the following reactions (if you believe no reaction will occur, indicate this!), paying attention to regio/stereochemistry where applicable. In cases of two or more isomeric products, indicate the major isomer. (6 pts)

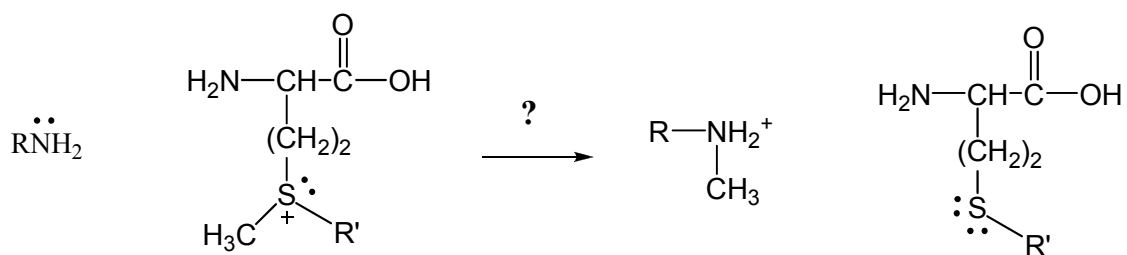


(34pts)

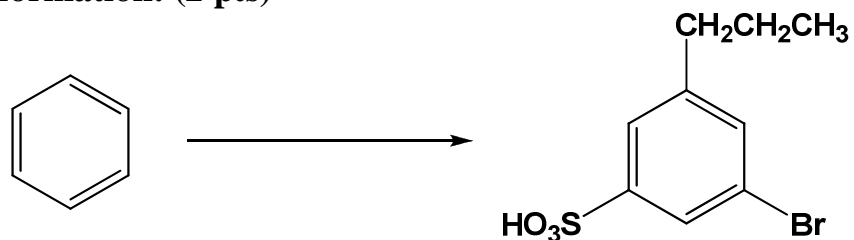
9. A student tried to prepare the compound on the left but found another product, whose molecular formula is given. Write the structure of the product. (2pts)



10. Draw the mechanism for this biochemical methylation reaction and write the name of the mechanism over the reaction arrow. (2 pts)



11. Provide reagents in the proper order to achieve the following transformation: (2 pts)



(40pts)

***Bonus questions* (1pt, each)**

1) Write the structure of a “nitrogen mustard”, which is an analogous compound to a sulfur mustard ‘gas’, give the products after reaction with water, and give its mechanism.

2) Write the molecular structure of a lachrymator and its reaction in eyes.

Part B

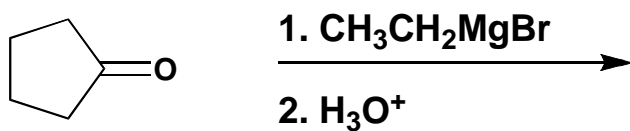
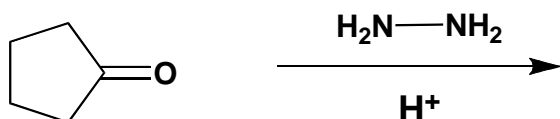
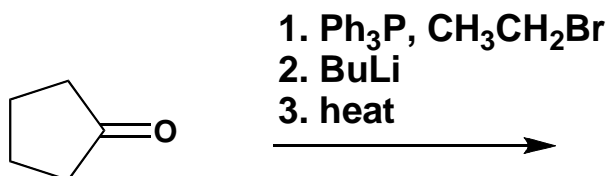
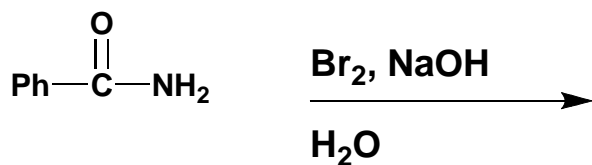
- 1) Give the name and show the mechanism for the following reaction. Include the structure of the intermediate and supply lone pairs and “curly” arrows. (2 pts)



Name: _____

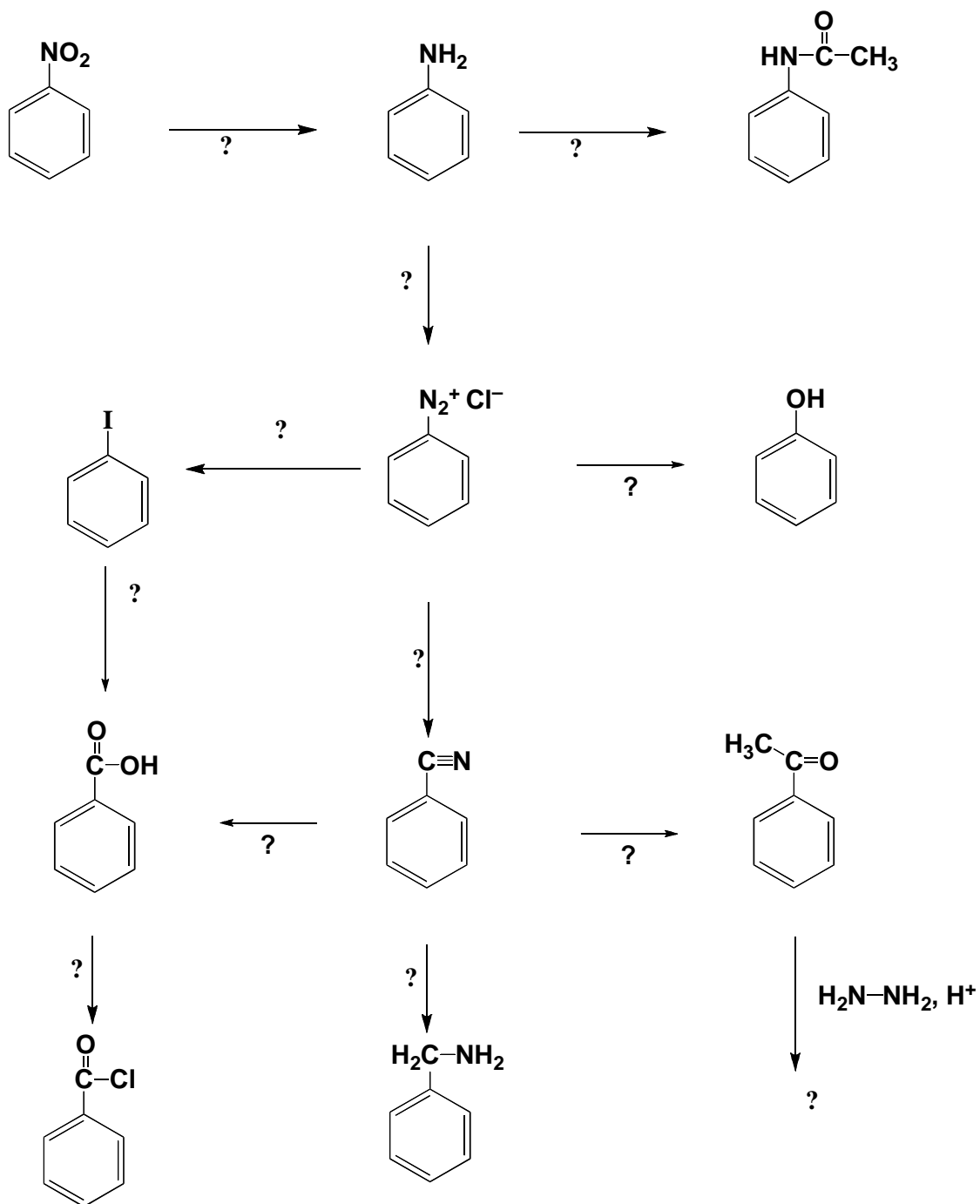
- 2) Write both mechanisms for the **acid** and **base** catalyzed hydration of propanone (acetone). (4 pts)

3) Give the products formed in **all** of the following reactions. (2 pts)



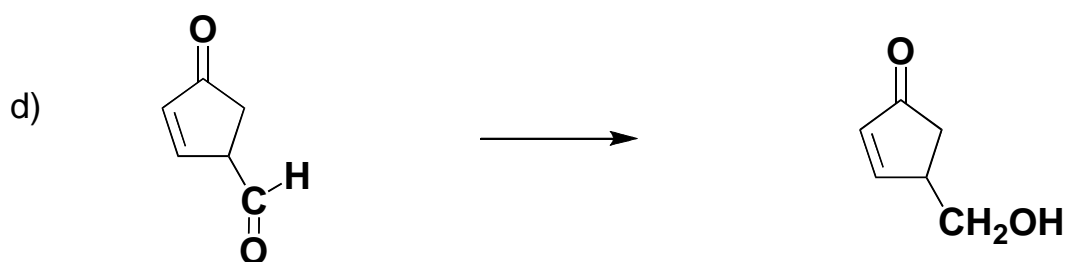
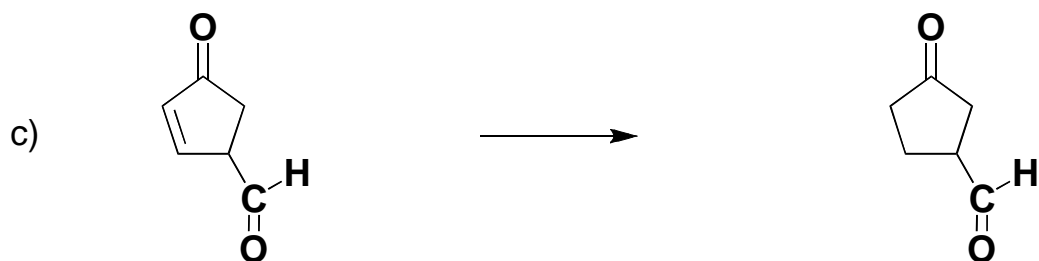
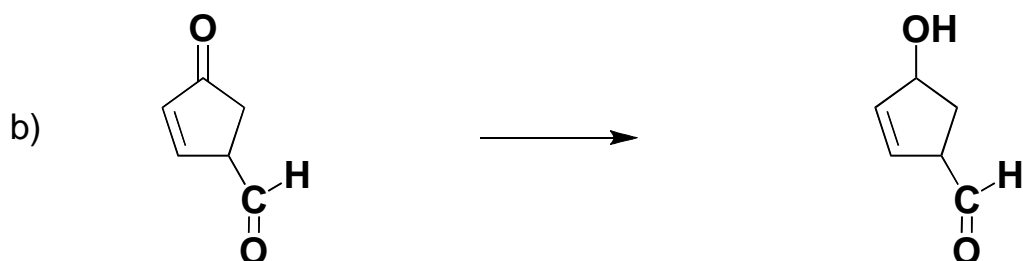
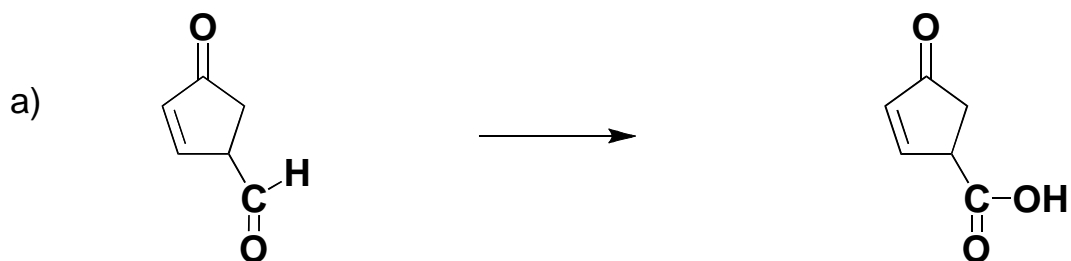
(48pts)

Fill in the blanks of the following scheme. (6 pts)



(54pts)

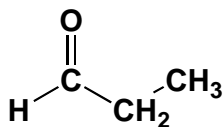
- 4) Give reagents for the following oxidations and reductions, bearing in mind the (in)compatibility of some of the functional groups. (4 pts)



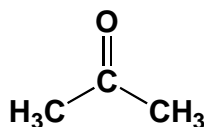
(58pts)

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- 5) Explain why propanal is more reactive towards nucleophilic attack than propanone. [Hint: it's not steric hindrance.](1 pt.)



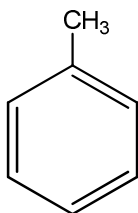
propanal



propanone

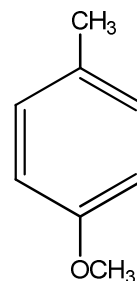
- 6) Explain why NaOCH_3 is not used as a reagent to make methoxy substituted phenyl groups directly from diazonium salts. (2pts. Show mechanism for full credit.)

- 7) Draw the synthesis of p-methoxytoluene from toluene using a diazonium salt as an intermediate step. Several steps and arrows are involved. (2pts)



→ ???

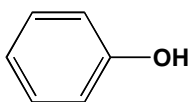
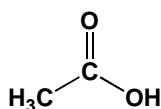
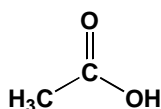
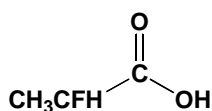
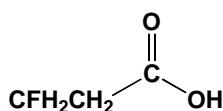
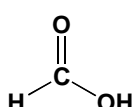
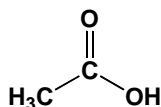
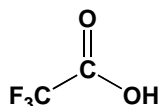
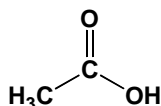
→



(63pts)

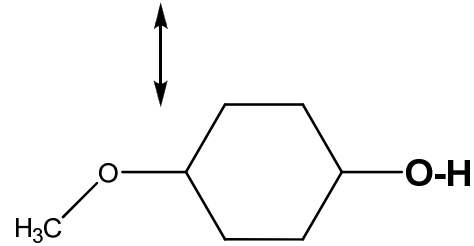
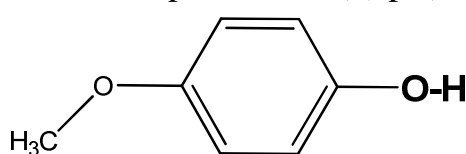
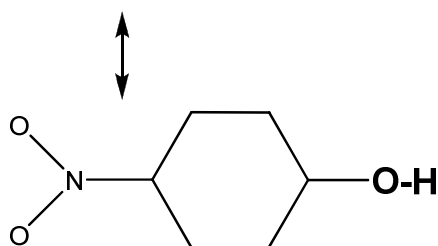
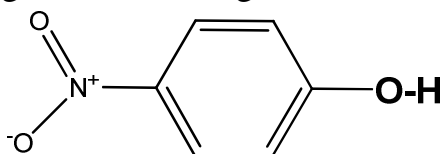
Part C

1) Circle the stronger acid in the following pairs. (3 pts)



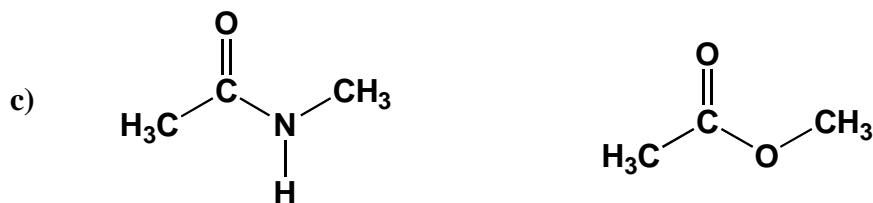
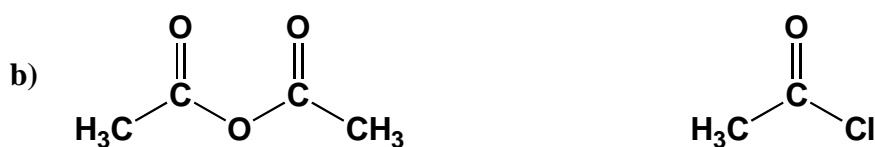
Not a bonus:

2) Circle the stronger acid, p-nitrophenol or p-methoxyphenol. Explain with resonance pictures (Use curly arrows on the molecule above and give the resulting resonance structure on the template below.)(2pts)



(68pts)

3) Circle the more reactive molecule with respect to nucleophilic acyl substitution. (2 pts)



4) Fill in the missing words from your notes on chapter 21 in the section describing the Interconversion of Acid Derivatives, (1 pt)

“The overall reaction is _____.”
(one missing word)

(next line, two missing words)

“This is another example of a(n)

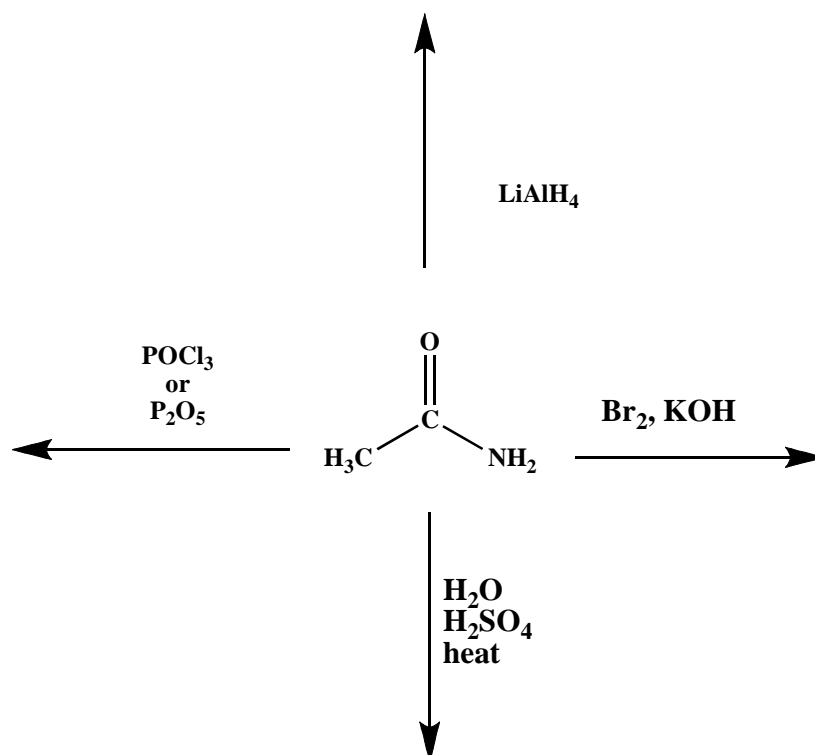
_____ -

_____ mechanism.”

(71pts)

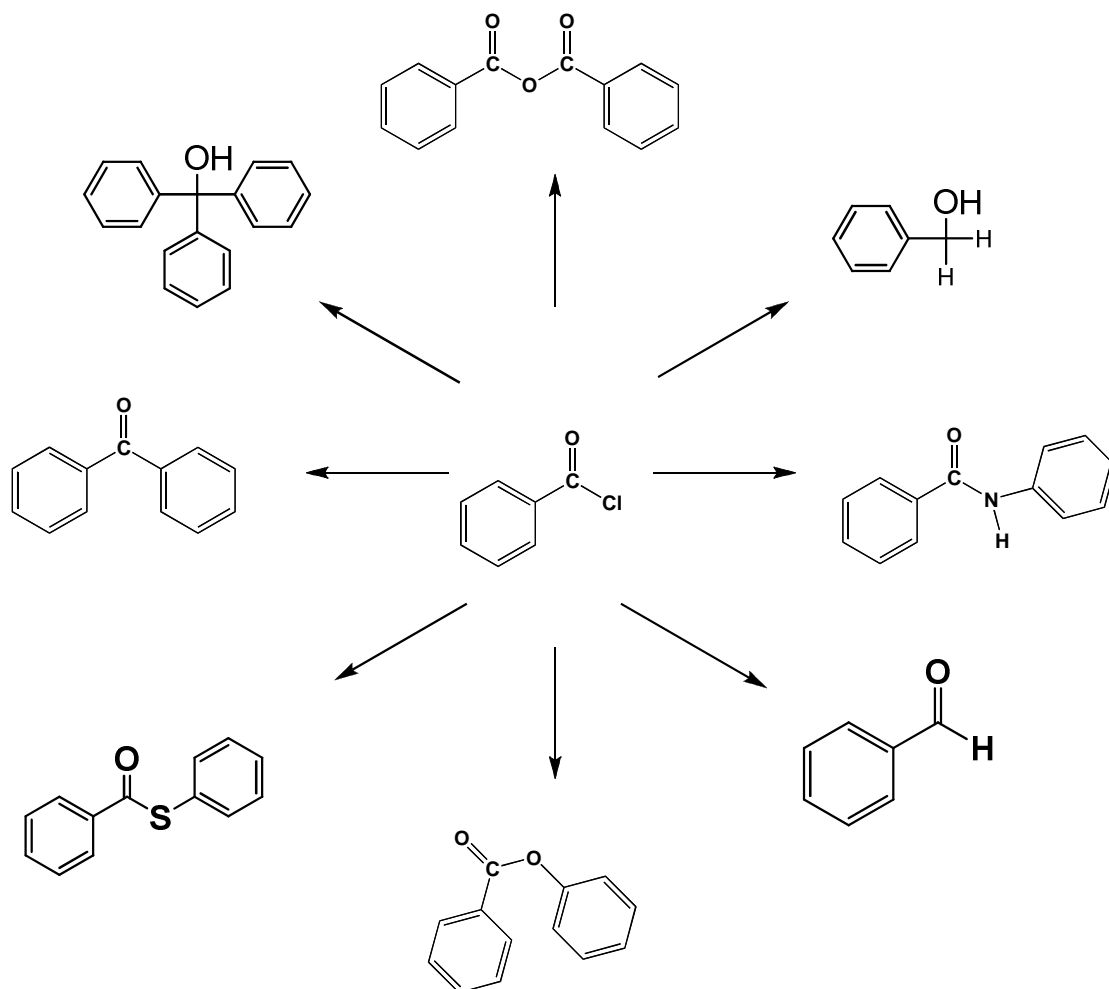
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5) Fill in all the missing products. (4 pts)



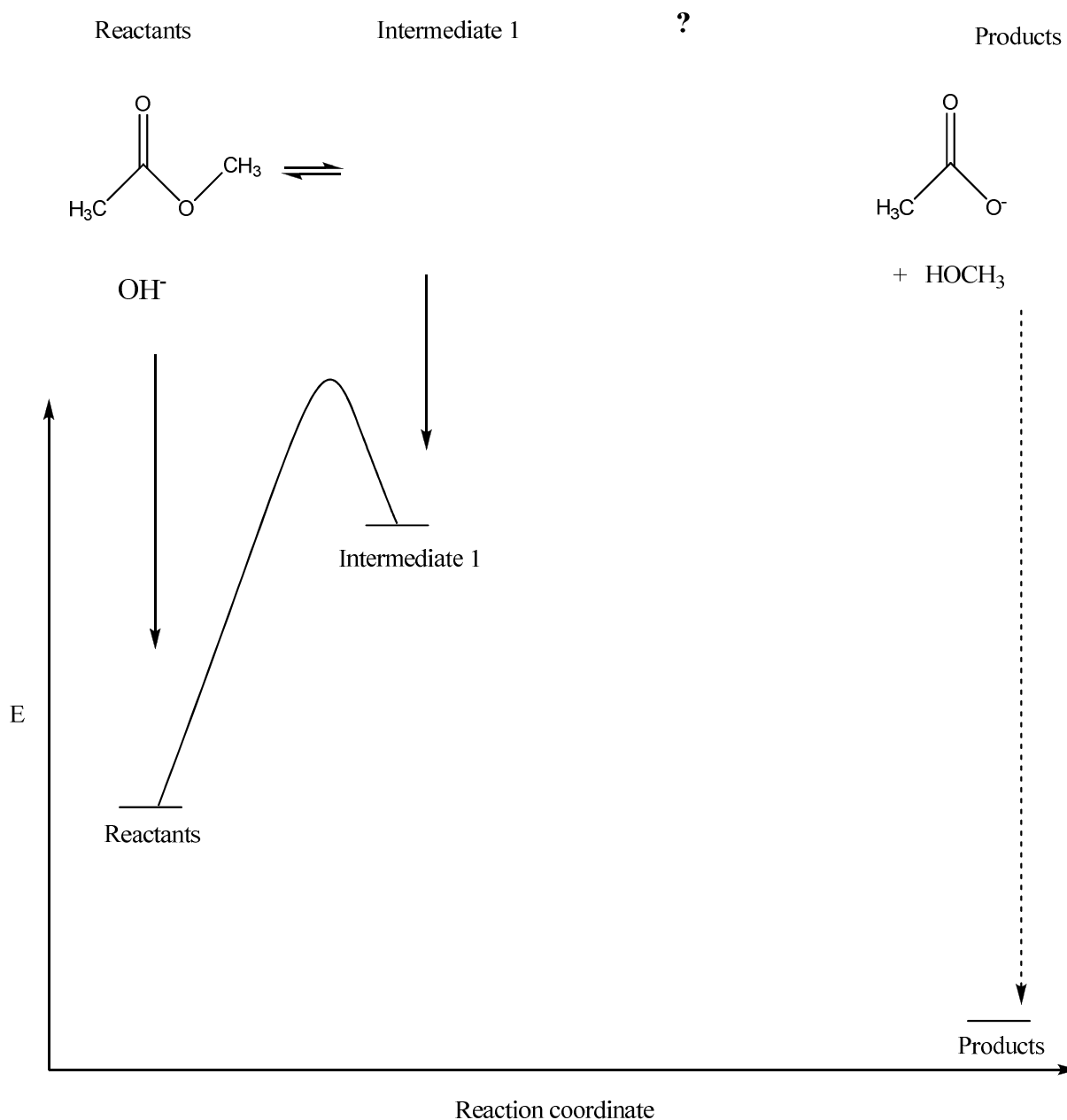
(75pts)

6) Fill in all the missing reagents. (8 pts)



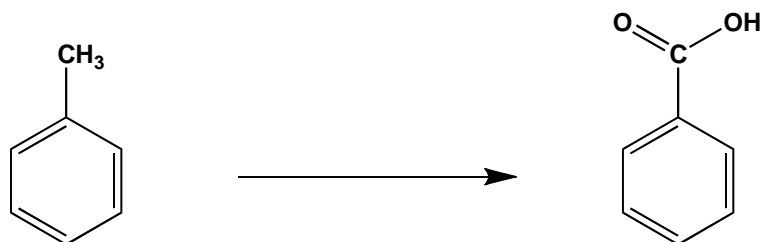
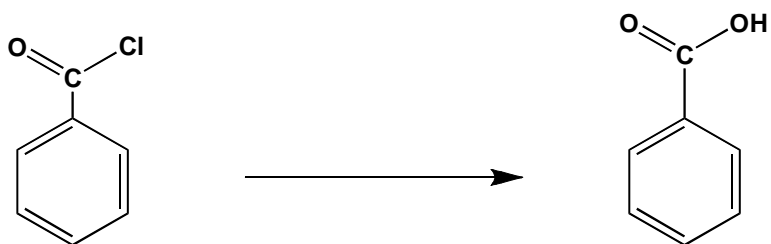
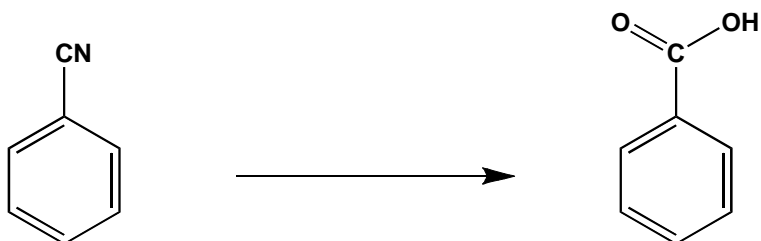
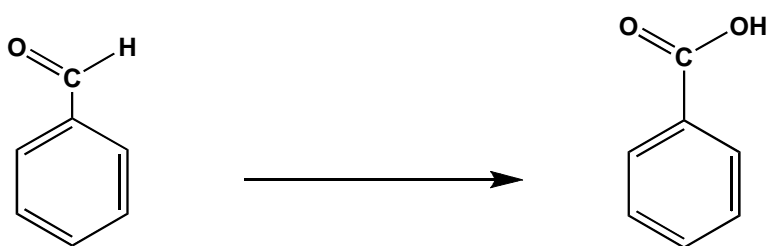
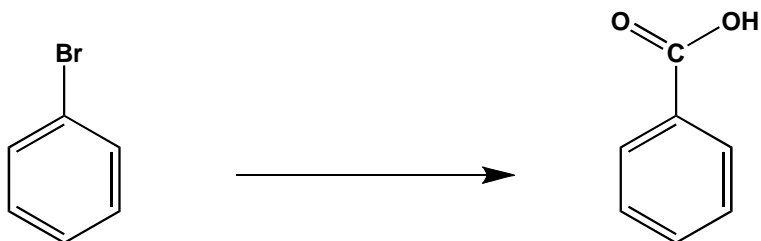
(83pts)

- 7) **Draw the mechanism for** the nucleophilic acyl substitution of methyl acetate by OH^- . Include *all* species, i.e. leaving groups, etc. Complete the energy diagram below by pointing to the reactants, products, and *all* intermediates from your mechanism. Explain in *one* sentence why the overall reaction is exothermic. (4 pts)



Explanation:
(87pts)

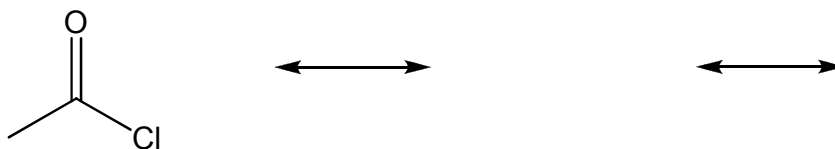
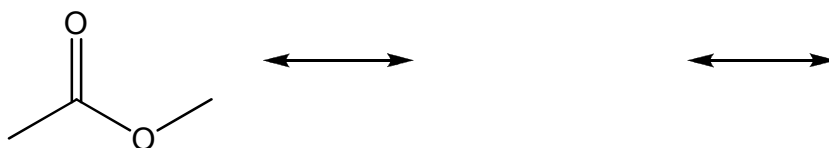
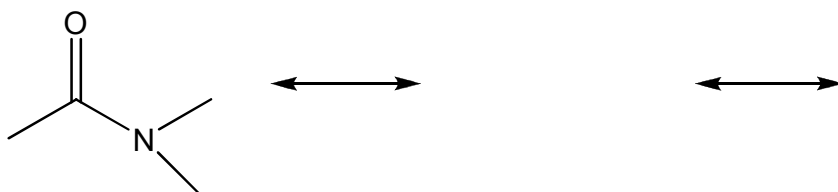
8) Benzoic acid can be made from a wide variety of benzene derivatives. Fill in the missing reagents. (3 pts)



(90pts)

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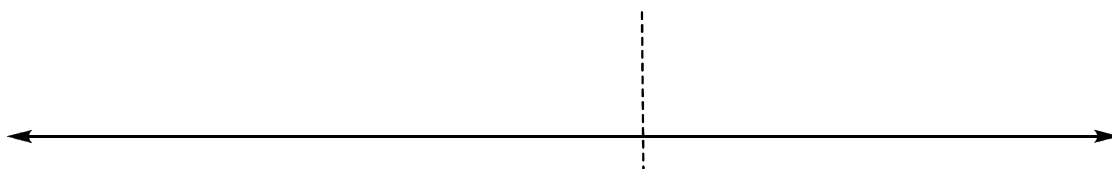
- 9) Draw the two resonance structures that describe the π delocalization in amides, esters, and acid chlorides. Draw *all* lone pairs. Indicate the major, minor, and very minor resonance structures. (3pts)



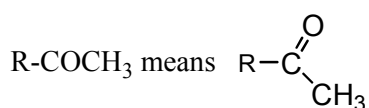
BONUS: Explain why thioesters are more reactive towards nucleophilic acyl substitution relative to esters. (2pts)

- 10) I put numbers under the following substituents, -X so that you would have room to write them over the line that indicates how strongly the group activates or deactivates a phenyl ring relative to benzene in an electrophilic aromatic substitution reaction. (Most activating left; most deactivating right) (4pts)

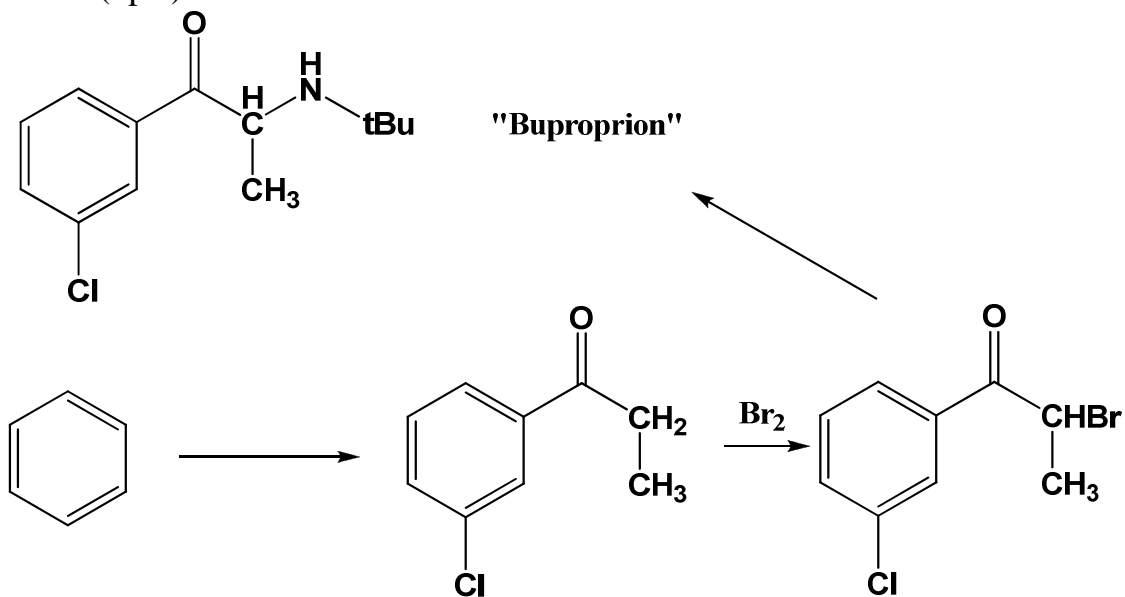
benzene



-NH₂ -NHCH₃ -NHCOCH₃ -NH₃⁺ -NO₂ -OH -OCH₃ -OCOCH₃ -F -Cl -Br -COCH₃
 1 2 3 4 5 6 7 8 9 10 11 12

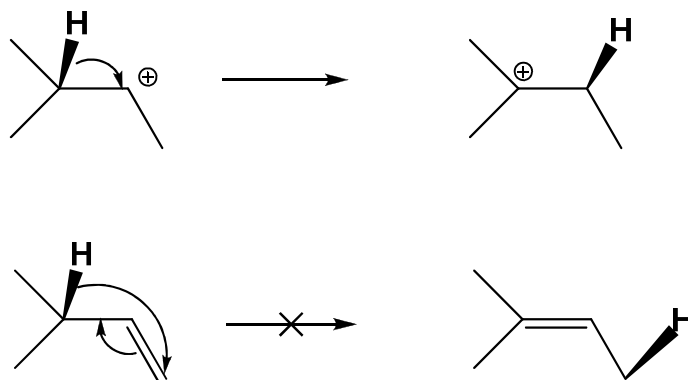


- 11) Fill in the missing reagents in the synthesis of bupropion.
 (3pts)



BONUS BONIBUS

As we were learning to write “H shifts” from secondary cations to the more stable tertiary cations, there were situations where we might be tempted to write “H shifts” in allylic systems to move a double bond to the more stable, “more substituted” position. The barrier to the shift in allylic systems is too high. Explain. (3pts)



- 1) Chemistry is all about pushing electrons, thus charge.
- 2) The three effects that stabilize or destabilize charge are:
 - i) _____
 - ii) _____
 - iii) _____
- 3) Of these, the strongest is: _____
- 4) Its *antithesis* is called: _____ (*hint*)
- 5) A “curly” arrow means _____ electrons are being moved. (Pick a number from 0 to 10)
- 6) Two “curly” arrows mean _____ electrons are being moved. (Pick a number from 0 to 10)
- 7) The two C atoms and the H atom in the cation form a triangle or ring and it has _____ electrons moving around. (The number you chose in 5)
- 8) The three C atoms and the H atom in the allylic ring have _____ electrons moving around. (The number you chose in 6)

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- 9) The cation has an “_____” number, and the allylic ring has an “_____” number. Et voilà. Fini. Merci et bonne chance!