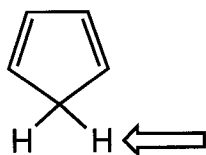


PAGE 1 Short questions 1-8; 3 points each)

1. Estimate the pK_a of the proton indicated.

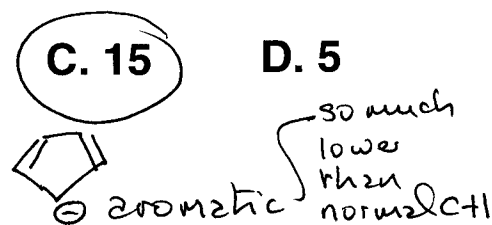


A. 50

B. 30

C. 15

D. 5



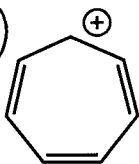
2. Which of the following compounds is likely to adopt a planar conformation?

A.



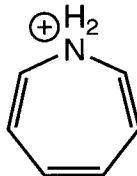
anti aromatic
will go
non-planar

B.



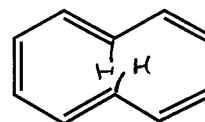
aromatic

C.



N tetrahedral
so non-planar

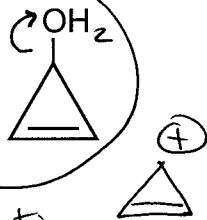
D.



cannot be planar -
H's bump
into each other

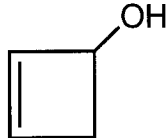
3. Which of the following is the most likely to lose water upon protonation with HCl?

A.



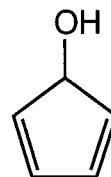
aromatic

B.

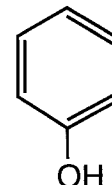


none of others are
after loss of H₂O

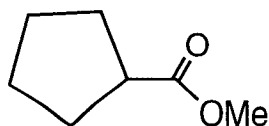
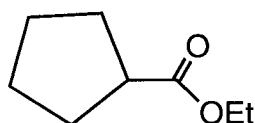
C.



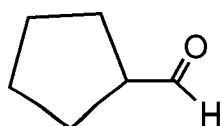
D.



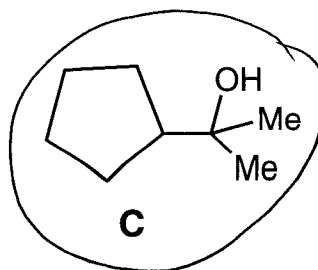
4. What would be the major organic product of the reaction scheme shown?



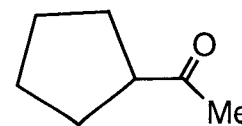
A



B



C



D

5. Which of the following statements about benzene is INCORRECT?

- A. It undergoes electrophilic substitution reactions rather than electrophilic addition reactions.
- B. It is less reactive than hexatriene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$)
- C. The carbon-carbon bond lengths are all the same.
- D. The carbon-carbon bond lengths are longer than ethane.

shocker

6. (3 points) Which of the following is the best description of a "catalyst"?

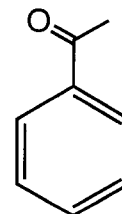
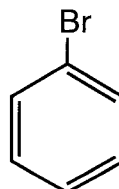
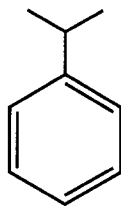
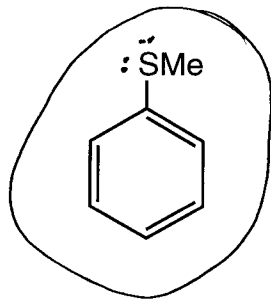
Catalysts alter the kinetics of a reaction by:

- A. Making the products more stable
- B. Making the reaction more exothermic
- C. Lowering the energy of activation for the reaction
- D. Providing a source of free radicals to initiate a reaction

7. What is the approximate magnitude of aromatic stabilization achieved by a simple compound like benzene?

- A. 5 kcal/mol B. 15 kcal/mol C. 25 kcal/mol D. 35 kcal/mol

8. Which of the following would be most reactive with Br_2 in the presence of FeBr_3 ?



PAGE 3 (9-11; 4 points each)

9. Rank the following compounds in order of increasing oxidation level (1 lowest, 4 highest)



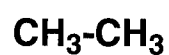
2



3

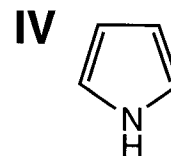
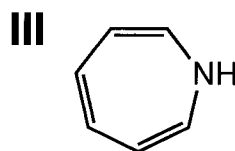
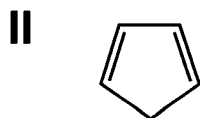
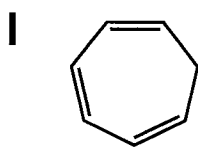


4



1

10. Of compounds I and II, II is the stronger acid and of compounds III and IV III is the stronger base.



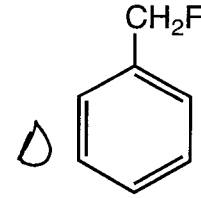
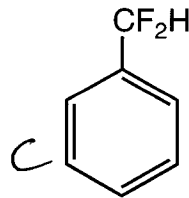
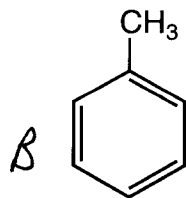
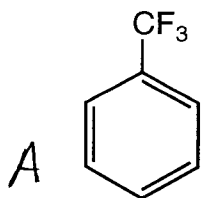
A. I and III

B. I and IV

C. II and III

D. II and IV

11. Rank the following in order of reactivity in electrophilic aromatic substitution



A

C

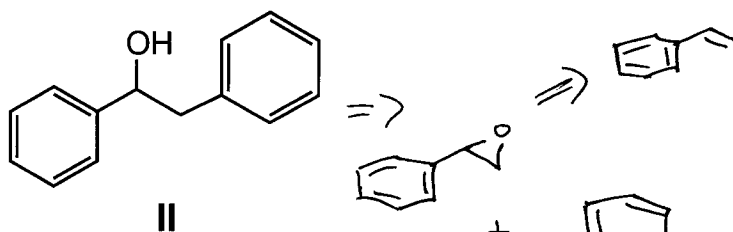
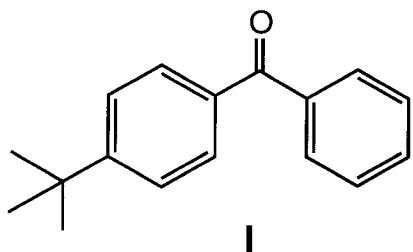
D

B

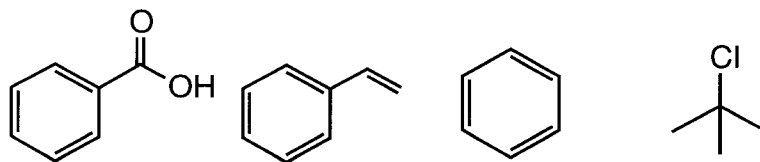
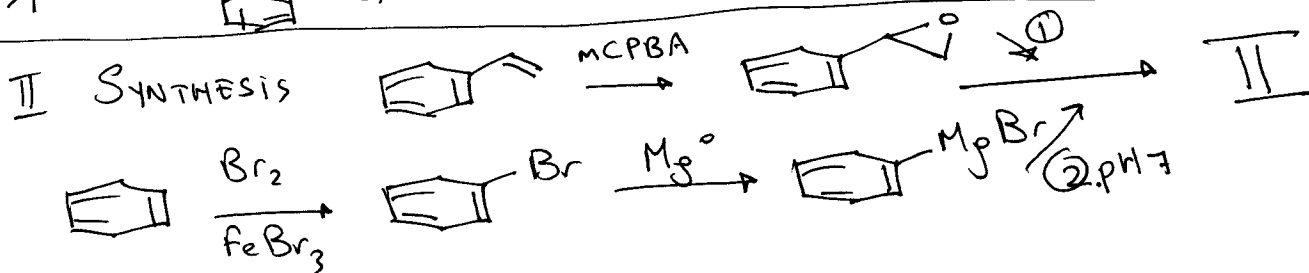
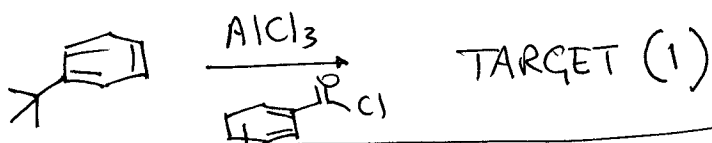
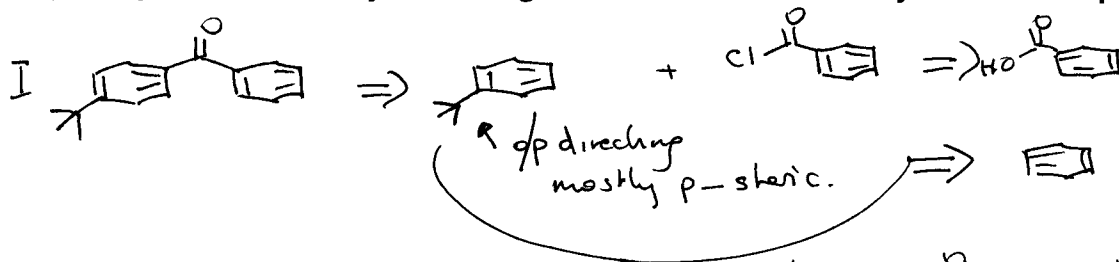
LEAST
REACTIVE

MOST
REACTIVE

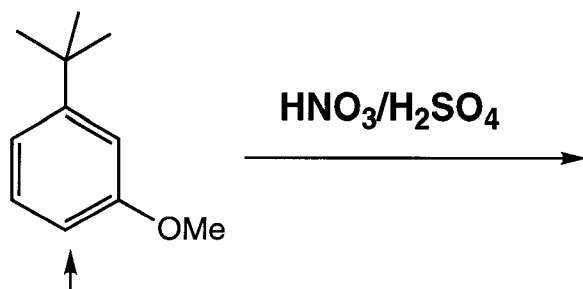
12. (30 points) Design syntheses of compounds I and II (15 points each).



You may only use the carbon containing starting materials in the square brackets
 Pay careful attention to directing effects in the key reactions that you plan to carry out on the benzene ring.
 A clear retrosynthetic analysis will help in planning the synthetic strategy and will be given partial credit if you don't get all the details of the synthesis completed.

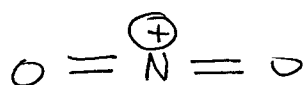


13. (26 points) The outcome of electrophilic aromatic substitution on functionalized benzene rings can be predicted by considering the effect of substituents on the intermediate formed in the rate determining step of the reaction.

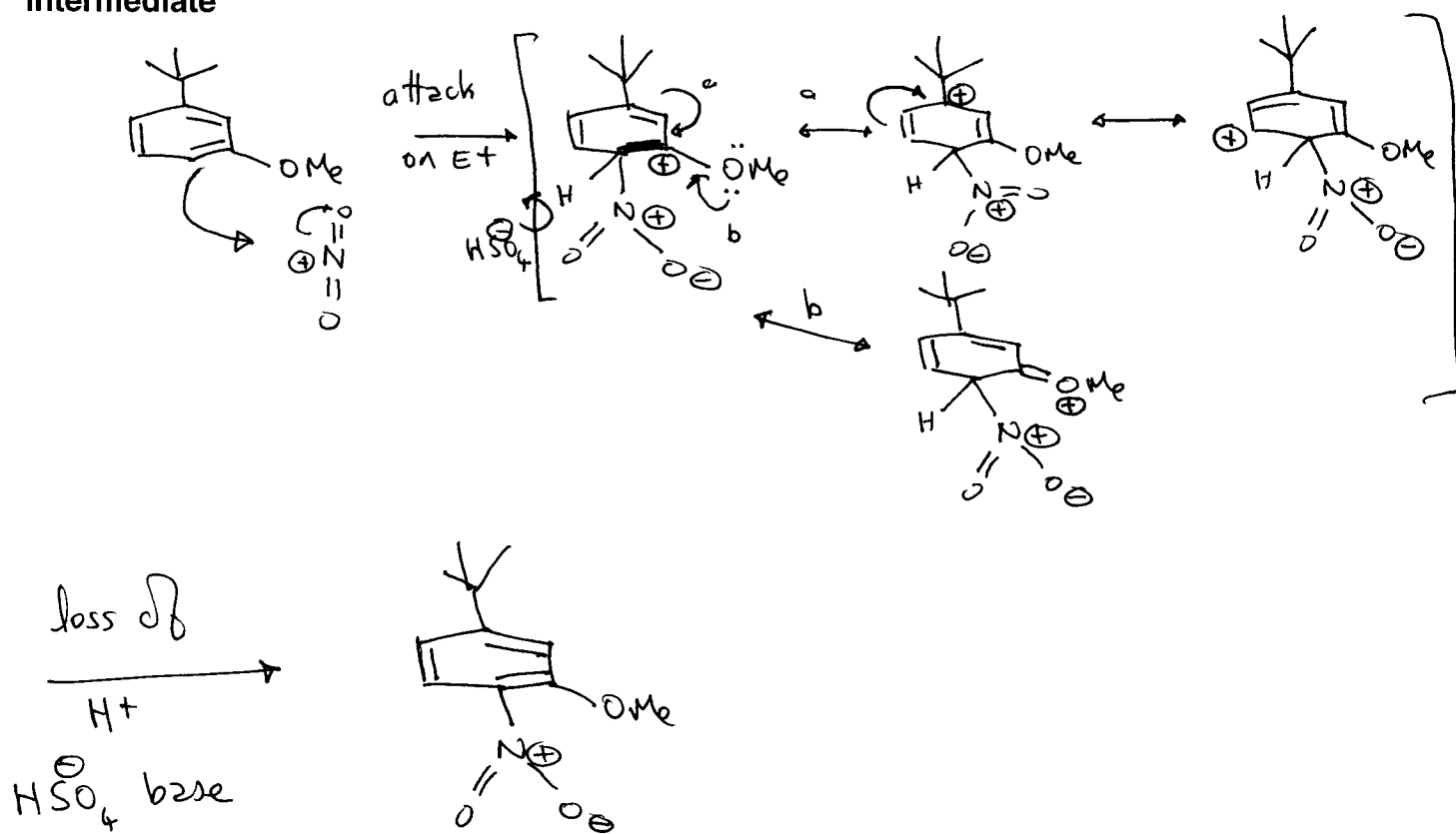


For the reaction shown above carry out the following:

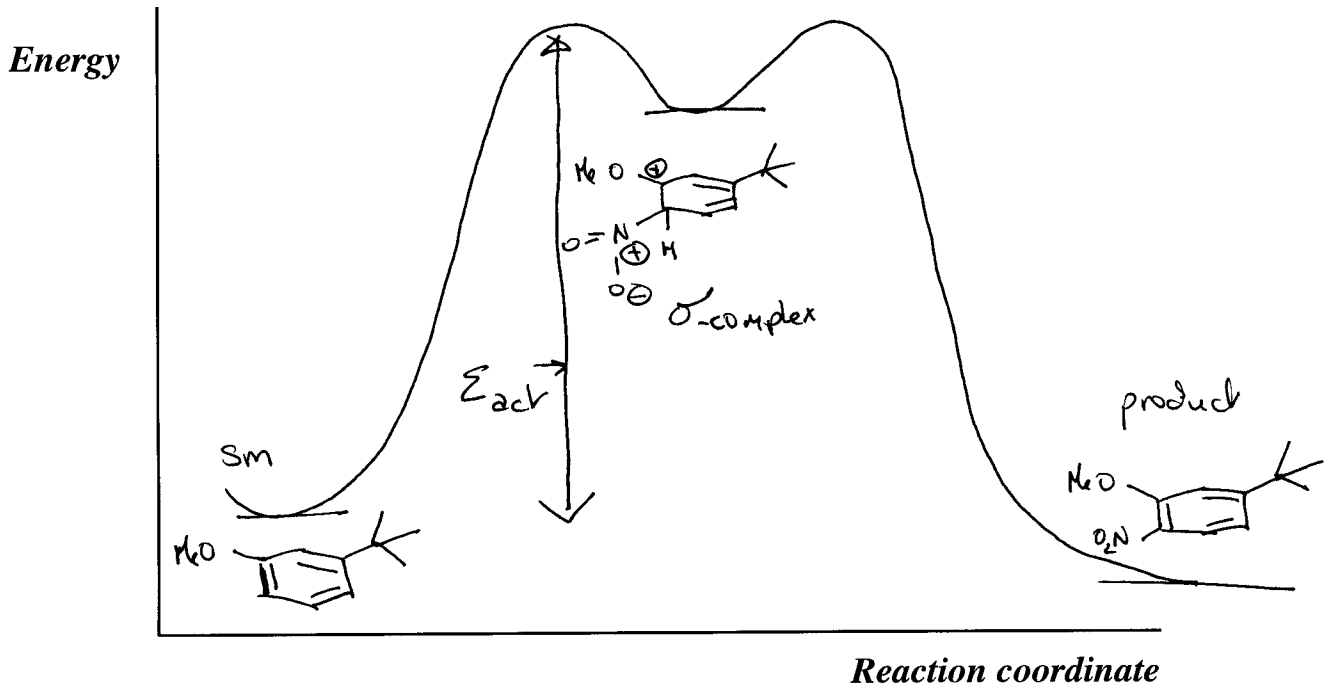
a) (3 points) Identify the active ELECTROPHILE in the reaction.



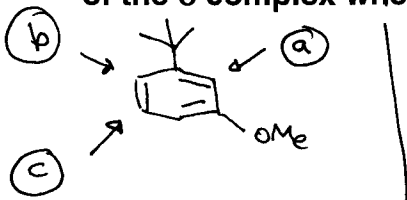
b) (9 points) Show the stepwise mechanism that accounts for the formation of a product in which the position indicated by the arrow is substituted with an $-\text{NO}_2$ group. You must identify all the important resonance structures in the positively charged intermediate



c) (6 points) Construct an energy diagram for this electrophilic aromatic substitution reaction. On the diagram you should indicate the starting material, the high energy intermediate (σ complex), the product and the energy of activation for the rate determining step.

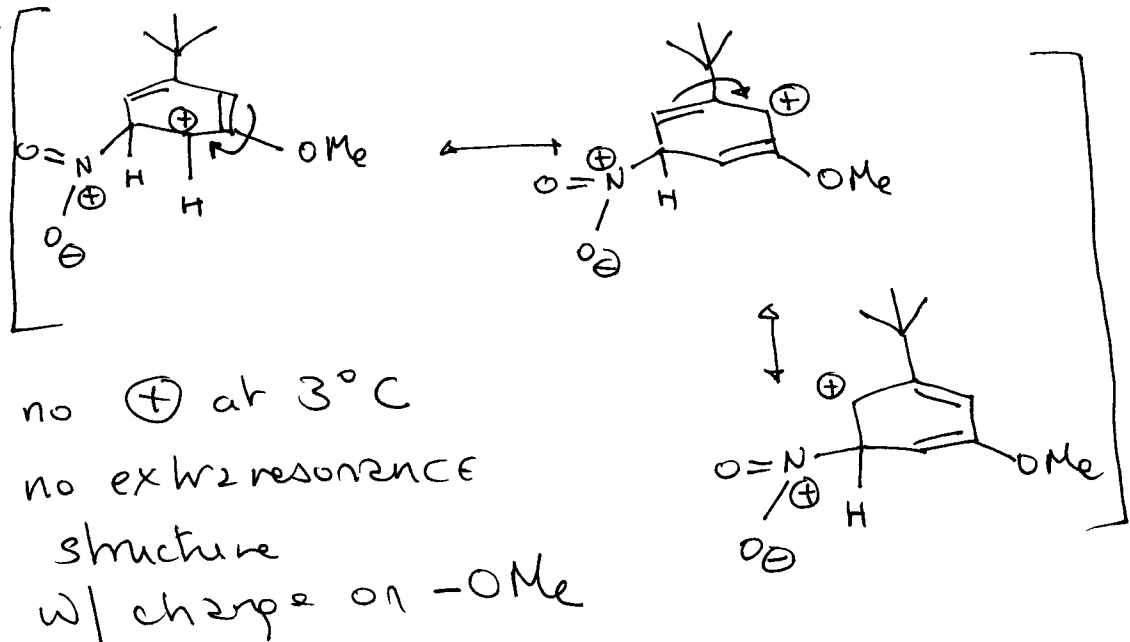


d) (8 points) Explain why a single major product is obtained by considering the features of the σ complex when attack occurs at the other sites on the ring.

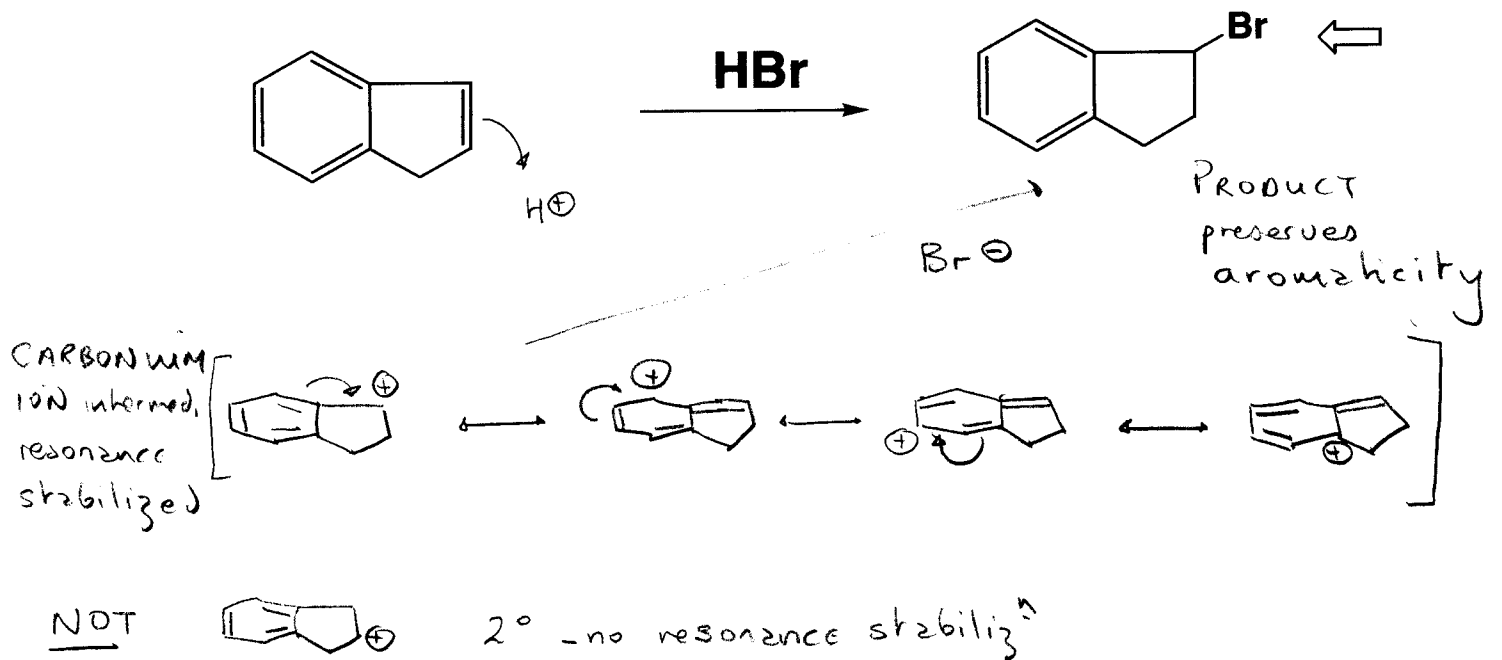


Attack at (a) sterically hindered (ortho to OMe +
 " " (b) " " ortho to
 " " " " + para to OMe

Attack at (c)



13. (8 points) Explain why the reaction shown affords only a single addition product upon treatment with HBr. In your answer you need to explain, by illustrating the intermediate formed in the reaction why none of the other double bonds in the starting material react and why the bromine adds to the carbon indicated in the scheme.



NONE OF ADDITION PRODUCTS TO BENZENE RING DOUBLE WOULD BE OBSERVED BECAUSE AROMATICITY WOULD BE LOST IN THE PRODUCT.