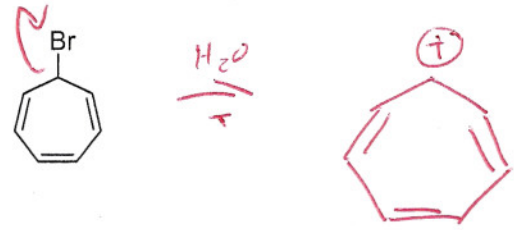
322 E1 Th 2010

1. (6 points) Explain why tropylium bromide is surprisingly water soluble for a halogenated hydrocarbon:



6 π e⁻
aromatic

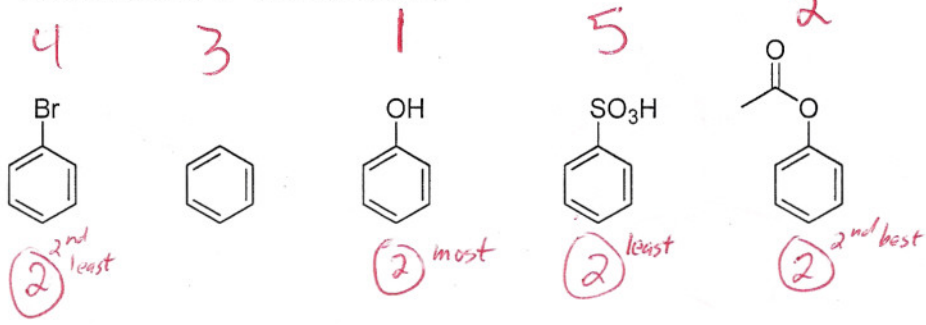
2. (8 points) Label each of the following molecules as being aromatic, antiaromatic, or neither:

a n a aa

3. (6 points) Explain why cyclic dienes (e.g. cyclopentadiene) are generally more reactive than acyclic dienes (e.g. butadiene) in Diels-Alder reactions.

100% s-cis
instead of only occasionally s-c.s.

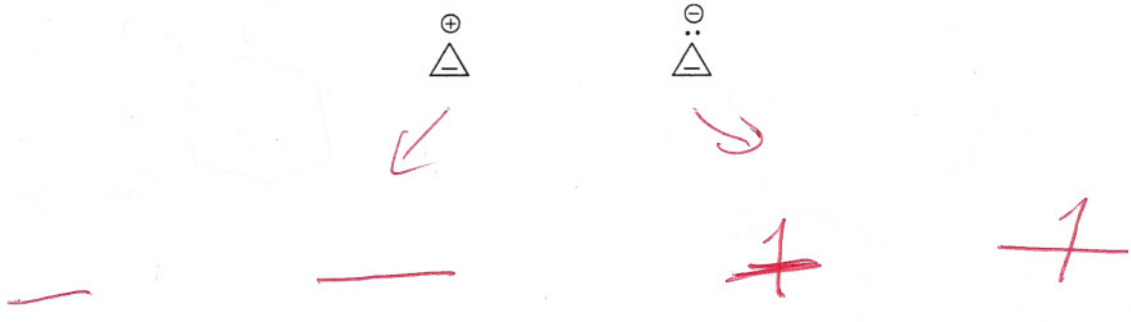
4. (8 points) Rank the following compounds in order of reactivity to electrophilic aromatic substitution (1 = most reactive, 5 = least reactive):



(2) 2nd least (2) most (2) least (2) 2nd best

Score based on relative order, not just correct ~~tt~~

5. (8 points) Give Molecular Orbital (MO) diagrams (hint: you can use a Frost circle) for the cyclopropenyl cation and anion. Using them, show which is aromatic and which is antiaromatic. Also using the MO diagrams, explain why the aromatic electron configuration is more stable than the antiaromatic.



2 π e⁻
full HOMO
aromatic

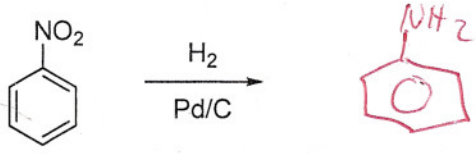
2 × (1) orbitals
2 × (1) e⁻
2 × (2) explanation.

4 π e⁻
half-filled HOMO
antiaromatic

24 4 ea

6. (24 points) Give the major organic product(s) for the following reactions:

a)

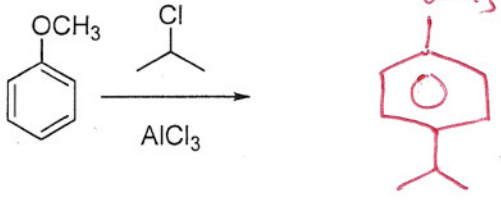


b)

anti. - mark. (2)

mark. (2)

c)



and/or o-

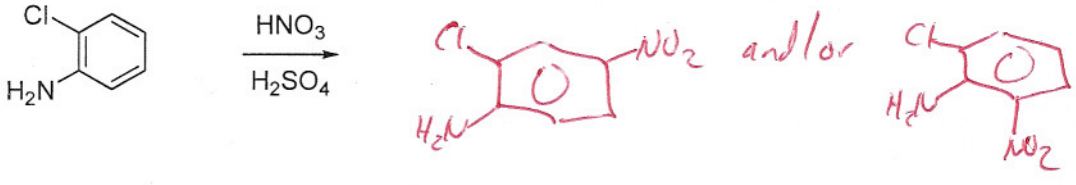
m- (2)

d)

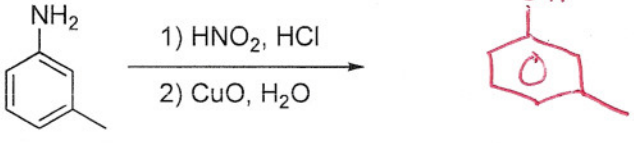
endo or enantiomer

exo - (3)

e)

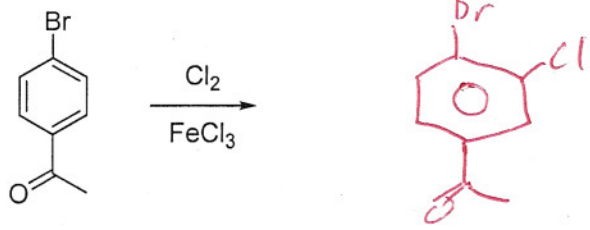


f)



4

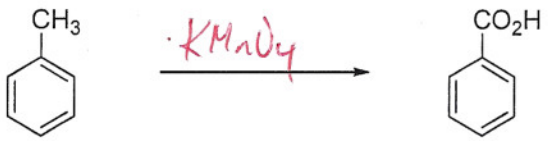
g)



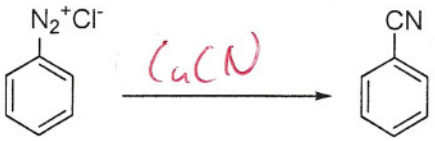
(4) wrong regio (2)

7. (12 points) Provide reagents for all the following transformations:

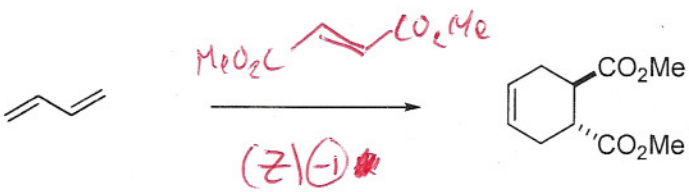
a)



b)

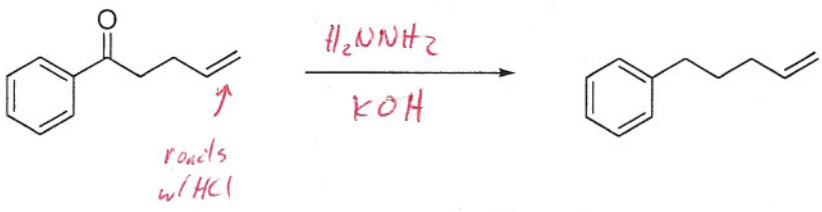


c)



(2)(-1)

d)

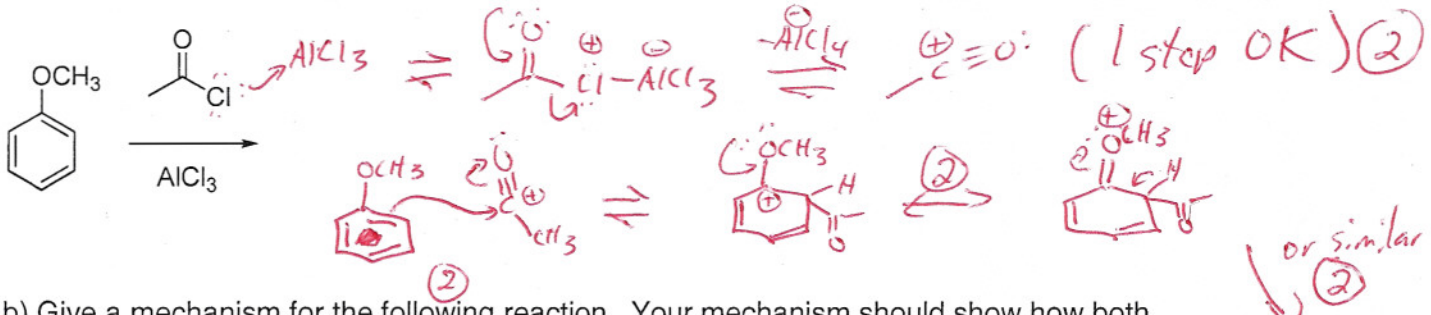


reacts w/ HCl

(-1) for Zn/Hg, HCl

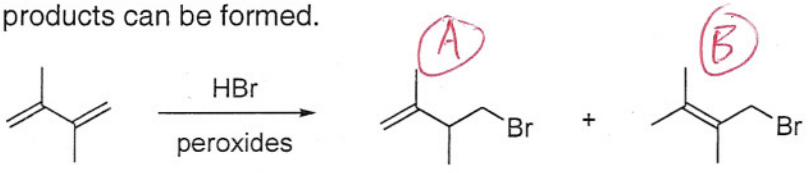
9. (12 points) Mechanisms: Choose ONE of the following TWO problems. If you work on more than one, CLEARLY indicate which you want to be graded for credit.

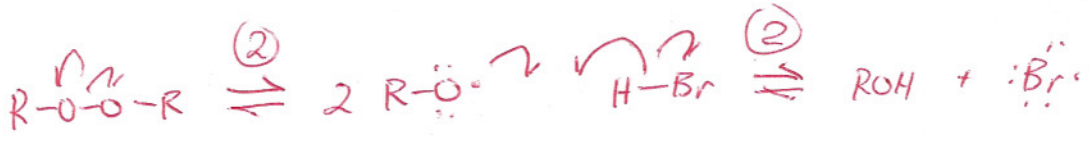
a) .Provide the major product or products for the acylation of anisole, as well as a mechanism for the formation for one such product. The mechanism should include the generation of the electrophile as well as the addition of the electrophile to the aromatic ring. Use the mechanism to explain the predicted regioselectivity (*o*-/*p*- or *m*- substitution) for the reaction.

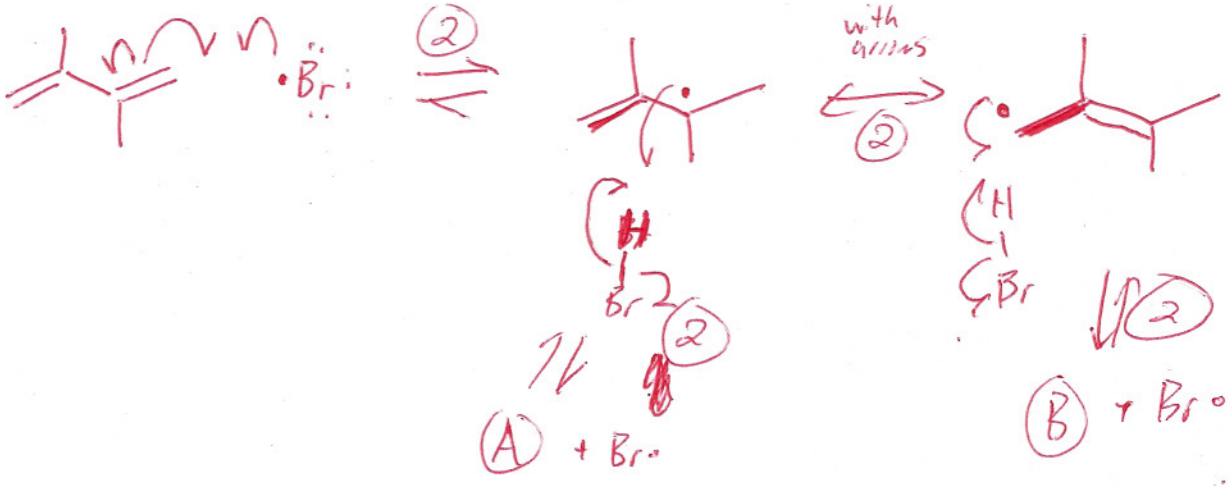


(2)

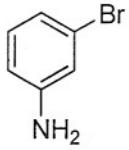
b) Give a mechanism for the following reaction. Your mechanism should show how both products can be formed.



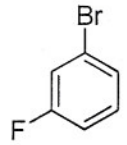




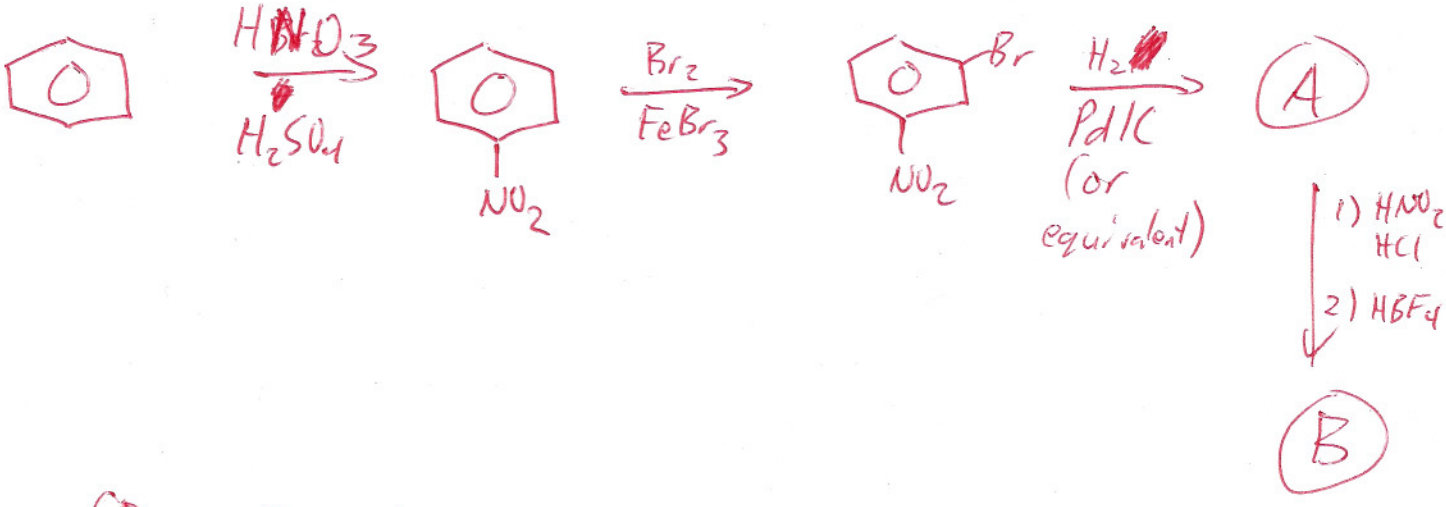
10. (12 points) Provide a synthesis for one of the following compounds from benzene. Retrosynthetic analysis may also be provided for partial credit. **If you show work on both, CLEARLY INDICATE WHICH SYNTHESIS YOU WANT GRADED.** Otherwise, the one first worked on will be graded.



(A)



(B)



(A): 4 pts/step

(B): 3 pts/step