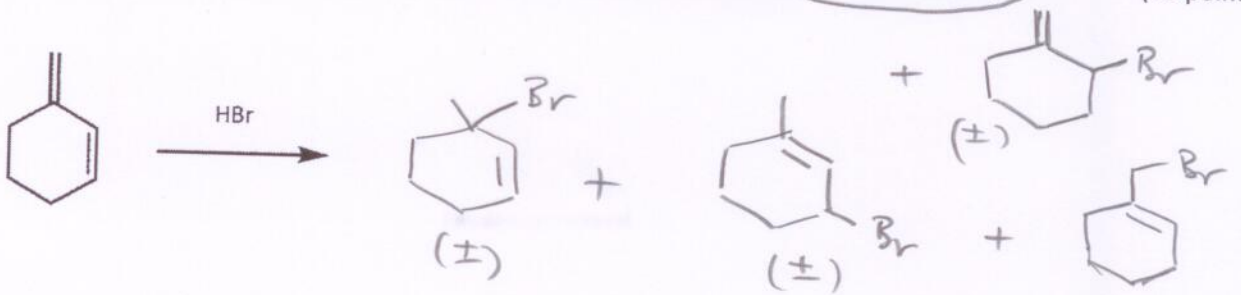
1. Show the product(s) from the following reactions. Remember to show all stereochemistry! (10 points)

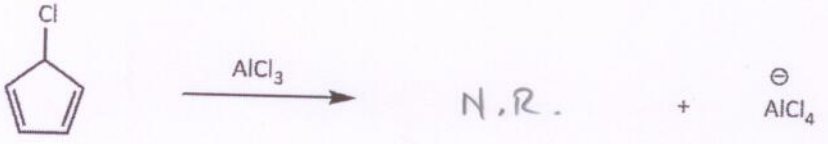
a. 

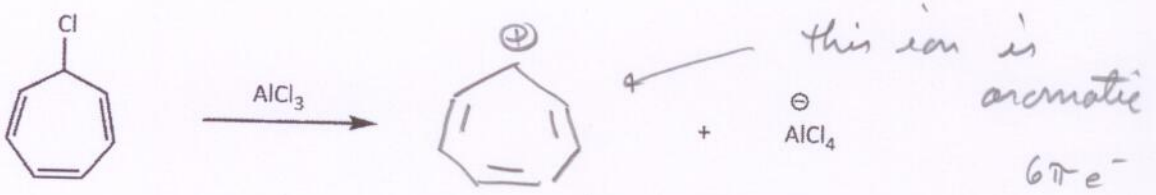
(7 products total)

b. 

conrotatory ring closure under photochemical

2. One of the reactions below work to produce a carbocation, the other one doesn't. Show the carbocation that is expected to form and write N.R. in the one that doesn't. In terms of the stability of the resulting ion (or lack thereof), explain your answer. (10 points)

a. 

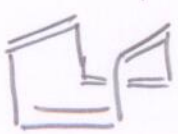
b. 

this ion is aromatic 6π e⁻

tropylium ion

3. Unlike benzene, 1,3,5,7-cyclooctatetraene has two different carbon-carbon bond lengths, 1.33 Å and 1.46 Å and it is definitely not planar. Clearly explain why (draw pictures if necessary). (6 points)

If this was flat, it would have 8 e⁻ in a conjugated ring - this is anti-aromatic and would be unstable. So, it adopts a "tub" shape.



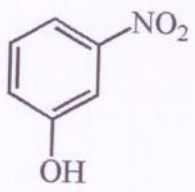
"Tub"

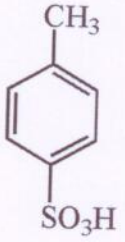
In this shape the double bonds are not conjugated, so the bonds alternate as single and double bonds, with corresponding single and double bond lengths.

4. What are the *requirements* (conditions) for a compound to be "aromatic?" (8 points)

1. cyclic
2. planar
3. conjugate
4. need $4n+2$ π electrons (where $n = 0, 1, 2, \ldots$)

5. Provide IUPAC names (*not common names*!) for the following compounds. (10 points)

a. 

b. 

no common names!

(p-toluenesulfonic)

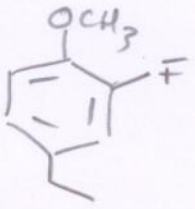
3-nitrophenol

(m-nitrophenol) ← common

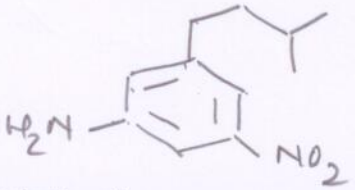
4-methylbenzenesulfonic acid

6. Draw the structure of the following compounds. (10 points)

a. 4-ethyl-2-fluoroanisole



b. 3-(3-methylbutyl)-5-nitroaniline

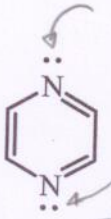


7. For each of the following molecules or ions indicate whether they are *aromatic*, *anti-aromatic* or *non-aromatic*. (16 points)

a. 

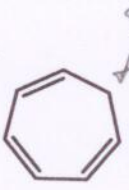
aromatic

$2e^-$ is a $4n+2$ case

b. 

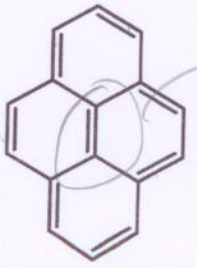
in sp^2! don't count

aromatic

c. 

sp^3

non-aromatic

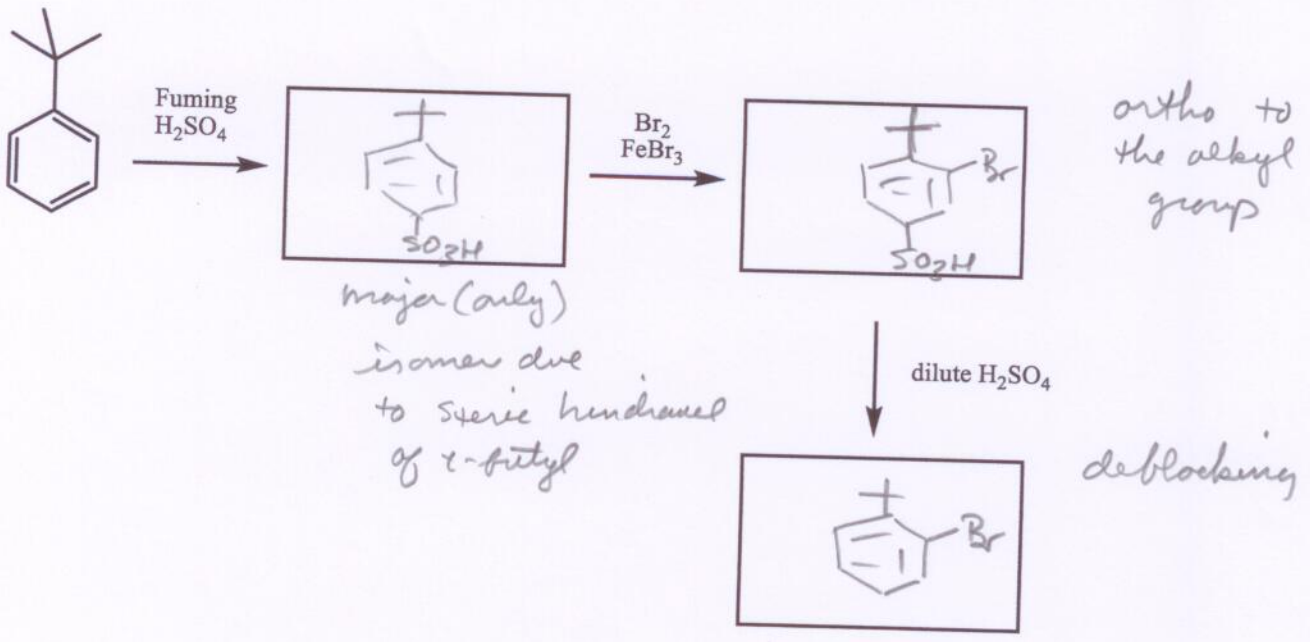
d. 

don't count these

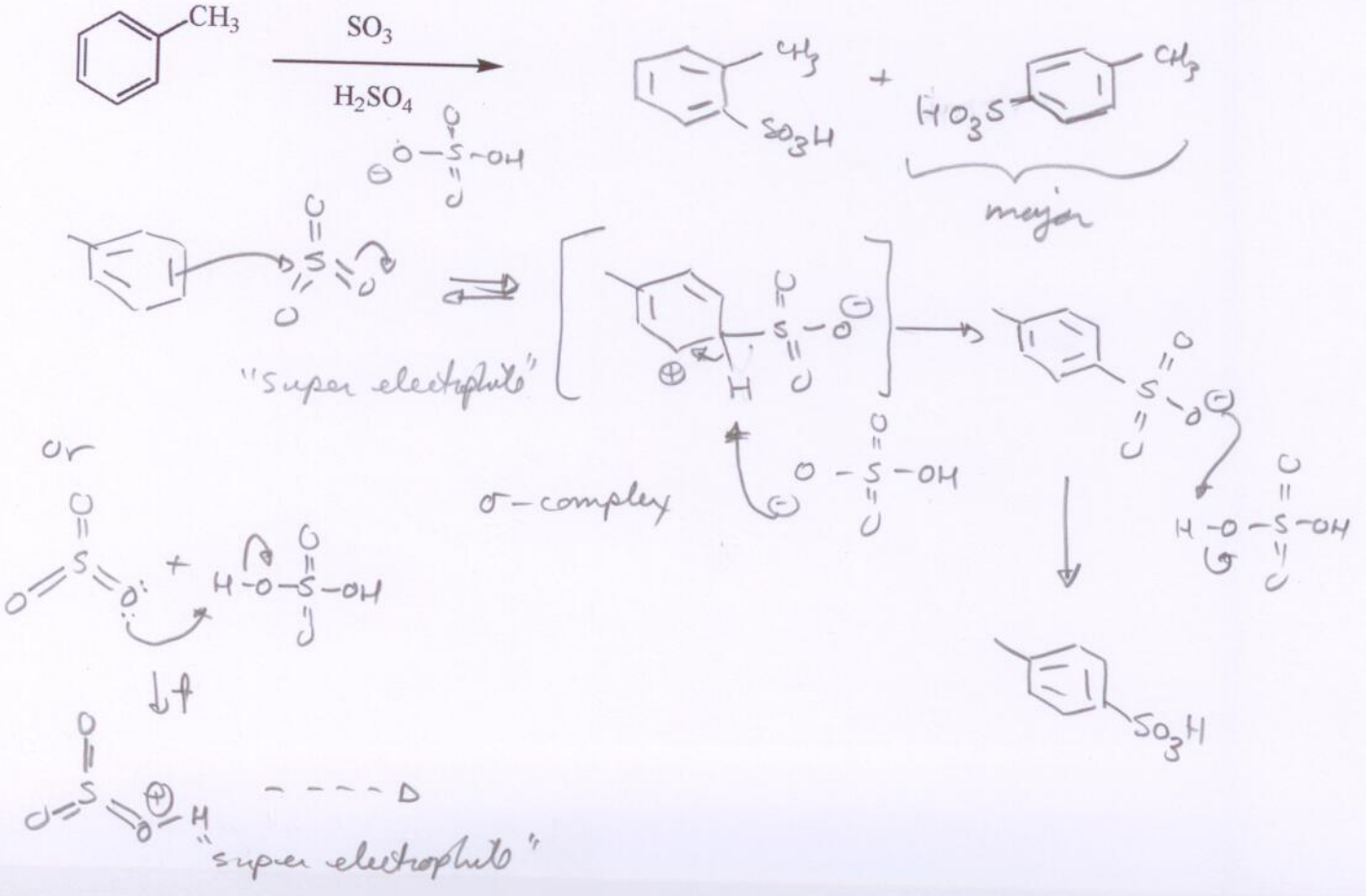
aromatic

$14e^-$

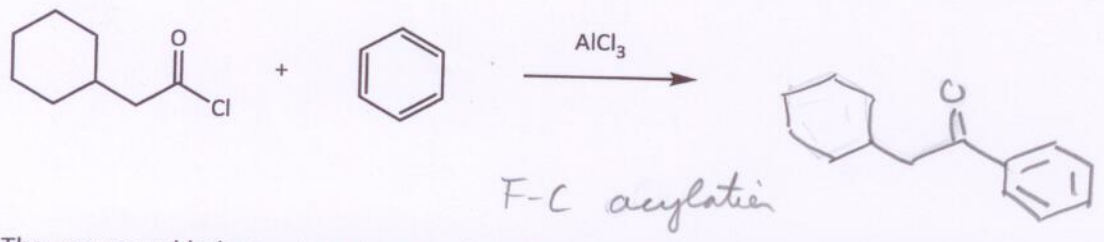
8. In the following synthesis, fill in the products or reagents. (15 points)



9. Show the product(s) and the complete *mechanism* (with electron-pushing) for the following reaction. (if more than one isomer is formed show the mechanism for only one of them, but be sure show all expected products) (20 points)

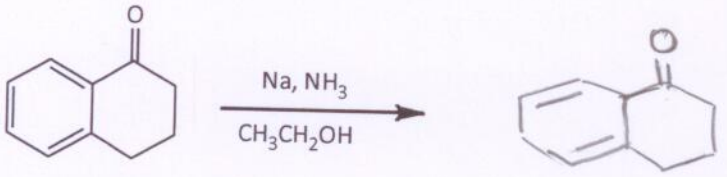


10. Show the product(s) from the following reaction. (5 points)



F-C acylation

11. The compound below, α-tetralone, undergoes Birch reduction to give a single product. Show the structure of the product. (10 points)

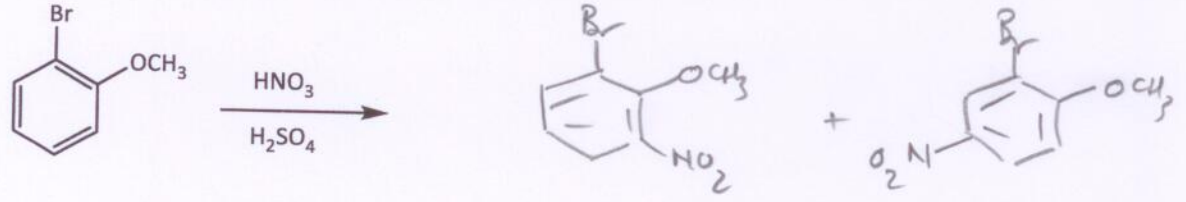


α-tetralone

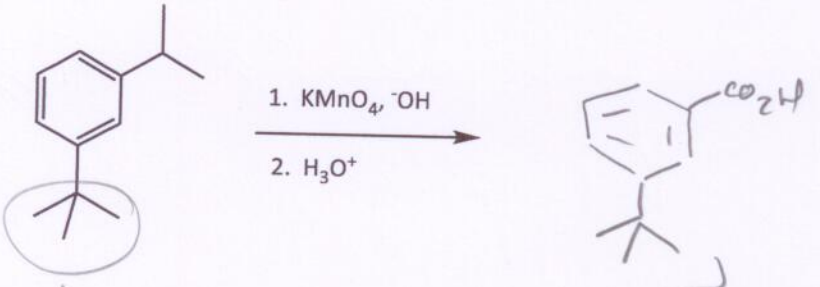
note the double bonds are not in conjugation with the ketone

12. Show the expected product (or products) from the following reactions. (10 points)

a.



b.

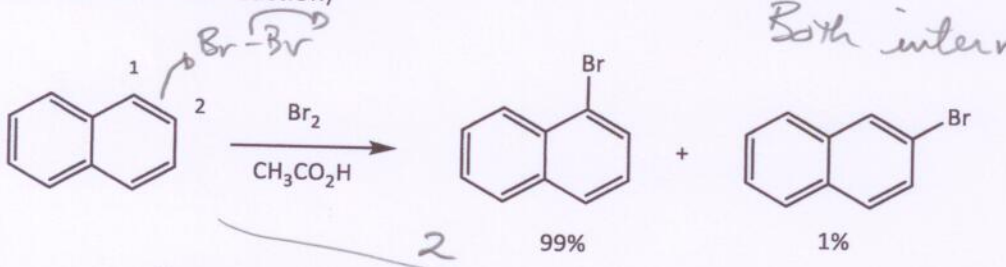


no H, so no oxidation

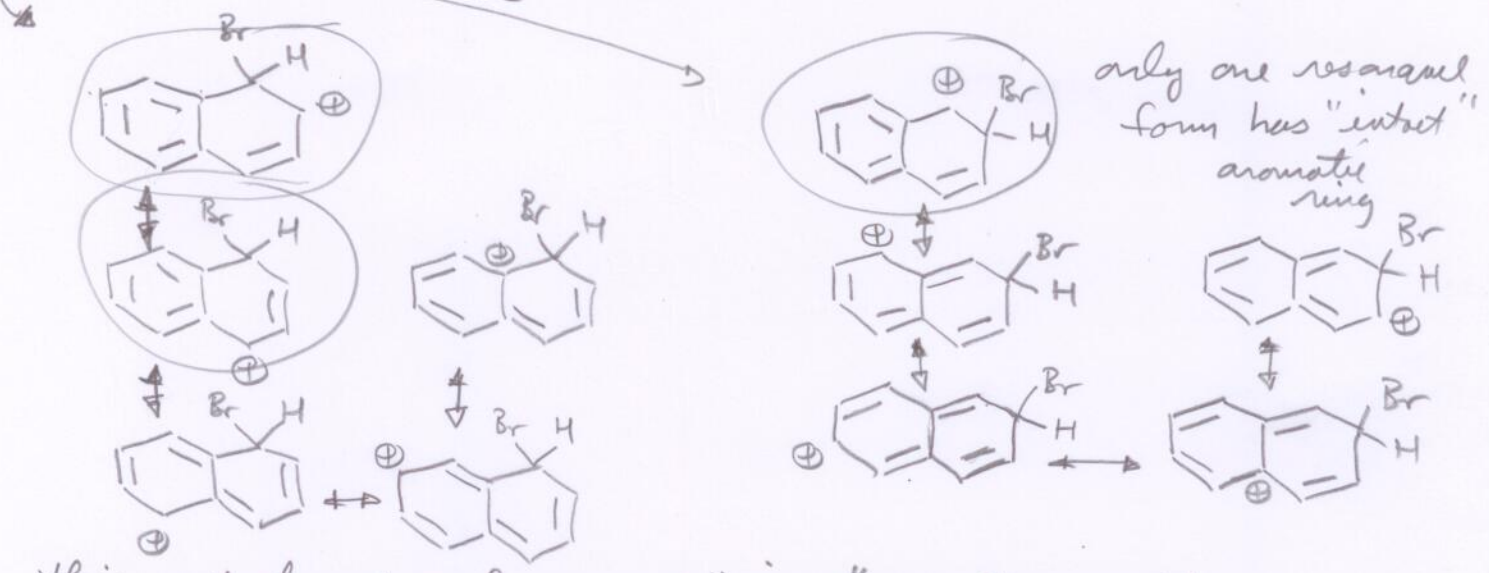
intact

13. Naphthalene is considerably more reactive than benzene toward bromine, although it still undergoes electrophilic aromatic substitution instead of reactions like alkenes, a strong Lewis acid catalyst is not required. Suggest an explanation for the observed *selectivity* for the bromination reaction. (Hint: consider the mechanism of the reaction)

(10 points)



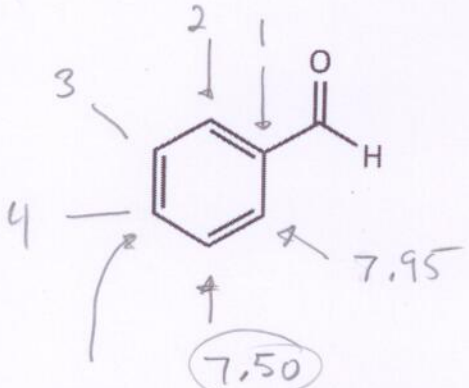
Both intermediates have 5 resonance forms



this set has two forms w/ "intact" aromatic ring!!

14. Use the NMR data sheets (from lecture) to calculate the proton and carbon chemical shifts for benzaldehyde. Explain how the chemical shift data indicate whether the aromatic substituent is an *activating* or *deactivating group* and whether it is an *ortho/para director* or a *meta director* in an Electrophilic Aromatic Substitution reaction (S_EAr). (Note: the entry in the ^1H NMR chart, Chart D.1, shows and aldehyde as CH(=O))

(15 points)



^1H NMR ^{13}C NMR

C-1 = 128.5 + 8.2 = 136.7
C-2 = 128.5 + 1.2 = 129.5
C-3 = 128.5 + 0.6 = (129.1)
C-4 = 128.5 + 5.8 = 134.0

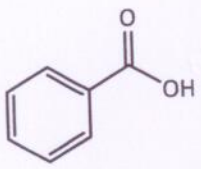
7.65 most electron rich proton — most shielded in NMR

The most e⁻ rich region undergoes electrophilic substitution, so the aldehyde is a meta director

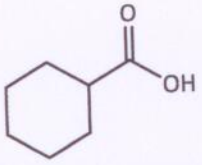
most e⁻ rich carbon — most shielded

all chemical shifts are deshielded relative to benzene so - deactivating

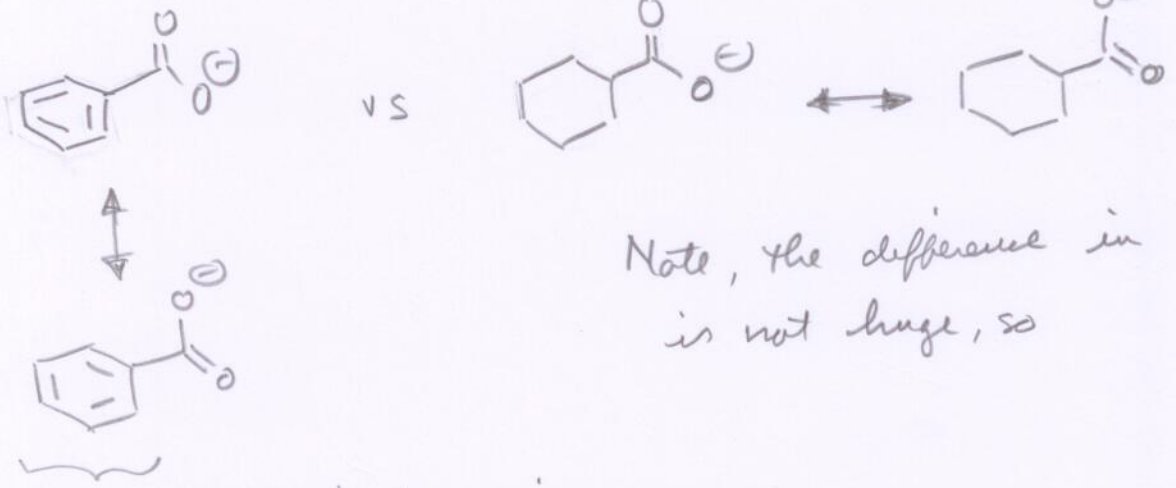
15. In terms of *conjugation* explain why benzoic acid ($pK_a = 4.1$) is more acidic than cyclohexanecarboxylic acid ($pK_a = 4.8$) (10 points)



benzoic acid

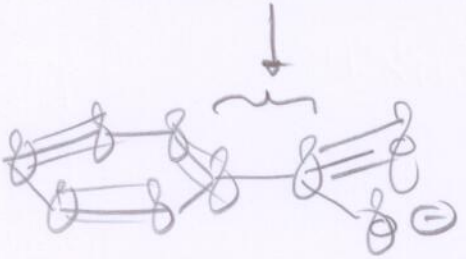


cyclohexanecarboxylic acid



Note, the difference in pka is not huge, so

the aromatic ring is in conjugation with the carboxylate since the π bond can overlap



this is a stabilizing feature for the carboxylate

Also, the sp^2 carbon, with greater S-character compared to sp^3 in cyclohexane-carboxylate, has an inductive effect

conjugation is the overlap of π systems and allows the π electrons to "spread out" into more space, so the benzoate is more stable than cyclohexane carboxylate!