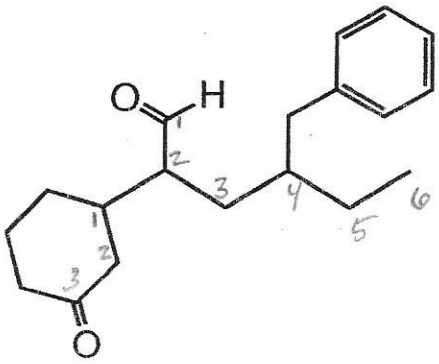
Exam 2, Sp24

A. Nomenclature: (12 points)
Give an acceptable IUPAC name for each of the compounds. in 1 and 2. Draw a structure for the compound in 3. Be sure to indicate the **stereochemistry** where appropriate.

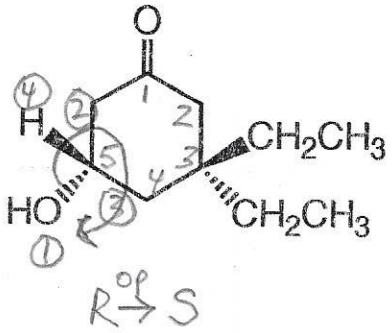
1.



4-benzyl-2-(3-oxocyclohexyl)hexanal

1 1 2

2.



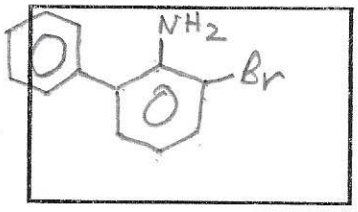
R → S

(S)-3,3-diethyl-5-hydroxycyclohexanone

1 1 2

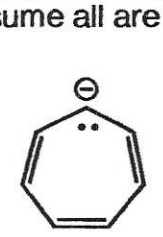
3. 2-bromo-6-phenylaniline

2 2

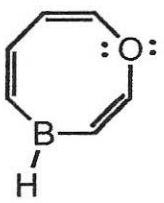


B. Facts: 20 points

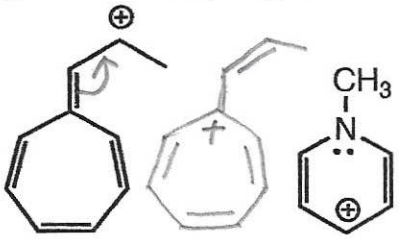
1. Label the molecules below as aromatic(**AR**), antiaromatic(**AA**), or nonaromatic(**NA**). Assume all are planar. (8 pts.)



AA



NA

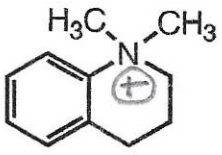


AR

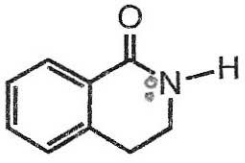
AR

2pts each

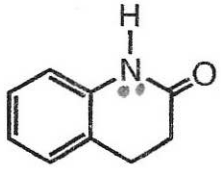
2. Rank the following substituted benzene compounds in order of increasing rate in the reaction with bromine and $FeBr_3$. (1=slowest rate, 3=fastest rate) (3 pts.)



1



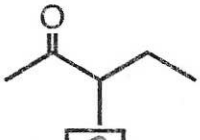
2



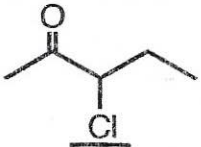
3

1pt each

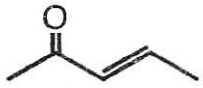
3. Rank the compounds in order of increasing amount of hydrate produced when reacted with H_3O^+. (1= smallest amount, 3=largest amount) (3 pts.)



2



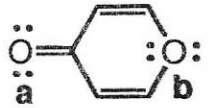
3



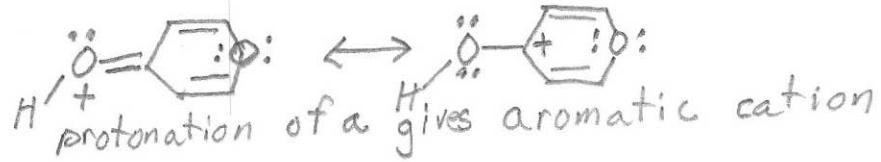
1

1pt each

4. Which oxygen atom is more basic, a or b? (2 pts.)



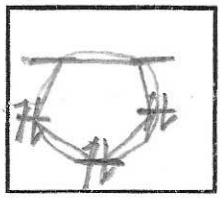
a



protonation of a gives aromatic cation

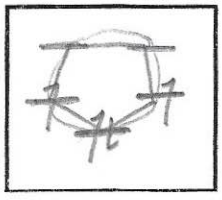
5. In the box below each ion, draw its energy level diagram using the polygon rule. Without using the Huckel equation, explain why the anion is aromatic while the cation is antiaromatic. (4 pts.)

6π e^- →



1pt

← $4\pi e^-$



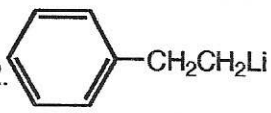
1pt

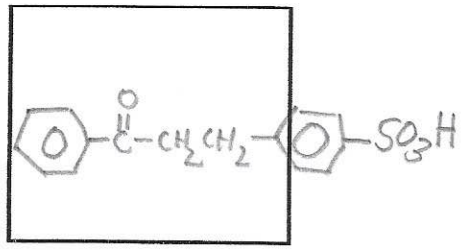
1pt [anion: all 6π e^- occupy low E bonding molecular orbitals.]

1pt [cation: has diradical character so is highly unstable]

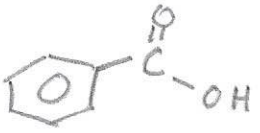
C. Reactions: Total = 36 points, 6 points each
Please provide the the major product in the answer box. Indicate **stereochemistry** if applicable. **Full credit is awarded only when the product of each step in a multi-step reaction is shown below the reaction.**

1.

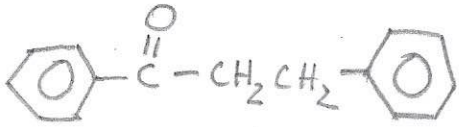
1. $Na_2Cr_2O_7$ / H_2SO_4 / 100°C
2.  (2 eq), then H_3O^+
3. fuming H_2SO_4



2pts

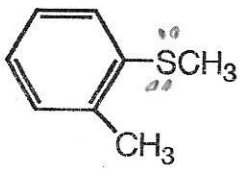


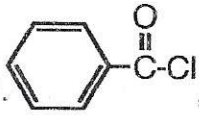
2pts

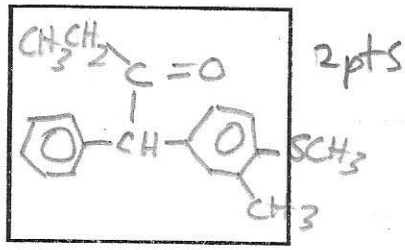


2pts

2.

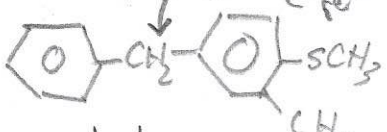


1.  , $AlCl_3$
2. $Zn(Hg)$ / HCl
3. NBS / Light
4. NaCN / acetone
5. CH_3CH_2MgBr, then H_3O^+

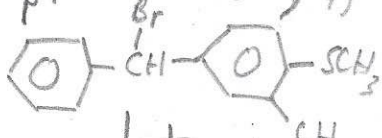


2pts

1pt



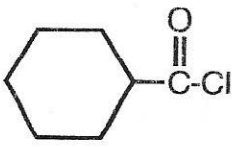
1pt

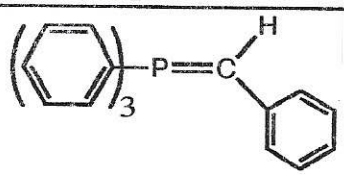


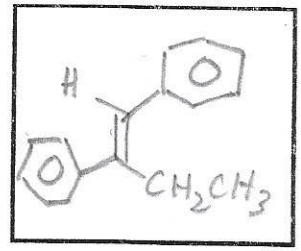
1pt

most reactive benzylic H (more resonance)

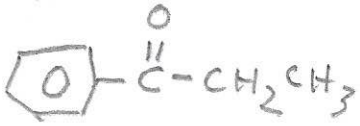
3.



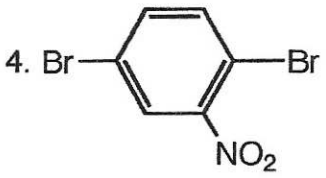
1. $(CH_3CH_2)_2CuLi$
2. 



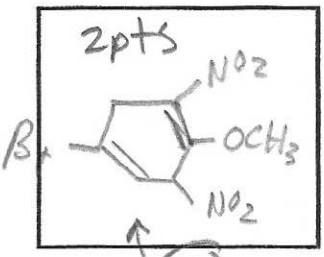
3pts (-1) incorrect or no stereo



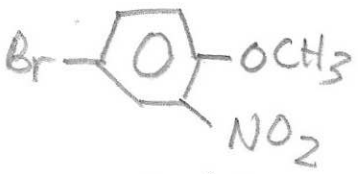
3pts

4. 

1. $CH_3O^-Na^+$ (2 eq) / 100 °C
2. HNO_3 / H_2SO_4
3. Na / NH_3 / CH_3OH

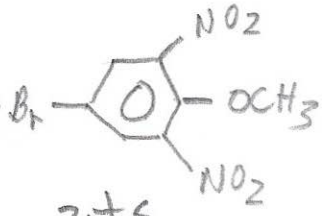


1)



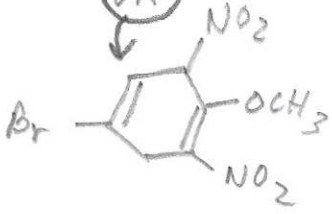
2pts

2)

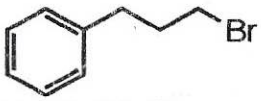


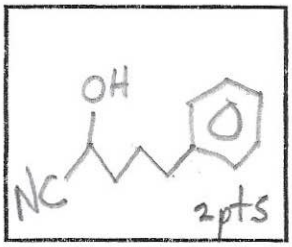
2pts

3)



5.

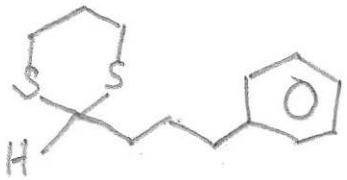
1. BuLi
2. 
3. H_3O^+ / $HgCl_2$
4. NaCN / H^+



1)

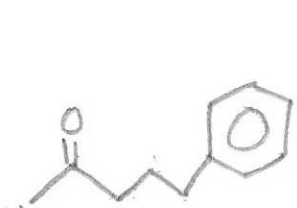
1pt

2)



1pt

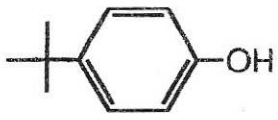
3)



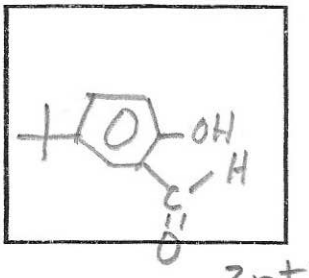
2pts

4)

6.

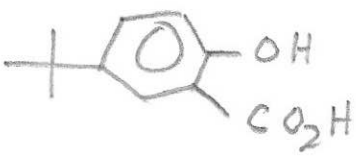


1. NaOH, CO_2, then H^+
2. $SOCl_2$
3. $LiAlH(OtBu)_3$



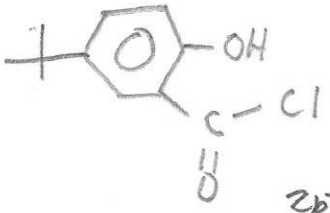
2pts

1)



2pts

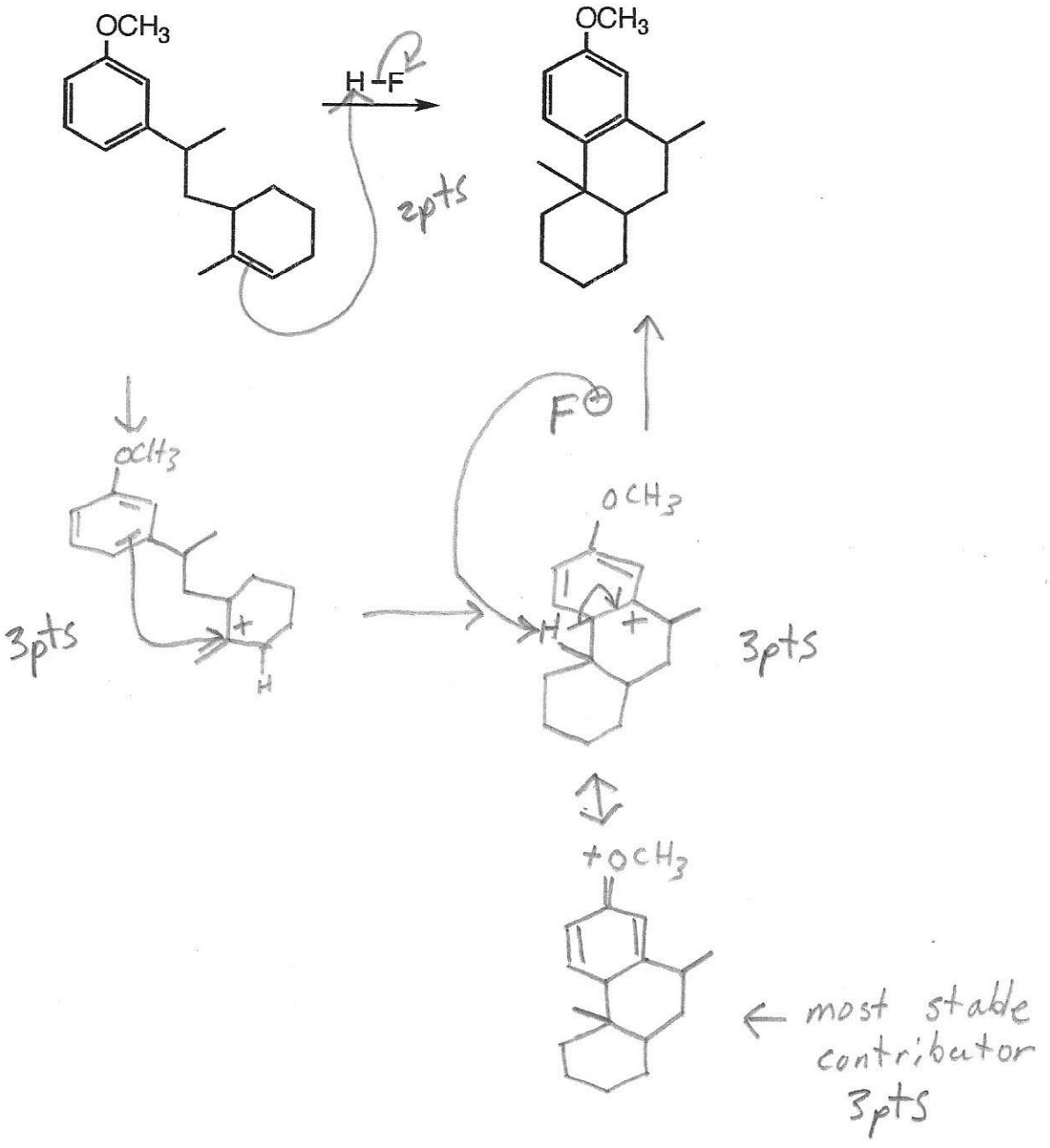
2)



2pts

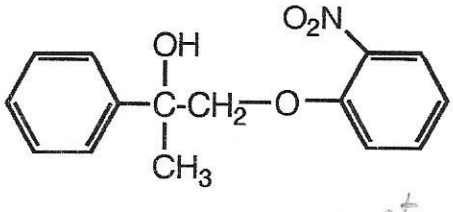
3)

D. Mechanism: (11 points)
Provide a clear mechanism to explain the formation of the product. Use curved arrows to indicate "electron flow". **Show all intermediates and all formal charges. When more than one resonance contributor may be drawn, be sure to draw the most stable contributor.**

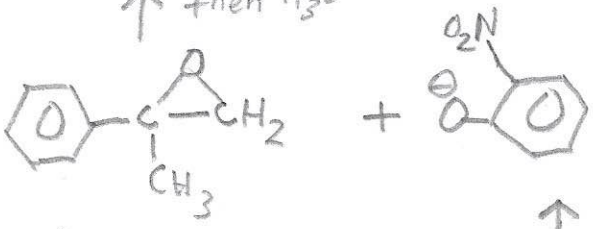


E. Synthesis: 11 Points

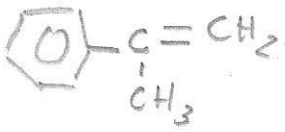
Synthesize the molecule below using **benzene**, **alcohols of two carbons or less**, any inorganic reagents, any oxidizing or reducing agents, and any peroxyacids.



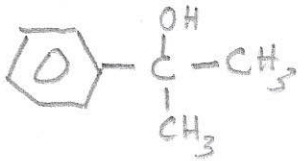
↑ then H_3O^+



↑ MCPBA

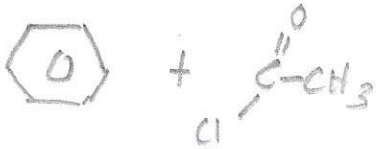


↑ H_2SO_4/Δ



↑ then H_3O^+

↑ $AlCl_3$



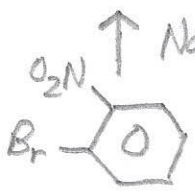
↑ Mg/Et_2O

CH_3Br

↑ PBr_3

CH_3OH

↑ $NaOH$ (2eq)/Δ

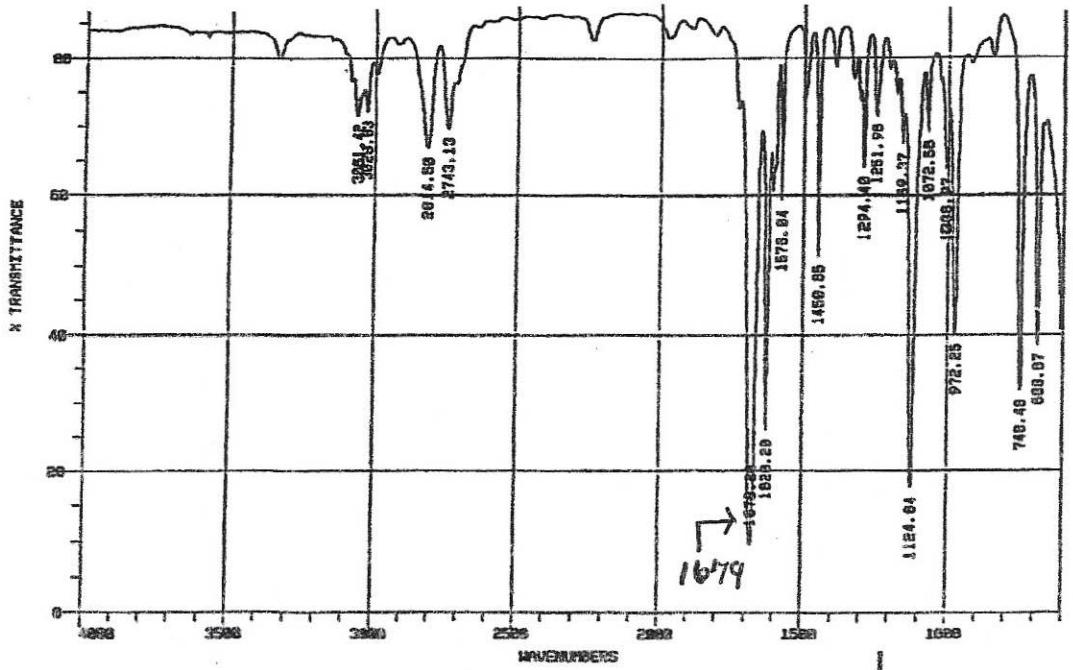


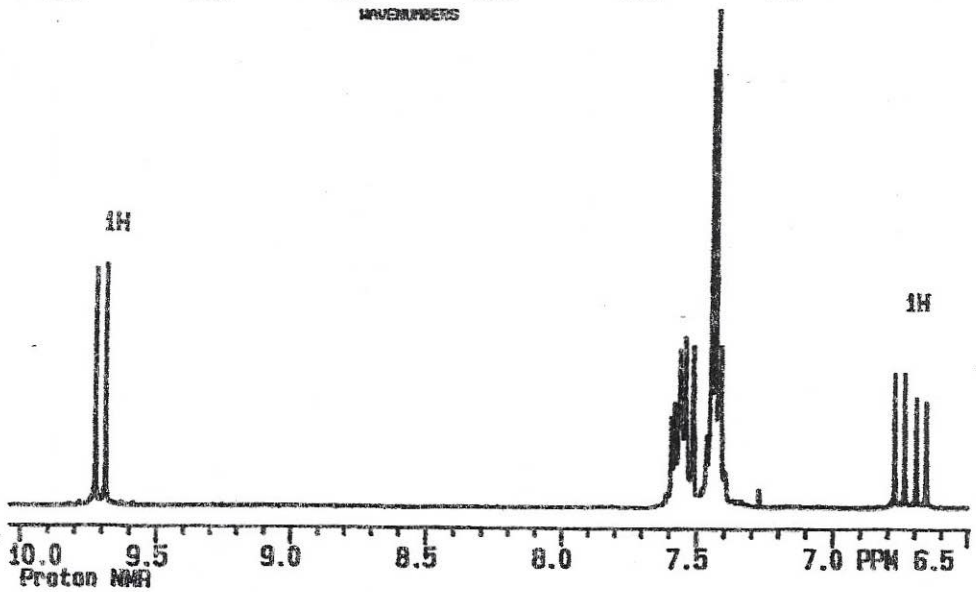
↑ HNO_3/H_2SO_4

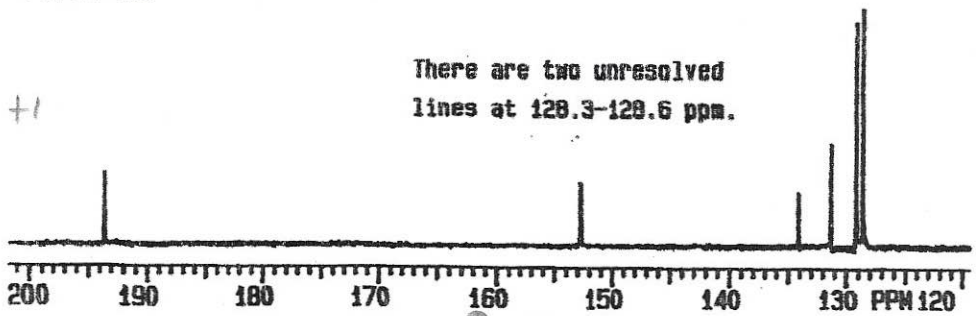
↑ $FeBr_3/Br_2$

F. Spectroscopy: 10 Points

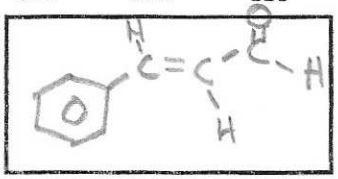
A compound with the formula C_9H_8O exhibits the IR, ^1H NMR and proton decoupled ^{13}C NMR spectra shown below. Identify this compound and draw the structure in the box provided below. NOTE: The multiplets at 7.4 - 7.6 ppm represent overlapping signals equivalent to 6 hydrogens. One signal is a 1 H doublet.







- benzene ring +1
- C=C +2
- aldehyde H adj. to 1 H +2
- other aldehyde +1
- NO points for ketone



trans or cis okay