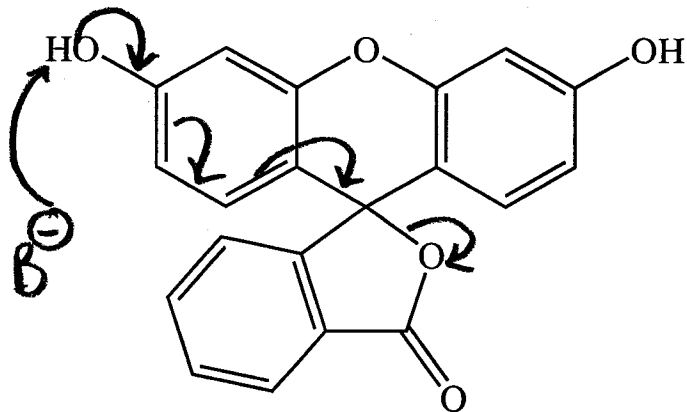
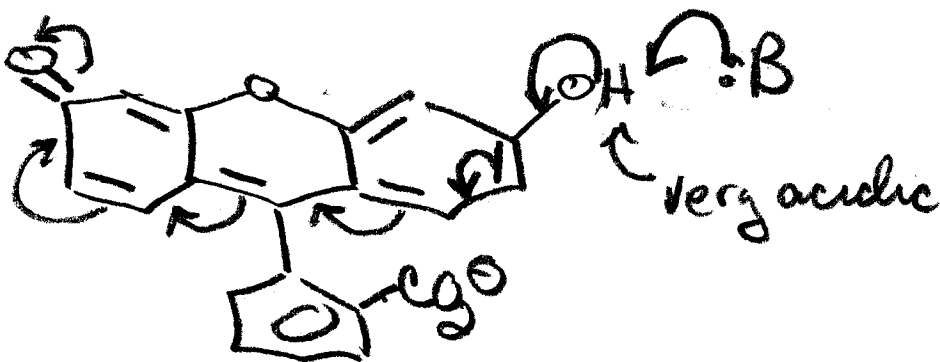


1. Isolated benzene rings generally absorb light in the UV and are colorless. The following compound is colorless but it turns red in aqueous base. Provide a detailed explanation for this result.

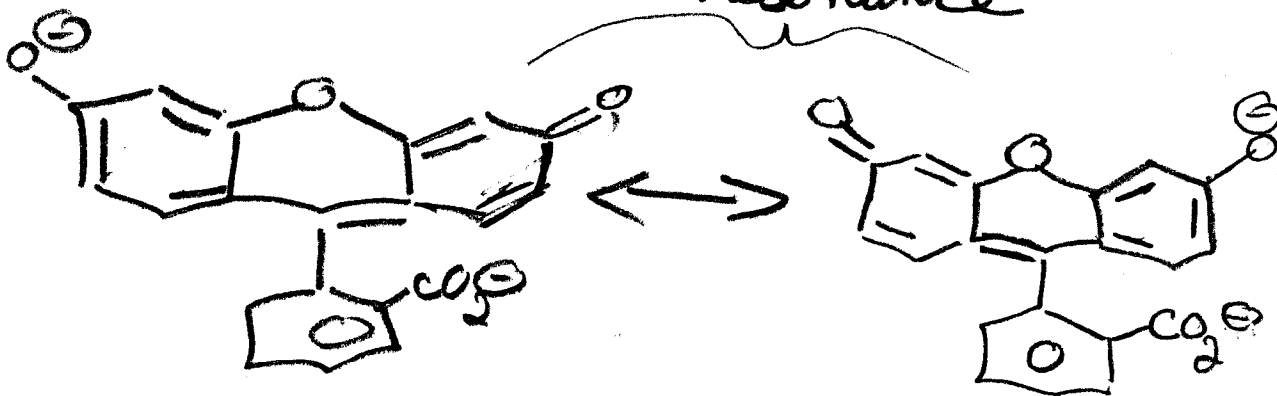


Parent Compound  
isolated benzen Rings  
No real Chromophore

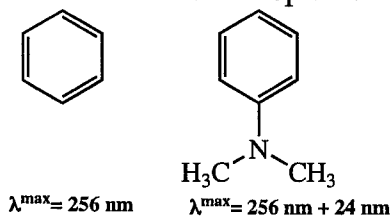
↓ With Base get expanded  
Chromophore



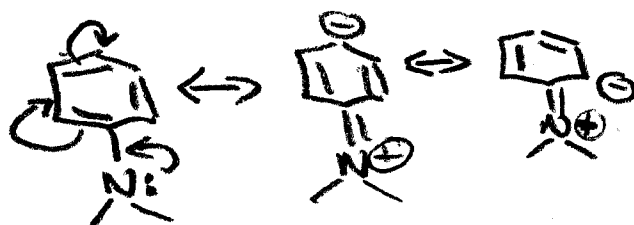
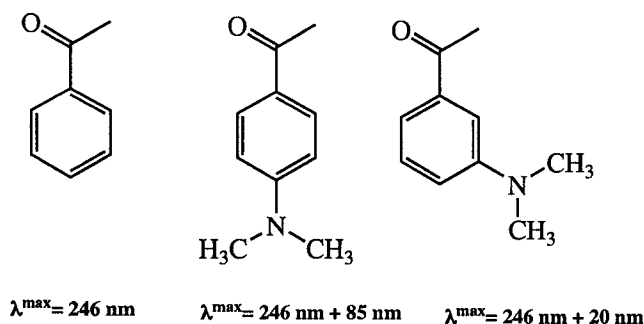
highly delocalized by  
resonance



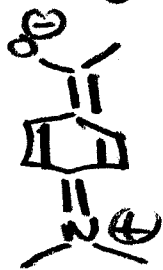
2. In addition to the diene examples given in class Woodward developed rules for benzene rings. Some representative examples are shown below. Suggest why in the second series the nitrogen substitution in the para position makes for a larger shift relative to the meta and to the top case which lacks the ketone.



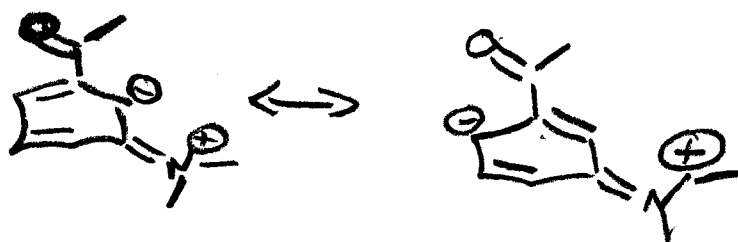
The amine donates into the ring and shifts the chromophore



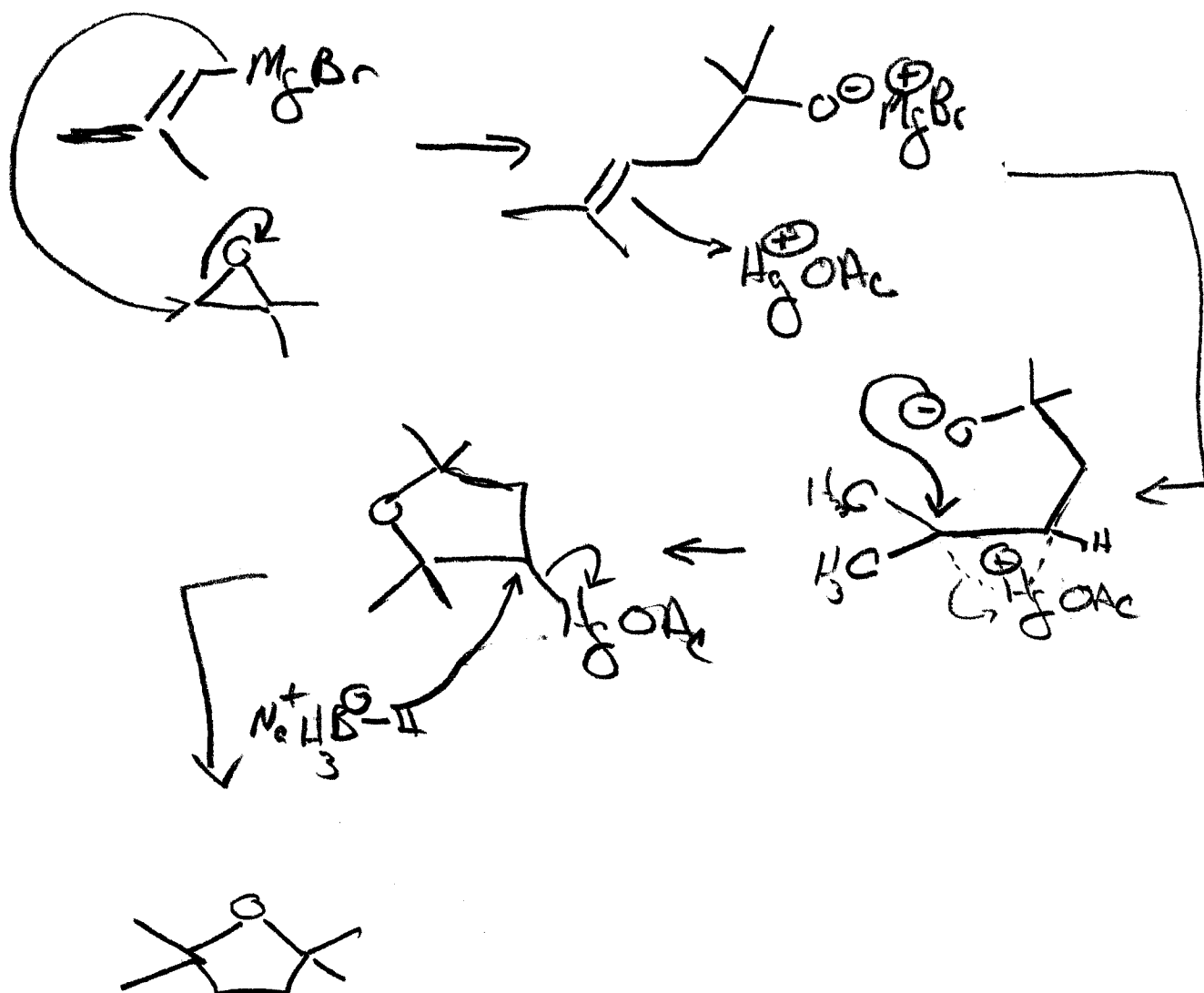
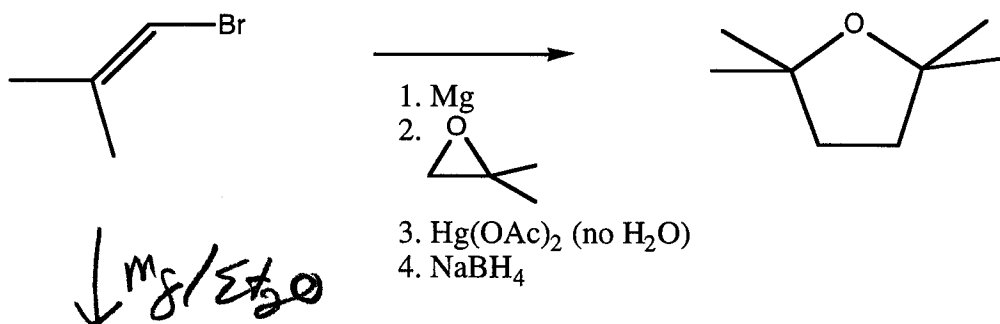
When a ketone is placed para to the amine we get an additional resonance structure



in which all of the atoms have filled octets and the electronegative Oxygen has a negative charge. When the amine is meta we do not have this possibility and we get an effect similar to the simple benzene

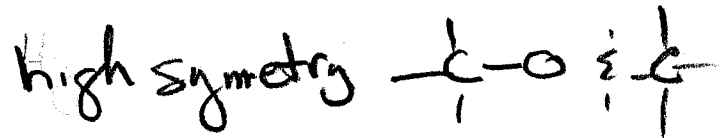
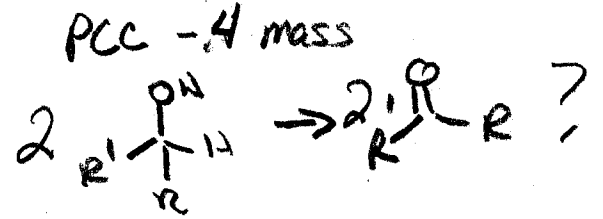
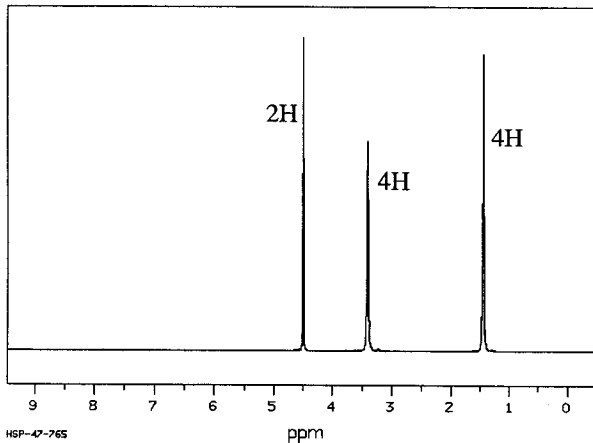
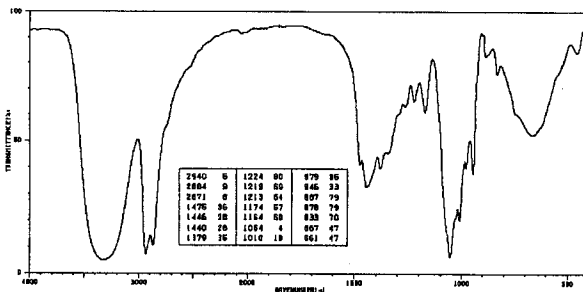
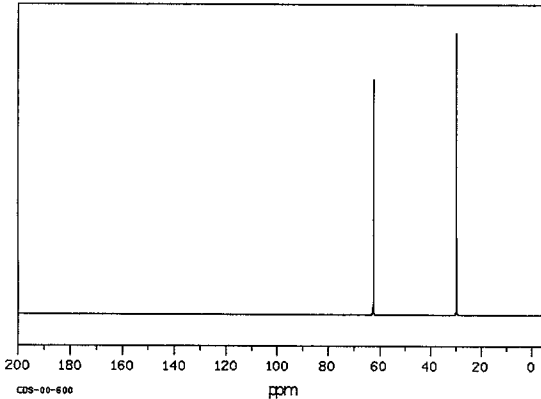


3. Show all of the intermediates and the mechanism for each step in the following transformation.

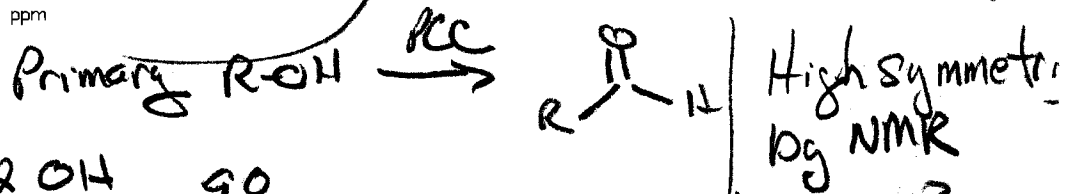
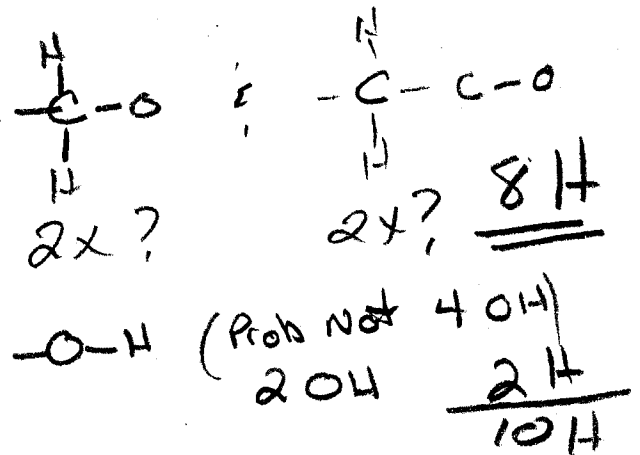


4. Compound A (F.W. = 90.1) is oxidized by pyridinium chlorochromate (PCC) in  $\text{CH}_2\text{Cl}_2$  to give compound B (F.W. = 86) which is then treated sequentially with  $\text{CH}_3\text{ONa}$ , and  $\text{CH}_3\text{I}$  to give compound C (F.W. = 132.2) with the spectra shown and a proton NMR of 4.5 (2H, t); 3.5 (6H, s), 1.35 (4H, m). Propose structures for A, B, and C and detail the reactions. Explain your structural assignment.

IR,  $^{13}\text{C}$ -NMR (decoupled),  $^1\text{H}$ -NMR of Compound A.



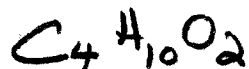
R-OH OH 3300  
 C-O 1050  
 Big } No alkene  
 sat. system  
 Need more  
 than 2 C



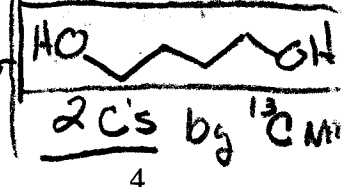
guess 2 OH

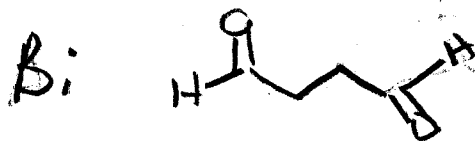
$$\begin{array}{r} 90 \\ - 34 \\ \hline 56 \end{array}$$

$$\begin{array}{r} \text{C}_4 \quad 48 \\ 4 \text{ H} \quad 8 \\ \hline 56 \end{array}$$



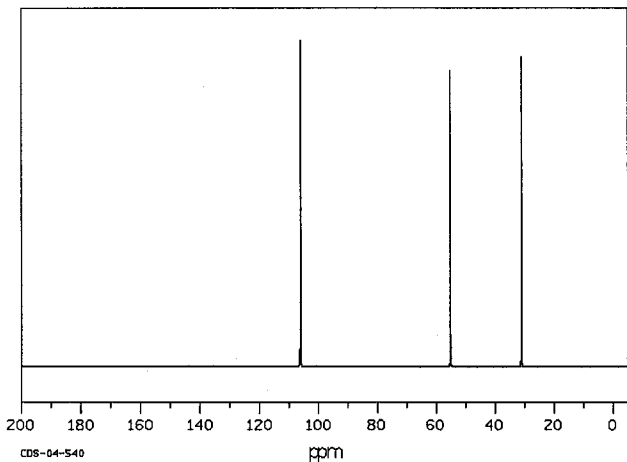
(A)





C  
No C-OH  
No C=O or alkene

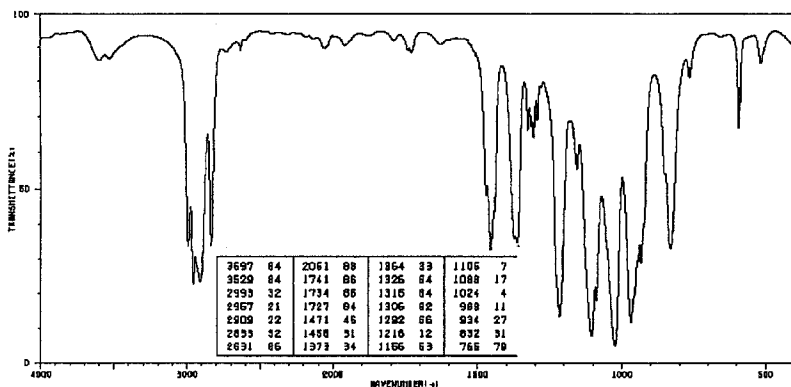
4. cont.  
IR, <sup>13</sup>C-NMR (decoupled) of Compound C



108 ppm more deshielded than typical C-O-

58 ppm -C-O

30 ppm -C-  
|  
H



lots of C-O action  
1455 cm<sup>-1</sup> - CH<sub>3</sub> (s)

Propose



<sup>1</sup>H 2x-O-CH<sub>3</sub>

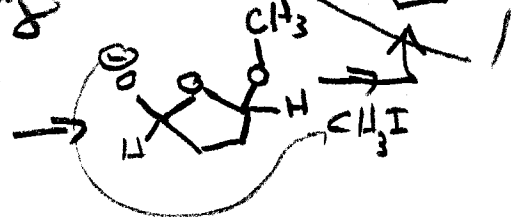
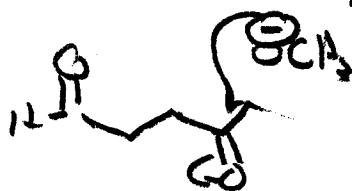
2x-CH<sub>2</sub>-



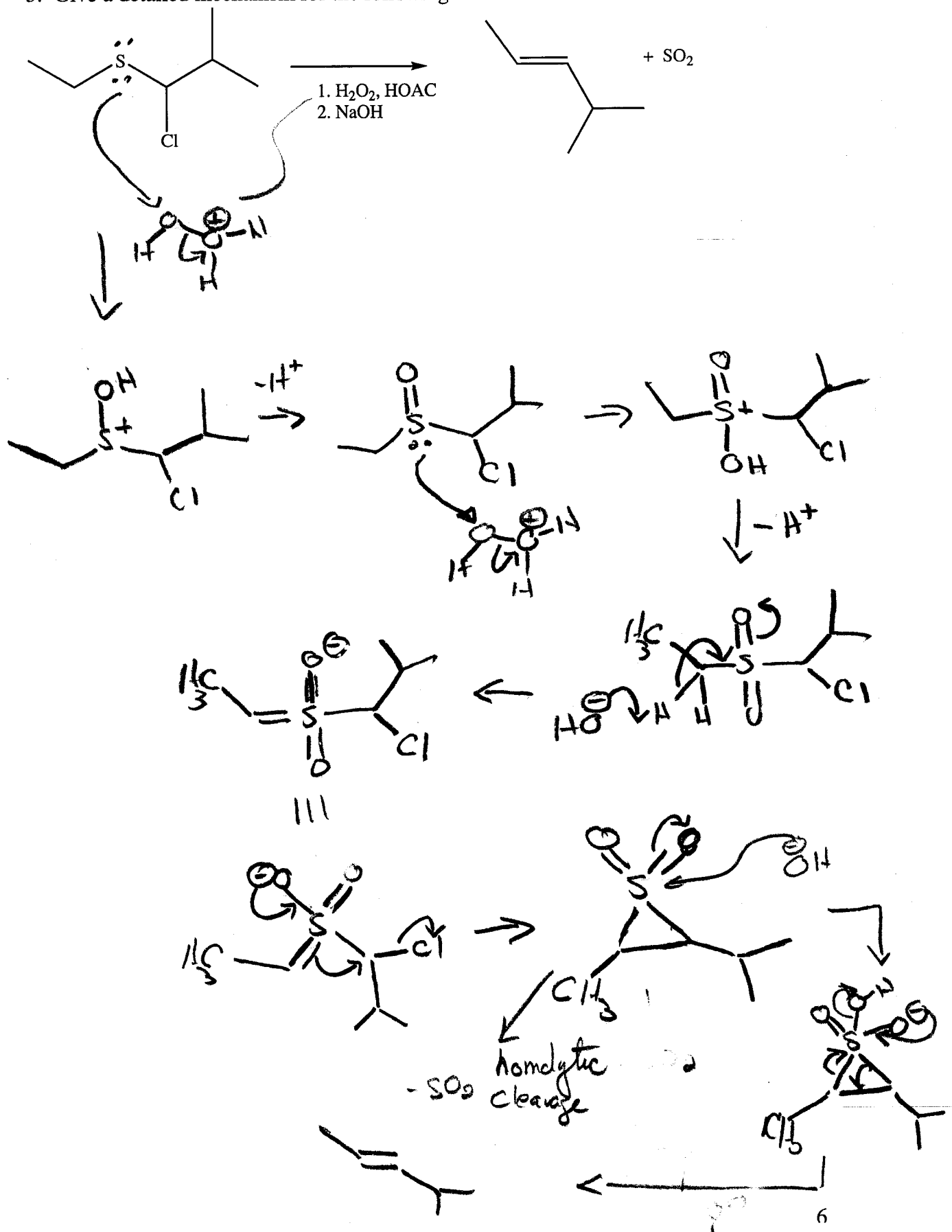
δ 4.5 very deshielded 2 O's

Again high Symmetry

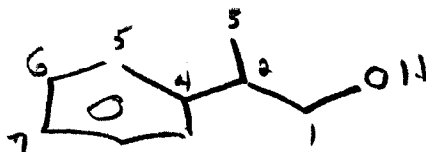
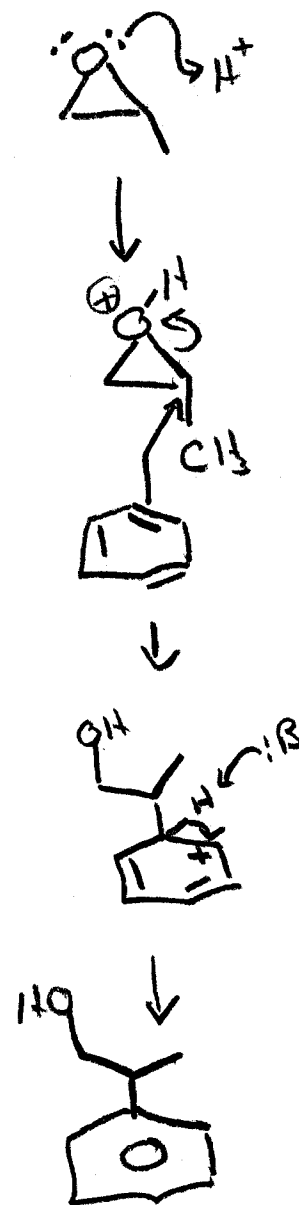
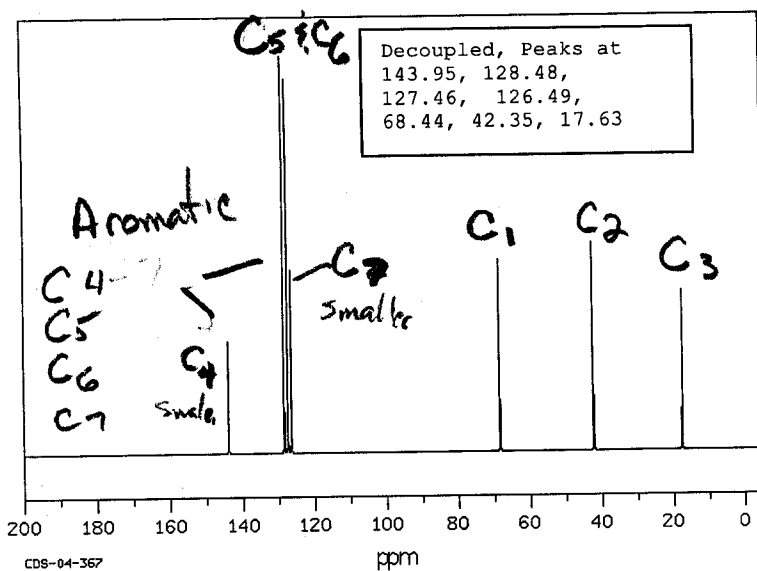
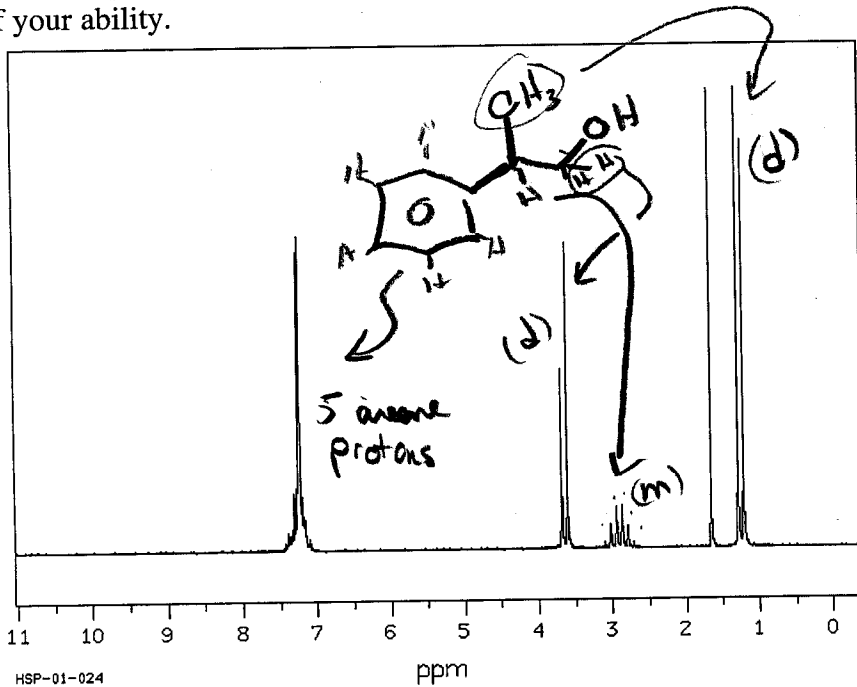
From B added  
4C, 2 mass units  
2xCH<sub>3</sub> + O



5. Give a detailed mechanism for the following reaction.



6. The following spectra are from a compound that is produced by the product of the acid catalyzed reaction with benzene and the epoxide formed from propene. Propose a structure, provide a detailed reaction mechanism, and assign the NMR signals to the best of your ability.



cts