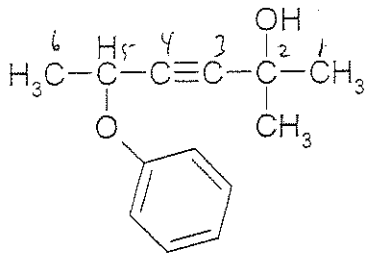
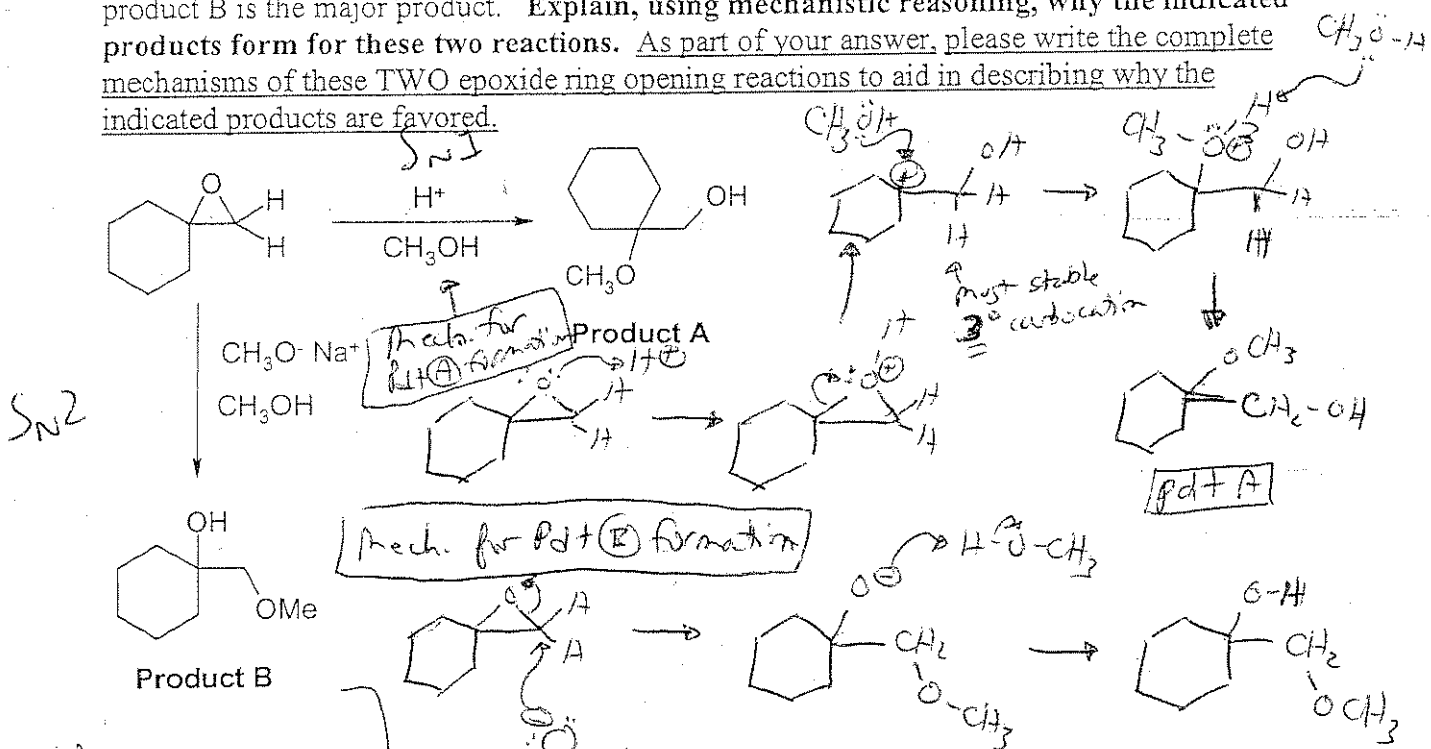


1. (4 pts) Give the IUPAC name for the following compound.



2-methyl-5-phenoxy-3-hexyn-2-ol

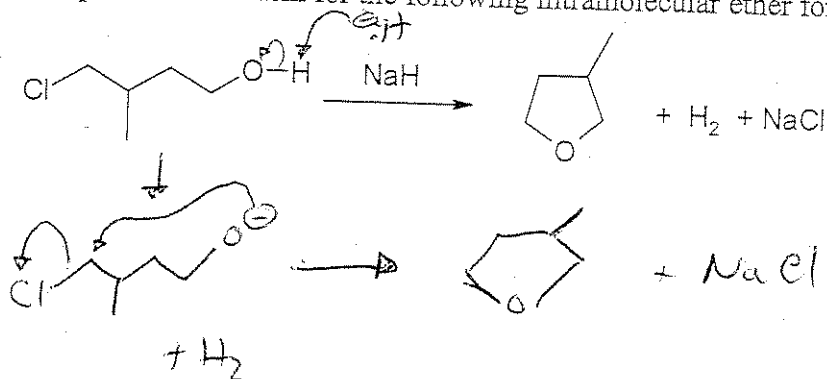
2. (9 pts) When the epoxide shown below is treated with acid and methanol product A is isolated as the major product. When the same epoxide is treated with sodium methoxide in methanol, product B is the major product. Explain, using mechanistic reasoning, why the indicated products form for these two reactions. As part of your answer, please write the complete mechanisms of these TWO epoxide ring opening reactions to aid in describing why the indicated products are favored.



The ring opening rxn that forms $\text{pd}(\text{A})$ goes by an $\text{S}_{\text{N}}1$ mechanism because the nucleophile is weak (CH_3OH) and the oxygen is protonated (Carbocation will form on most highly subst. carbon: 3° vs 1°) make a better leaving group. As can be seen in the mech. above, this pathway is mainly $\text{pd}(\text{A})$.

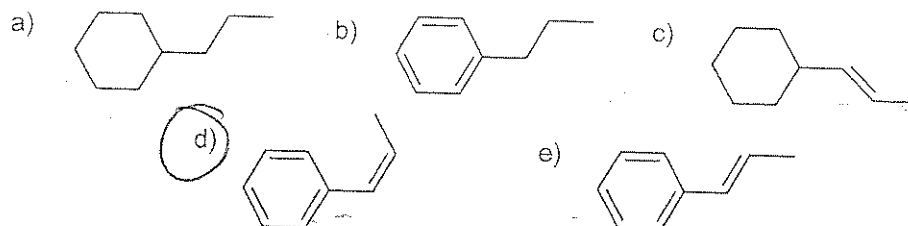
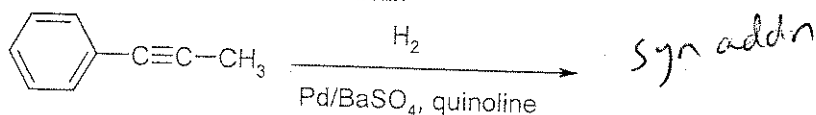
In the ring opening rxn that forms $\text{pd}(\text{B})$ the strong nucleophile, CH_3O^- , attacks the less hindered carbon (1° vs 3°) because the rxn takes place by an $\text{S}_{\text{N}}2$ mechanism. This pathway gives $\text{pd}(\text{B})$ as the major $\text{pd}(\text{t})$.

3. (5 pts) Draw a stepwise mechanism for the following intramolecular ether formation reaction.



4. Multiple Choice. Circle the best answer. (15 pts; 3 each).

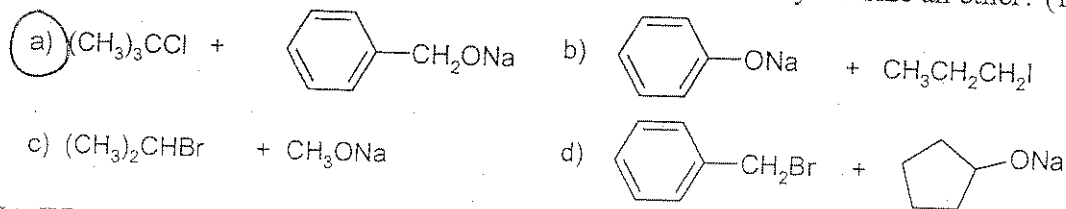
I. What is the product of this reaction?



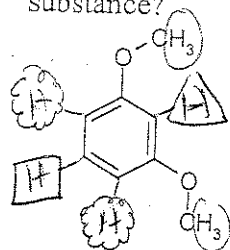
II. Compared to ^1H -NMR spectroscopy, why do ^{13}C -NMR spectra usually require using more sample and/or collecting more scans?

- a) Carbon has a higher atomic weight than hydrogen
- b) ^{13}C has a lower natural abundance relative to hydrogen
- c) ^{13}C resonates over a larger range on the chemical shift scale
- d) The ^{13}C spectrometer frequency is larger than for ^1H
- e) The ^1H spectrometer frequency is lower than for ^{13}C

III. Which of these reaction conditions could NOT be used to synthesize an ether? (1 answer)

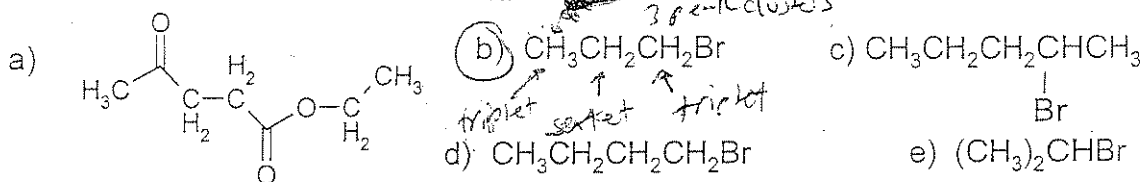
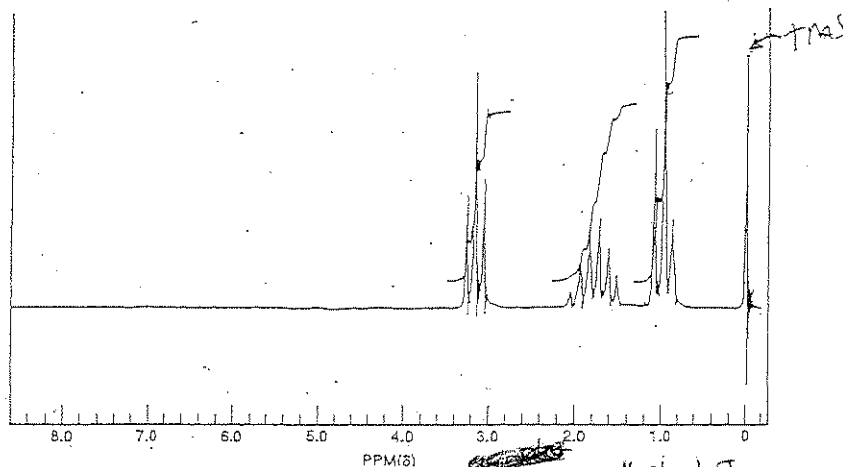


IV. What is the number of chemical shift equivalent groups of hydrogen atoms in this substance?



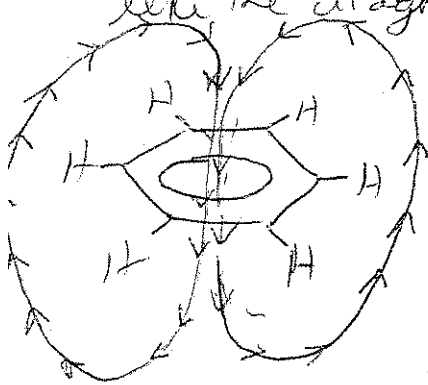
- a) 2 b) 3 c) 4 d) 5 e) 6

V. To which of these substances does the following $^1\text{H-NMR}$ spectrum correspond?



5. (8 pts) An alkene hydrogen atom has a chemical shift that ranges from 3.8–6.5 ppm while a hydrogen on an aromatic ring has a chemical shift that can range from 6.0–8.8 ppm. (See Table 11.3). Both of these types of hydrogen atoms are attached to sp^2 hybridized carbon atoms and consequently the electronegativity of these carbon atoms are similar. The difference in the chemical shifts for these two types of H atoms can be explained by magnetic anisotropy. Please explain what magnetic anisotropy is in relation to aromatic rings and how it causes the aromatic hydrogen signals to be observed further downfield compared to alkene hydrogen atoms.

In aromatic rings the electrons that move around the ring cause the formation of a magnetic field that has field lines that look like the diagram below (if you could see them, which you can't).



In the region outside of the ring (where the aromatic ring hydrogens are) this ring current induced magnetic field is in the SAME direction as the external magnetic field (it reinforces it). This

extra magnetic field produced by the circulating electrons in the ring causes the aromatic hydrogens to appear to be more deshielded + hence the aromatic proton signals are more downfield (higher ppm).

6. (16 pts) The following is a listing of the $^1\text{H-NMR}$ spectral data of a compound with a molecular formula of $\text{C}_{10}\text{H}_{12}\text{O}_2$.

δ 1.30, 3H, triplet; δ 2.35, 3H, singlet; δ 4.29, 2H, quartet; δ 7.17, 2H, doublet; δ 7.85, 2H, doublet

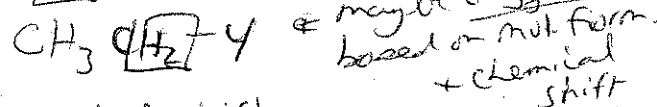
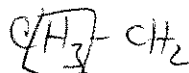
a) How many elements of unsaturation are in this compound?

$$\frac{2C + 2 - H + N - X}{2} = \frac{2(10) + 2 - 12}{2} = \frac{10}{2} = 5$$

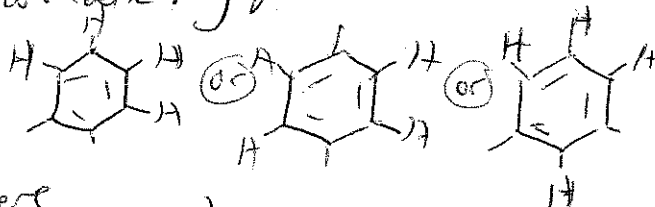
b) Propose a structure for this compound and place your final answer in the box. Be sure to show any partial structures you determine below and correlate these structures to their chemical shifts in order to receive partial credit.

ppm	Integration	Splitting
1.30	3H	triplet
2.35	3H	singlet
4.29	2H	quartet
7.17	2H	doublet
7.85	2H	doublet

X = electroneg. group
Y = electronegative groups

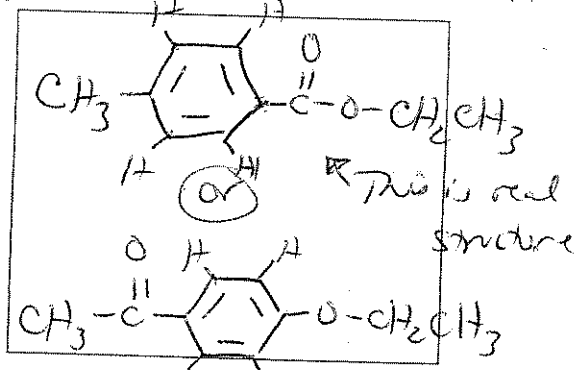
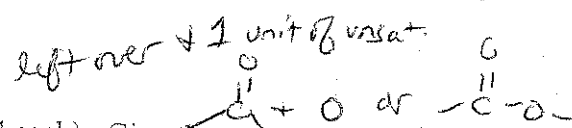
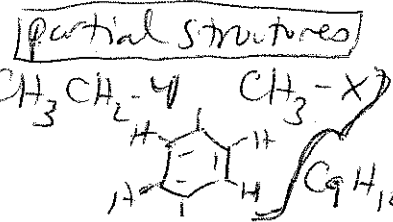
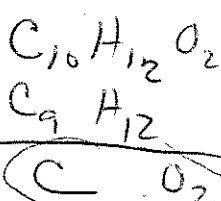


Chemical shift + units of unsat. indicates aromatic ring protons (See Table 11.3)

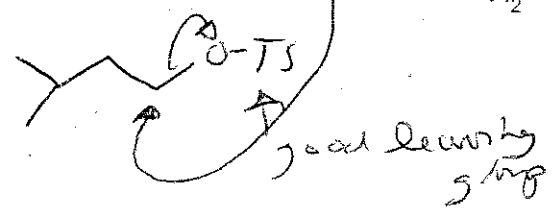
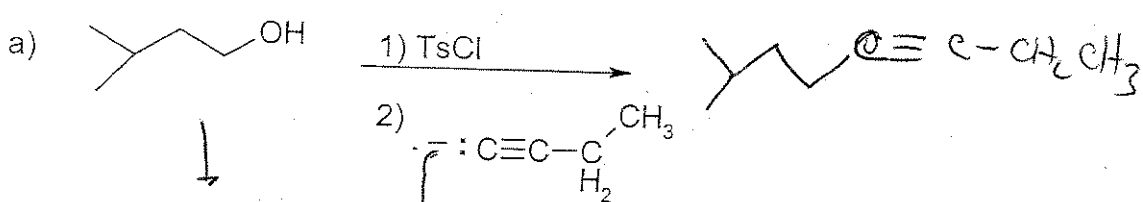


This subst. pattern of aromatic ring best fits splitting pattern observed here

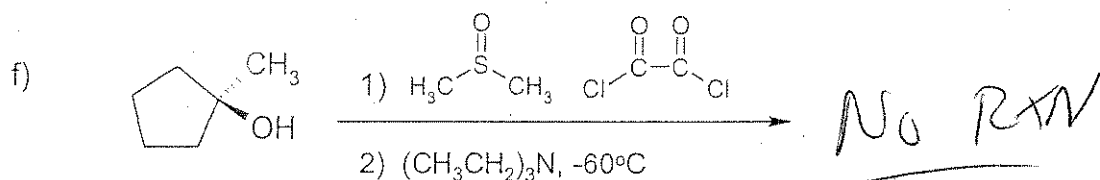
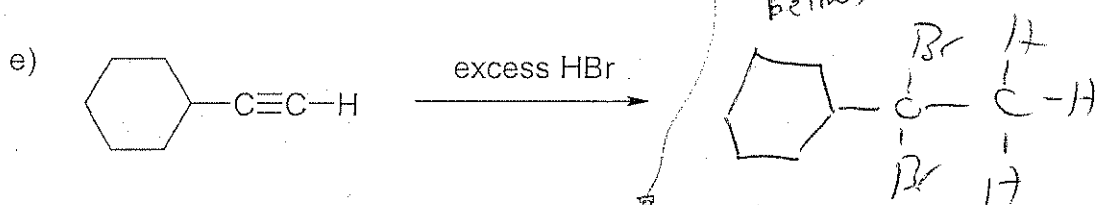
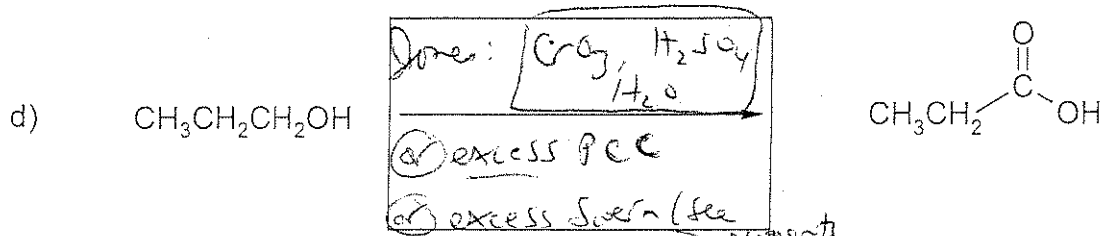
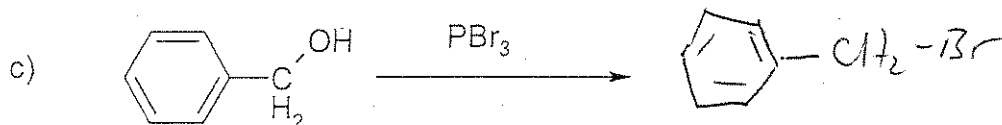
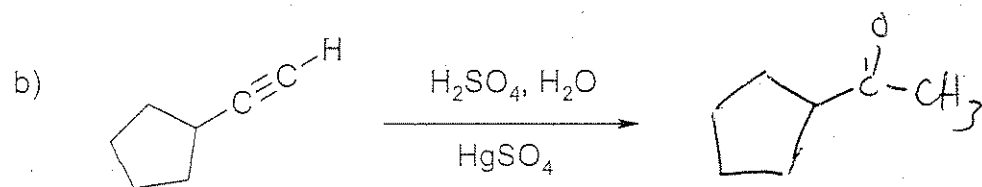
(4 units of unsat. used)



7. (24 pts, 4 each) Give the major product(s) or reagents needed for the following transformations. Be sure to show stereochemistry when necessary.

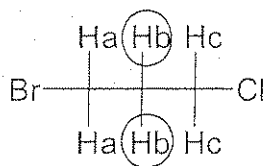


Either structure above is full credit

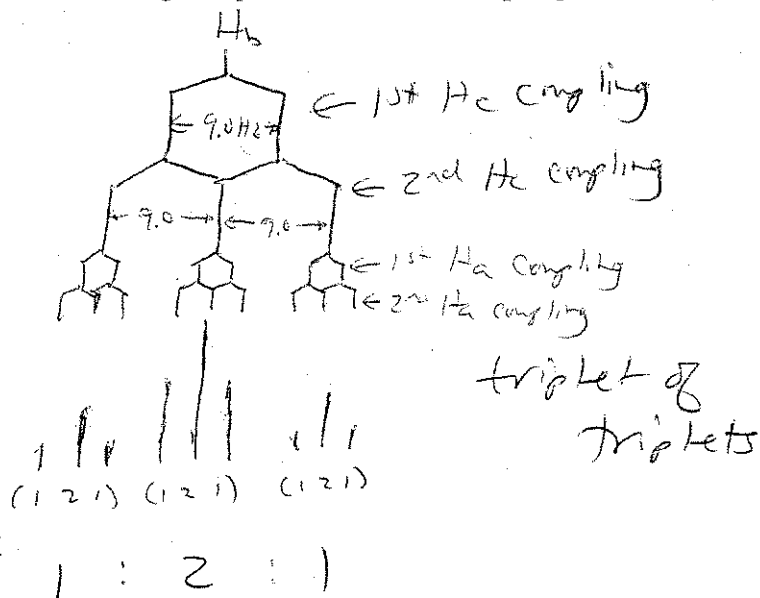


8. (1 pt) True or False An alcohol is more highly oxidized than an aldehyde.

9. (6 pts) Draw a branching diagram to show the expected splitting pattern that would be observed for the H_b hydrogens, circled below, in the following compound. Note the coupling constants given below for J_{ab} and J_{bc} .



$J_{ab} = 2.0 \text{ Hz}; J_{bc} = 9.0 \text{ Hz}$



10. (12 pts) **Multistep synthesis.** Show how you would synthesize 4-methylpentanal (shown below) starting from acetylene (ethyne) and 1-bromo-2-methylpropane. You can use any reagents you deem necessary for your synthesis. Be sure to show the structures of intermediate structures along the pathway to the final product. (Note: You don't need to write any mechanisms here.)

