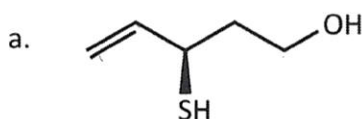


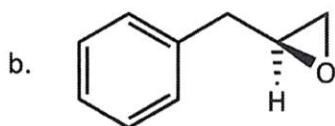
1. Provide IUPAC names for the following compounds.

(20 points)



(R)-3-mercapto-4-penten-1-ol
or

(R)-3-sulfamylpent-4-en-1-ol



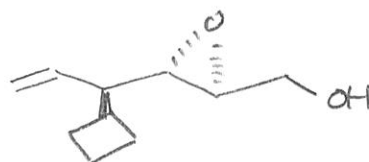
((S)-2,3-epoxypropyl) benzene
or

(S)-2-benzyl oxirane

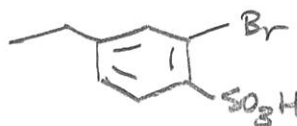
2. Provide structures for the following compounds.

(30 points)

a. (2S,3S,4R)-2,3-epoxy-4-cyclobutylhex-5-en-1-ol



b. 4-ethyl-2-bromobenzenesulfonic acid



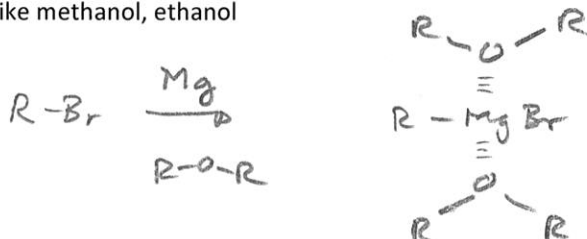
c. ethylene oxide



aka oxirane aka epoxyethane

3. Explain why ether solvents, such as Et₂O and THF, are used for preparing and using Grignard reagents, instead of solvents like methanol, ethanol

(5 points)



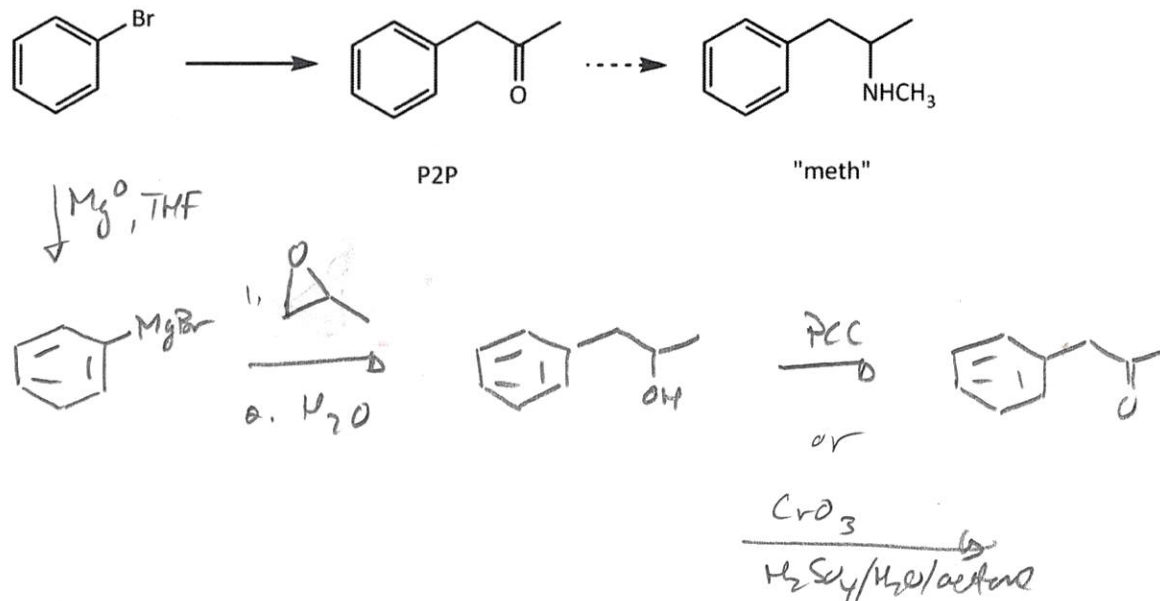
ethers offer stabilization to the metal center of the Grignard reagent



Grignard reagents are exceedingly basic and will simply deprotonate alcohol solvents, before they can do any type of addition reaction - they are incompatible!

4. The ketone shown below, P2P, is an infamous starting material for the street drug methylamphetamine ("meth"). Show how to convert bromobenzene into this ketone using any reagents that you want, but the synthesis must include an *epoxide* at some point. Show all intermediates.

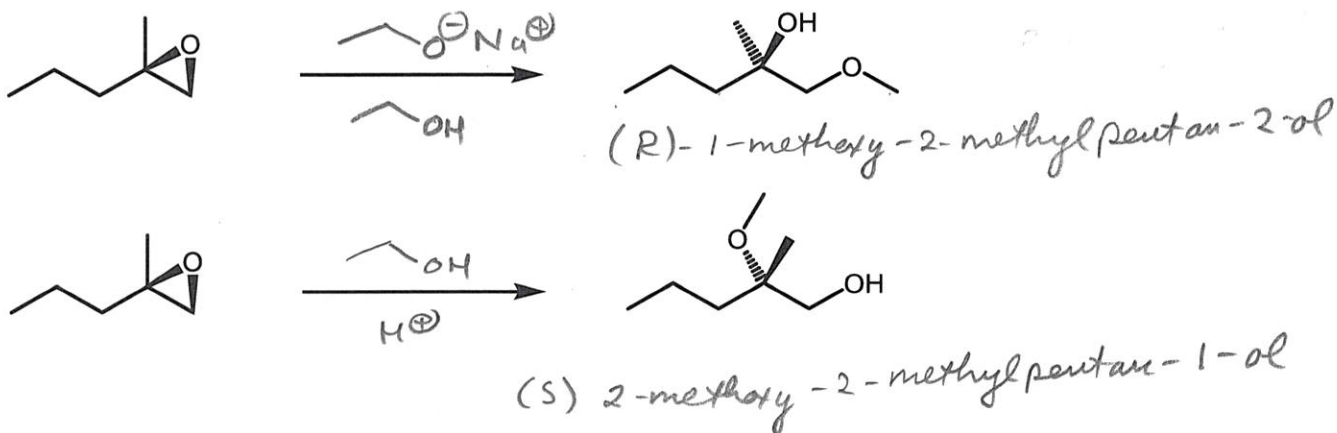
(20 points)



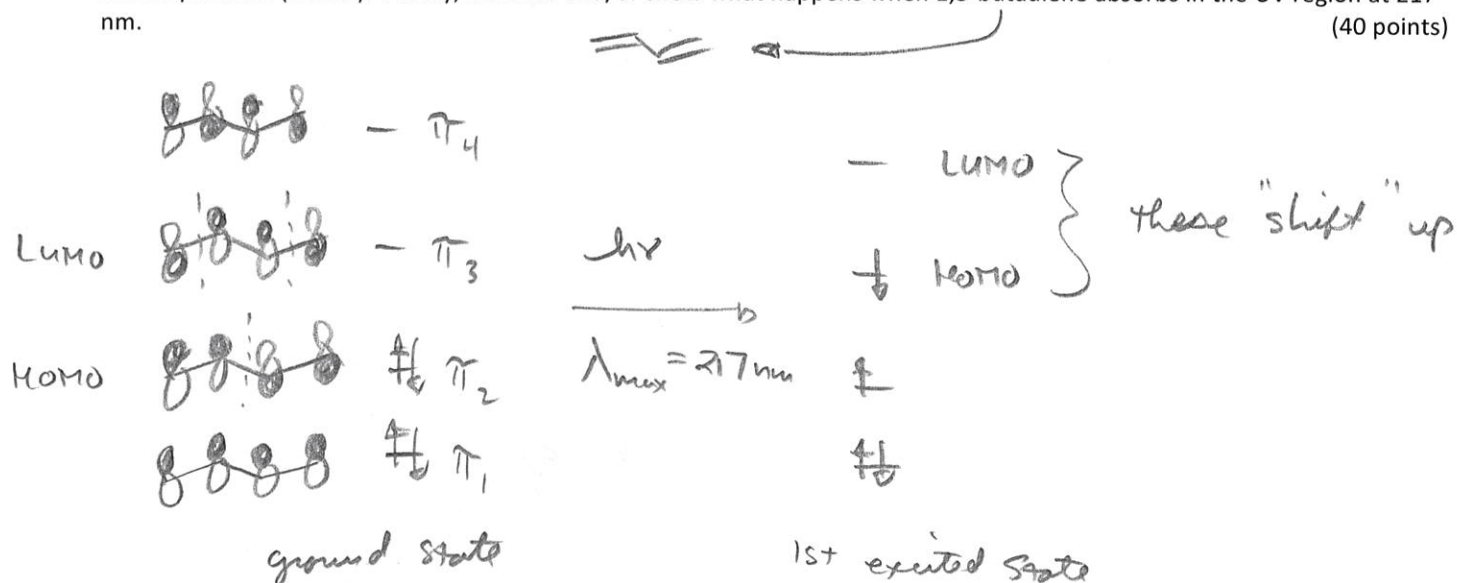
5. Show the reagents necessary to accomplish the two transformations. Explain your reasoning behind the choice of reagents, i.e., why they give the different products (20 points)

Extra Credit: Provide IUPAC names for the products (including stereochemistry)

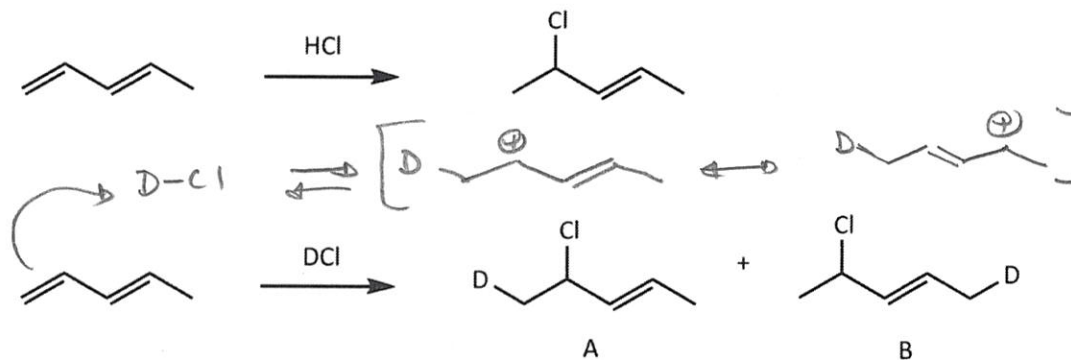
(10 EC points)



6. Draw the pi molecular orbitals of 1,3-butadiene and their relative energy levels. Show how these orbitals are filled with electrons in the ground state. Indicate which orbital is the *Highest Occupied MO* (HOMO) and which is the *Lowest Unoccupied MO* (LUMO). Finally, describe and/or show what happens when 1,3-butadiene absorbs in the UV region at 217 nm. (40 points)



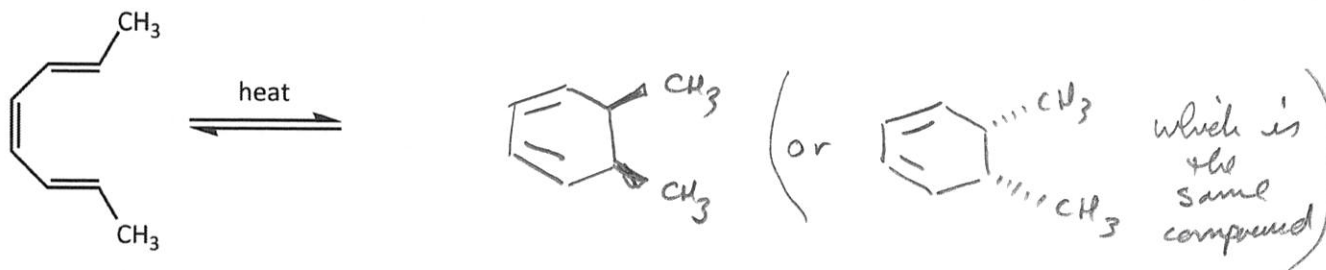
7. The reaction of 1,3-pentadiene with hydrogen chloride (HCl) gives only one product (shown as a *racemate*). However, the reaction with deuterium chloride (DCI) produces two products, A and B (also as *racemates*), and the ratio of these is temperature dependent. Which product, A or B is favored at low temperatures (0°C) and what happens to the ratio at higher temperatures (40°C)? Explain in terms of *kinetic vs thermodynamic control*. (20 points)



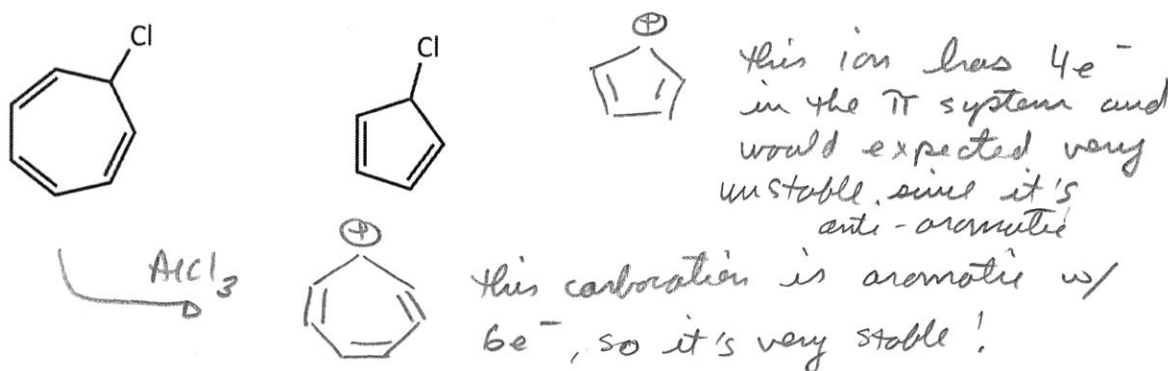
Product A is from 1,2-addition of the DCI and is formed faster than B, which is from 1,4-addition, at all temperatures. However, products A and B are same in terms of stability — both are disubstituted alkenes + 2°-allylic halides. The placement of the deuterium is insignificant in energy terms.

So, product A is favored at lower temperatures since it is formed irreversibly. At higher temperatures the reaction is reversible so Product A and B are in equilibrium and since they are the same stability would be 50/50 in concentration.

8. Show the product (or products) from the following *electrocyclic* reaction. Clearly show the stereochemistry of the product. (10 points)



9. One of the two compounds below reacts with aluminum chloride (AlCl_3) to form a stable carbocation easily and the other one doesn't. Which one is it? Explain. (10 points)

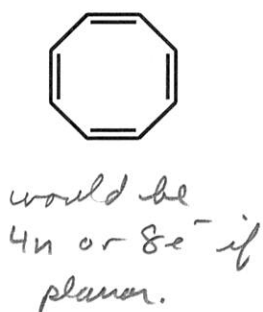


10. Unlike benzene, 1,3,5,7-cyclooctatetraene has two different carbon-carbon bond lengths, 1.33 Å and 1.46 Å and it is definitely not planar. Clearly explain why (draw pictures if necessary). (10 points)

Extra Credit: Suggest an alternate name for this compound.

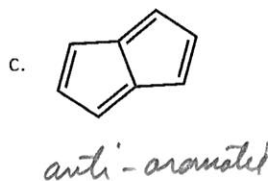
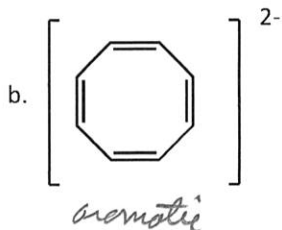
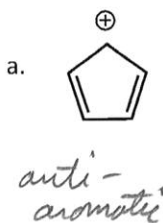
[8]annulene

(5 EC points)

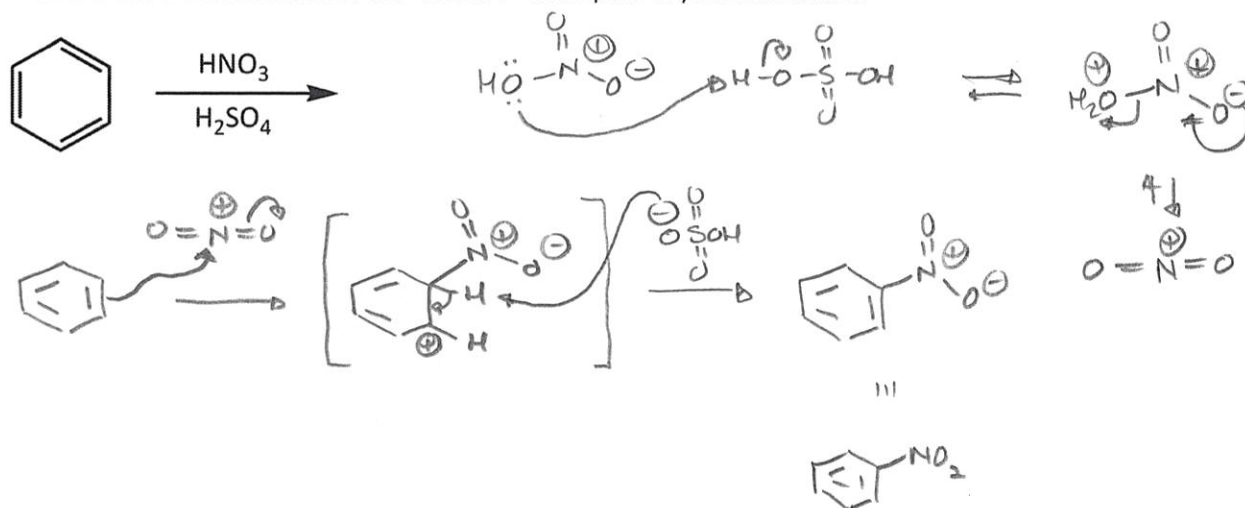


adopts the "tub" shape. This shape prevents the overlap and conjugation of adjacent π bonds, which in this case would give an anti-aromatic π system. The lack of conjugation leads to alternating short and longer C-C bonds.

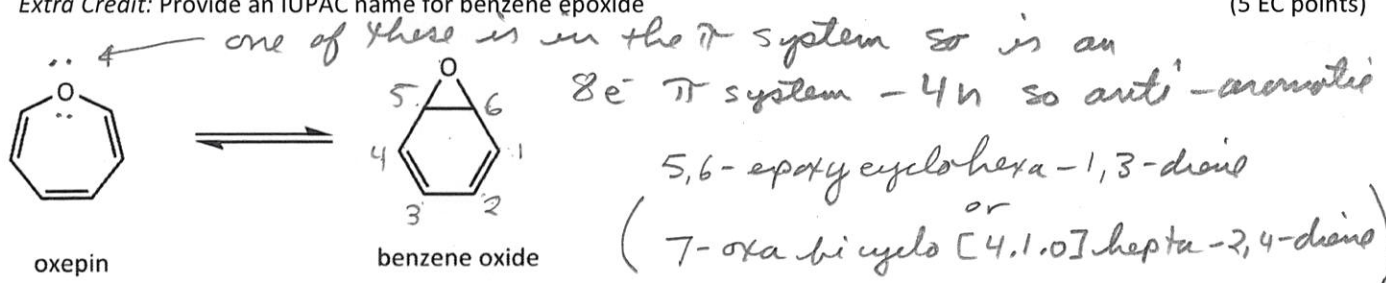
11. For each of the following molecules or ions indicate whether they are aromatic, anti-aromatic or non-aromatic. (20 points)



12. Show the product and complete mechanism for the following electrophilic aromatic substitution reaction. (15 points)
Be sure to show the formation of the "reactive" electrophile in your mechanism.

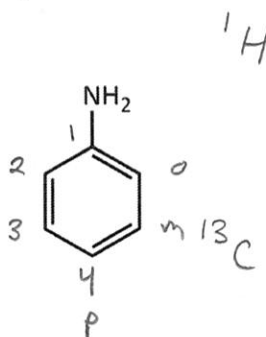


13. Oxepin is not a very stable compound! It undergoes rapid equilibrium with benzene oxide (the "epoxide" of benzene), which itself is not the most stable compound. Suggest a reason for the tendency of oxepin to undergo this equilibrium. (10 points)
Extra Credit: Provide an IUPAC name for benzene epoxide (5 EC points)



with the two lone pairs of electrons on the oxygen, one of which is in resonance w/ the π system, the ring is officially anti-aromatic

14. Use the NMR data sheets (from lecture) to calculate the proton (^1H) and carbon (^{13}C) NMR chemical shifts for aniline (shown below). Explain how the calculated chemical shift values for the *ortho* position can predict the electron density of that position relative to benzene, i.e., is it more or less electron rich than benzene? (20 points)



Handwritten calculations for NMR chemical shifts:

^1H

ortho: $7.36 - 0.71 = 6.65$

meta: $7.36 - 0.22 = 7.14$

para: $7.36 - 0.62 = 6.74$

^{13}C

C-1: $128.5 + 19.2 = 147.20$

C-2: $128.5 - 12.4 = 116.10$

C-3: $128.5 + 1.3 = 129.80$

C-4: $128.5 - 9.5 = 119.00$

the *ortho* positions are shielded relative to benzene therefore they are more electron rich than benzene