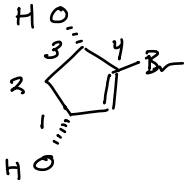
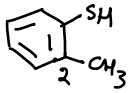
Name Key

1. Provide structures for the following compounds (don't forget stereochemistry!). (20 points)

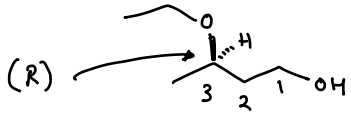
a. (1*R*,3*S*)-4-bromocyclopent-4-ene-1,3-diol



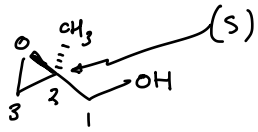
b. 2-methylbenzenethiol



c. (*R*)-3-ethoxybutan-1-ol

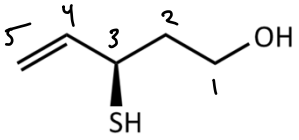


d. (2*S*)-2,3-epoxy-2-methylpropan-1-ol



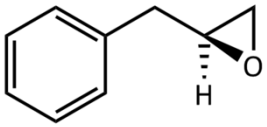
2. Provide IUPAC names for the following compounds. (10 points)

a.



(R)-3-mercaptopent-4-en-1-ol
or
(R)-3-sulfanylpent-4-en-1-ol

b.

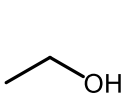


(S)-2-benzyloxirane
or
(S)-2-(phenylmethyl)oxirane
or
(S)-(2,3-epoxypropyl)benzene
or
(S)-1,2-epoxy-3-phenylpropane

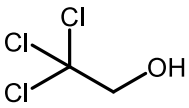
3. Explain the two trends in acidity for the following compounds (10 points)

always compare the conjugate base stability!

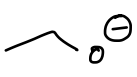
Trend 1



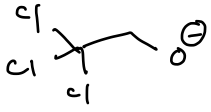
pK_a = 16



pK_a = 12.2



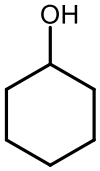
vs.



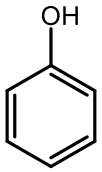
more stable

inductive effect of the CCl_3 withdraws electron density from the oxygen

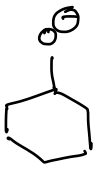
Trend 2



pK_a = 18



pK_a = 10



vs

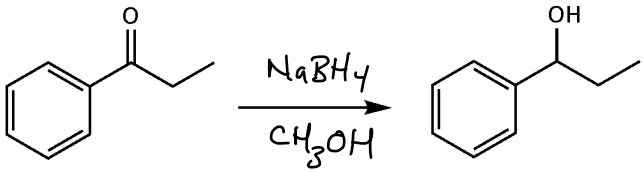
3 resonance forms

more stable

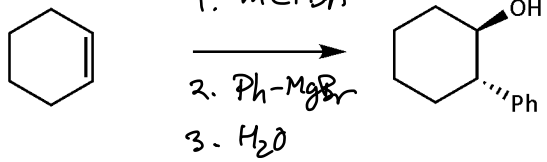
resonance effect provides for delocalization of ⊖ charge

4. Show the reagents and conditions to accomplish the following (more than one step may be necessary). (15 points)

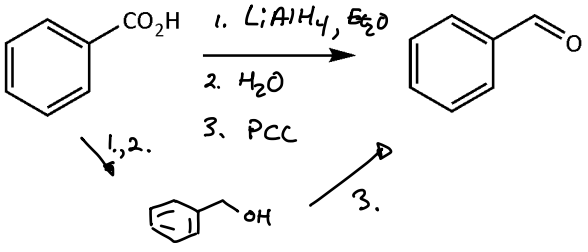
a.



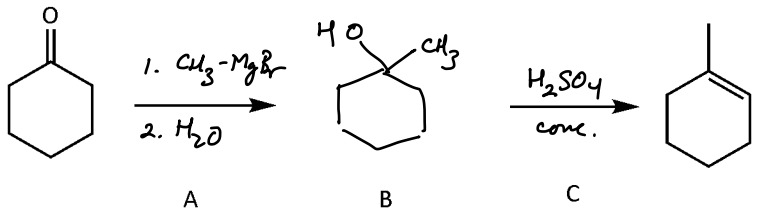
b.



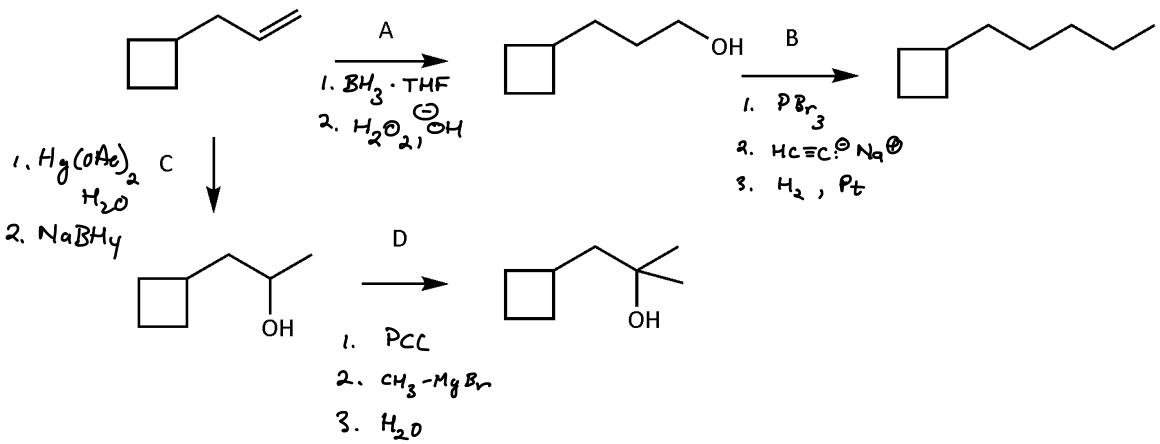
c.



5. Show the reagents A and C, and the structure of B that leads to the product shown in the following synthesis. (15 points)



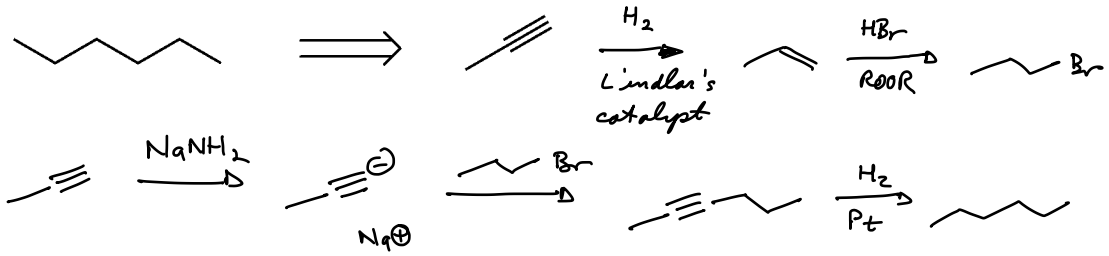
6. For the following series of reactions, fill in the reagents necessary to accomplish each transformation (some of them require more than one step – be sure to use numbers (1., 2., etc) to show separate steps when necessary. You do not need to show any intermediates. (40 points)



7. Explain why ether solvents, such as Et_2O and THF, are used for preparing and using Grignard reagents (R-MgBr), instead of solvents like methanol or ethanol. (5 points)

Grignard reagents are both strongly nucleophilic and strongly basic!
$R-Br \xrightarrow{Mg} R-MgBr$ which behaves like $R:^{\ominus}\ ^{\oplus}MgBr$ a carbanion
Since the pKa of the conjugate acid from any carbanion is in the range 50-25 (e.g. ethane to acetylene), any alcohol (pKa 16-19) will simply protonate the formed Grignard.

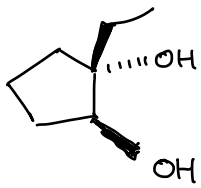
8. Devise a synthesis of hexane from the indicated starting compound. The synthesis should only use the starting material shown for the source of carbon. You can use any reagents needed, but the final six carbons of hexane must come from only 1-propyne. (10 points)



9. Starting with the epoxide shown below, show the product in each case. Be clear about the stereochemistry of the products material. Explain why they give the different products (20 points)

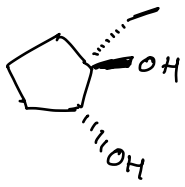
Extra Credit: Provide IUPAC names for the products (including stereochemistry) (10 EC points)

a. H_3O^+ → **A**



(1S,2S)-1-ethyl cyclopentane-1,2-diol

b. ^-OH, H_2O → **B**

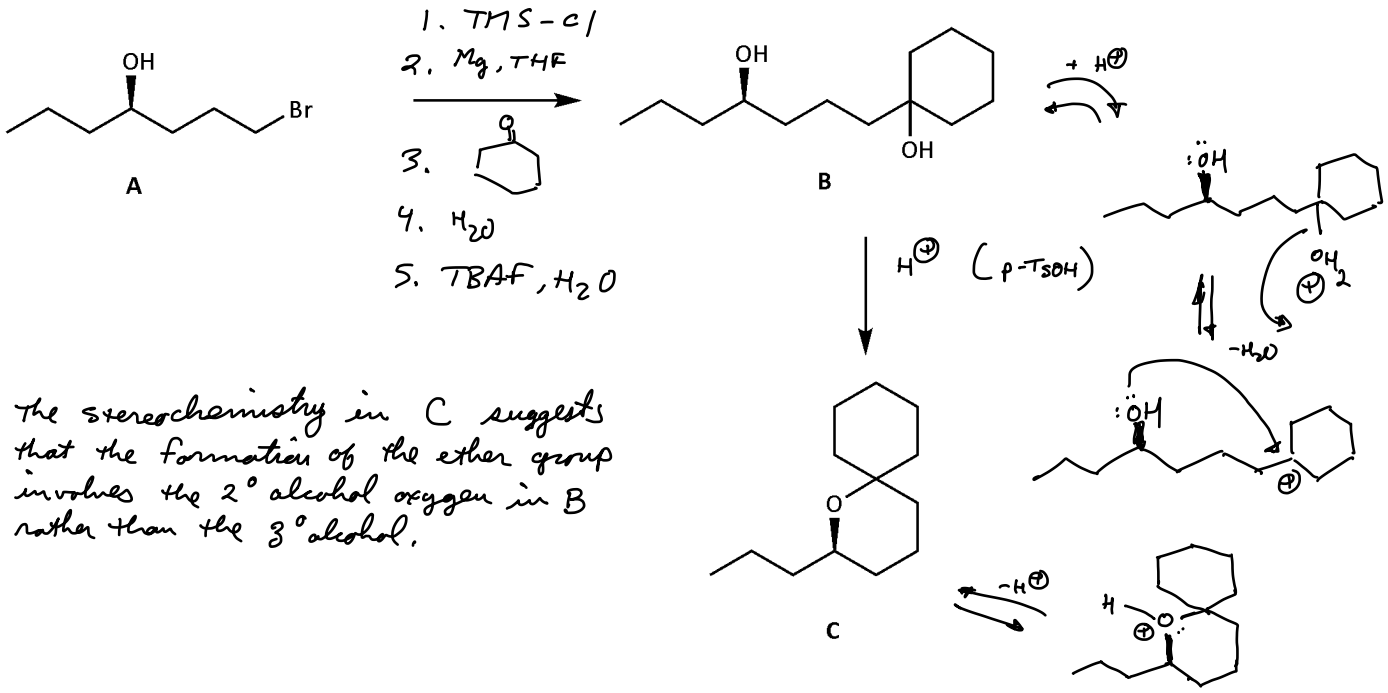


(1R,2R)-1-ethyl cyclopentane-1,2-diol

under basic conditions the nucleophile attacks the least hindered (less substituted) carbon

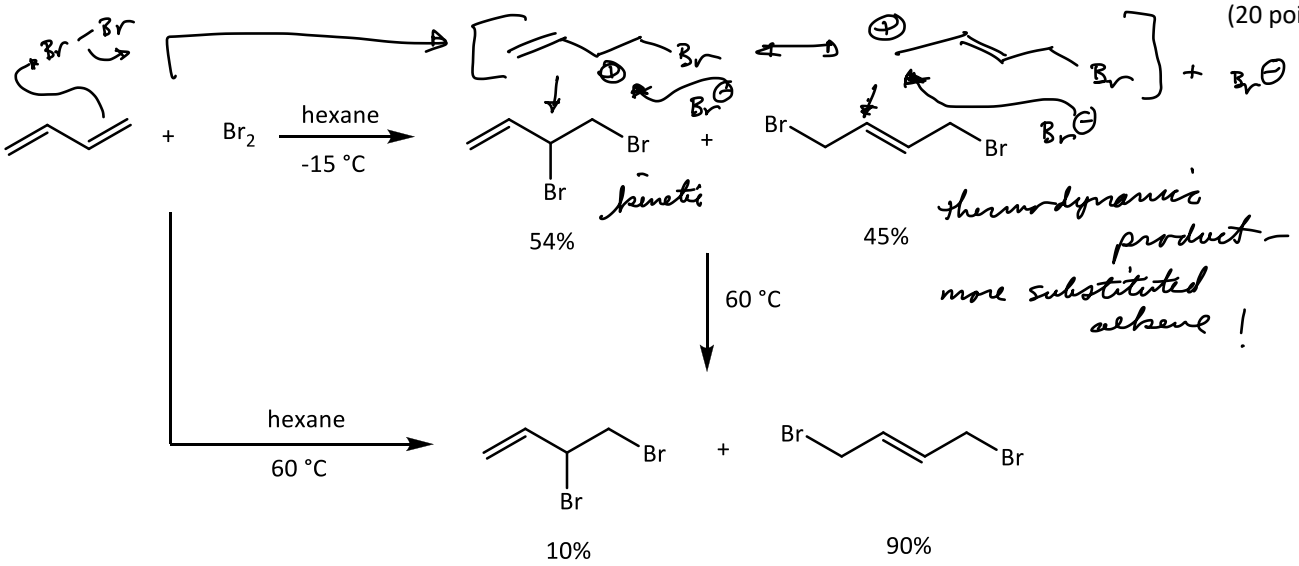
under acidic conditions, the epoxide is protonated and the more substituted carbon is most reactive

10. Show the reagents and conditions needed to convert **A** to **B** using a Grignard reaction – you will need to use a protecting group. Suggest how to prepare C from B. Note the stereochemistry in C. (10 points)



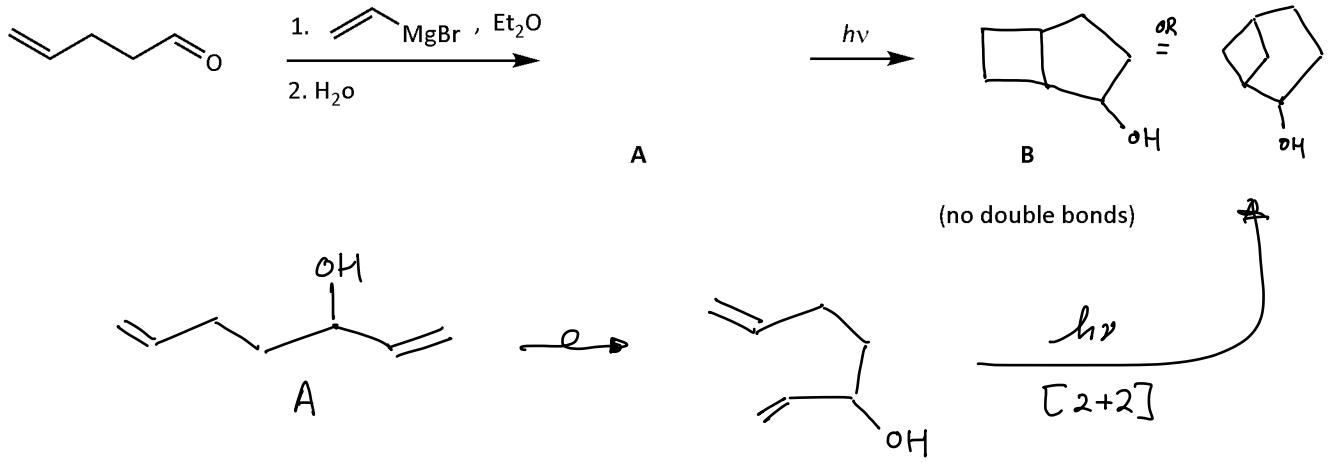
The stereochemistry in C suggests that the formation of the ether group involves the 2° alcohol oxygen in B rather than the 3° alcohol.

11. Consider the reaction shown below. In terms of the mechanism, clearly account for the formation of the two products and in the observed ratios at the different temperatures. Note that if the reaction is run at the colder temperature and then the mixture is warmed to 60 °C, the ratio of products is the same as if run only at the higher temperature (this is a hint). (20 points)

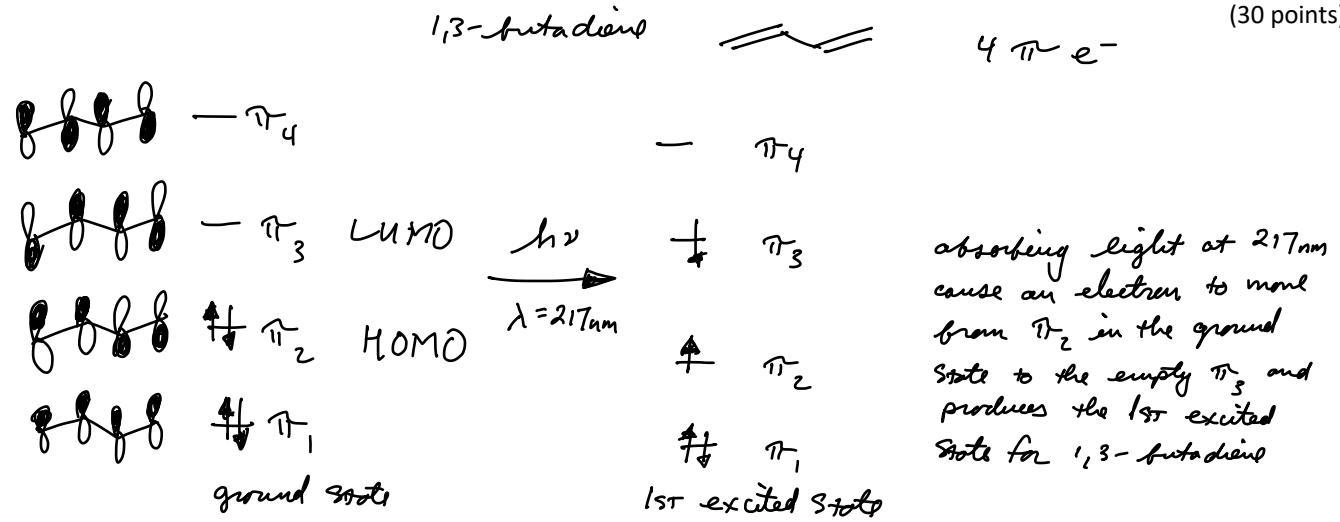


- at low temp. the bromide attacks the closest carbocation since it is faster – products are formed irreversibly
- at warmer temp. the formation of the dibromides are reversible so 1,2- and 1,4- products are in equilibrium and the more stable 1,4- product is favored

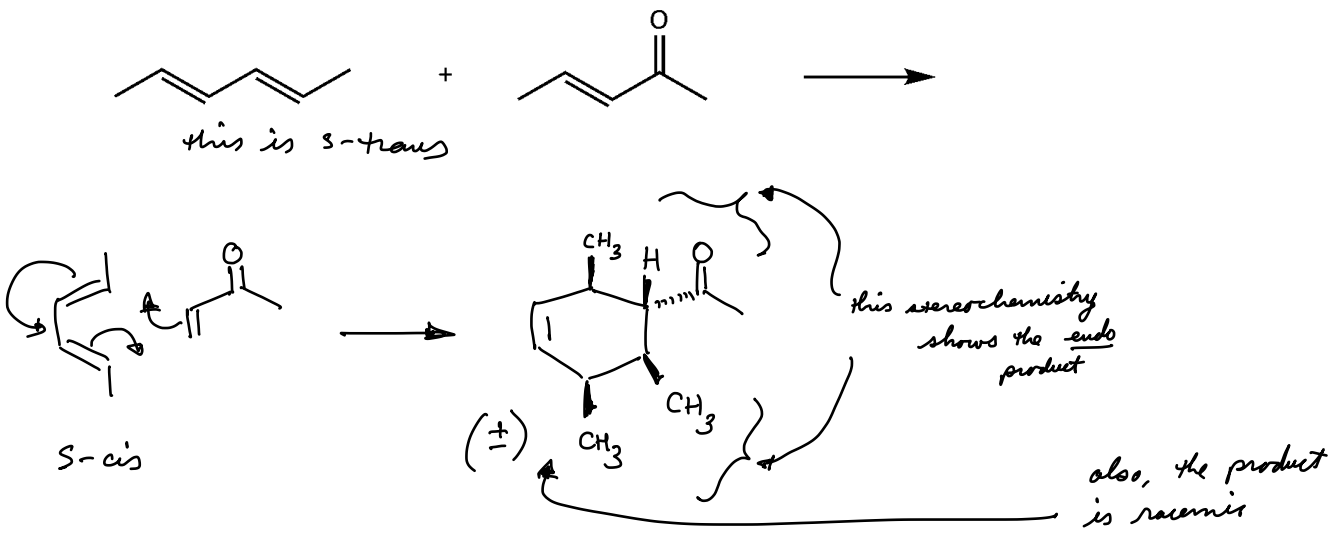
12. Consider the synthesis below. Suggest the structure of A and B – note that B has no double bonds (20 points)



13. Sketch 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 what happens when 1,3-butadienene absorbs in the UV region at 217 nm. (30 points)

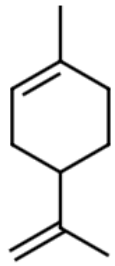


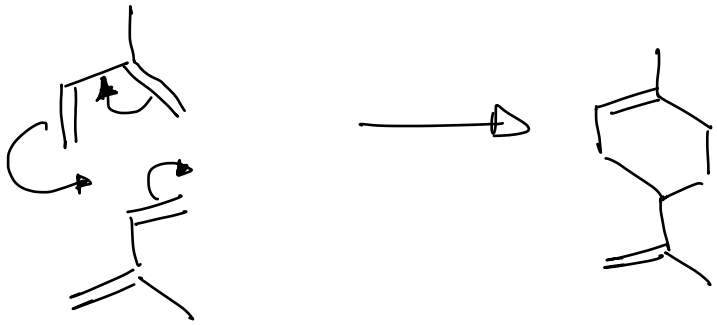
14. Show the *major* product from the following reaction. Be very clear about the stereochemistry of the product and the number and type of any isomers that may (or may not be) produced. (15 points)



15. The natural product limonene (below) is found in many plants and herbs, most notably in orange peels (guess what it smells like…). Although Nature uses a completely different approach than Diels and Alder would use, how might you prepare limonene using the Diels-Alder reaction? What would the starting materials look like?

    Also, provide an IUPAC name for limonene. (10 points)





1-methyl-4-(1-methylethenyl)cyclohex-1-ene

or

1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene