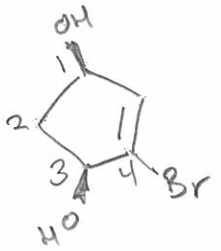
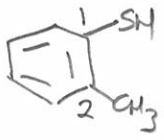
1. Provide structures for the following compounds (don't forget stereochemistry!). (20 points)

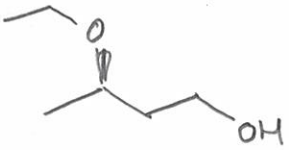
a. (1*R*,3*S*)-4-bromocyclopent-4-ene-1,3-diol



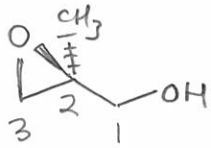
b. 2-methylbenzenethiol



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

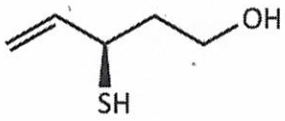


d. (2*S*)-2,3-epoxy-2-methylpropan-1-ol



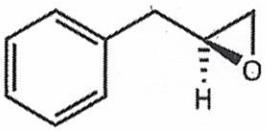
2. Provide IUPAC names for the following compounds. (10 points)

a.



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

b.



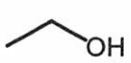
(S)-2-benzyloxirane

or

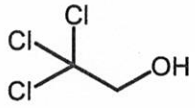
(2S)-1,2-epoxy-3-phenylpropane

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

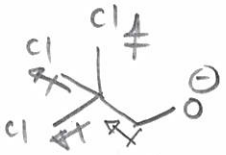
Trend 1



$pK_a = 16$

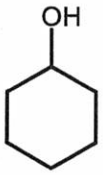


$pK_a = 12.2$

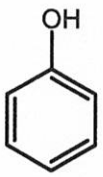


inductive withdrawal by chlorines stabilizes this conjugate more than  so the acid is more likely to give up its proton

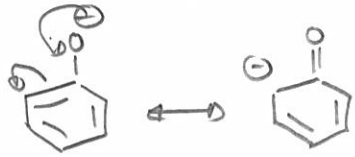
Trend 2



$pK_a = 18$

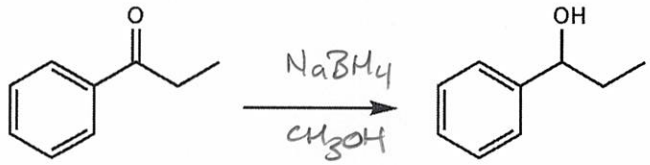


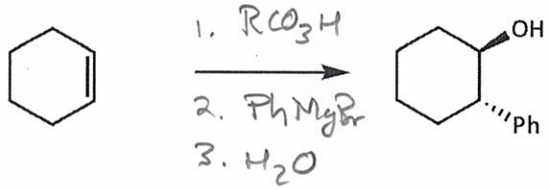
$pK_a = 10$

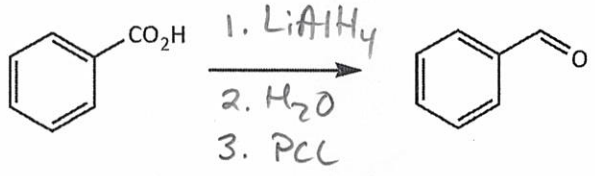


resonance stabilization of the conj. base makes it more stable than the conjugate from cyclohexanol. So phenol is more likely to give up its proton.

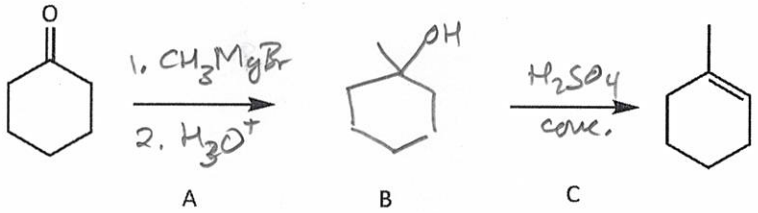
4. Show the reagents and conditions to accomplish the following (more than one step may be necessary). (15 points)

a. 

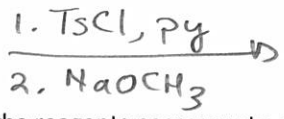
b. 

c. 

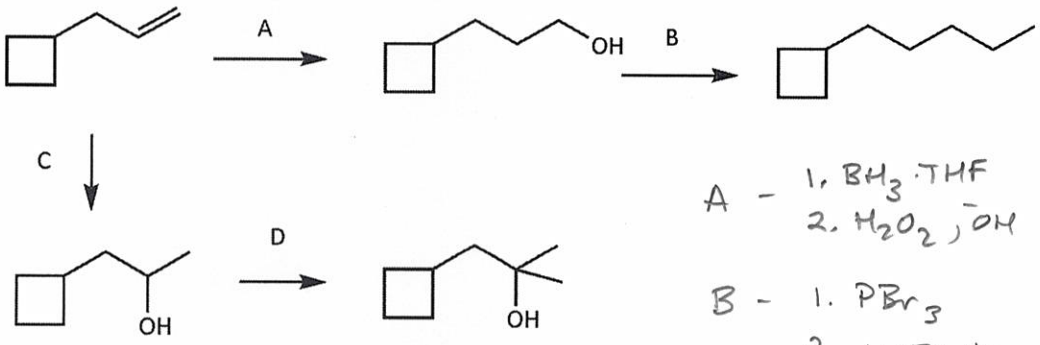
5. Show the reagents A and C, and the structure of B that leads to the product shown in the following synthesis. (15 points)



or



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)



A – 1. $BH_3 \cdot THF$
2. H_2O_2, ^-OH

B – 1. PBr_3 (or HBr, Δ)
2. $HC{\equiv}CNa$
3. H_2, Pt

C – 1. $Hg(OAc)_2$, H_2O
2. $NaBH_4$

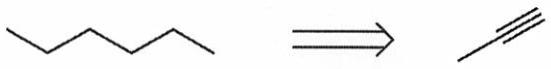
D – 1. PCC
2. CH_3MgBr
3. H_3O^+

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, ethanol. (5 points)

answers published elsewhere

8. For following two problems, devise a synthesis of hexane from the indicated starting compound. Each synthesis should only use the starting material as shown for the source of carbon. You can use any reagents needed but the six carbons of hexane must come from either 1-propyne (in a.) or propanoic acid (in b.) (20 points)

a.



e.g.

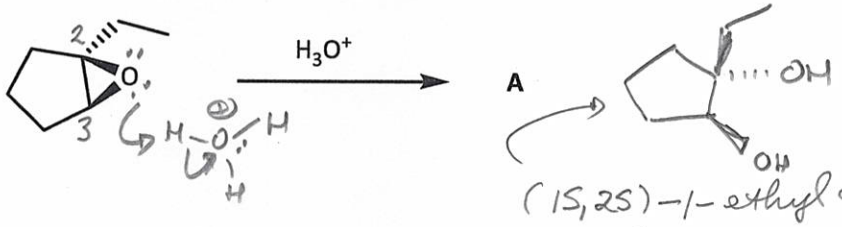
b.

e.g.

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)

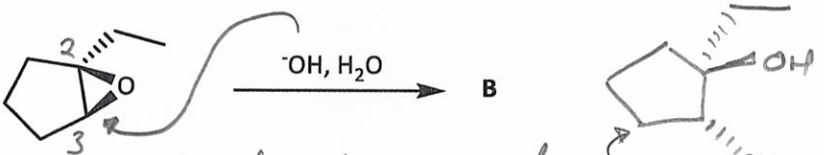
a.



nucleophile attacks carbon 2

(1S,2S)-1-ethylcyclopentane-1,2-diol

b.



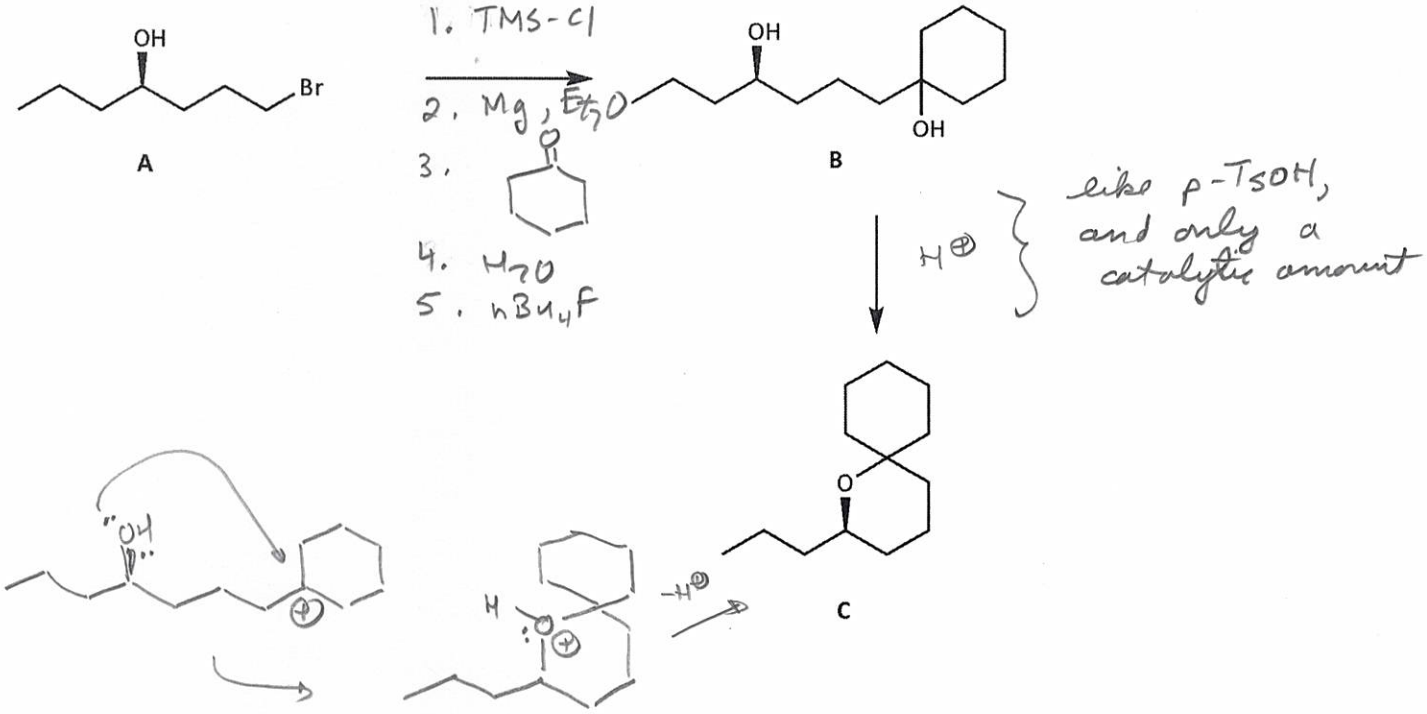
nucleophile attacks carbon 3

(1R,2R)-1-ethylcyclopentane-1,2-diol

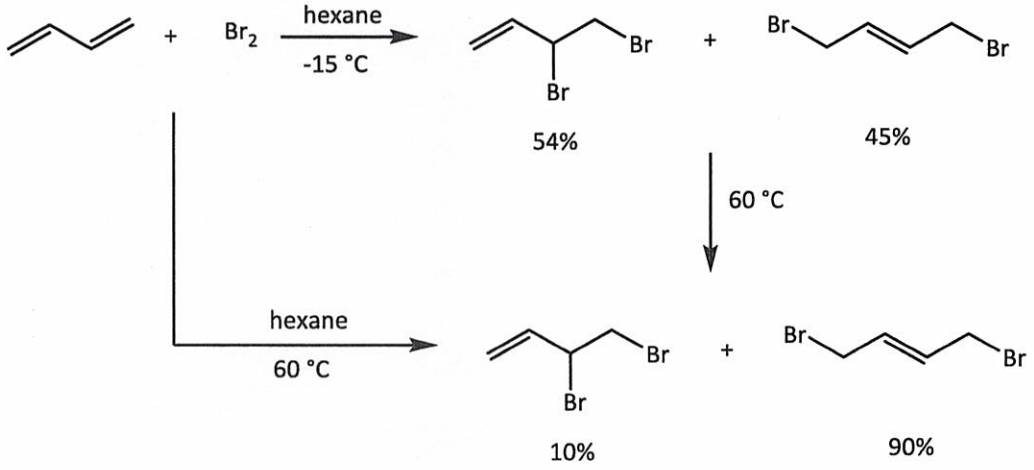
under basic, strongly nucleophilic conditions the epoxide is opened at least hindered carbon – backside attack gives shown stereochemistry

with weak nucleophiles like water, acidic conditions are required to protonate the epoxide and make the oxygen a better leaving group. This results in the electronic effect of creating a greater $\delta^{\oplus}$ at more substituted carbon.

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)

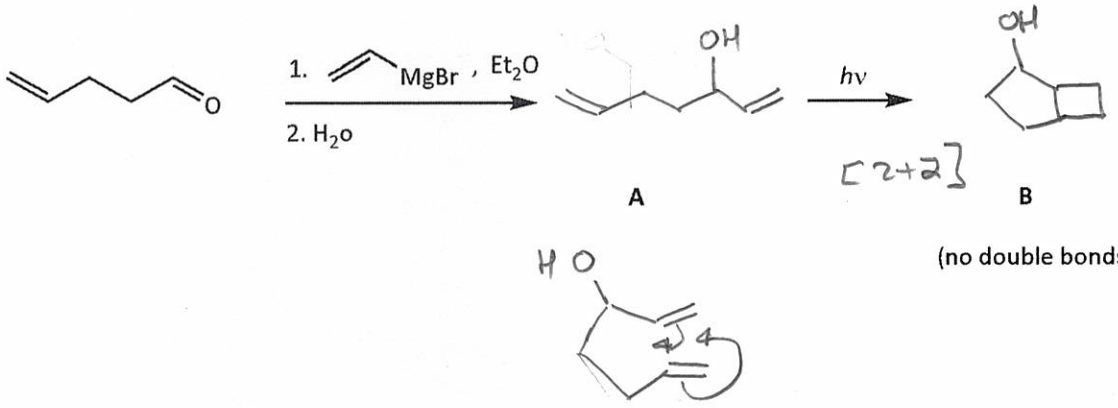


11. Consider the reaction shown below. In terms of the mechanism, clearly account for the formation of the two products and in the observed ratios at the different temperatures. Note that if the reaction is run at the colder temperature and then the mixture is warmed to 60 °C, the ratio of products is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

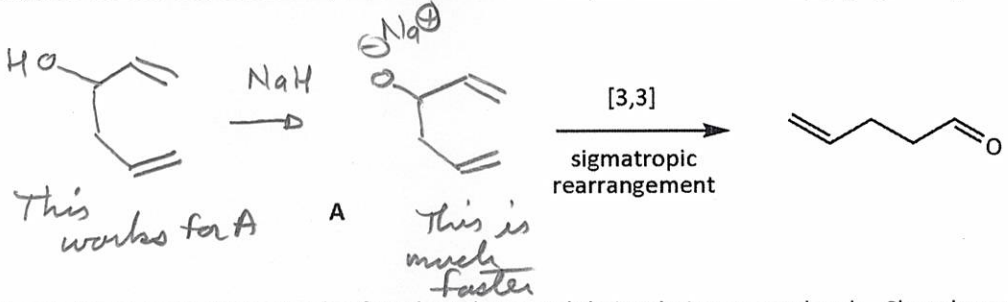


answers already pasted elsewhere

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



13. Suggest the starting material A, that leads to the aldehyde which is from a [3,3] sigmatropic rearrangement. (5 points)



14. 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 258 nm. (30 points)

already posted elsewhere

217 nm

15. Show the major product from the following reaction. Be very clear about the stereochemistry of the product. (10 points)