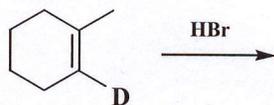
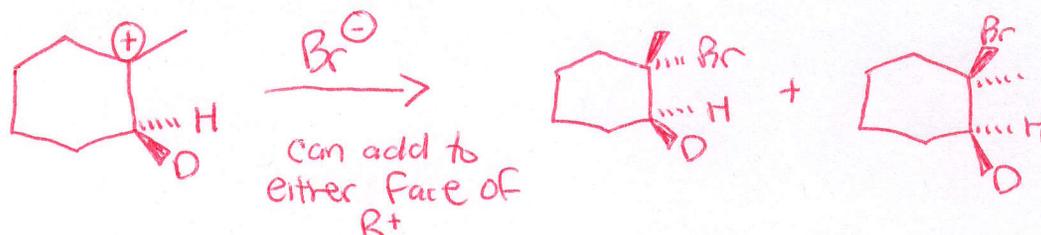


1. Does the addition of HBr to the following alkene give syn addition, anti addition or a mixture of both? Briefly explain your answer using the structure of the intermediate formed in this addition. How/why is this different from addition of Br₂? H₂?

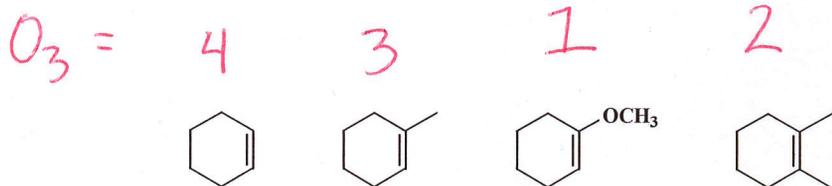
Produces a mixture of both syn and anti addition via R⁺ intermediate



Br₂ anti only
H₂ syn only



2. Rank the following compounds from most reactive (1) to least reactive (4) towards O₃. Also rank their reactivity towards BH₃. Briefly explain your answers.



most electron rich = most reactive to O₃

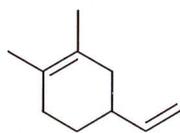


least hindered is most reactive to BH₃

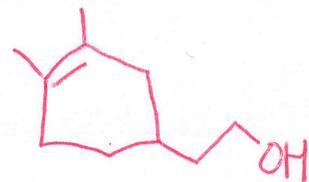
3. In the addition of electrophiles to alkenes, most electrophiles will add to the most reactive alkene first (most electron rich alkene). The two exceptions to this generalization are H₂ and BH₃. Provide the products when the following alkene reacts with the two reagents shown below. Be sure to draw correct stereochemistry where necessary and explain why the electrophile added to the position you indicated.



Br₂ (1 equiv)



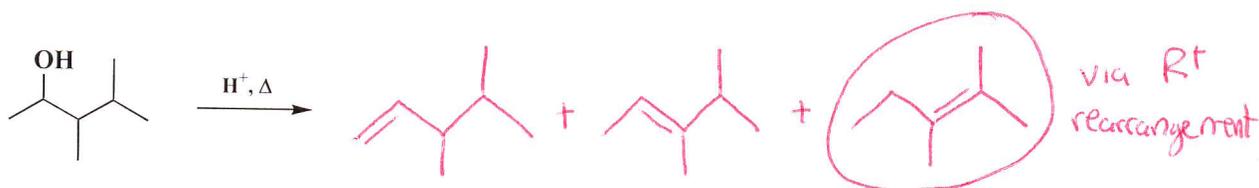
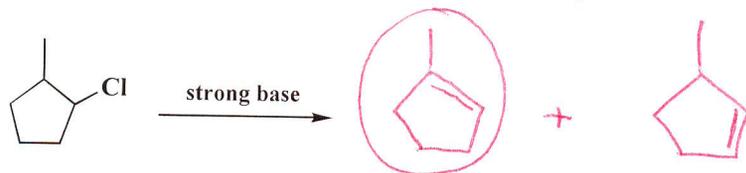
1. BH₃ (1 equiv)
2. H₂O₂, ⁻OH



tetra-sub is more electron rich than mono-sub

mono-sub is less hindered than tetra-sub

4. Preparation of Alkenes. The main way to prepare an alkene is to perform an elimination reaction of an alcohol (via carbocation) or an alkyl halide. For the two reactions shown below draw all possible products and then circle the one that is favored under thermodynamic conditions. We will see mechanisms for these reactions in a later chapter.

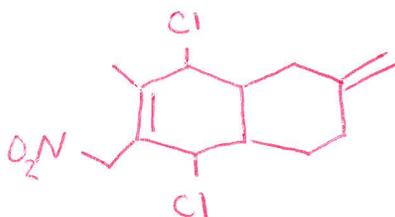


5. A compound with molecular formula $C_{13}H_{19}Cl_2NO_2$ reacts with 2 equivalents of H_2 upon hydrogenation, how many rings are present in this compound? Upon ozonolysis, one equivalent of CO_2 is produced. Draw a structure that fits this data.

Degree of unsat = 4

of π bonds = 2

1 terminal alkene
to give CO_2

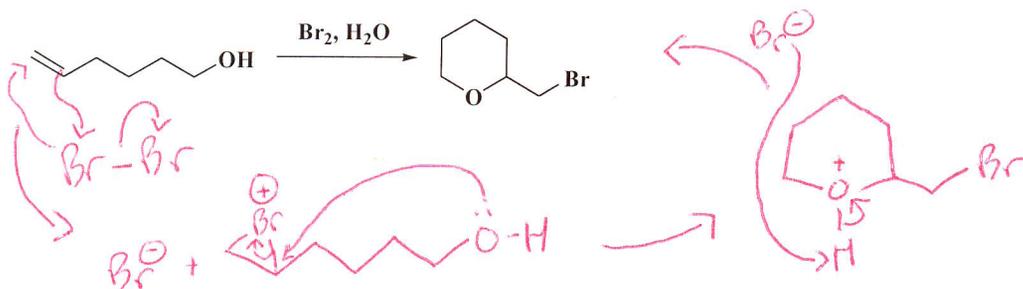


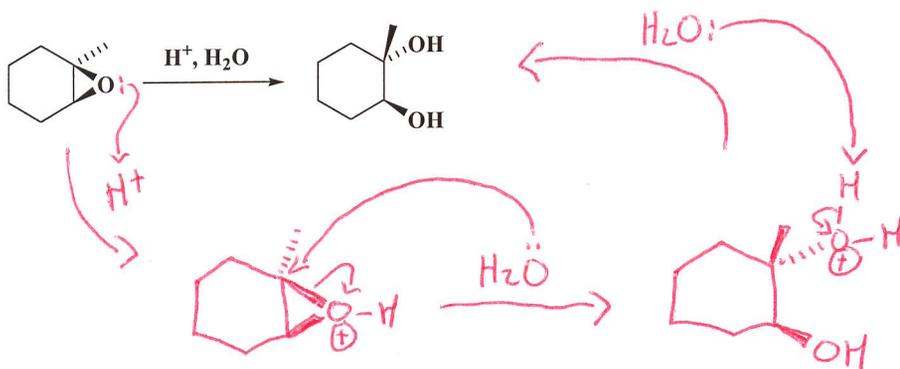
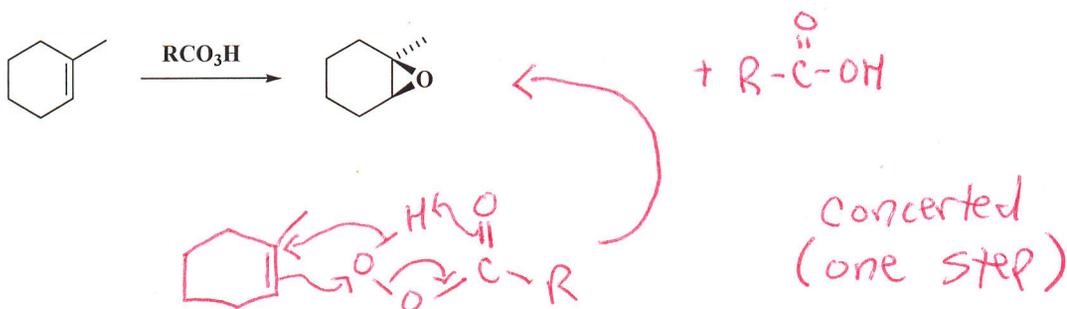
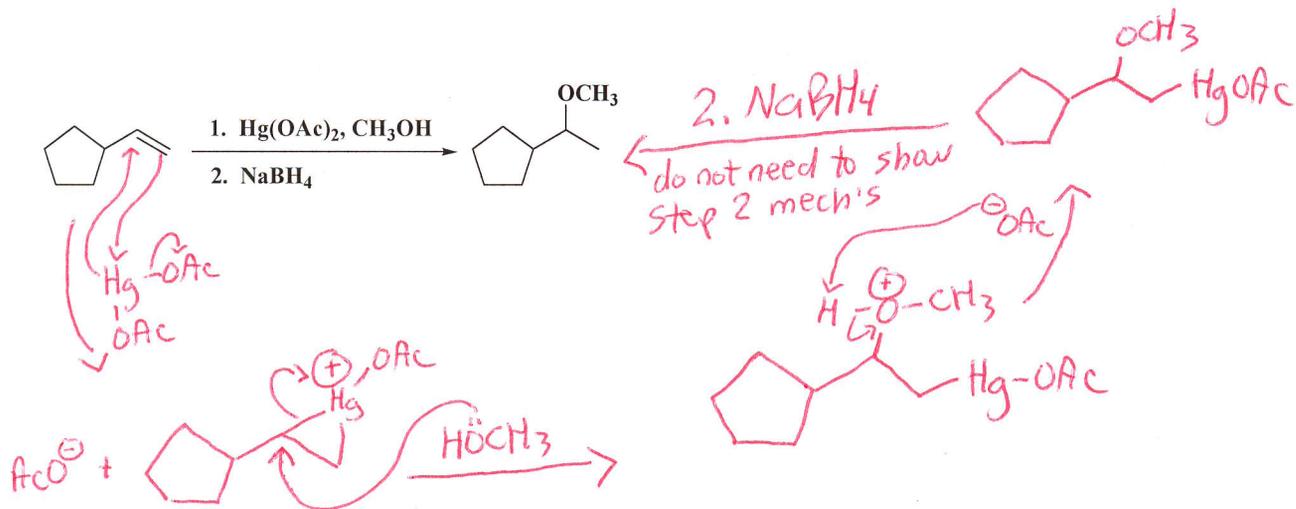
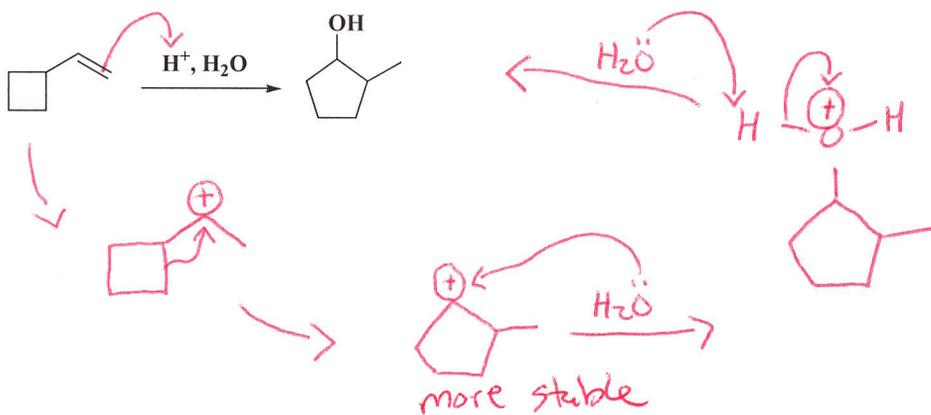
6. Which reagents give anti addition to alkenes? What do they all have in common? Which reagents give syn addition? What do they all have in common?

Anti Addition = X_2 ; $X_2 + H_2O$; $Hg(OAc)_2, H_2O$. All have 3-ring int adding the two pieces in 2 steps

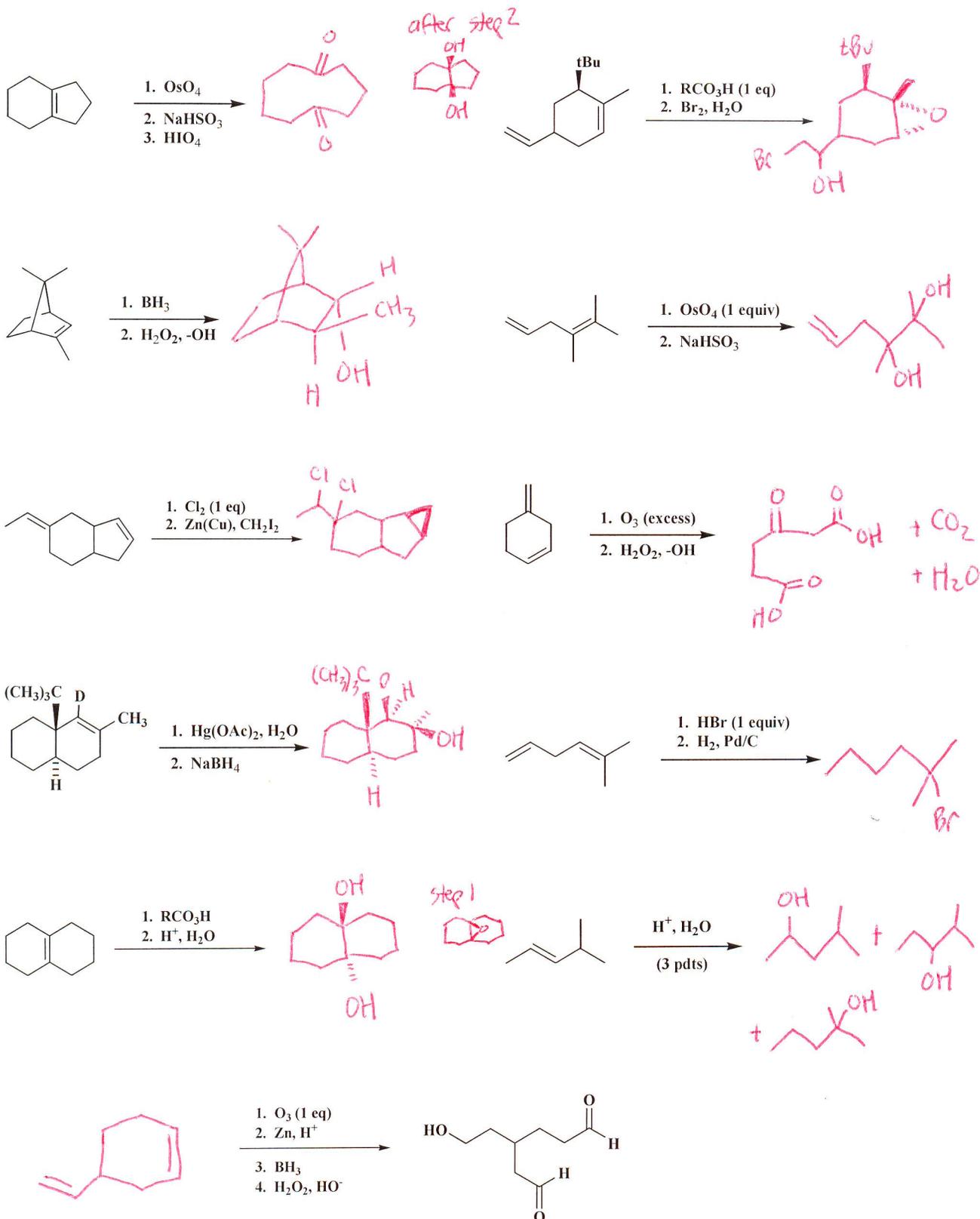
Syn Addition = H_2 ; BrH_3 ; O_3O_4 ; O_3 . All add the two pieces at same time in a concerted step. also MCPBA; $:CH_2$

7. **Mechanisms.** Provide a complete mechanism for each of the following reactions.



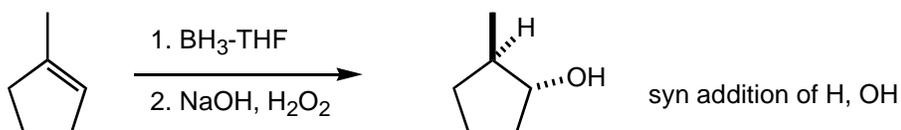


8. **Reactions.** Give the structure of the major organic product(s) expected from each of the following reactions. If necessary, indicate product stereochemistry.

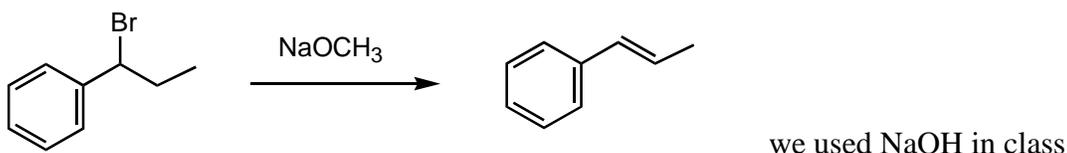


9. Supply the missing reagent, reactant, or product. If more than one product can be formed, give all possible products, and indicate which would be the major product. Be sure to indicate the stereochemistry and regiochemistry of the products where appropriate. The last three are particularly challenging.

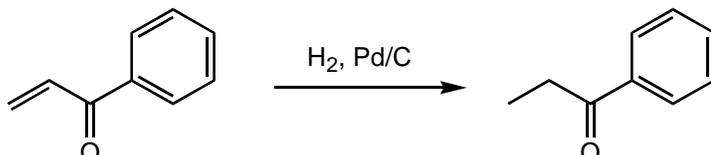
a.



b.

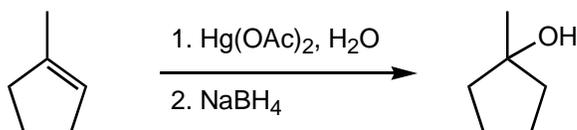


c.

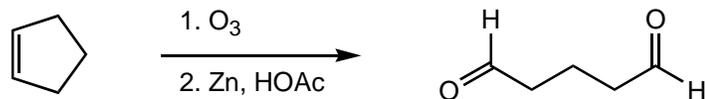


note: these conditions only reduce ordinary alkenes -- not carbonyls or benzene rings

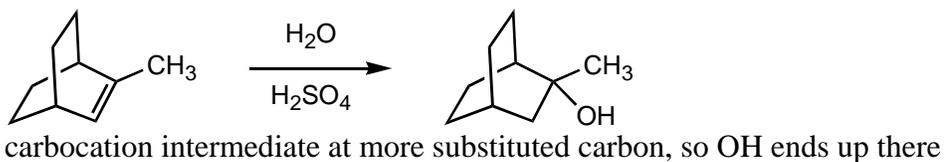
d.



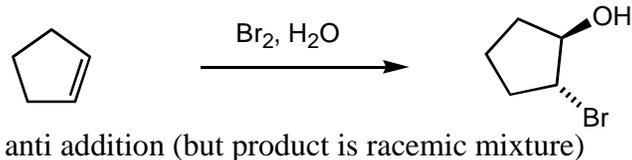
e.



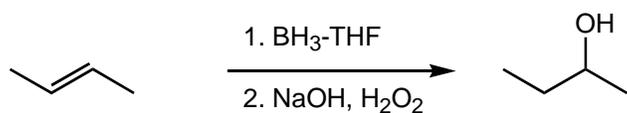
f.



g.

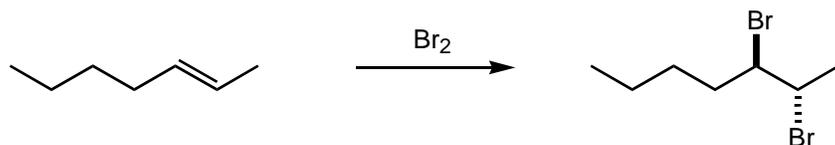


h.



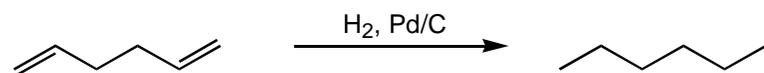
note that 1-butene would give 1-butanol, not 2-butanol as given

i.



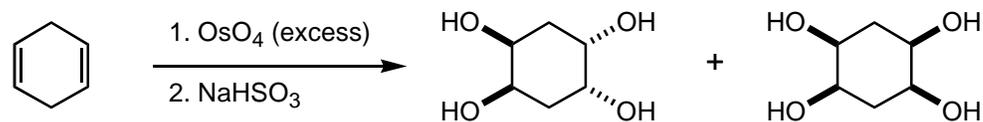
anti addition (but product is racemic mixture)

j.



H_2 gas always in excess, so both π bonds will react

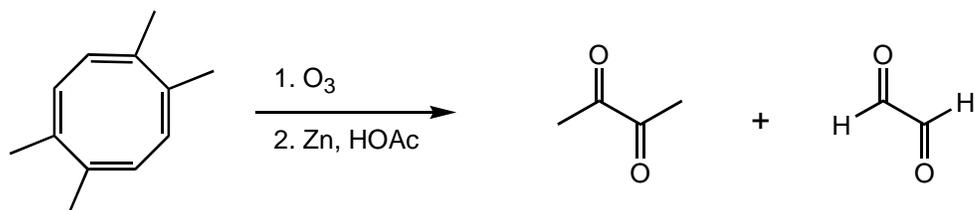
k.



major product

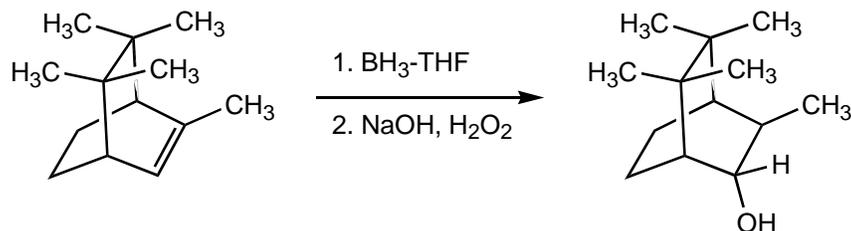
syn addition for each diol; second addition more likely from opposite side

l.



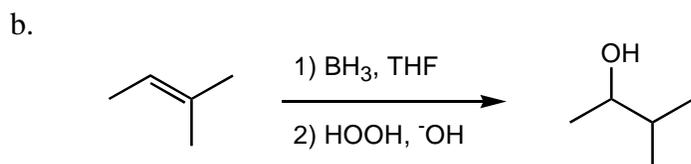
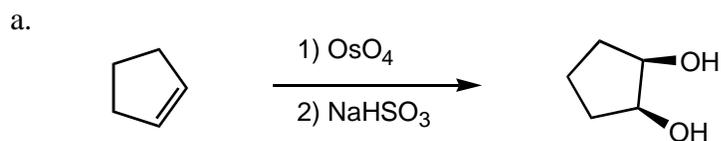
ozone always in excess; 2 moles of each product are formed

m.

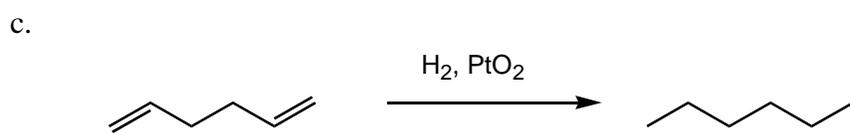


borane addition from less sterically-hindered side of alkene

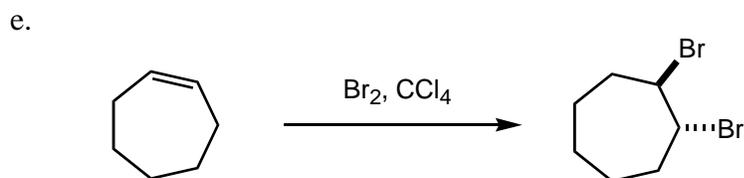
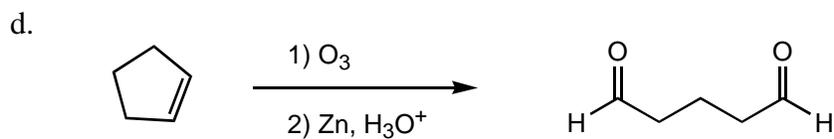
10. Give the missing products, reactants, or reagents for the following reactions.



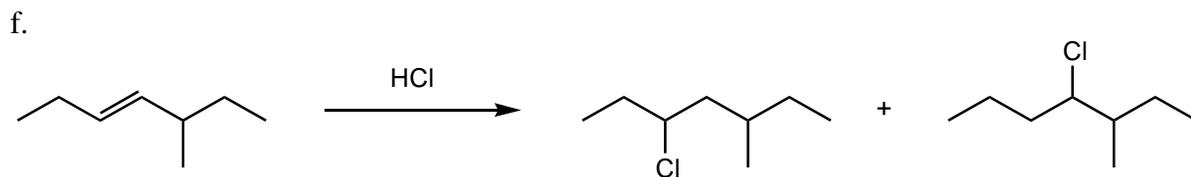
don't worry about THF, just a solvent



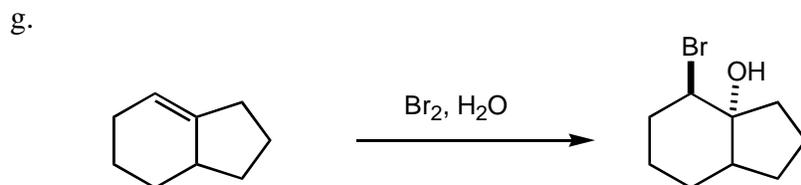
we use Pd/C in class



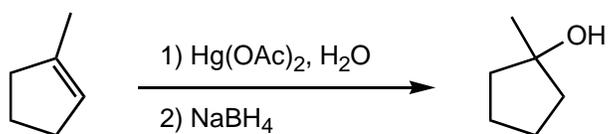
don't worry about CCl_4 , just solvent



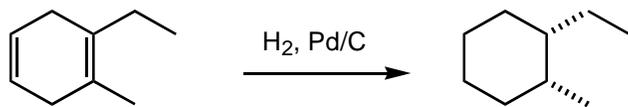
and likely get a third product via carbocation rearrangement



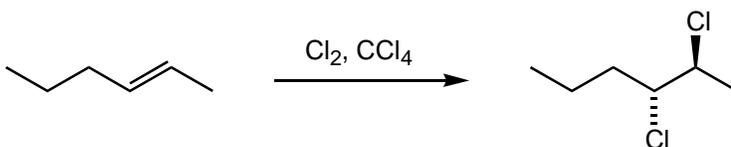
h.



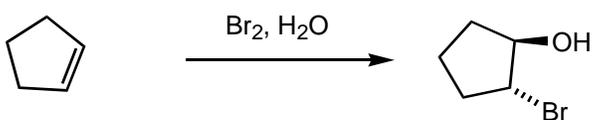
i.



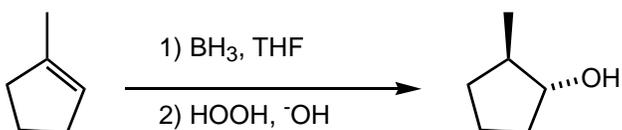
j.



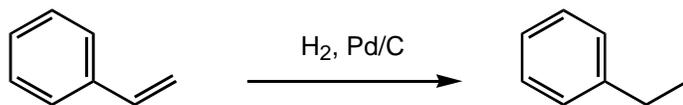
k.



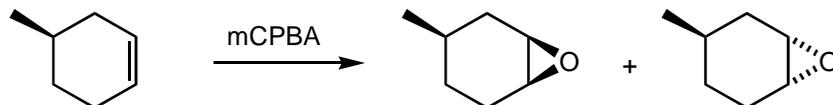
l.



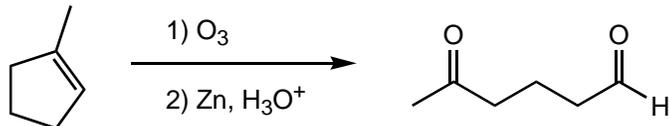
m.



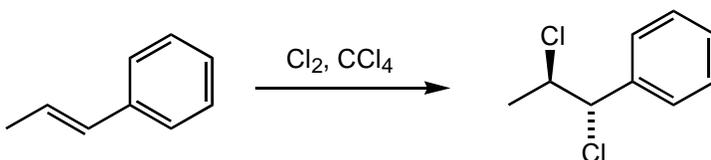
n.



o.

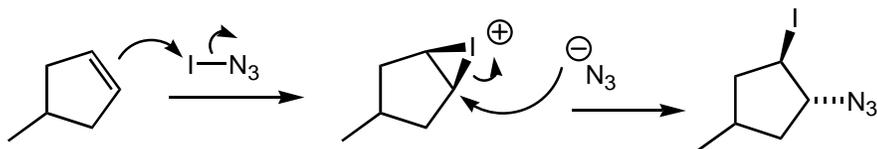


p.

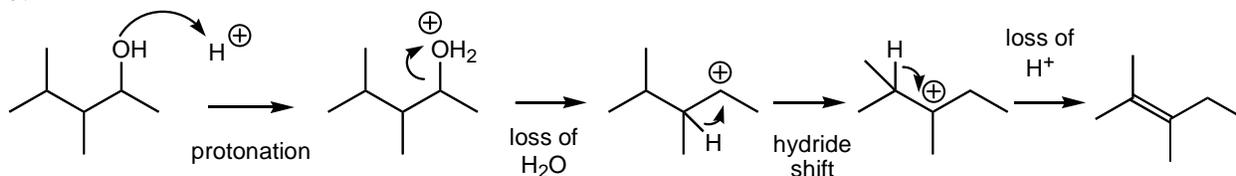


11. Using mechanistic arrows, draw a detailed mechanism for the following reactions.

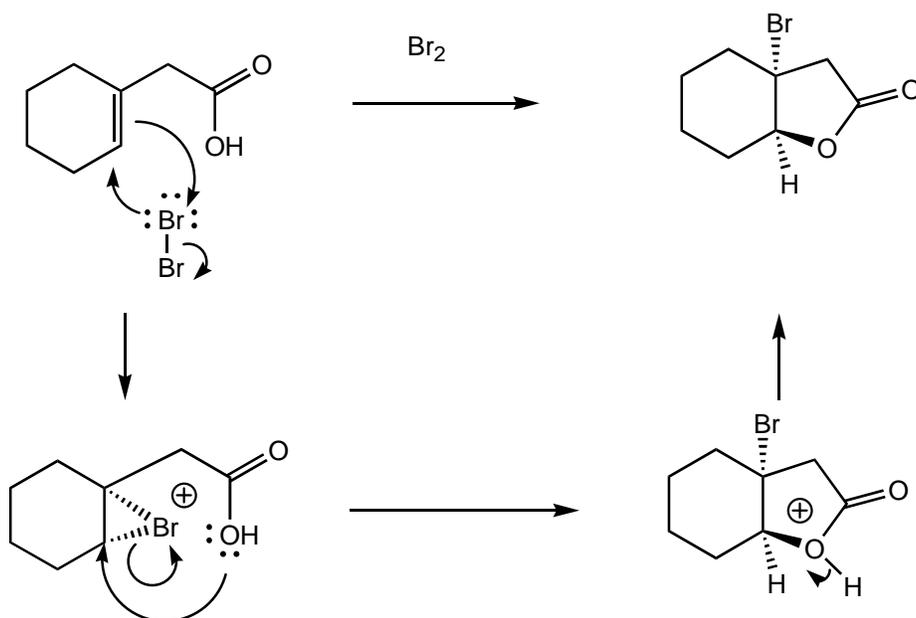
a.



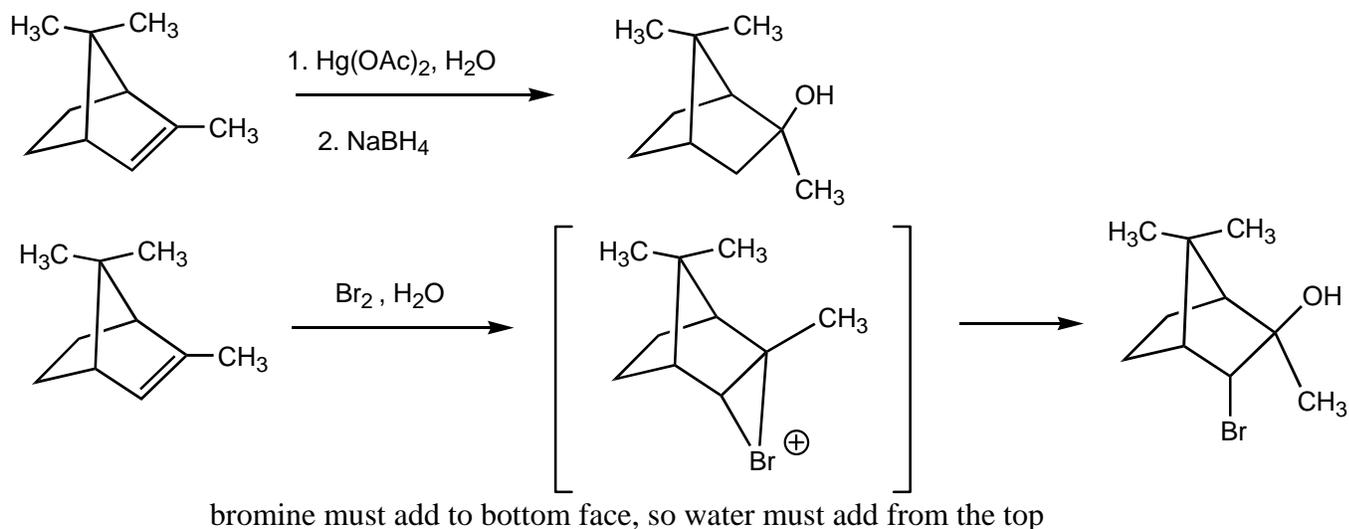
b.



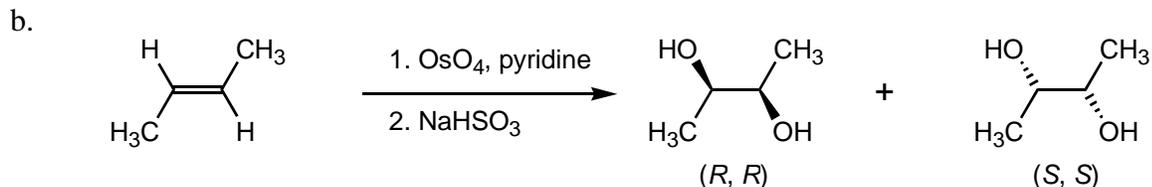
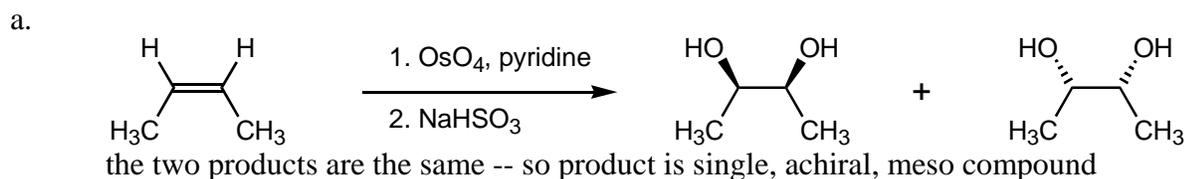
12. Draw a reasonable mechanism to explain the outcome of the following reaction. Be sure that your mechanism explains the observed stereochemistry.



13. Given the results from the oxymercuration reaction below, predict the products from treating the same alkene with Br_2 and H_2O . Draw a mechanism that explains the regiochemistry and stereochemistry of the product.



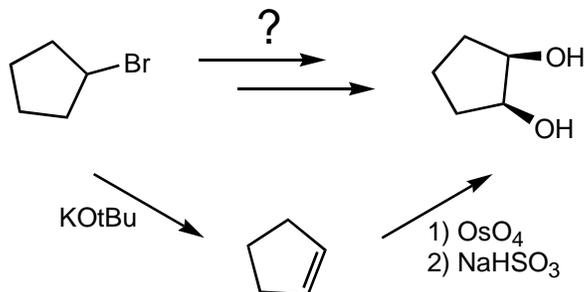
14. Give the stereochemical relationship of the products formed (i.e. enantiomers, diastereomers, etc) in the reactions below. Recall that the method we use is to look at the products from both top and bottom face attacks and then to determine the stereochemical relationship between them.



The two products are enantiomers; overall we get a racemic mixture

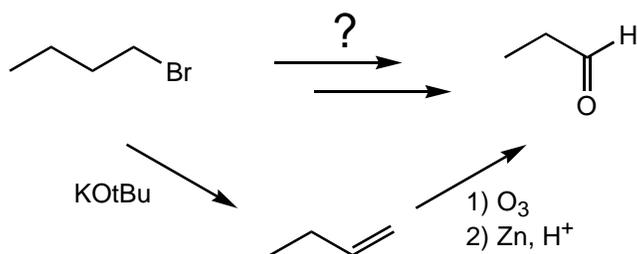
15. Provide a synthetic sequence to go from the given starting material to the desired product. Show all reagents and synthetic (not reaction) intermediates. All these syntheses can be accomplished in two or three steps.

a.

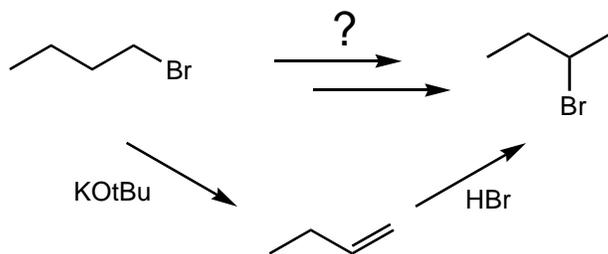


we use NaOH for step 1 in a and b and c

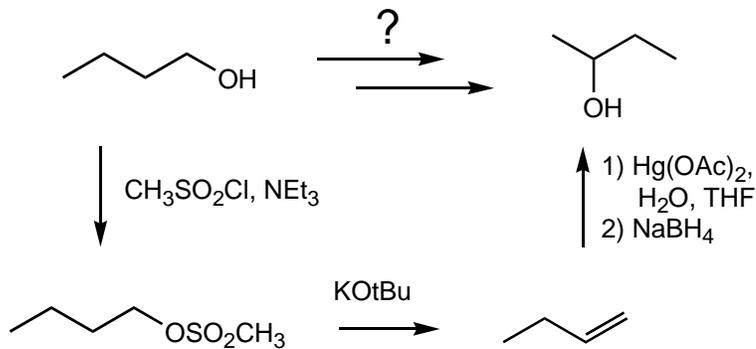
b.



c.

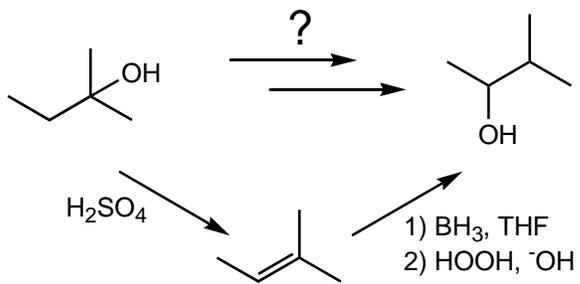


d.

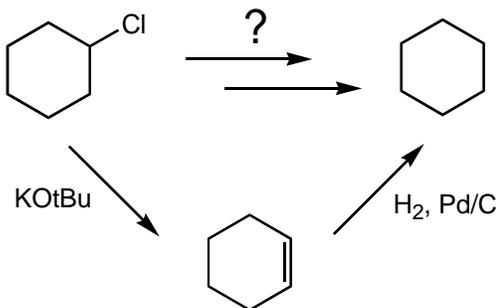


don't worry about this step 1

e.

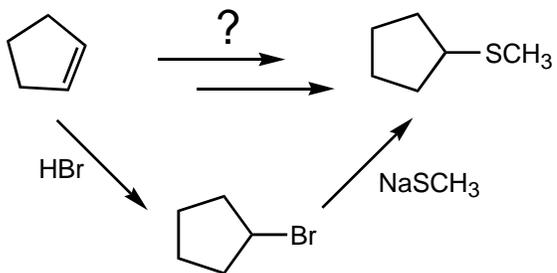


f.



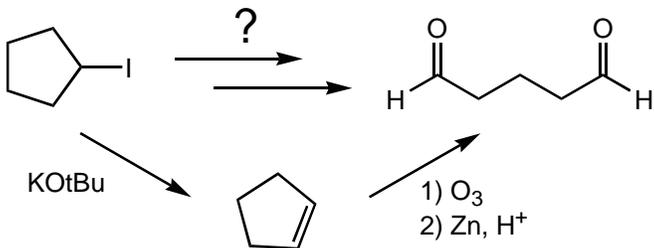
again, we use NaOH in step 1

g.



don't worry about step 2

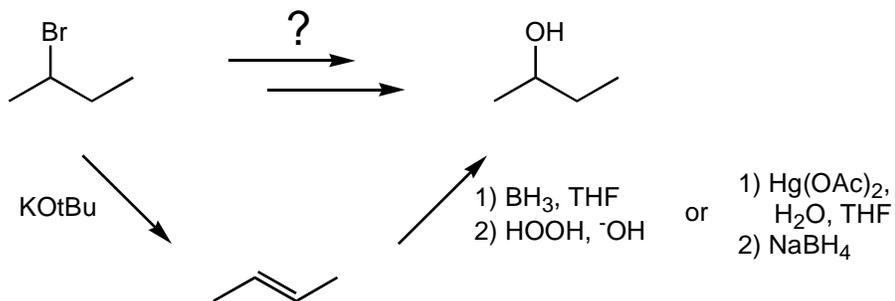
h.



again, NaOH for step 1

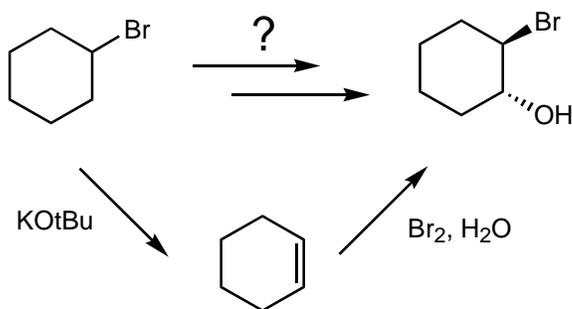
16. Propose syntheses to accomplish the following transformations. Each transformation can be done in two or three steps.

a.



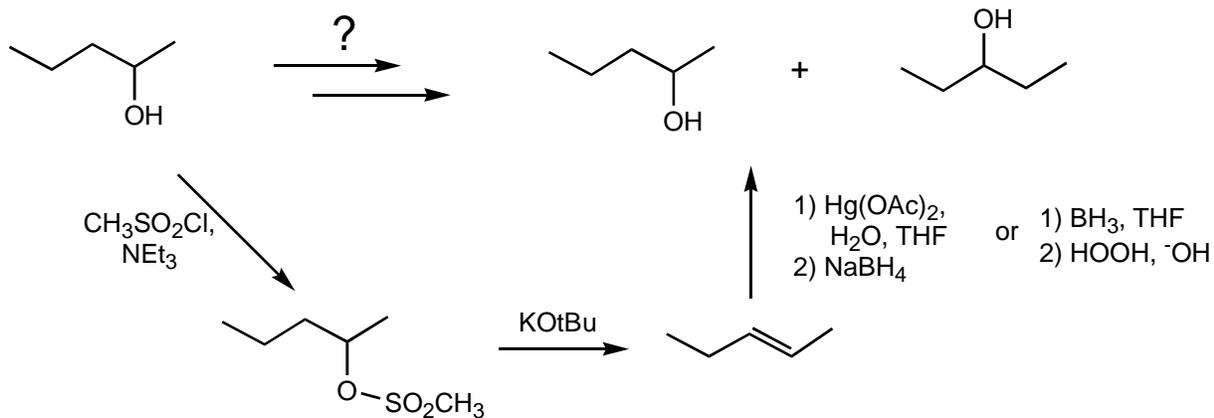
NaOH
step 1

b.



NaOH step 1

c.



Don't worry about step 1; use NaOH for step 2

17. Treatment of compound **A** ($C_6H_{14}O$) with H_2SO_4 gave two alkene products, with **B** as the major product. Catalytic hydrogenation of **B** gave 2-methyl-pentane as the only product. Hydroboration (1. BH_3 -THF; 2. H_2O_2 , NaOH) of **B** gave a single compound, alcohol **C**. Ozonolysis (1. O_3 ; 2. Zn, HOAc) of **B** gave a ketone and an aldehyde (no formaldehyde): compounds **D** and **E**. Show the structures of all the compounds: **A**, **B**, **C**, **D**, and **E**.

