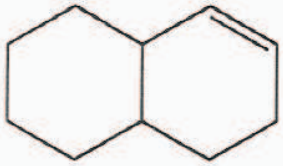
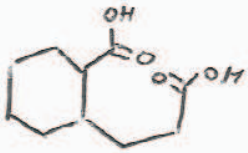
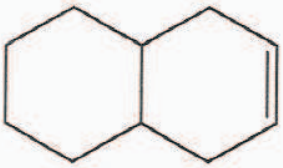
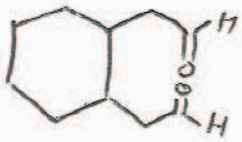
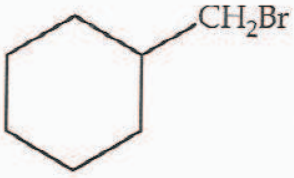
Chemistry 3311-100
Organic Chemistry / Dr. Barney Ellison
Thursday: March 11th @ **7:00pm → 9:00** / 2nd Exam / Math 100)

Name: Key (please print)

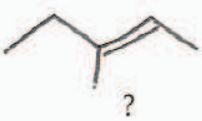
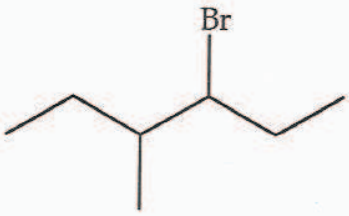
1. (12 pts) Give the missing reactant or product in each of the following equations.

a)  O_3 $H_2O/HOOH$? 

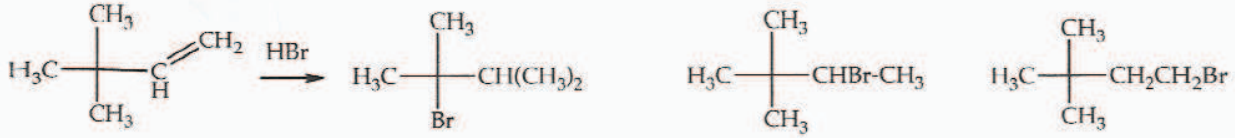
b)  O_3 CH_3SCH_3 ? 

c)  ? HBr → peroxides 

3 points each

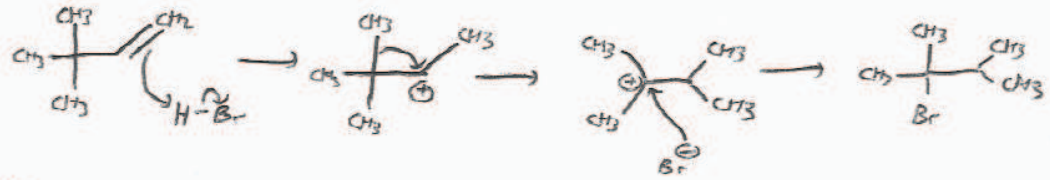
d)  ? HBr → peroxides 

2. (8 pts) When HBr is added to 3,3-dimethyl-1-butene, the following products are observed. Explain why different conditions give different products. Show a mechanism.

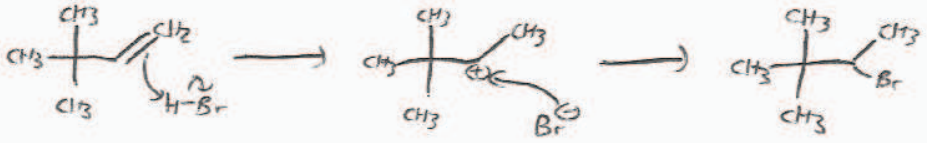


no peroxides	71%	29%	0%
peroxides	0%	0%	100%

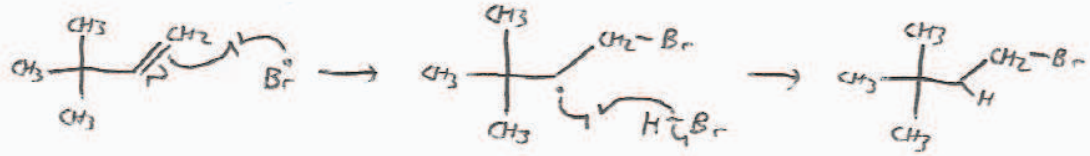
No peroxides:



or



Peroxides: $RO\overset{\curvearrowright}{-}OR \longrightarrow 2RO^{\cdot} \overset{\curvearrowright}{H-Br} \longrightarrow ROH + Br^{\cdot}$



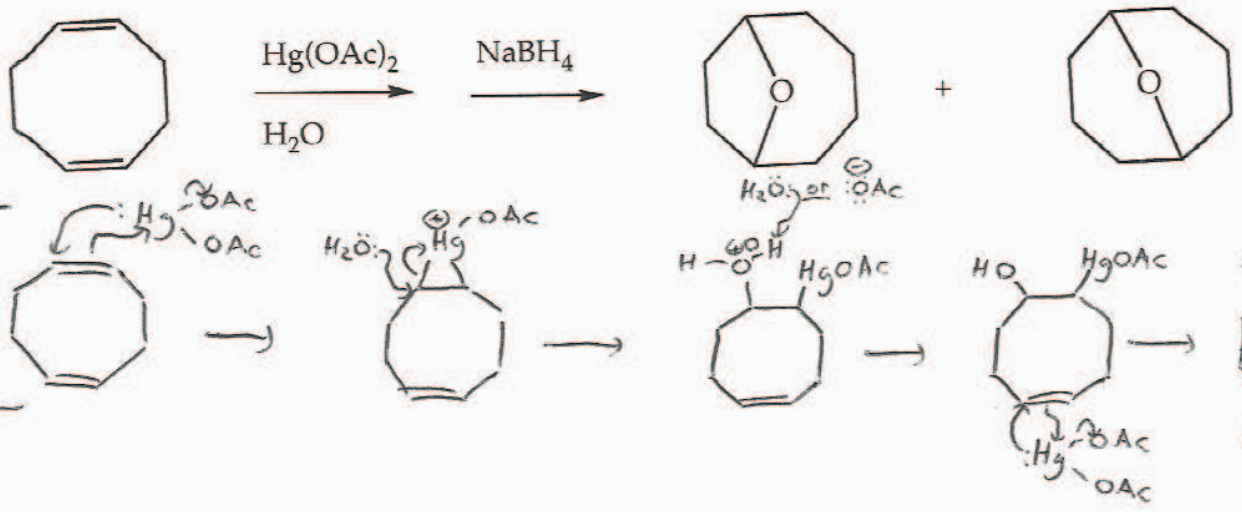
In the absence of peroxides, HBr reacts by a regular arrow-pushing mechanism to add Markovnikov-style. A carbocation rearrangement is likely to occur.

In the presence of peroxides, there's a radical mechanism that makes HBr add anti-Markovnikov-style.

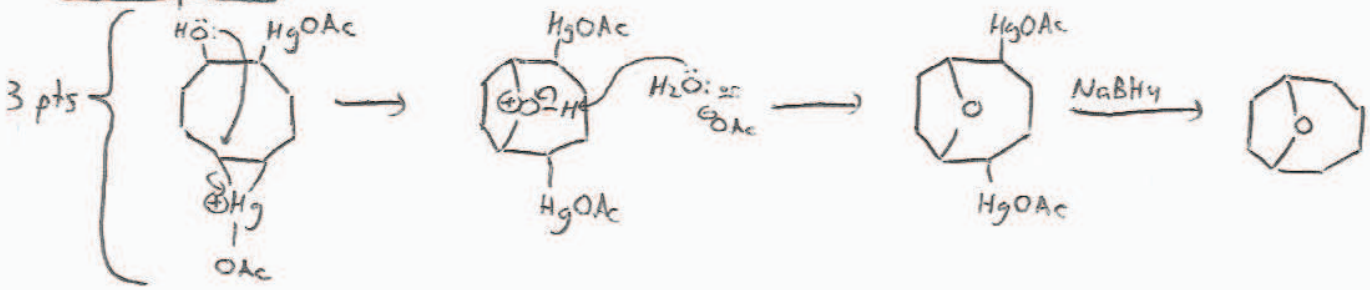
2 pts for each mech
2 pts for explanation

−1 for wrong charges
−1 for bad half-arrows
−3 if mech gives wrong regiochem.

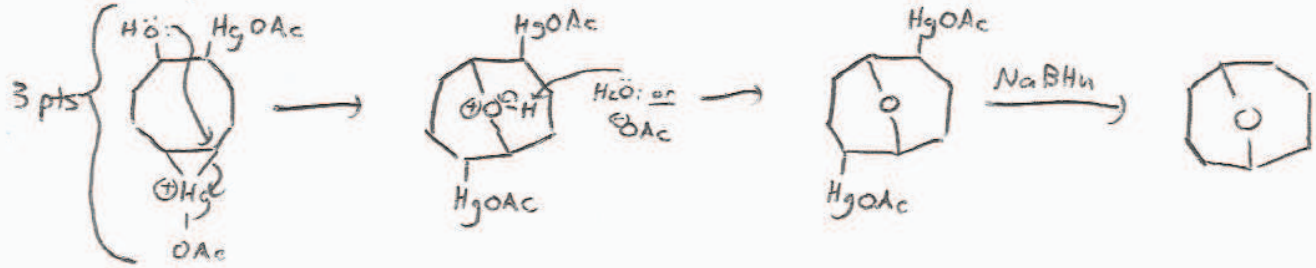
3. (10 pts) Show a mechanism for the following reaction.



First product:



Second product:

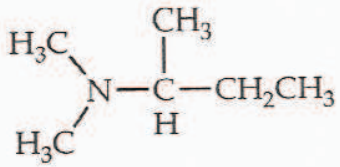


-3 for not using Hg on 2nd alkene

-2 if H_2O attacks both  at once

-6 if 2 separate H_2Os add to ring

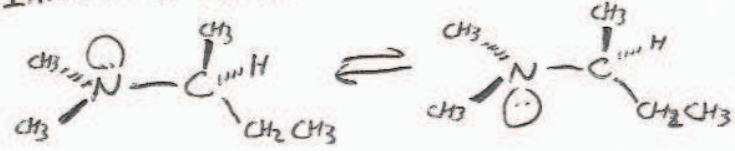
4. (10 pts) The following compound has the (S) configuration at the asymmetric carbon.



a) What is the isomeric relationship between the two forms of this compound that are interconverted by amine inversion?

5 pts

Inversion of amine:



The nitrogen is not a stereocenter regardless of which way the lone pairs are pointing, so they are identical.

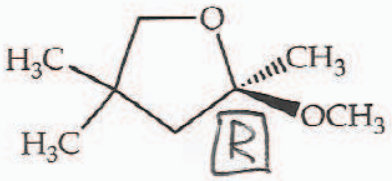
b) Can this compound be resolved into enantiomers?

5 pts

No, since the compound has the S configuration at the carbon and no other stereocenters.

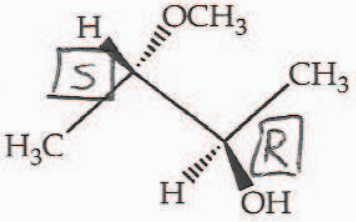
5. (10 pts) Give the configuration (R or S) of each asymmetric center in the following.

a)



3 1/3 pts each, rounded to nearest integer.

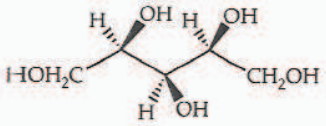
b)



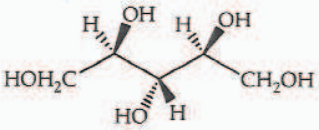
6. (10 pts) Give the stereochemical relationship between each pair of compounds below. (enantiomers, diastereomers, or the same ?)

Are any of these species meso compounds?

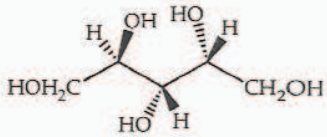
Which compounds will be optically active?



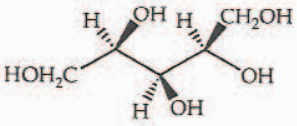
A



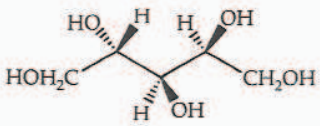
B



C



D

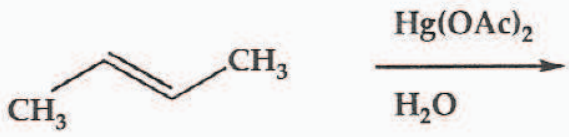


E

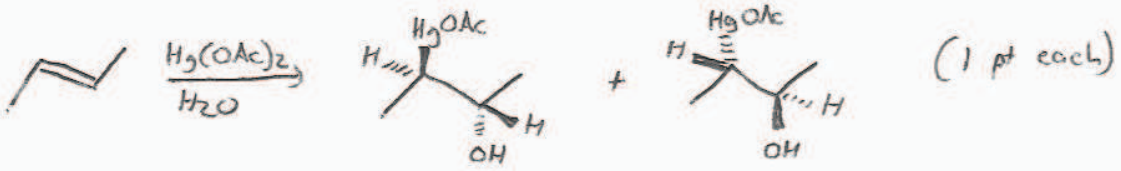
	A	B	C	D	E
A	Id	Di	Di	Di	Di
B	Di	Id	Di	Di	Di
C	Di	Di	Id	Id	En
D	Di	Di	Id	Id	En
E	Di	Di	En	En	Id

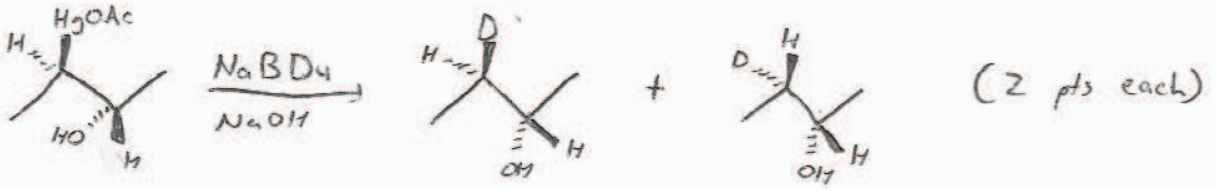
A & B are meso; C, D & E are optically active.

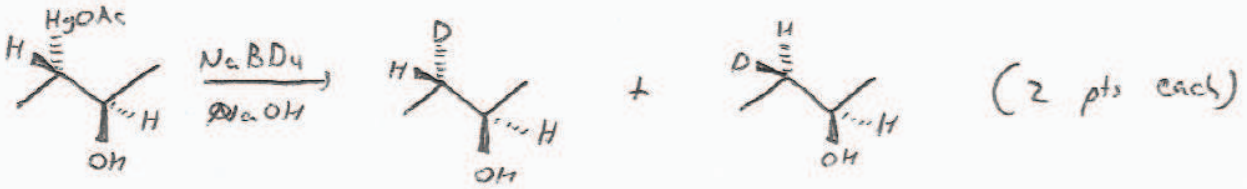
7. (10 pts) Give the products and their stereochemistry when *trans*-2-butene reacts with $Hg(OAc)_2 + H_2O$.



What products result when these products are treated with $NaBD_4$ in aqueous NaOH?



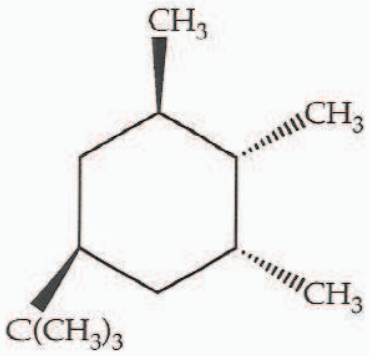


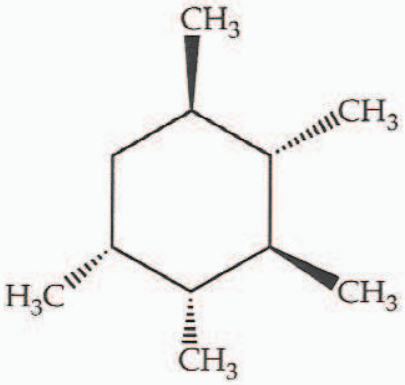


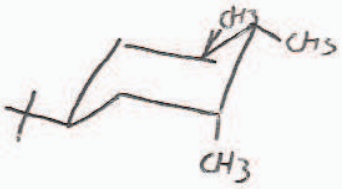
Oxymercuration goes by anti addition, but reduction is random. must add a D from $NaBD_4$.

-8 if no D or not stereochem shown at all

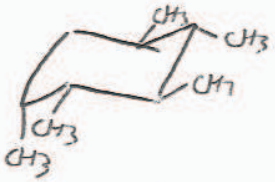
8. (10 pts) Draw the structure of the most stable chair conformation.







$C(CH_3)_3$ group must be equatorial

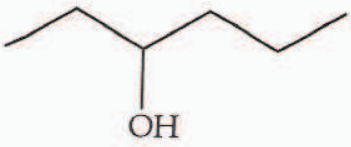


1 group axial & 4 groups equatorial is better than the other way round.

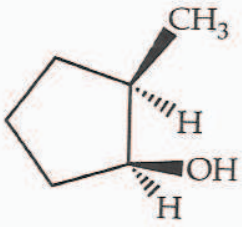
9. (10 pts) Which of the following alcohols can be synthesized free of constitutional isomers and diastereomers by

a) hydroboration-oxidation A + D (5 pts)

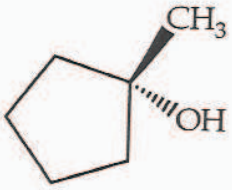
b) oxymercuration-reduction A + C (5 pts)



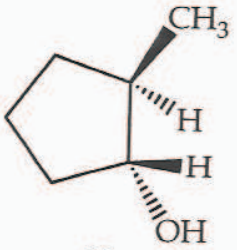
A



B

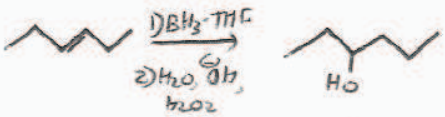


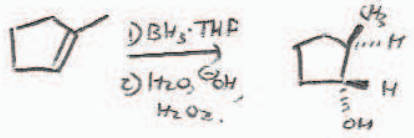
C



D

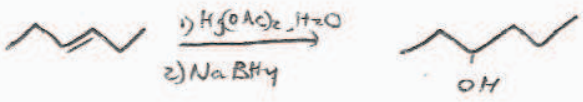
a) Hydroboration-oxidation

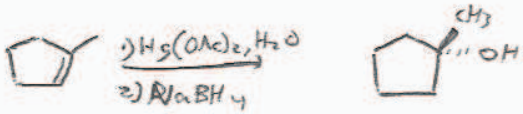
A: 

D: 

Must be giving anti-Markovnikov-style addition, w/ syn stereochem. This rules out B & C.

b) Oxymercuration-reduction.

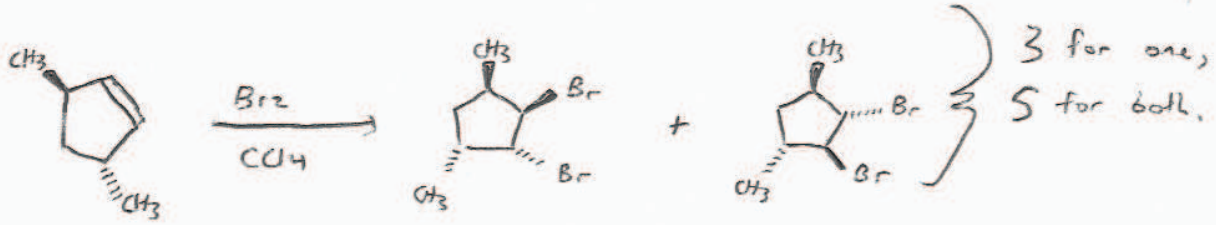
A: 

C: 

Must give Markovnikov-style addition, so B & D are ruled out.

10. (10 pts) Give the structure and stereochemistry of the products of:

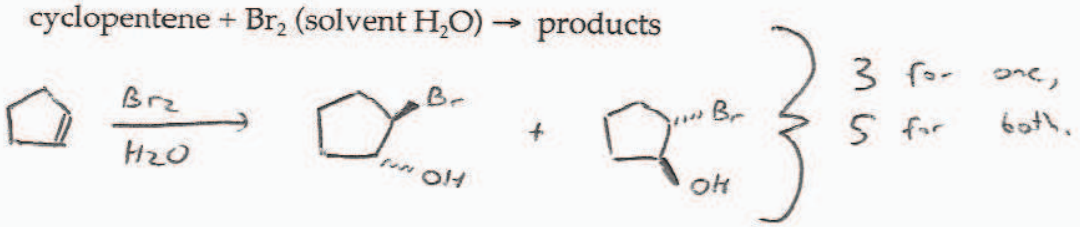
a) (3R,5R)-3-5-dimethylcyclopentene + Br_2 (solvent $CC\ell_4$) → products



3 for one,
5 for both.

-2 for CH_3's syn
-1 for each extra, wrong structure
-2 wrong starting material

b) cyclopentene + Br_2 (solvent H_2O) → products



3 for one,
5 for both.

-3 for adding CH_3's.
-1 for repeats of a structure
-2 for each extra wrong structure.