Dr. Steven Pedersen December 11, 2002

Chemistry 3A
Final Exam

Student name: _____

Student's signature: _____

TA's name or section number:_____

M Problem 1 _____ (31 pts)

I Problem 2 _____ (51 pts)

D Problem 3 _____ (18pts)

T Problem 4 _____ (52 pts)

E Problem 5 _____ (48 pts)

R

M

Problem 6 _____ (74 pts)

Problem 7 _____ (73 pts)

Problem 8 _____ (73 pts)

Total Points _____ (420 pts)

No Calculators Allowed
Be Sure Your Exam has 17 Pages
Be Sure To Try All Parts of a Problem!

1.

A. Provide one, and only one, real example for each of the following terms or draw a structure for a given chemical name. (31 pts)

an epoxide

diisopropyl ether

MCPBA

Z-2,3-dimethyl-2-penten-1-ol

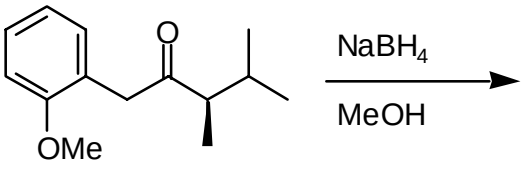
cis-3-heptene

1B. Calculate the degree of unsaturation for the molecular formula shown below. You must show your work to receive any credit. Draw TWO REAL molecules that are consistent with your calculation.

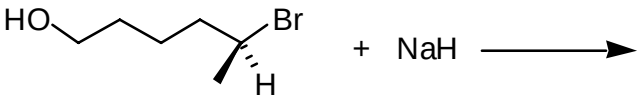
C_4H_6ClN

Don't forget to draw two real molecules that fit this formula.

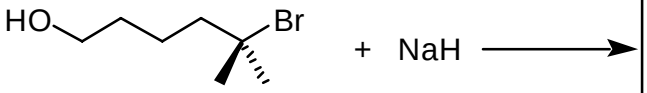
2. Predict the product(s) from the following reactions. (51 pts)



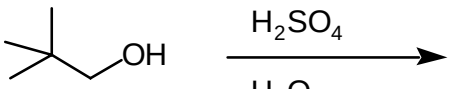
all possible stereoisomers
(be sure to show wedges and dashes)



an optically ACTIVE product
(be sure to show appropriate stereochemistry)



an optically INACTIVE ACYCLIC product



$C_5H_{12}O$

$C_5H_{12}O$ (different from starting material)

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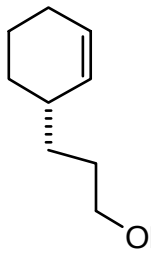
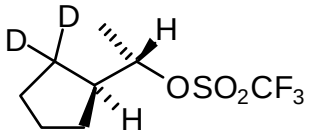
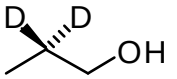


+ HBr



the product is an alkene



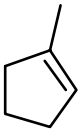
H_2SO_4

heat

reaction proceeds through a carbocation intermediate

+ H_2O

4 alkenes



1. BH_3

2. H_2O_2, H_2O, $HO^{\ominus}$

two major stereoisomers (be sure to show wedges and dashes)

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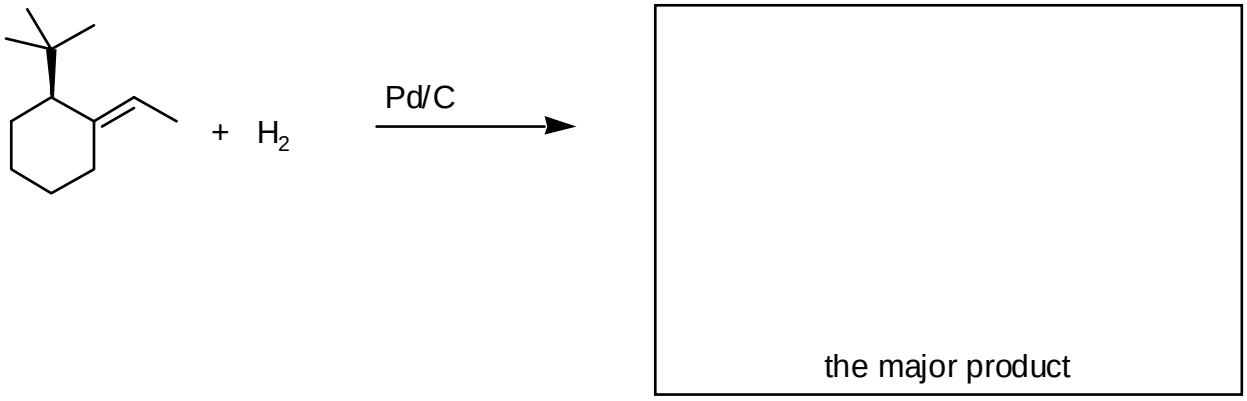
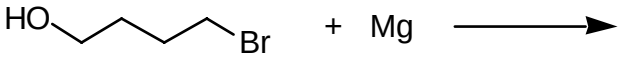
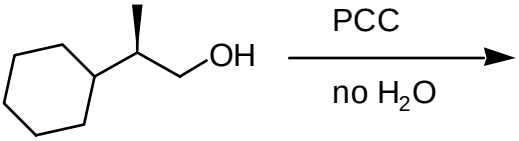


the major product



an optically active product
(be sure to show appropriate
stereochemistry)



3. Match the molecules shown below with the statements. (18 pts)

a. Want some gypsy moths in your car? _____

b. A liver carcinogen and monomer for a very long-lived polymer. _____

c. This molecule tells some bees to “back off boy”! _____

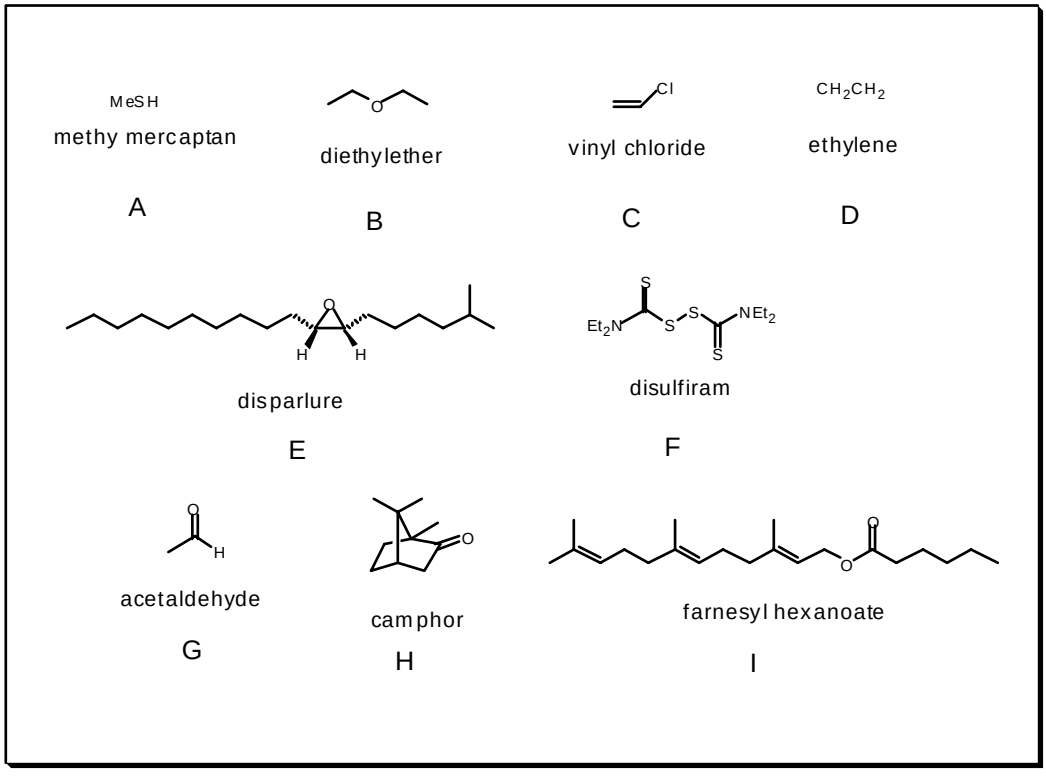
d. This molecule is produced in many ripening fruits. _____

e. Before this molecule’s introduction to medicine, the thought of surgery was more than many a patient and doctor could handle. _____

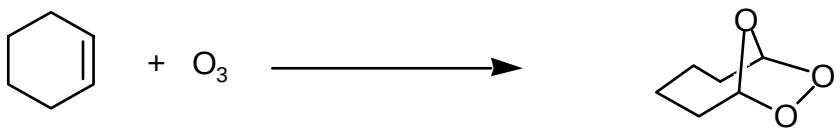
f. Both of these molecules can lead to terrible hangovers. _____ and _____

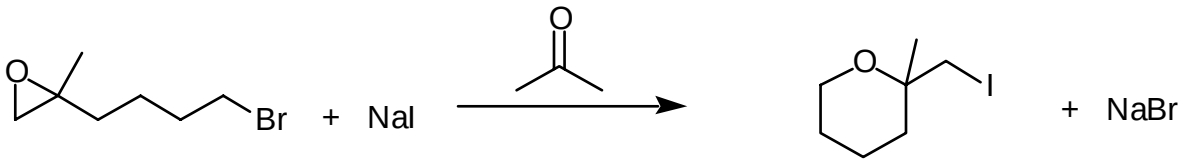
g. The worlds smelliest molecule! _____

h. The shipwreck preserver. _____



4. Write logical arrow-pushing mechanisms for the following reactions. (52 pts)





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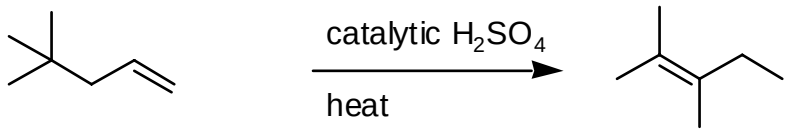
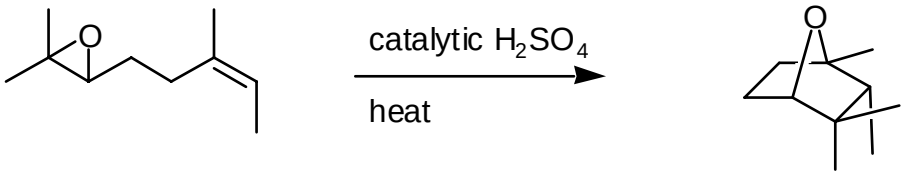
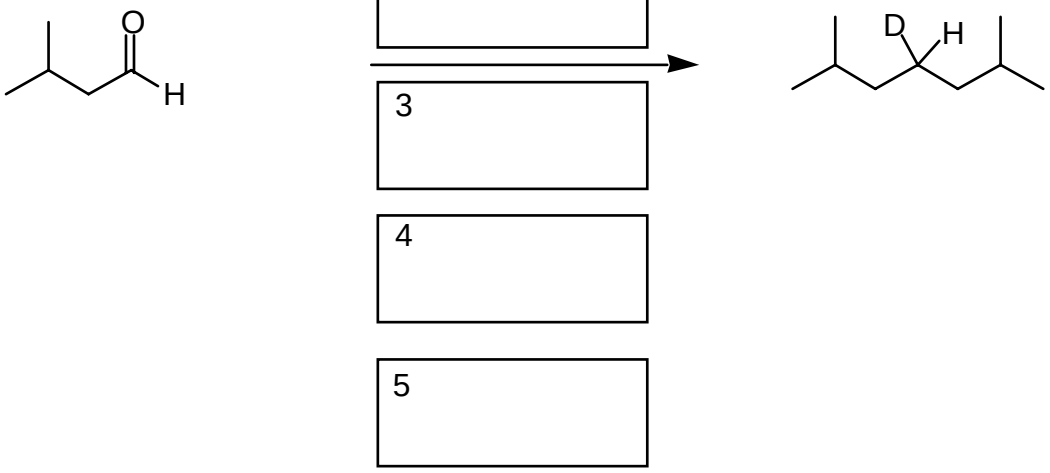
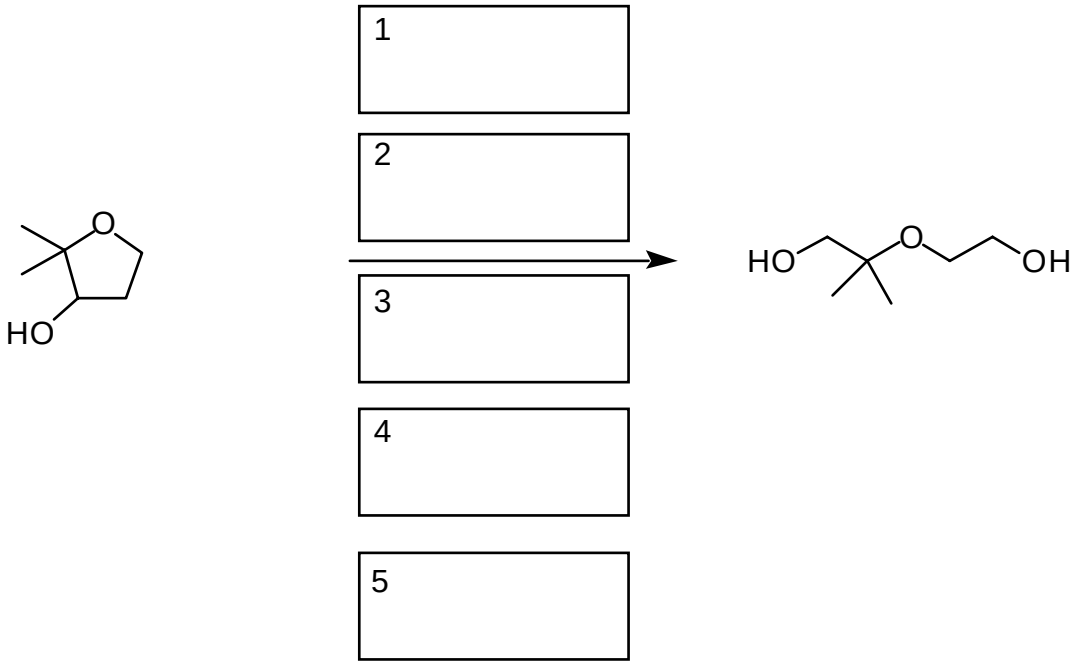




5. Provide the reagents and any other organic compounds necessary to synthesize the indicated product from the starting material shown. For each problem, five boxes are provided in which to place each step of your synthesis. **No synthesis will require more than five steps. However, some or all, may require**

fewer than five steps. (48 pts)





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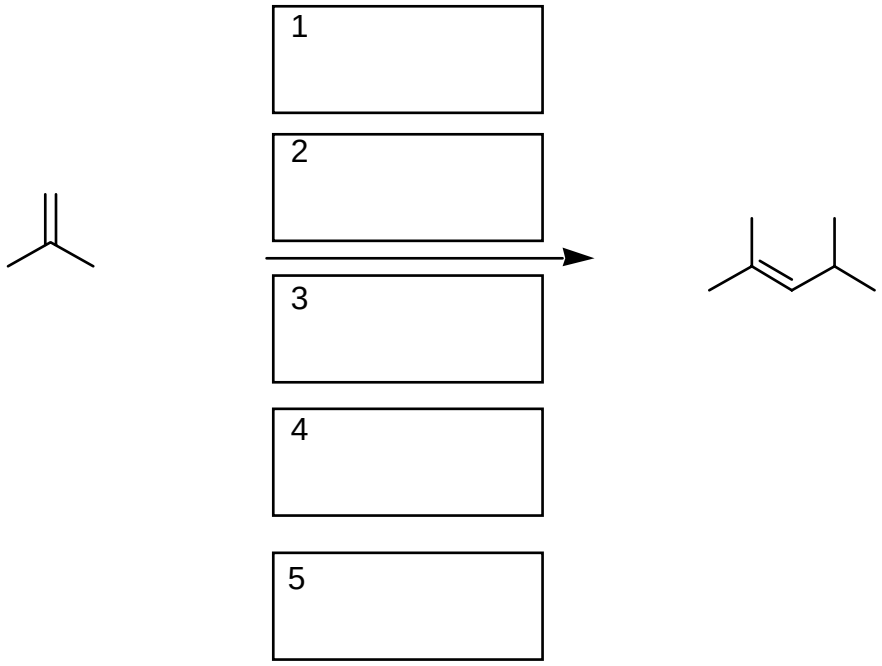
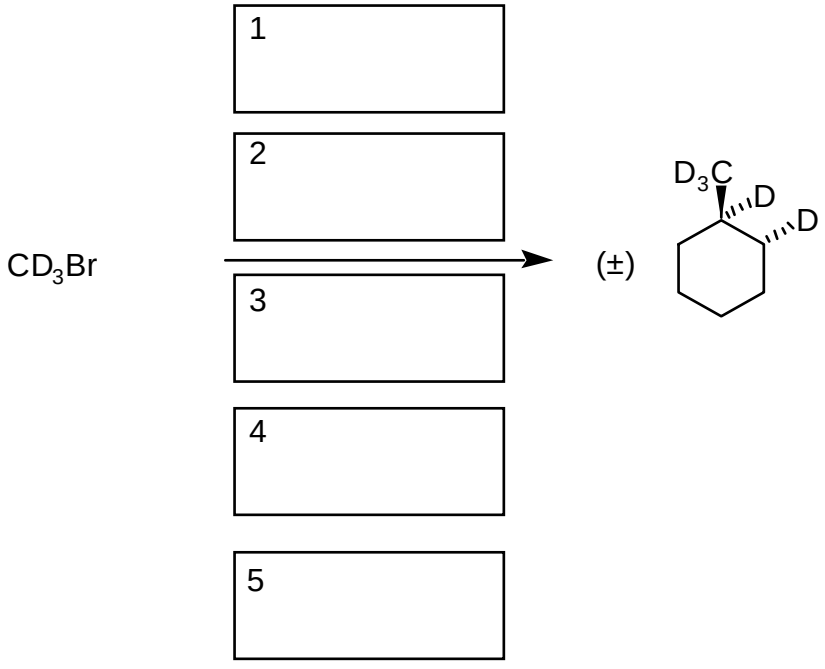




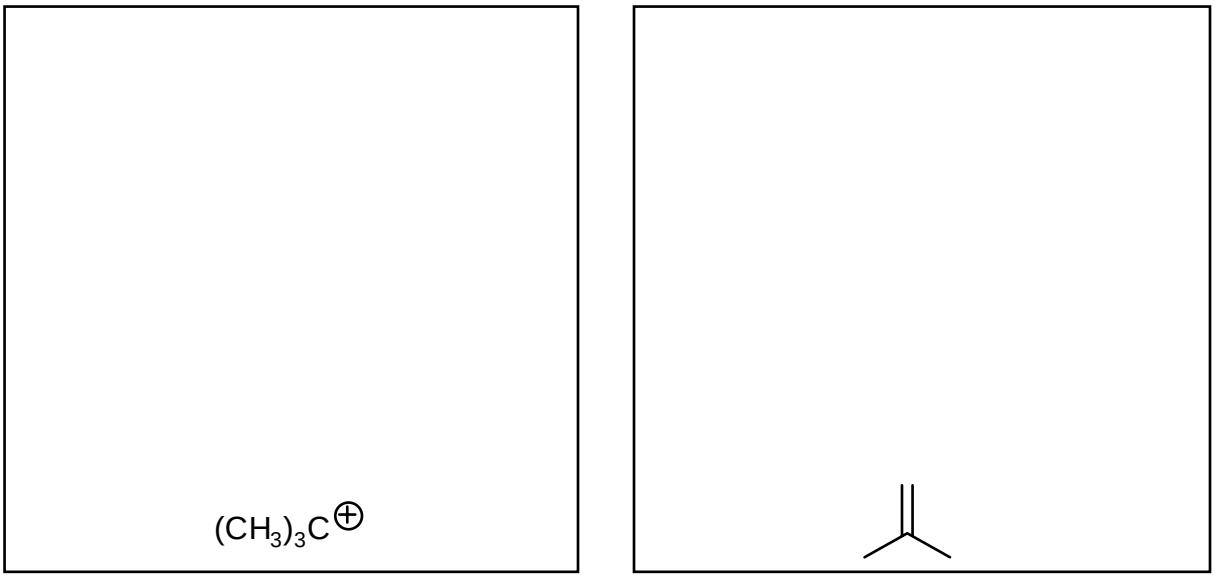
Carbocations!

6. (74 pts)

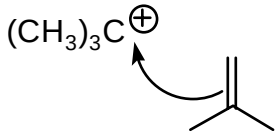
A. Draw the molecular orbital energy level diagram of the tertiary-butyl carbocation (only draw the energy levels not the orbitals themselves). Label the levels as σ C-H, σ C-C, etc. Fill in all of the electrons and label the HOMO and LUMO.

B. Draw the molecular orbital energy level diagram of 2-methylpropene (only draw the energy levels not the orbitals themselves). Label the levels as σ C-H, σ C-C, etc. Be careful to order your various levels making use of what you know about the influence of hybridization on bond strengths. Fill in all of the electrons and label the HOMO and LUMO.

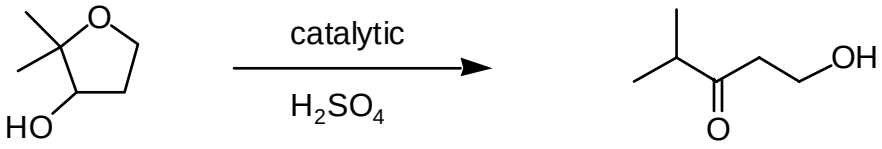
Molecular orbital energy level diagrams

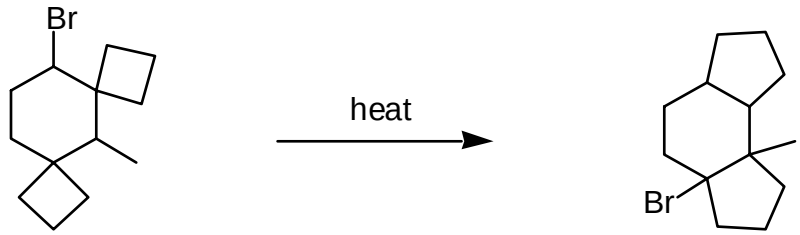


C. Based on what you know about Frontier Molecular Orbital Theory, on the diagrams above, draw a dashed line between the two orbitals involved in the reaction shown below.



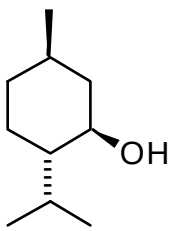
D. Write logical arrow-pushing mechanisms for the following reactions. Remember that the theme of this entire problem is carbocation chemistry.





Menthol

7. Let's revisit that cool MOD menthol. (73 pts)



menthol

A. Provide an IUPAC name for menthol. Be sure to include R and S nomenclature.

A. How many possible stereoisomers of menthol are there?

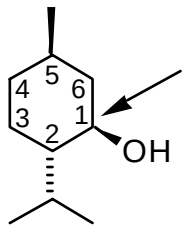
B. Draw three of these stereoisomers, not including menthol. (Every redundant answer cancels a right answer)

C. In the boxes below show:
1) The two chair conformations of menthol
2) Calculate $\Delta G°$ for the ring flip, YOU MUST SHOW YOUR WORK TO RECEIVE ANY CREDIT
3) Show the direction of the equilibrium using arrows

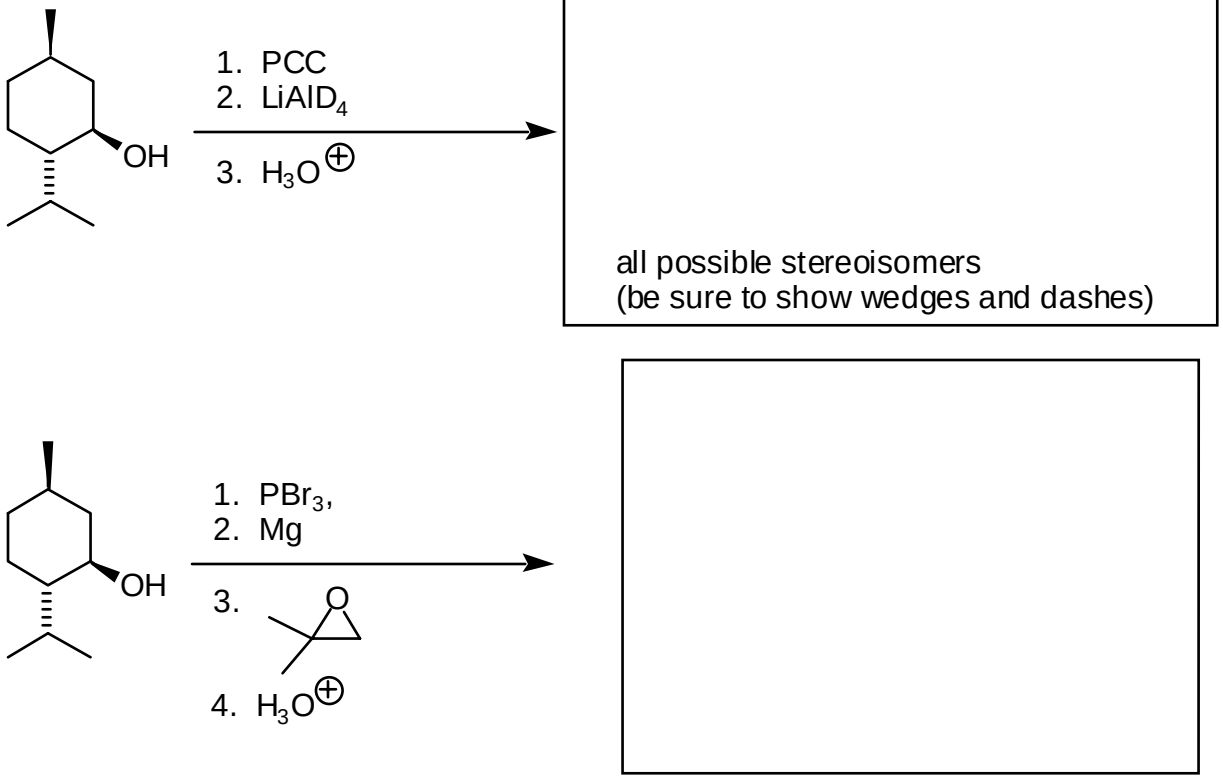
	$\Delta G° =$	
	$K_{equilibrium}$	

Show your work for calculating $\Delta G°$ here:

D. Using the numbering scheme below, draw a Newman projection looking down the C1-C2 bond of menthol in its lowest energy chair conformation.

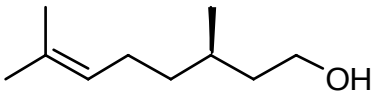


E. Predict the products from the following reactions involving menthol.



Citronellol

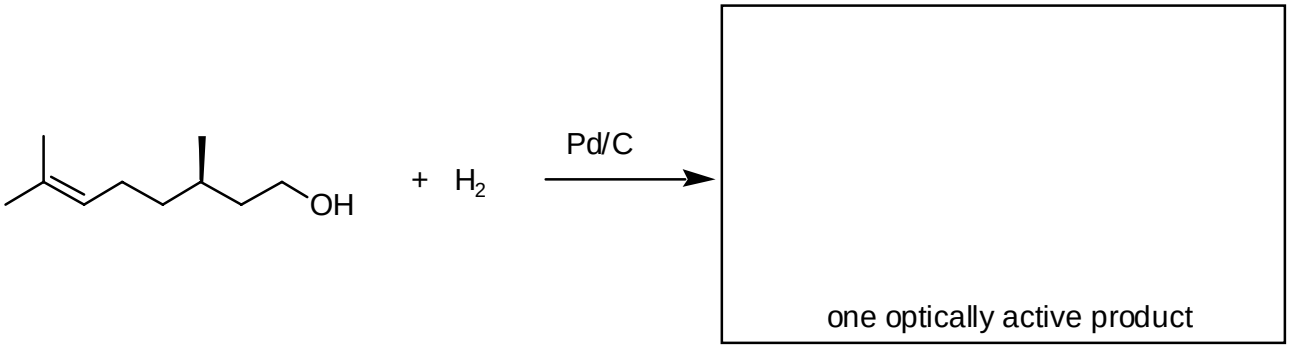
7. Citronellol is one of the main constituents of lemongrass oil and is an “all natural” insect repellant. (73 pts)



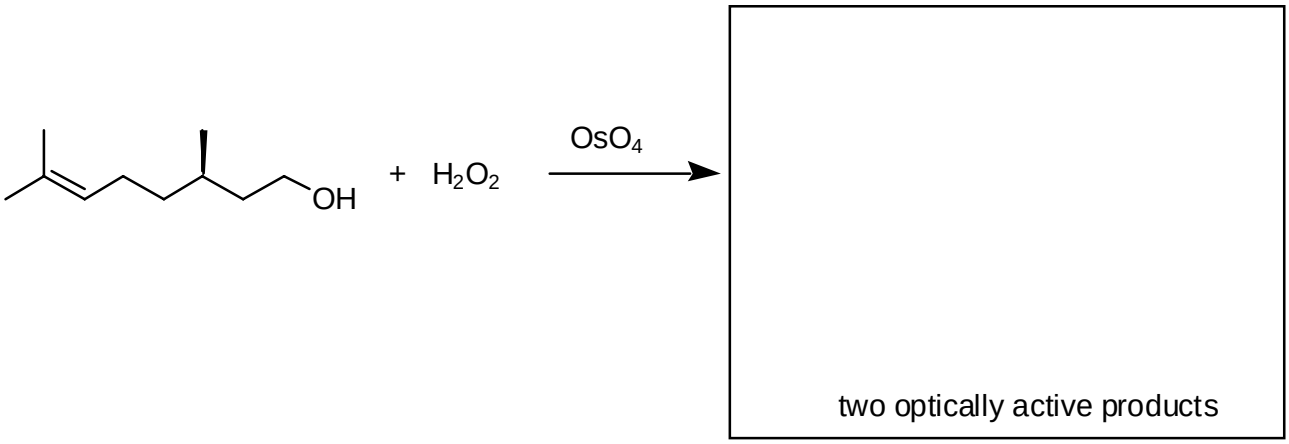
citronellol

A. Provide an IUPAC name for citronellol. Be sure to include R and S nomenclature.

B. Only one optically active product is generated from the hydrogenation of citronellol. Show that product below.

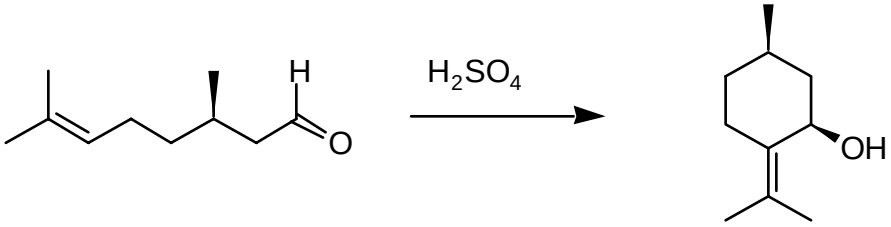


C. Two optically active products are generated from the dihydroxylation of citronellol. Show these two products below.



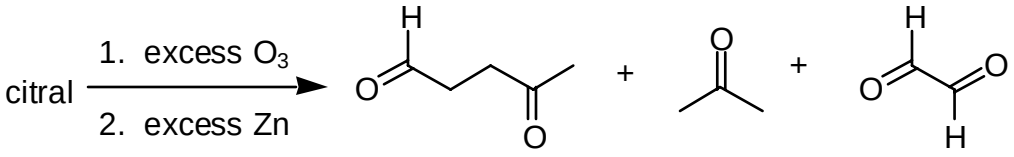
D. Explain why only one optically active product is formed in part B and two optically active products are formed in part C.

E. Citronellal, an oxidation product of citronellol reacts with sulfuric acid to give the product shown below. Provide a rational arrow pushing mechanism for this reaction. (Hint: think about analogies and how other double bonds might react with acid)



F. Citral, a close relative of citronellol, is actually a mixture of two stereoisomers. The molecular formula is $C_{10}H_{16}O$. How many degrees of unsaturation does citral have? You must show all of your work to receive full credit.

G. Ozonolysis of citral followed by reduction with zinc gave the following products (the products are in no particular order). What are the two stereoisomers that make up the citral mixture? (HINT: CITRAL IS AN OXIDIZED FORM OF CITRONELLOL)



two stereoisomers making up the citral mixture

"I have learned that you shouldn't compare yourself to the best others can do, but to the best you can do."
Live and Learn and Pass it On by H. Jackson Brown

HAVE A GREAT WINTER BREAK. YOU HAVE EARNED IT!!!!