

## Chemistry 3A Final Exam

Student name: \_\_\_\_\_ *Key* \_\_\_\_\_

Student's signature: \_\_\_\_\_

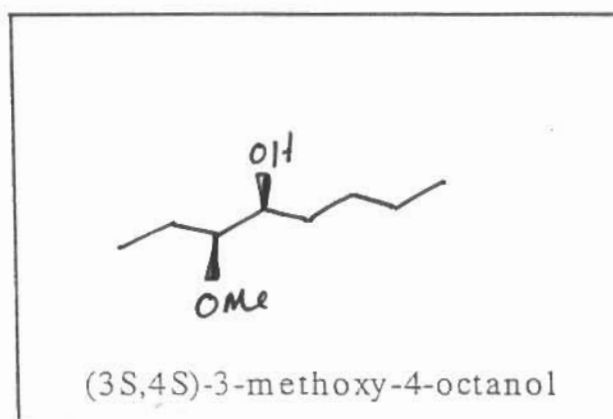
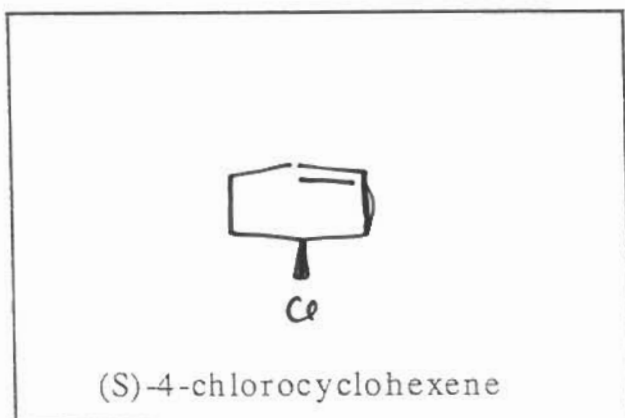
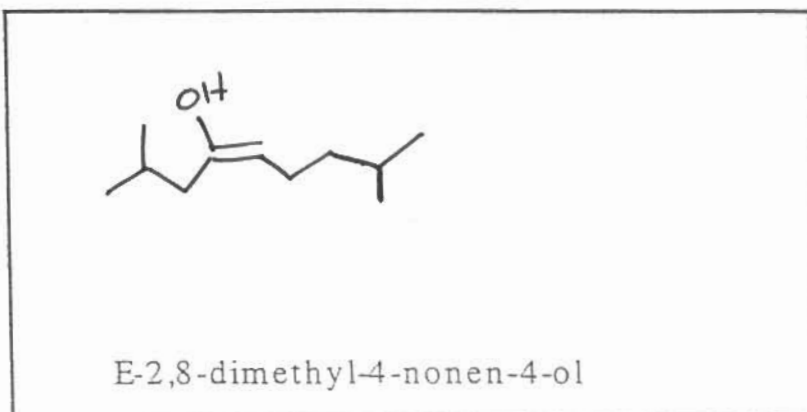
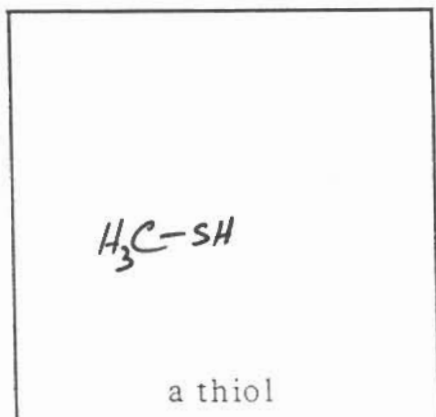
TA's name or section number: \_\_\_\_\_

<b>M</b>	Problem 1	_____	(7 pts)
<b>I</b>	Problem 2	_____	(20 pts)
<b>D</b>	Problem 3	_____	(5pts)
<b>T</b>	Problem 4	_____	(24 pts)
<b>E</b>	Problem 5	_____	(20 pts)
<b>R</b>	Problem 6	_____	(24 pts)
<b>M</b>			
	Problem 7	_____	(25 pts)
	Problem 8	_____	(35 pts)
	Problem 9	_____	(40 pts)
	Total Points	_____	(200 pts)

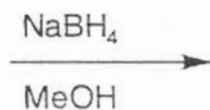
**No Calculators Allowed**  
**Be Sure Your Exam has 20 Pages**  
**Be Sure To Try All Parts of a Problem!**

1.

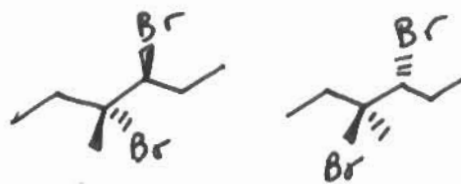
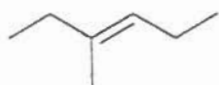
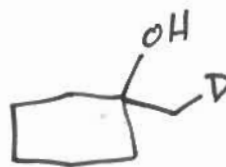
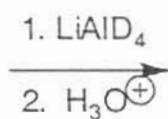
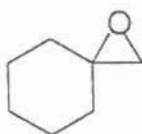
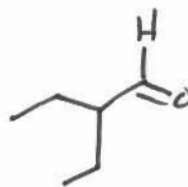
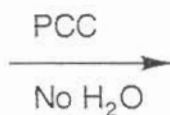
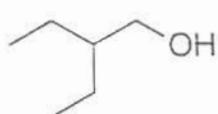
A. Provide one, and only one, real example for each of the following terms or draw a structure for a given chemical name. (7 pts)



2. Predict the product(s) from the following reactions. (20 pts)

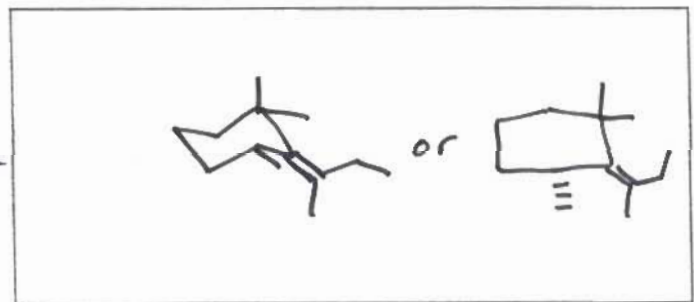
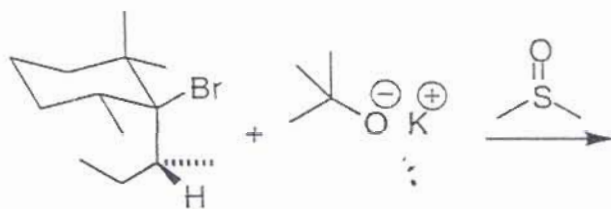
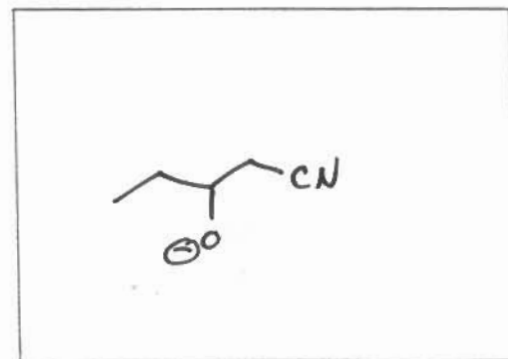
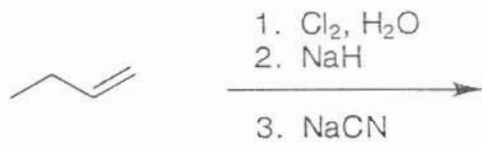
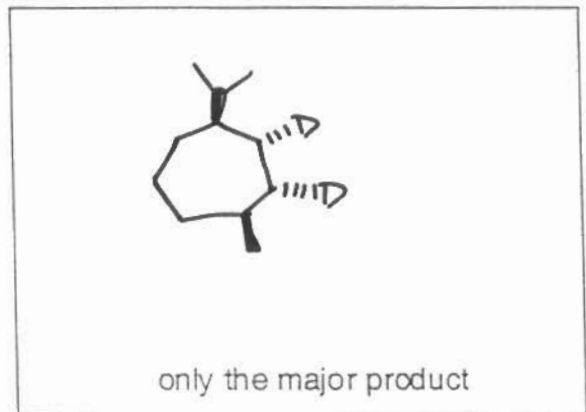
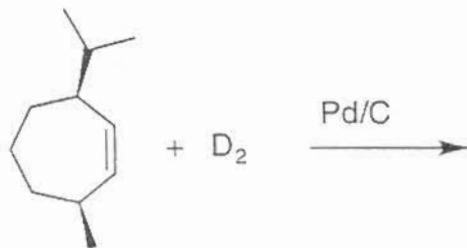
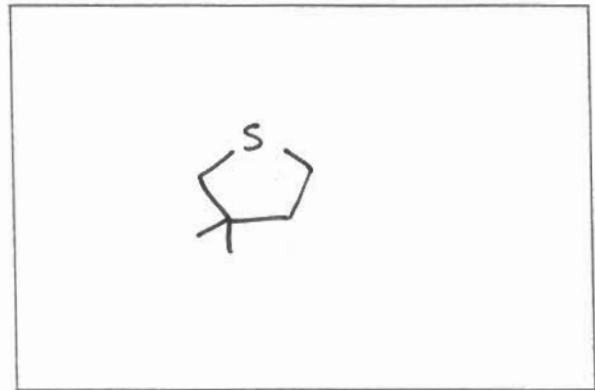
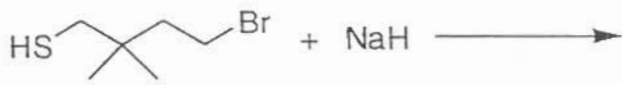


all possible stereoisomers  
(be sure to show wedges and dashes)



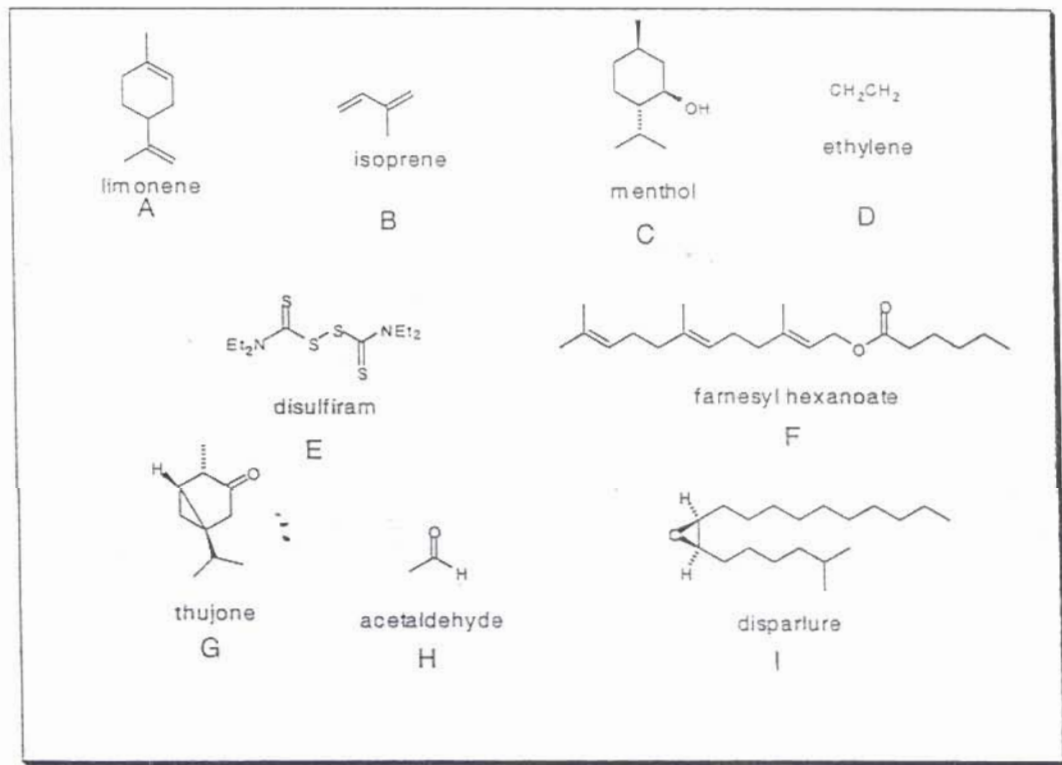
all expected stereoisomers  
(be sure to show wedges and dashes)

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3. Match the molecules shown below with the statements. (5 pts)

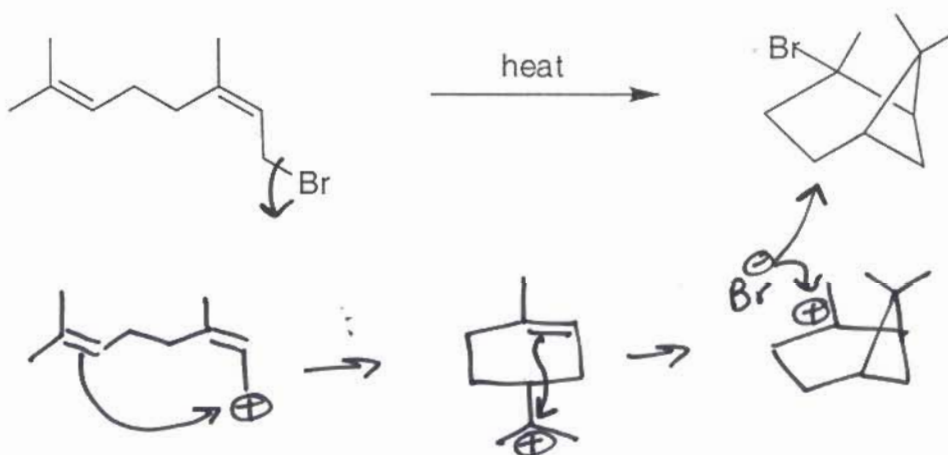
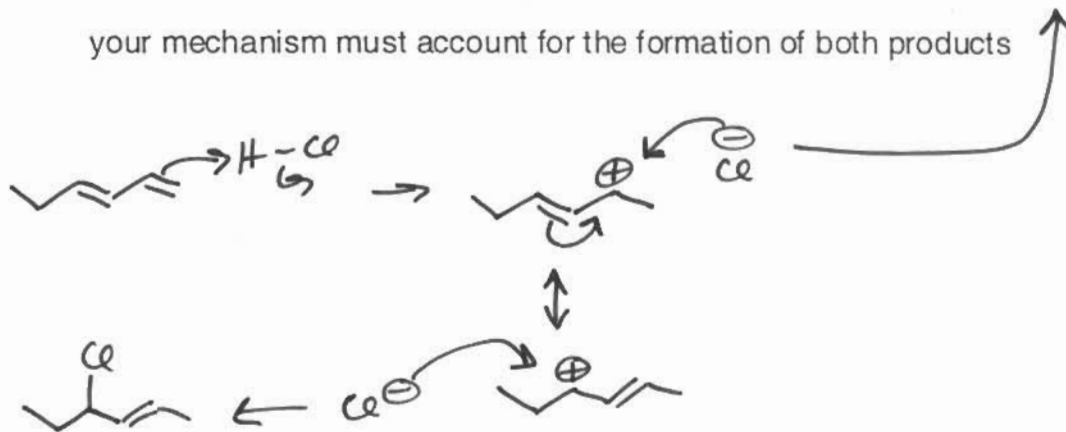
- a. Partly responsible for the Blue in the Blue Ridge Mountains? B
- b. Grandma said "don't put green banana's next to ripe banana's". D
- c. A very cool (actually cooling) molecule. C
- d. Gypsy moths! I
- e. A molecule that tells male bees to "go away, I'm not interested". F
- f. Hangover (I drank to much) molecules. E and H
- g. Absinthe! G
- h. Responsible for the miniature flame throwing ability of orange peels. A



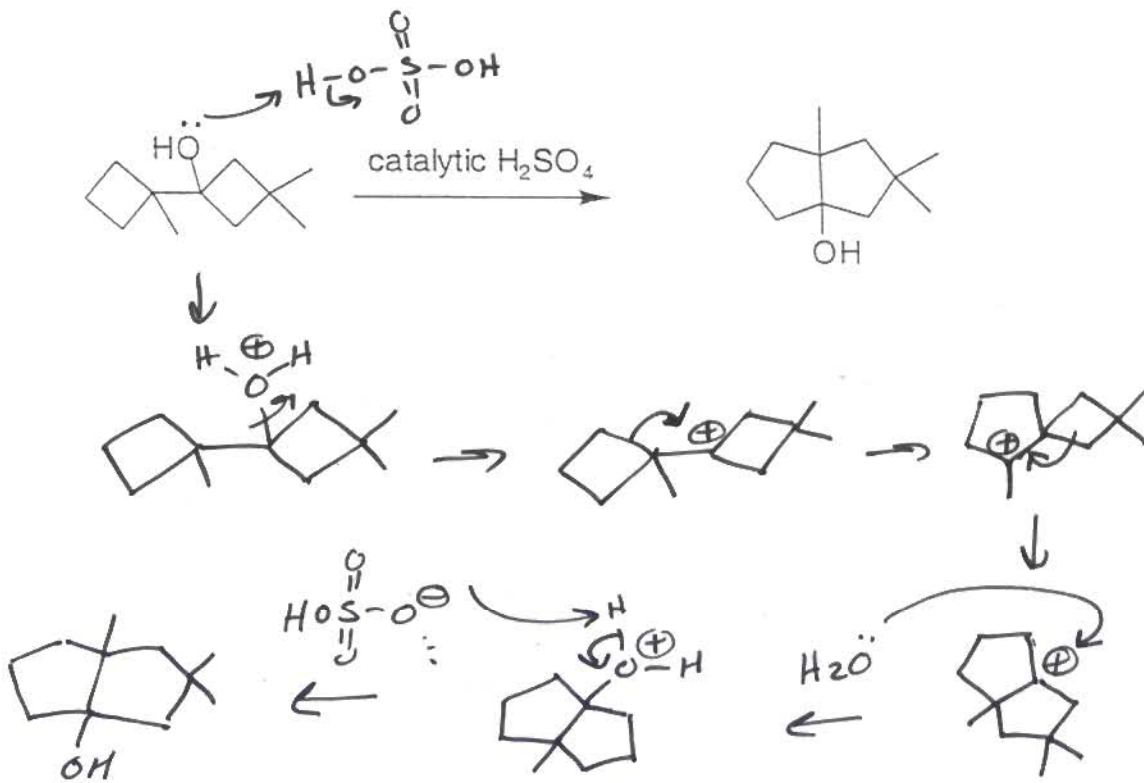
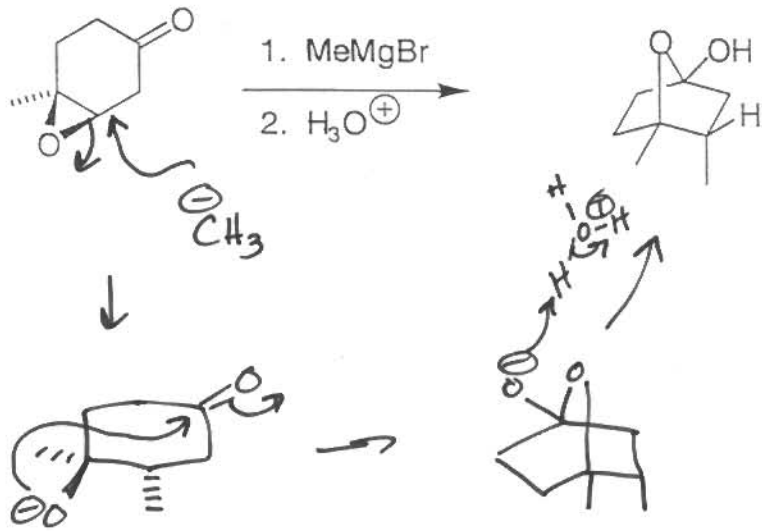
4. Write logical arrow-pushing mechanisms for the following reactions. (24 pts)



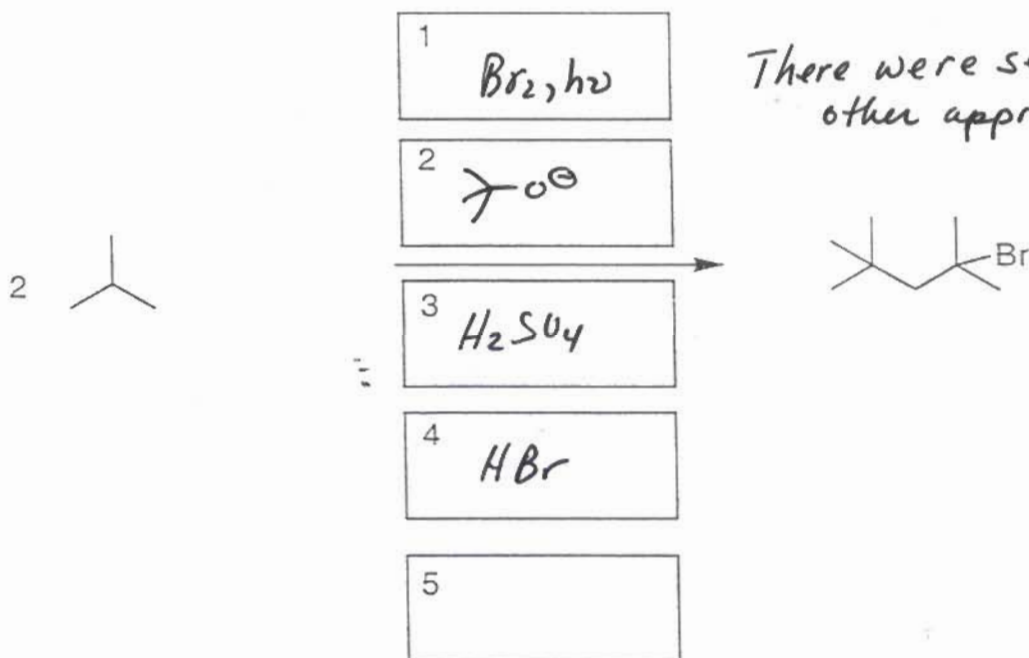
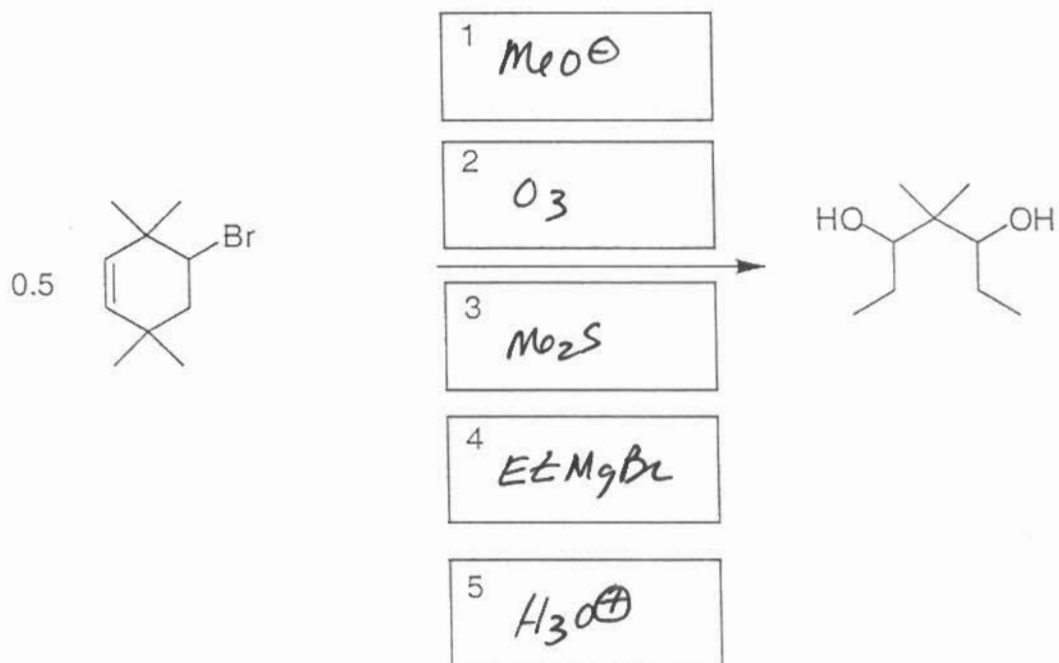
your mechanism must account for the formation of both products



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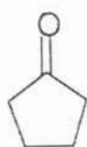


5. Provide the reagents and any other organic compounds necessary to synthesize the indicated product from the starting material shown. For each problem, five boxes are provided in which to place each step of your synthesis. **No synthesis will require more than five steps. However, some or all, may require fewer than five steps.** (20 pts)



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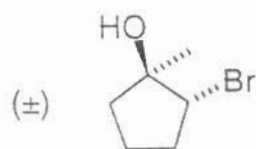
1  
 $\text{CH}_3\text{MgBr}$

2  
 $\text{H}_2\text{SO}_4, \Delta$

3  
 $\text{Br}_2, \text{H}_2\text{O}$

4

5



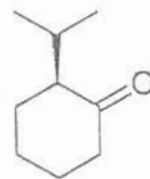
1  
MCPBA

2  
 $\text{LiAlH}_4$

3  
 $\text{H}_3\text{O}^+$

4  
PCC

5

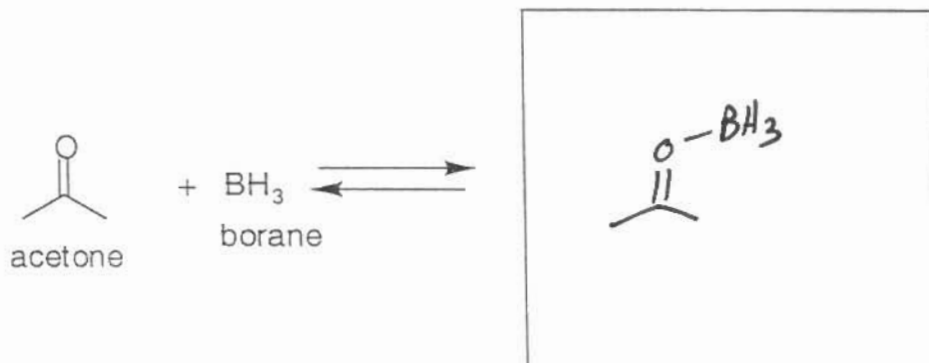


(hint: hydroboration or hydration are not acceptable approaches)

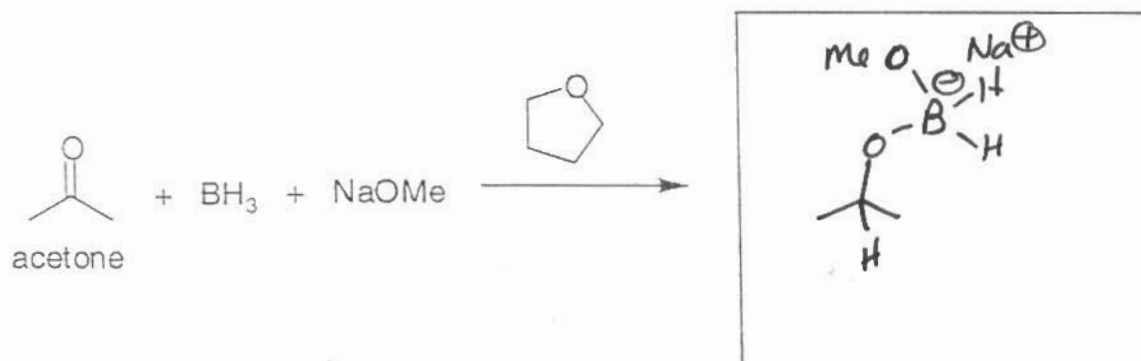
## Boron is not Boring!

6. (24 pts)

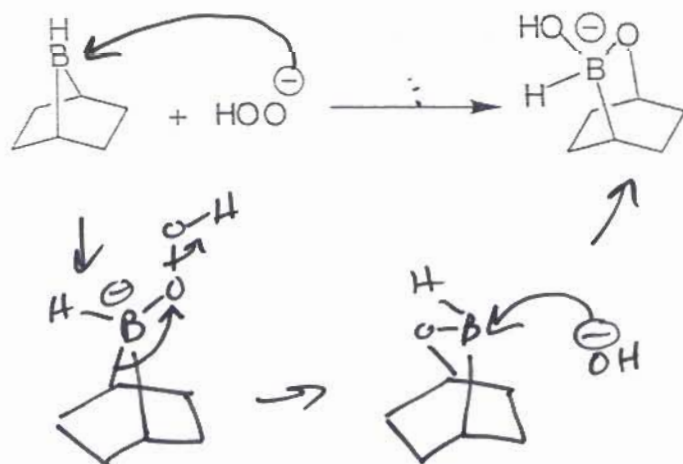
A. Borane does not reduce acetone, but will react with it to form a compound that is in equilibrium with the starting materials. Draw this compound in the box below.



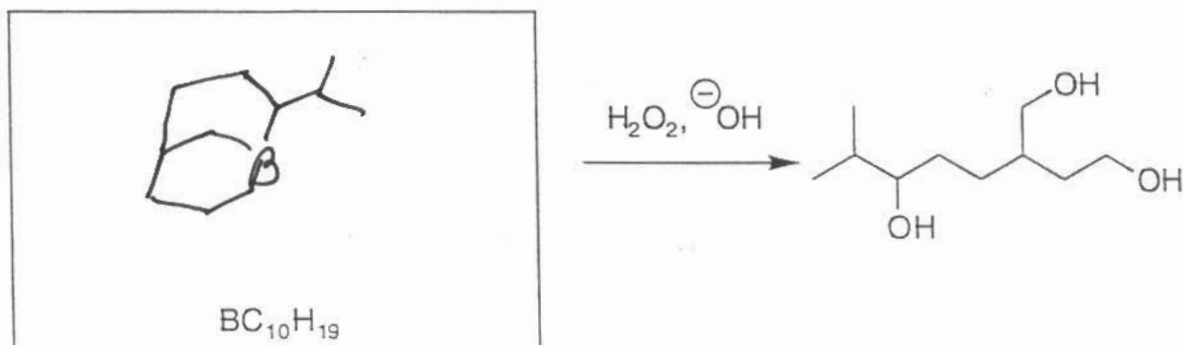
B. Borane, in the presence of sodium methoxide, will reduce acetone. Show the boron containing product resulting from the reaction shown below. Note the reaction is being run in tetrahydrofuran, not methanol.



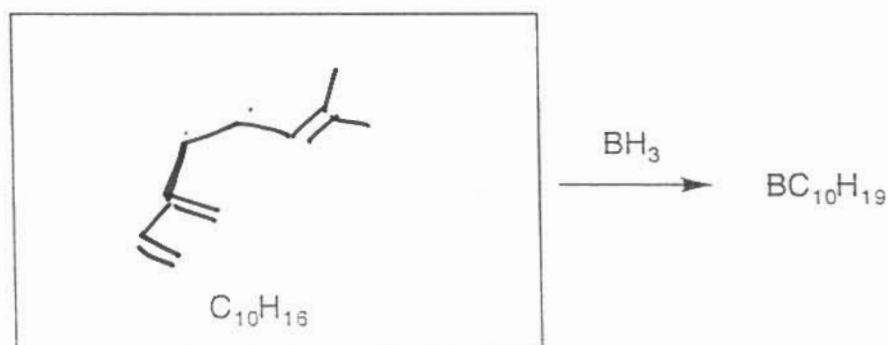
C. Write a logical arrow-pushing mechanism for the following reaction.



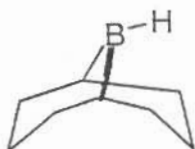
D. The triol shown below was prepared by oxidizing a compound with the molecular formula,  $BC_{10}H_{19}$ . Show the structure of this compound in the box below.



E. In the box below, provide the structure of the triene (a molecule with three alkenes) that led to the boron containing compound in part D.



F. When is it best to use 9-BBN instead of  $BH_3$ ? Place an X to the left of the correct answer.

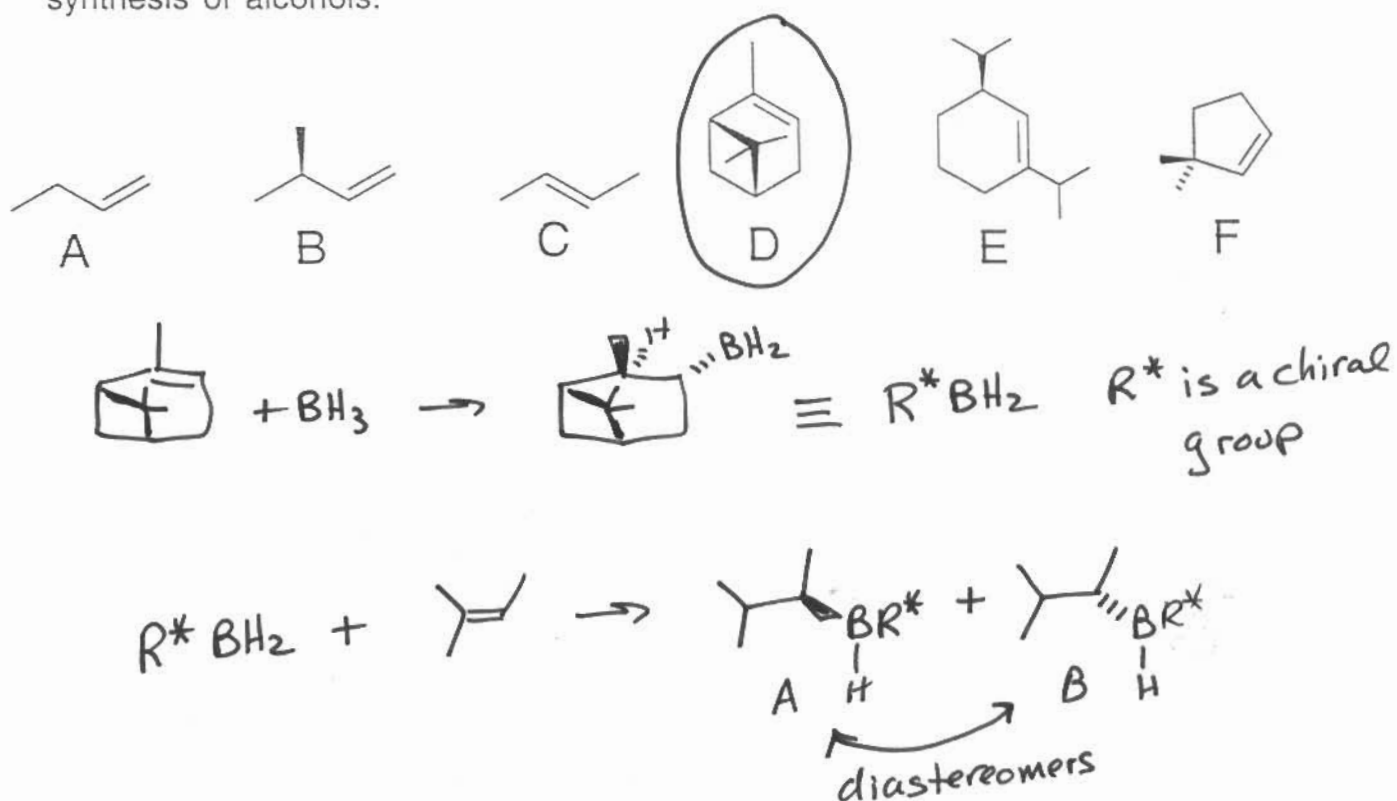


9-BBN

- When you have mono- and tri-substituted alkenes in the same molecule and you wish to only react at the tri-substituted alkene.
- When you have mono- and tri-substituted alkenes in the same molecule and you wish to only react at the mono-substituted alkene.
- When you want to form a chiral alcohol.
- When you want to form an alkyl bromide from an alcohol.
- When you want to oxidize a primary alcohol to an aldehyde.

G. The enantioselective synthesis of alcohols from ACHIRAL alkenes has been accomplished using appropriate alkyl boranes,  $\text{RBH}_2$ . Such boranes are prepared by the addition of a borane to an alkene. This species is then added to an ACHIRAL alkene, followed by oxidation.

- Which alkene below has the potential of leading to an alkyl borane that can then be used in the enantioselective synthesis of alcohols from ACHIRAL alkenes?
- Rationalize your choice by showing the reagent you would form by adding borane to the alkene you chose;
- and then show the products you would get by adding this alkyl borane to an ACHIRAL alkene.
- Explain why this method has the potential for leading to an enantioselective synthesis of alcohols.



Enantioselective synthesis of alcohols is possible using this approach because we formed diastereomeric products. Under the right circumstances, these products could be formed in significantly different amounts leading to differing amounts of enantiomeric alcohols after oxidation of A and B.

# The Basics

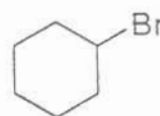
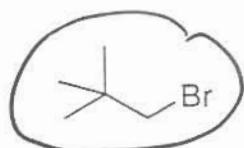
7. (25 pts)

A. How many neutrons are in  $^{18}\text{O}$ ? *10*

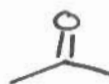
B. What does each letter and number in the acronym  $\text{S}_{\text{N}}1$  stand for?

*S = Substitution N = nucleophilic 1 = unimolecular*

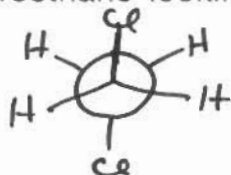
C. Which of the following electrophiles would NOT be suitable in an  $\text{S}_{\text{N}}2$  reaction? Circle one.



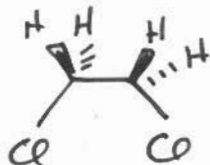
D. Draw the structure of a polar aprotic solvent.



E. Show the Newman projection of the most stable conformation of 1,2-dichloroethane looking down the carbon-carbon bond.



F. Show the bond-line representation of 1,2-dichloroethane in its least stable conformation.



G. Draw the major contributing resonance structure of the azide ion:



H. Draw the  $\pi$ -antibonding molecular orbital of ethylene (i.e. ethene).



I. The ideal bond angles associated with an  $\text{SP}^2$  hybridized carbon are?

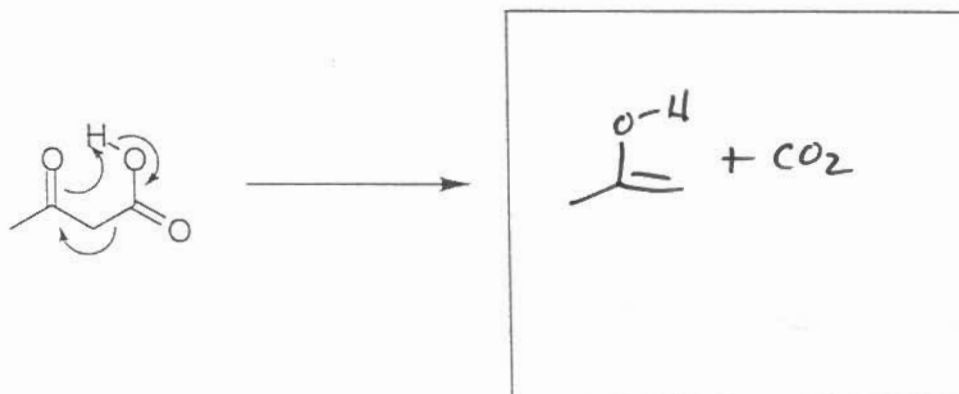
*120°*



K. What do the letters in the acronym LUMO stand for?

*L = lowest U = unoccupied M = molecular O = orbital*

L. Show the expected products from the following arrow-pushing mechanism.



M. Which statement best describes Hammond's postulate for an endothermic reaction? Place an X to the left of the correct answer.

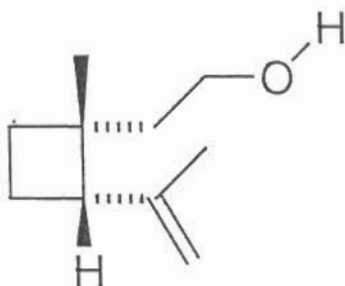
- The transition state looks more like the product(s) than the starting material(s).
- There is no transition state for an endothermic reaction.
- The transition state looks more like the starting material(s) than the product(s).
- Endothermic reactions are always "downhill".
- The transition state is considered "early".

N. A polarimeter is used to: (place an X to the left of the correct answer).

- Measure the thickness of ice in the Polar regions of our planet.
- Measure the degree to which a chiral molecule rotates plane-polarized light.
- Measure the polarity of a molecule.
- Make polarized sun glasses.

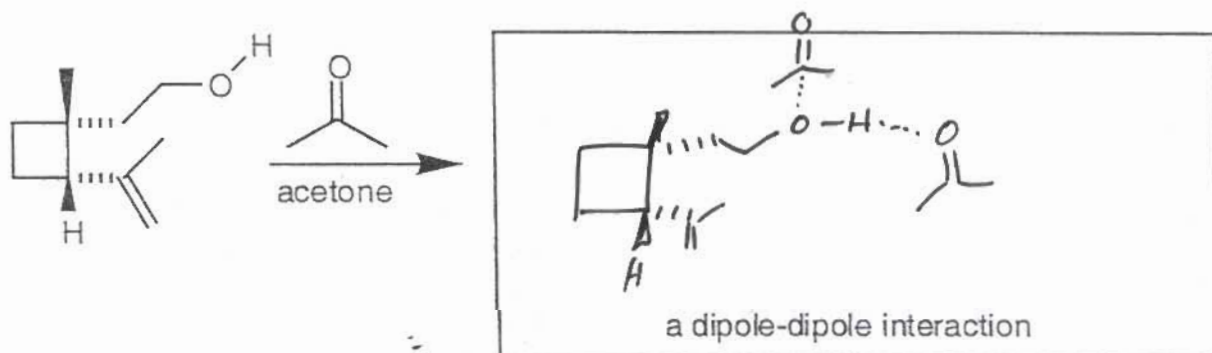
## Grandisol

8. Grandisol is the major component of grandlure, the sex attractant of the boll weevil. (35 pts)

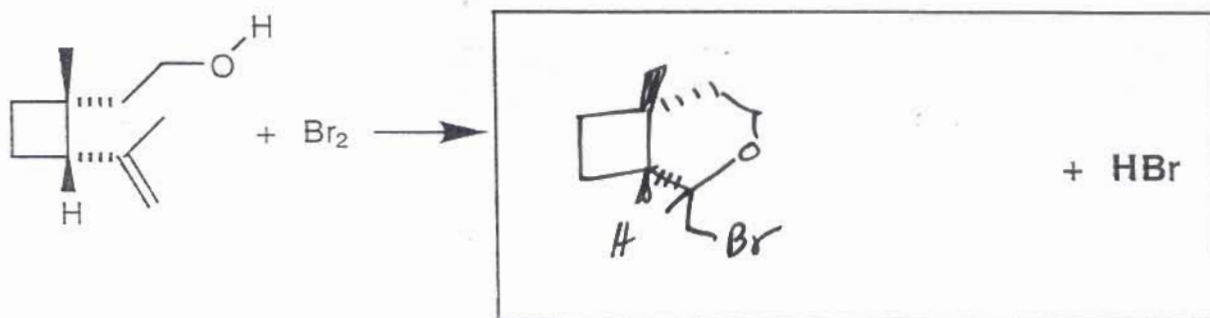


grandisol

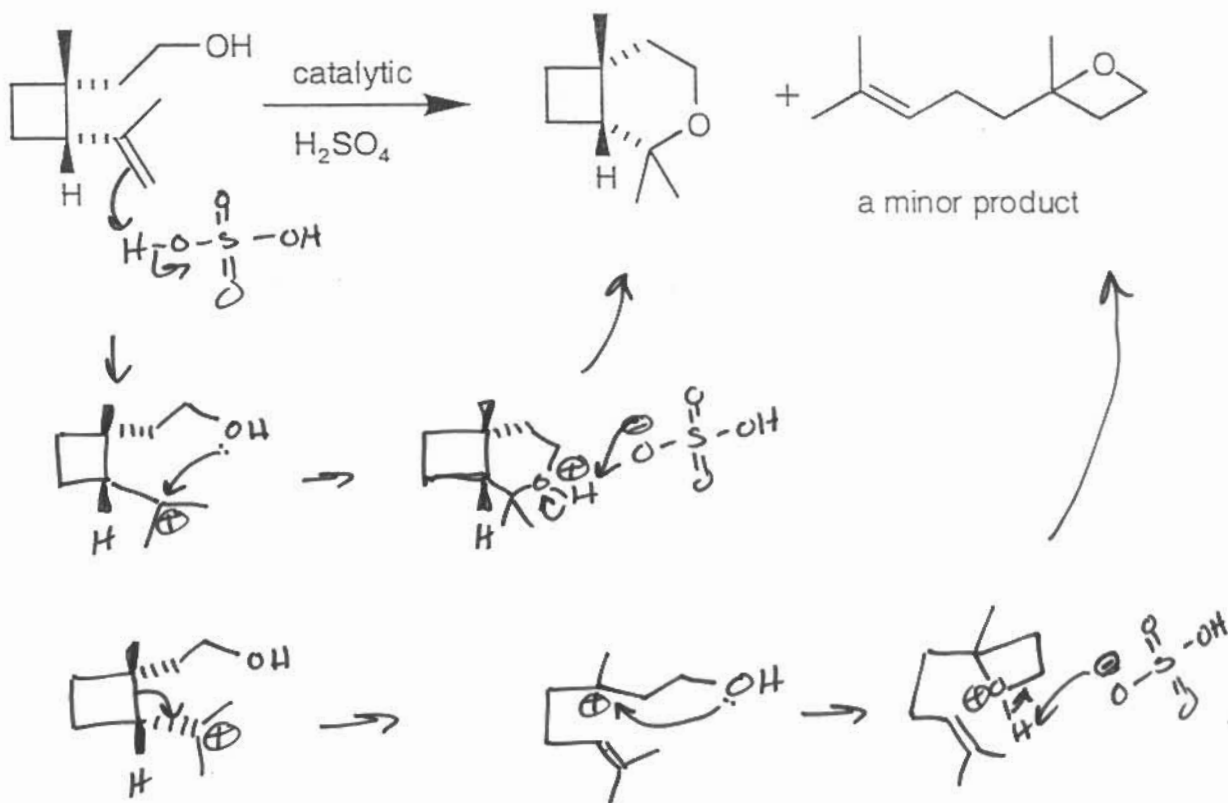
- On the diagram above, label each stereocenter as R or S.
- On the diagram above, circle a quaternary carbon and label it 4°.
- On the diagram above identify the most polar bond in grandisol and label it polar.
- How many possible stereoisomers are there of grandisol?
- Dissolving grandisol in acetone would lead to several types of Van der Waals interactions between the two molecules. Clearly draw a dipole-dipole interaction between these two molecules. Indicate your interaction using a dotted line. Your drawing must be specific to receive any points.



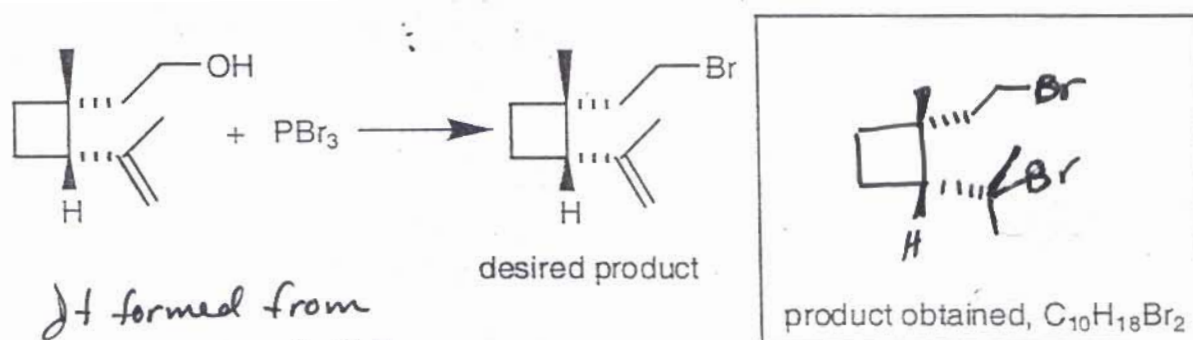
F. Predict the product.



G. Write a logical arrow-pushing mechanism for the following reaction. Be sure that your mechanism accounts for the formation of both products shown.



H. John T. wanted to make the bromo analog of grandisol shown below. However, after reacting grandisol with  $\text{PBr}_3$  he obtained a different compound with the molecular formula,  $\text{C}_{10}\text{H}_{18}\text{Br}_2$ . What is this compound and why did it form? Words are satisfactory here. You do not need to write mechanisms!



It formed from any residual  $\text{HBr}$  or  $\text{Br}_2\text{P-OH}$  (an acid).

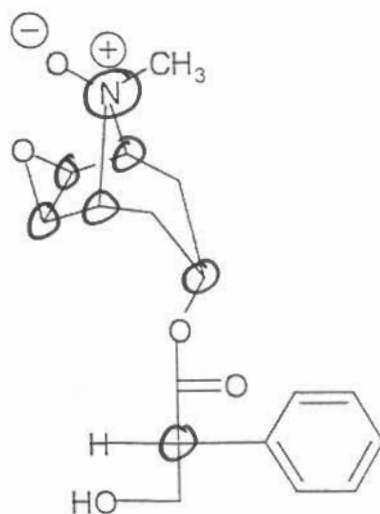


# Naturally Natural Product Chemistry

9. (40 pts)

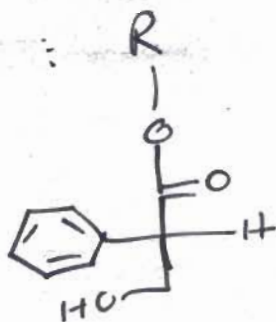
A. Scopolamine N-oxide is a synthetic derivative of scopolamine, a naturally occurring plant alkaloid that has been used as a sedative in surgery as well as a treatment for motion sickness (consult a physician before using!!).

Circle all of the stereocenters in scopolamine N-oxide shown below. Every wrong circle cancels a right circle.

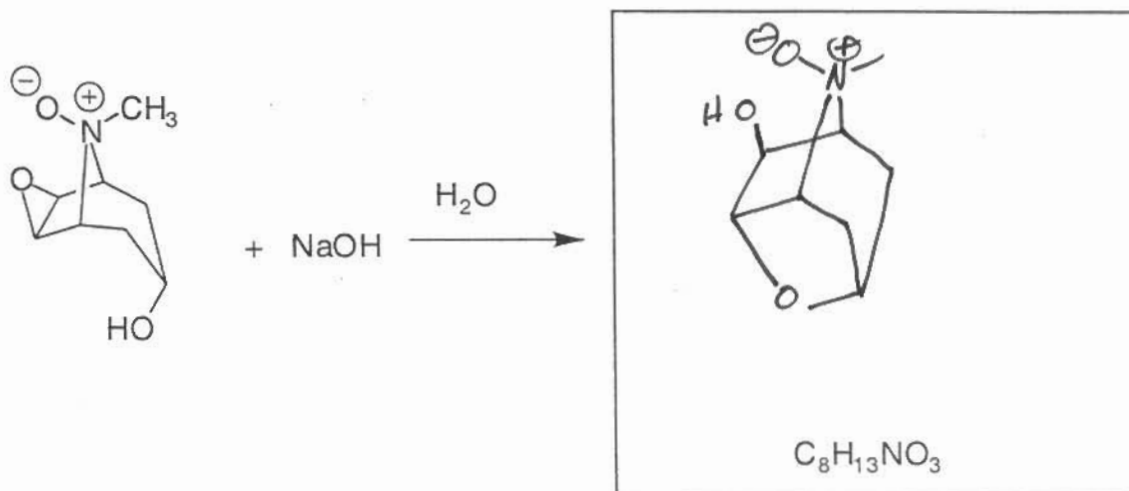


scopolamine N-oxide

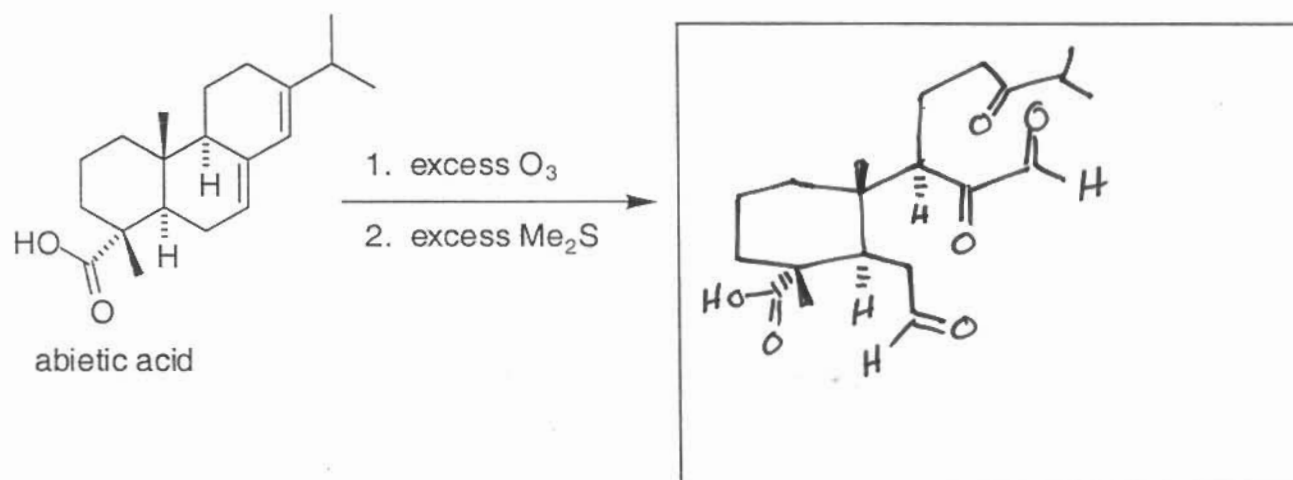
B. Draw one diastereomer of scopolamine N-oxide.



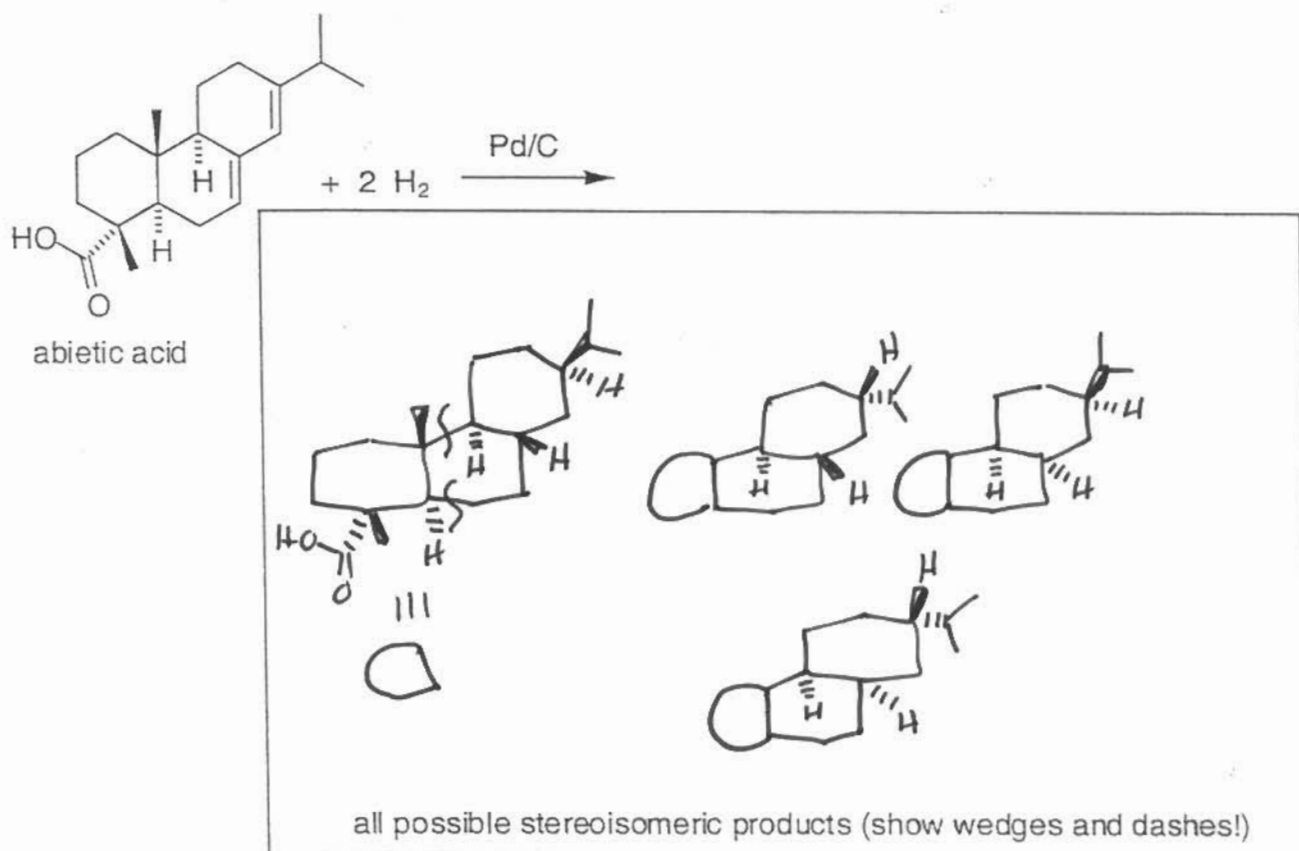
C. Predict the product.



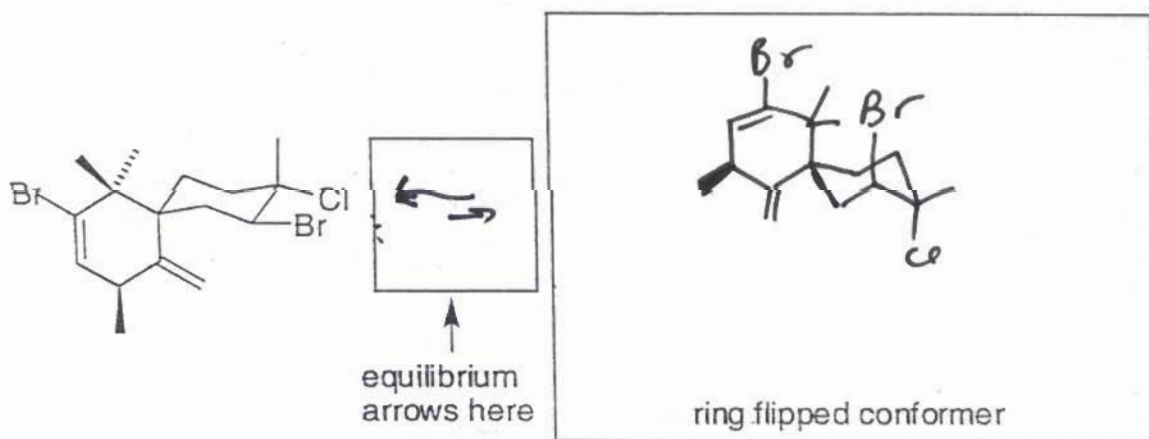
D. Show the product(s) of ozonolysis of abietic acid.



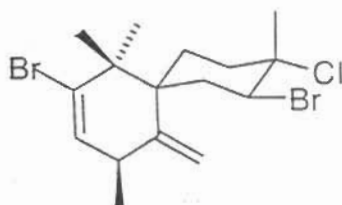
E. Show the products of complete hydrogenation of abietic acid.



F. One of many compounds isolated from red algae is shown below. Draw the ring flipped conformer of this compound. In the small box indicate which conformer is favored using equilibrium arrows (you do not need a table of data to figure this out).



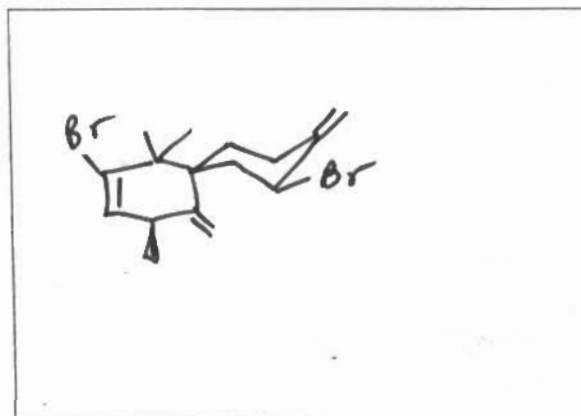
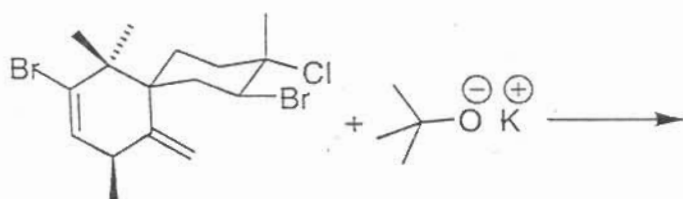
G. Which word(s) describe the relationship between the bromine and chlorine atoms in the cyclohexane ring of the compound shown below. Place an X to the left of every answer that is correct. Every wrong answer cancels a right answer.



compound from red algae

- cis
- diastereomeric
- trans
- enantiomeric
- syn
- eclipsed
- staggered
- diequatorial

H. Predict the product.



*Have a great winter break!*  
*S. Pedersen*



## Table of select pKa's

Acid	pKa	Acid	pKa
HI	-5.2	CH <sub>3</sub> CO <sub>2</sub> H	4.7
H <sub>2</sub> SO <sub>4</sub>	-5.0	HCN	9.2
HBr	-4.7	NH <sub>4</sub> <sup>+</sup>	9.2
HCl	-2.2	CH <sub>3</sub> SH	10.0
H <sub>3</sub> O <sup>+</sup>	-1.7	CH <sub>3</sub> OH	15.5
CH <sub>3</sub> SO <sub>3</sub> H	-1.2	H <sub>2</sub> O	15.7
HF	3.2	NH <sub>3</sub>	35

**THE PERIODIC TABLE**

IA												VIIIA							
H	He											B	C	N	O	F	Ne		
1 1.01 Hydrogen	2 4.00 Helium											5 10.81 Boron	6 12.01 Carbon	7 14.01 Nitrogen	8 16.00 Oxygen	9 19.00 Fluorine	10 20.18 Neon		
IIA												III A	IV A	VA	VIA	VII A			
3 6.94 Lithium	4 9.01 Beryllium											13 26.98 Aluminum	14 28.09 Silicon	15 30.97 Phosphorus	16 32.07 Sulfur	17 35.45 Chlorine	18 39.95 Argon		
		IIIB	IVB	VB	VIB	VII B	VIII B				IB	II B							
11 22.99 Sodium	12 24.31 Magnesium	21 44.96 Scandium	22 47.88 Titanium	23 50.94 Vanadium	24 52.00 Chromium	25 54.94 Manganese	26 55.85 Iron	27 58.93 Cobalt	28 58.93 Nickel	29 63.55 Copper	30 65.39 Zinc	31 69.72 Gallium	32 72.61 Germanium	33 74.92 Arsenic	34 78.96 Selenium	35 79.90 Bromine	36 83.80 Krypton		
37 85.47 Rubidium	38 87.62 Strontium	39 88.91 Yttrium	40 91.22 Zirconium	41 92.91 Niobium	42 95.94 Molybdenum	43 95.94 Technetium	44 101.07 Ruthenium	45 101.07 Rhodium	46 106.42 Palladium	47 107.87 Silver	48 112.41 Cadmium	49 114.82 Indium	50 118.71 Tin	51 121.76 Antimony	52 127.60 Tellurium	53 126.90 Iodine	54 131.29 Xenon		
55 132.91 Cesium	56 137.33 Barium	57 138.91 Lanthanum	58 172.49 Hafnium	59 180.95 Tantalum	60 183.85 Tungsten	61 186.21 Rhenium	62 193.22 Osmium	63 193.22 Iridium	64 197.04 Platinum	65 197.04 Gold	66 200.59 Mercury	67 204.38 Thallium	68 207.2 Lead	69 208.98 Bismuth	70 208.98 Polonium	71 208.98 Astatine	72 222 Radon		
87 223.02 Francium	88 226.03 Radium	89 227.03 Actinium	104 (261) Rutherfordium	105 (262) Dubnium	106 (263) Seaborgium	107 (262) Bohrium	108 (265) Hassium	109 (266) Meitnerium	Unannounced Discovery 110 Nov. 1984	Unannounced Discovery 111 Nov. 1984	Unannounced Discovery 112 1985	Unannounced Discovery 114 Nov. 1985	Unannounced Discovery 115 1985	Unannounced Discovery 116 1985	Unannounced Discovery 118 1985	Unannounced Discovery 119 1985	Unannounced Discovery 120 1985		
ALKALI METALS		LANTHANIDES										ACTINIDES						HALOGENS	NOBLE GASES
		58 140.12 Cerium	59 140.91 Praseodymium	60 144.24 Neodymium	61 (145) Promethium	62 150.36 Samarium	63 152.97 Europium	64 157.25 Gadolinium	65 158.93 Terbium	66 162.50 Dysprosium	67 164.93 Holmium	68 167.26 Erbium	69 168.93 Thulium	70 173.04 Ytterbium	71 174.97 Lutetium				
		90 232.04 Thorium	91 231.04 Protactinium	92 238.03 Uranium	93 237.05 Neptunium	94 (240) Plutonium	95 243.06 Americium	96 (247) Curium	97 (248) Berkelium	98 (251) Californium	99 252.08 Einsteinium	100 257.10 Fermium	101 (257) Mendelevium	102 259.10 Nobelium	103 262.11 Lawrencium				

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**TABLE 1-2** Electronegativities of Selected Elements

H						
2.2						
Li	Be	B	C	N	O	F
1.0	1.6	2.0	2.6	3.0	3.4	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.3	1.6	1.9	2.2	2.6	3.2
K						Br
0.8						3.0
						I
						2.7

Note: Values established by L. Pauling and updated by A. L. Allred (see *Journal of Inorganic and Nuclear Chemistry*, 1961, 17, 215).

**TABLE 3-1** Bond-Dissociation Energies of Various A-B Bonds  
 $(DH^\circ \text{ in kcal mol}^{-1})$ 

A in A-B	B in A-B						
	-H	-F	-Cl	-Br	-I	-OH	-NH <sub>2</sub>
H	104	136	103	87	71	119	108
CH <sub>3</sub> -	105	110	85	70	57	93	84
CH <sub>3</sub> CH <sub>2</sub> -	101	111	84	70	56	94	85
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> -	101	110	85	70	56	92	84
(CH <sub>3</sub> ) <sub>2</sub> CH-	98.5	111	84	71	56	96	86
(CH <sub>3</sub> ) <sub>3</sub> C-	96.5	110	85	71	55	96	85

Note: These numbers are being revised continually because of improved methods for their measurement. Some of the values given here may be in (small) error.

**TABLE 3-2** Bond-Dissociation Energies for Some Alkanes

Compound	$DH^\circ$ (kcal mol <sup>-1</sup> )	Compound	$DH^\circ$ (kcal mol <sup>-1</sup> )
CH <sub>3</sub> -H	105	CH <sub>3</sub> -CH <sub>3</sub>	90
C <sub>2</sub> H <sub>5</sub> -H	101	C <sub>2</sub> H <sub>5</sub> -CH <sub>3</sub>	89
C <sub>3</sub> H <sub>7</sub> -H	101	C <sub>2</sub> H <sub>5</sub> -C <sub>2</sub> H <sub>5</sub>	88
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> -H	101	(CH <sub>3</sub> ) <sub>2</sub> CH-CH <sub>3</sub>	88
(CH <sub>3</sub> ) <sub>2</sub> CH-H	98.5	(CH <sub>3</sub> ) <sub>3</sub> C-CH <sub>3</sub>	87
(CH <sub>3</sub> ) <sub>3</sub> C-H	96.5	(CH <sub>3</sub> ) <sub>2</sub> CH-CH(CH <sub>3</sub> ) <sub>2</sub>	85.5
		(CH <sub>3</sub> ) <sub>3</sub> C-C(CH <sub>3</sub> ) <sub>3</sub>	78.5

Note: See footnote for Table 3-1.