Dr. Steven Pedersen December 10, 2003

Chemistry 3A
Final Exam

Student name: Key

Student's signature: _____

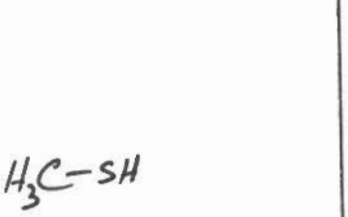
TA's name or section number: _____

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

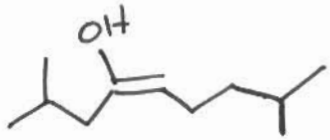
No Calculators Allowed
Be Sure Your Exam has 20 Pages
Be Sure To Try All Parts of a Problem!

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)

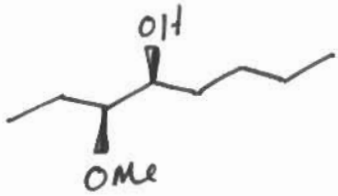


a thiol



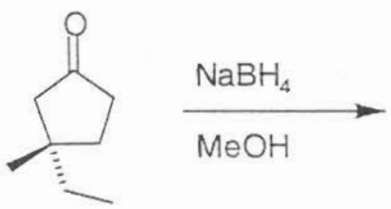
E-2,8-dimethyl-4-nonen-4-ol

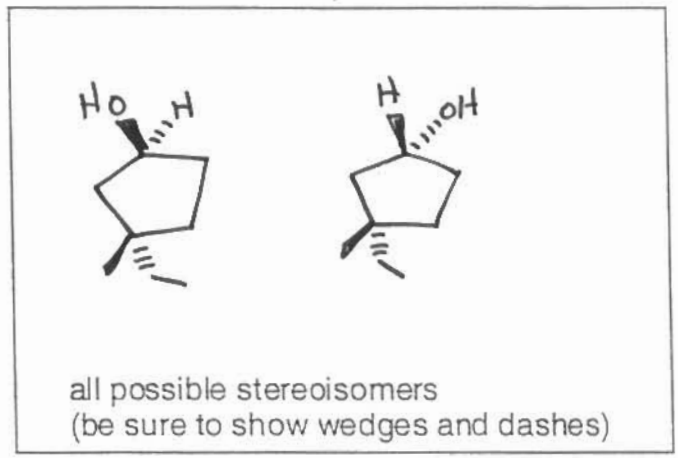
(S)-4-chlorocyclohexene

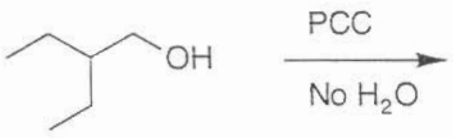


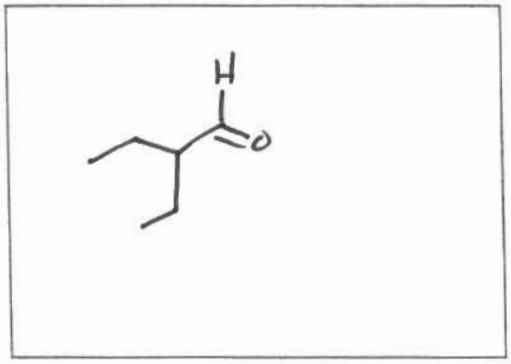
(3S,4S)-3-methoxy-4-octanol

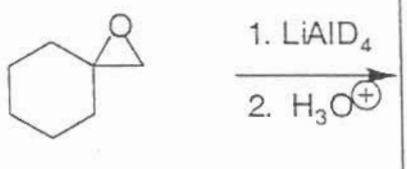
2. Predict the product(s) from the following reactions. (20 pts)

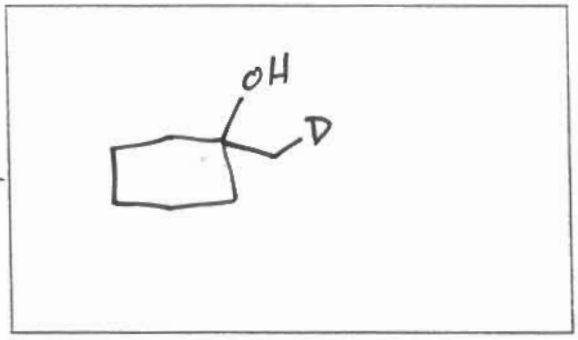


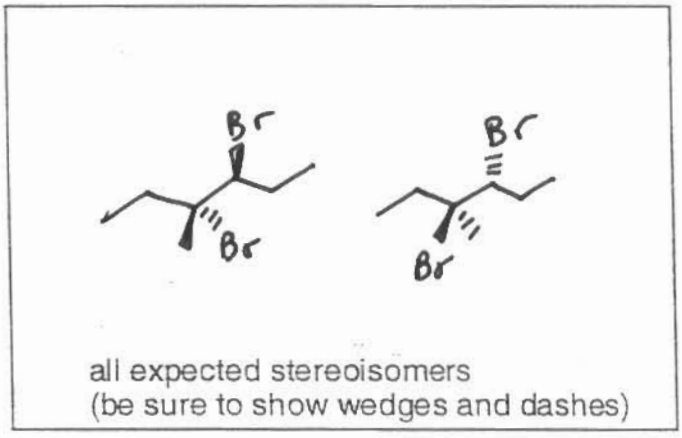












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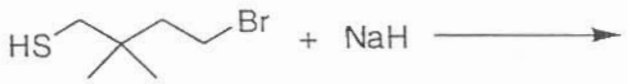
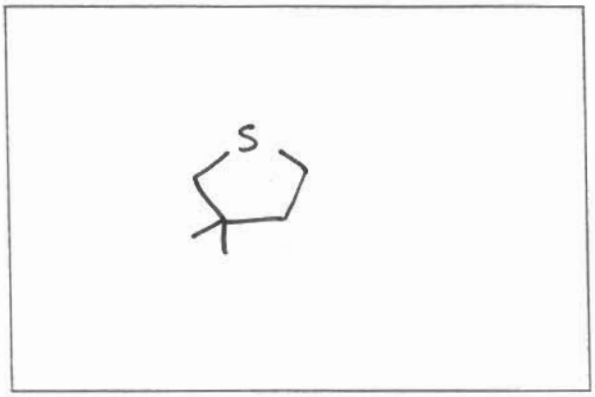
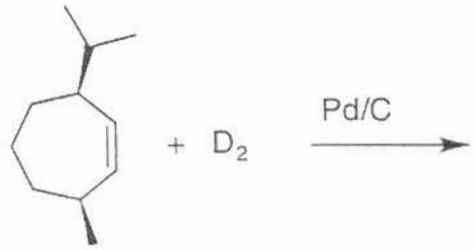
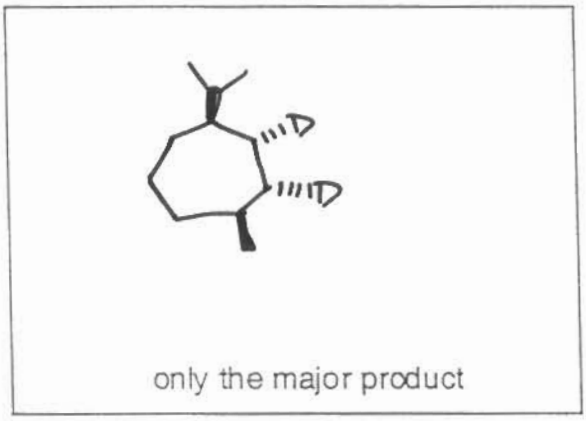
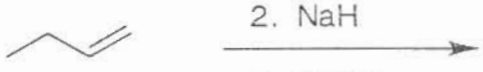
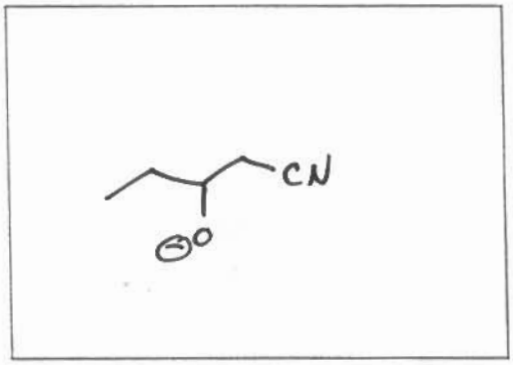

HS
Br
+ NaH

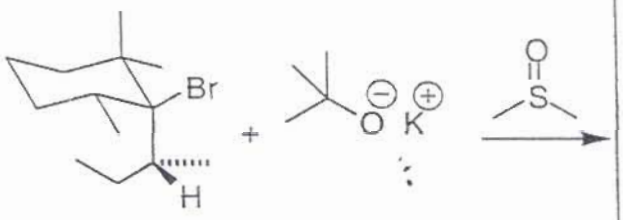

S

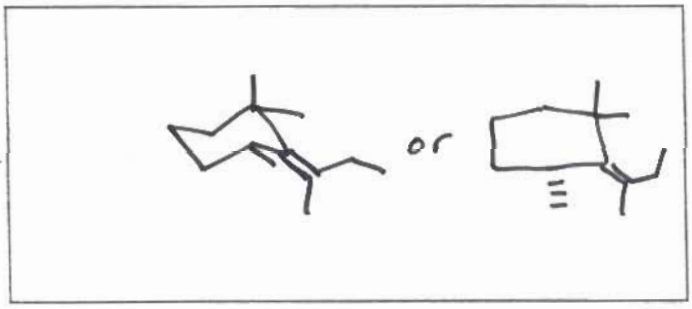

+ D_2
Pd/C


only the major product


1. Cl_2, H_2O
2. NaH
3. NaCN


CN
O


Br
H
+
O
K
O
S


or

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

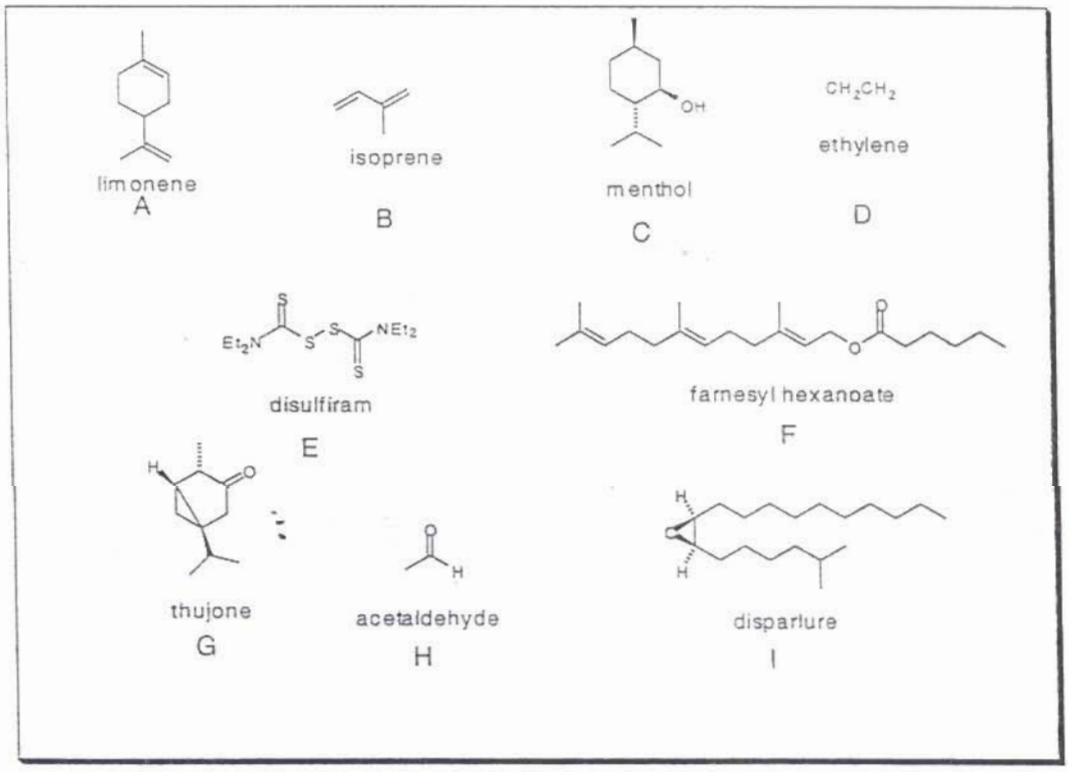
d. Gypsy moths! I

e. A molecule that tells male bees to "go away, I'm not interested". F

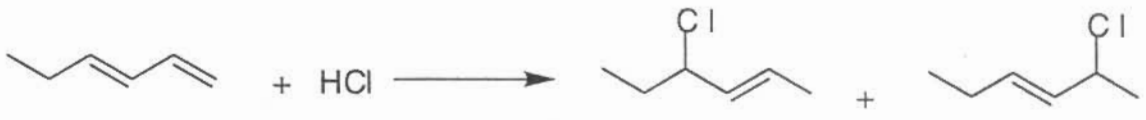
f. Hangover (I drank to much) molecules. E and H

g. Absinthe! G

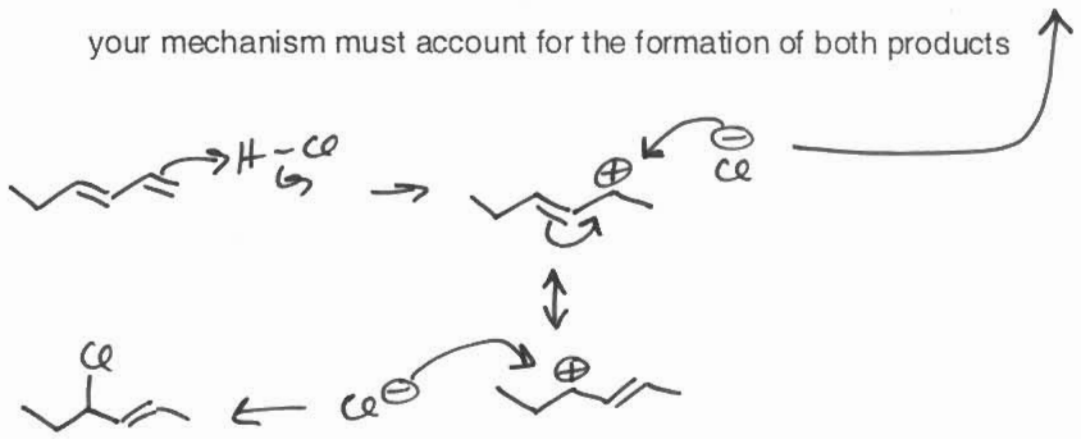
h. Responsible for the miniature flame throwing ability of orange peels. A

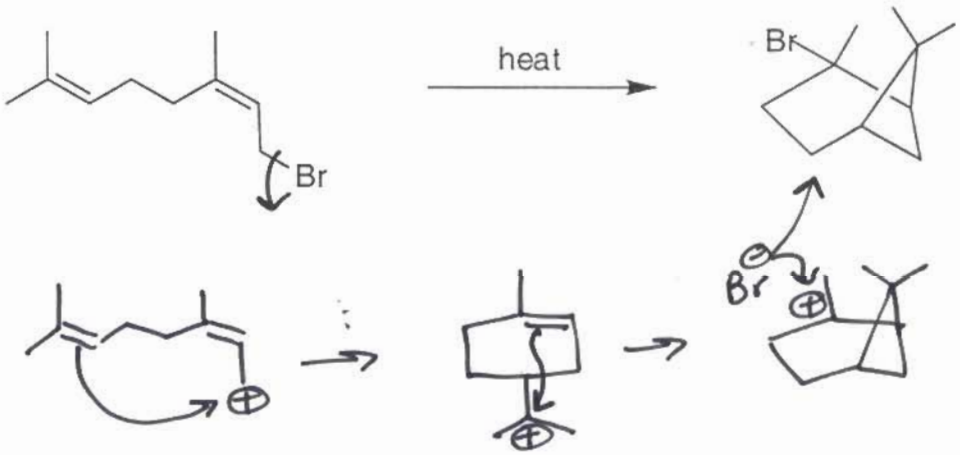


4. Write logical arrow-pushing mechanisms for the following reactions. (24 pts)



your mechanism must account for the formation of both products





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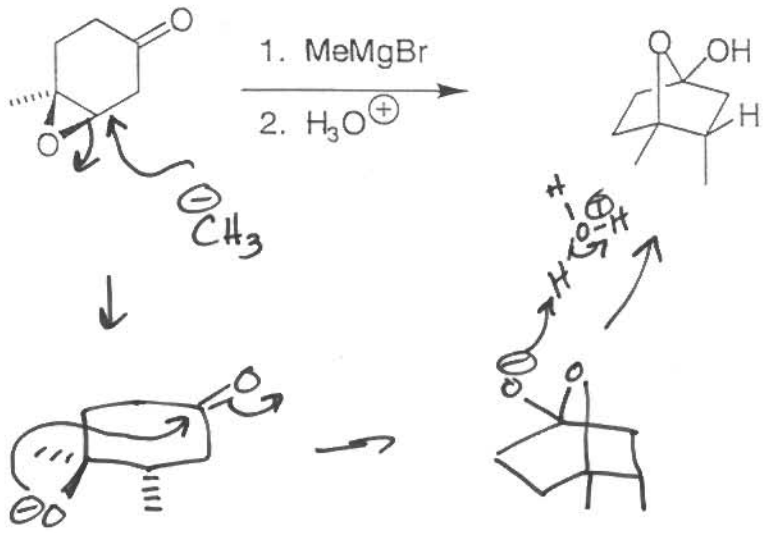
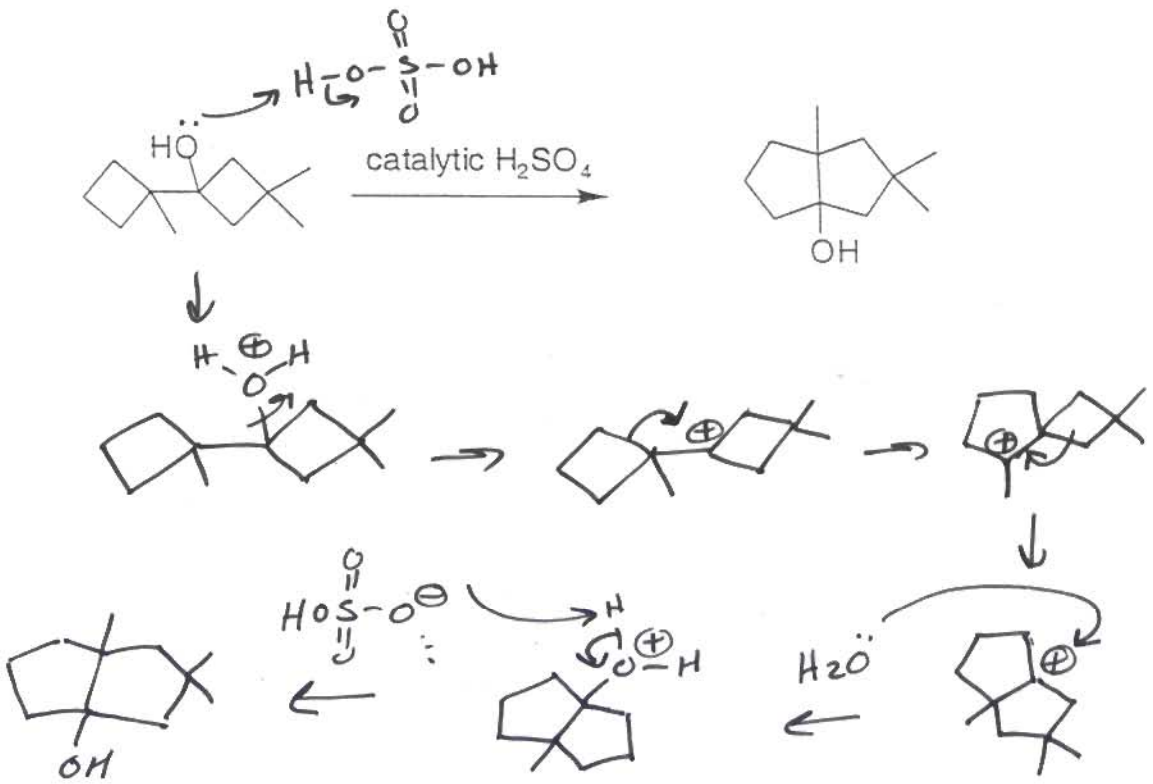
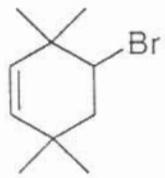

1. MeMgBr
2. $H_3O^{\oplus}$
OH
H


catalytic H_2SO_4
OH
H_2O

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)

0.5 

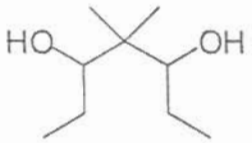
1 $MeO^{\ominus}$

2 O_3

3 Mo_2S

4 $EtMgBr$

5 $H_3O^{\oplus}$



2 

1 $Br_2, h\nu$

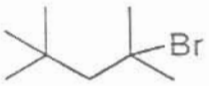
2 $^{\ominus}OH$

3 H_2SO_4

4 HBr

5

There were several other approaches.



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1 CH_3MgBr

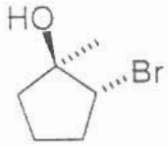
2 H_2SO_4, Δ

3 Br_2, H_2O

4

5

(±)



1 MCPBA

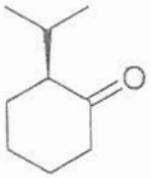
2 $LiAlH_4$

3 $H_3O^{\oplus}$

4 PCC

5

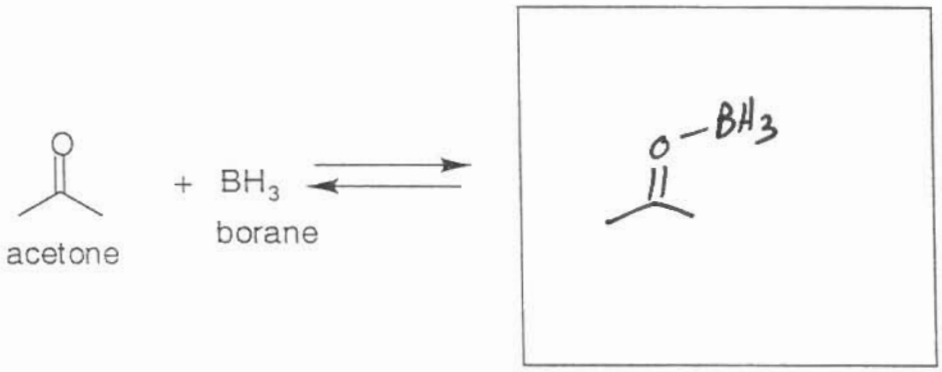
(hint: hydroboration or hydration are not acceptable approaches)



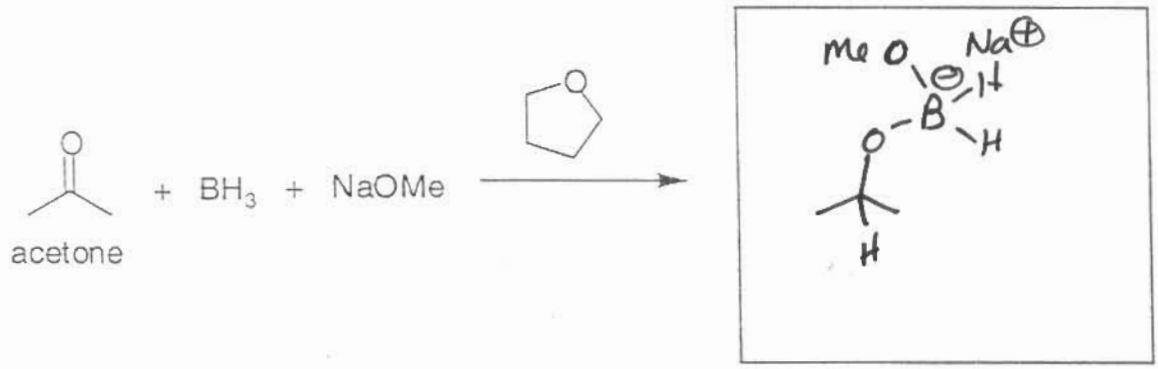
Boron is not Boring!

6. (24 pts)

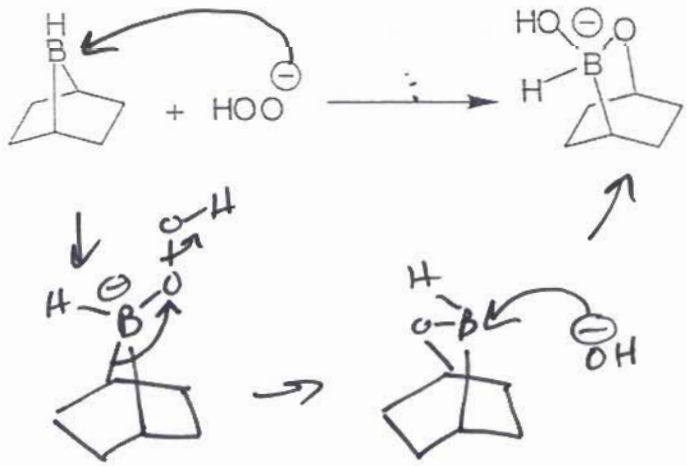
A. Borane does not reduce acetone, but will react with it to form a compound that is in equilibrium with the starting materials. Draw this compound in the box below.



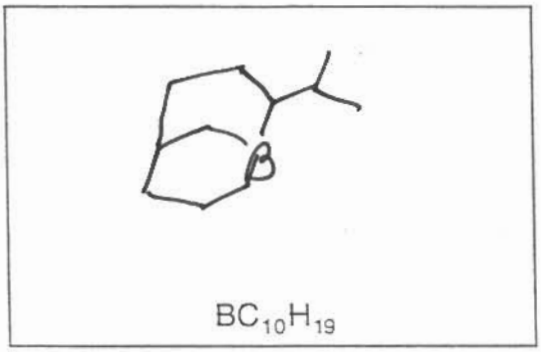
B. Borane, in the presence of sodium methoxide, will reduce acetone. Show the boron containing product resulting from the reaction shown below. Note the reaction is being run in tetrahydrofuran, not methanol.



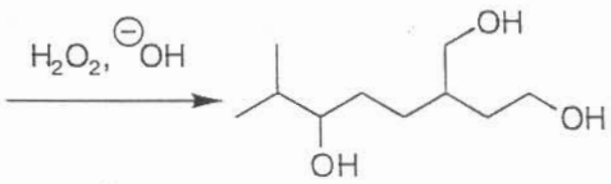
C. Write a logical arrow-pushing mechanism for the following reaction.



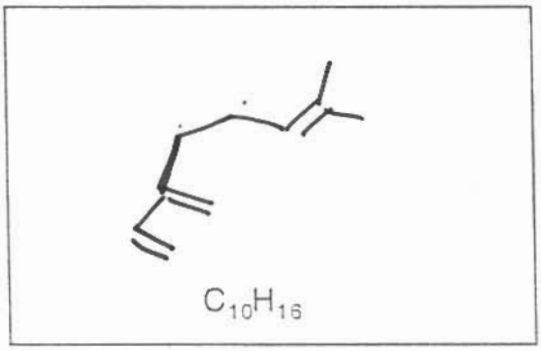
D. The triol shown below was prepared by oxidizing a compound with the molecular formula, $BC_{10}H_{19}$. Show the structure of this compound in the box below.



$BC_{10}H_{19}$



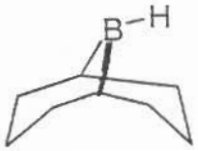
E. In the box below, provide the structure of the triene (a molecule with three alkenes) that led to the boron containing compound in part D.



$C_{10}H_{16}$

$BC_{10}H_{19}$

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

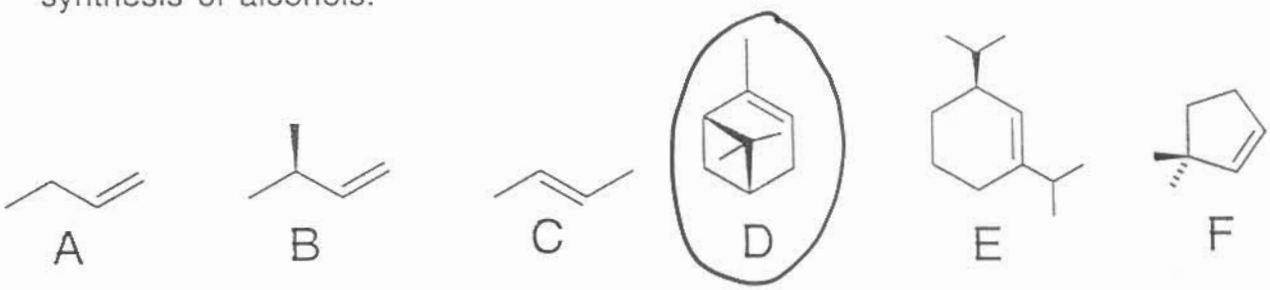


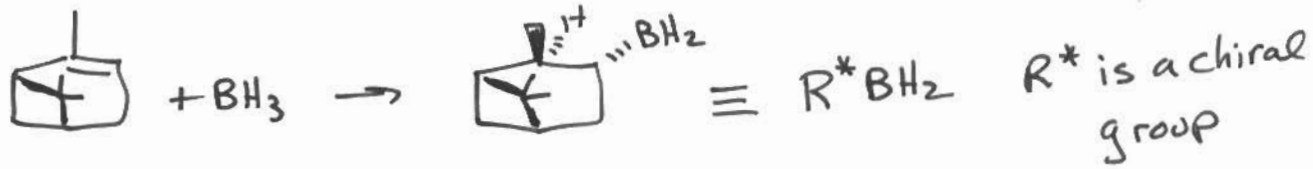
9-BBN

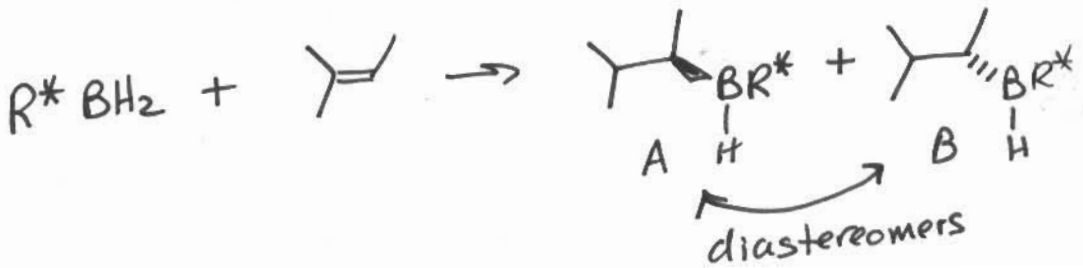
- ☐ When you have mono- and tri-substituted alkenes in the same molecule and you wish to only react at the tri-substituted alkene.
- ☒ When you have mono- and tri-substituted alkenes in the same molecule and you wish to only react at the mono-substituted alkene.
- ☐ When you want to form a chiral alcohol.
- ☐ 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, 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

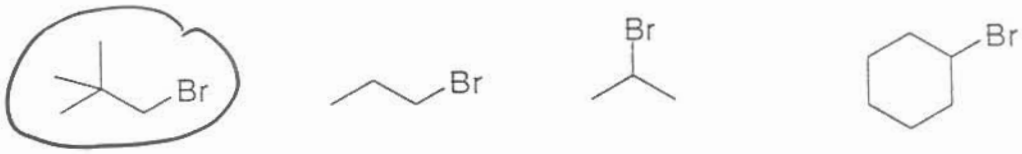
7. (25 pts)

A. How many neutrons are in ^{18}O? 10

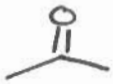
B. What does each letter and number in the acronym S_N1 stand for?

S = Substitution N = nucleophilic 1 = unimolecular

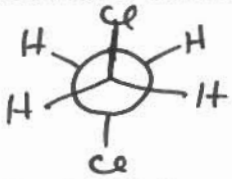
C. Which of the following electrophiles would NOT be suitable in an S_N2 reaction? Circle one.



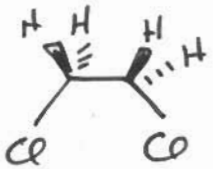
D. Draw the structure of a polar aprotic solvent.



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



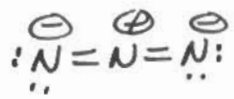
F. Show the bond-line representation of 1,2-dichloroethane in its least stable conformation.



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

$N_3^{\ominus}$

azide ion



H. Draw the π-antibonding molecular orbital of ethylene (i.e. ethene).

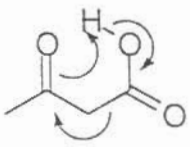
I. The ideal bond angles associated with an SP^2 hybridized carbon are?

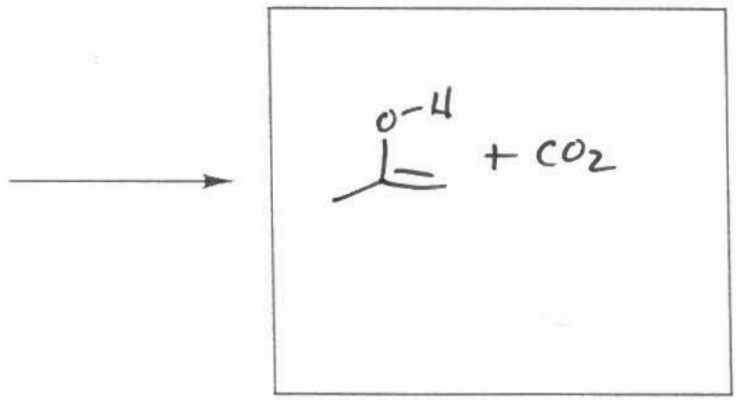
120°

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

L = lowest U = unoccuppied 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.

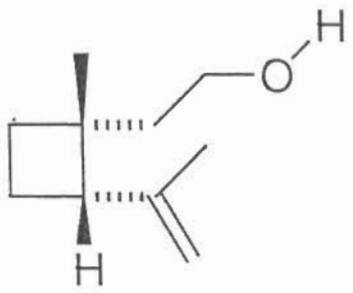
- [X] The transition state looks more like the product(s) than the starting material(s).
- [ ] There is no transition state for an endothermic reaction.
- [ ] The transition state looks more like the starting material(s) than the product(s).
- [ ] Endothermic reactions are always "downhill".
- [ ] The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

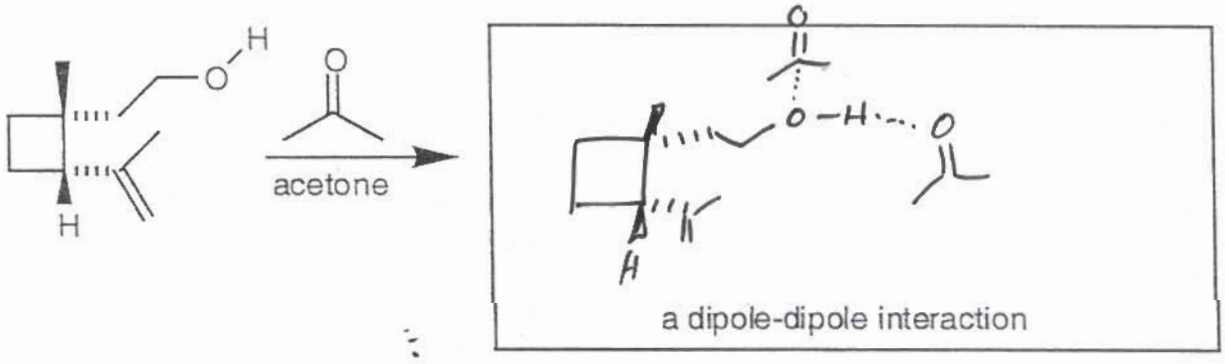
A. On the diagram above, label each stereocenter as R or S.

B. On the diagram above, circle a quaternary carbon and label it 4°.

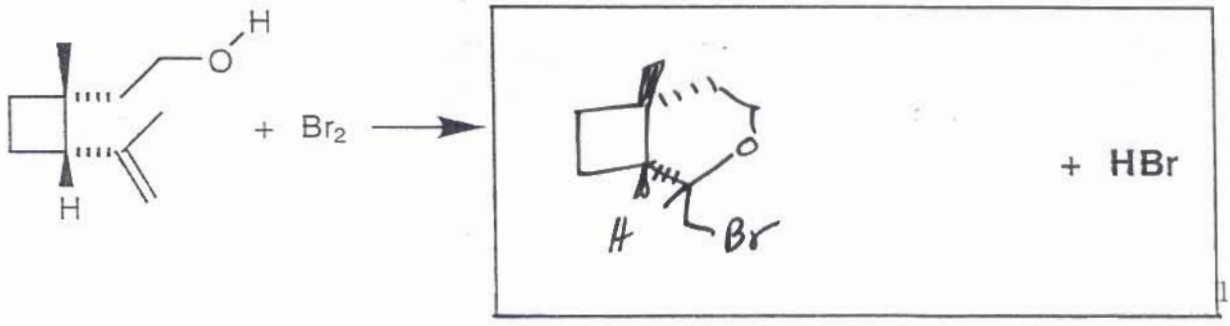
C. On the diagram above identify the most polar bond in grandisol and label it polar.

D. How many possible stereoisomers are there of grandisol?

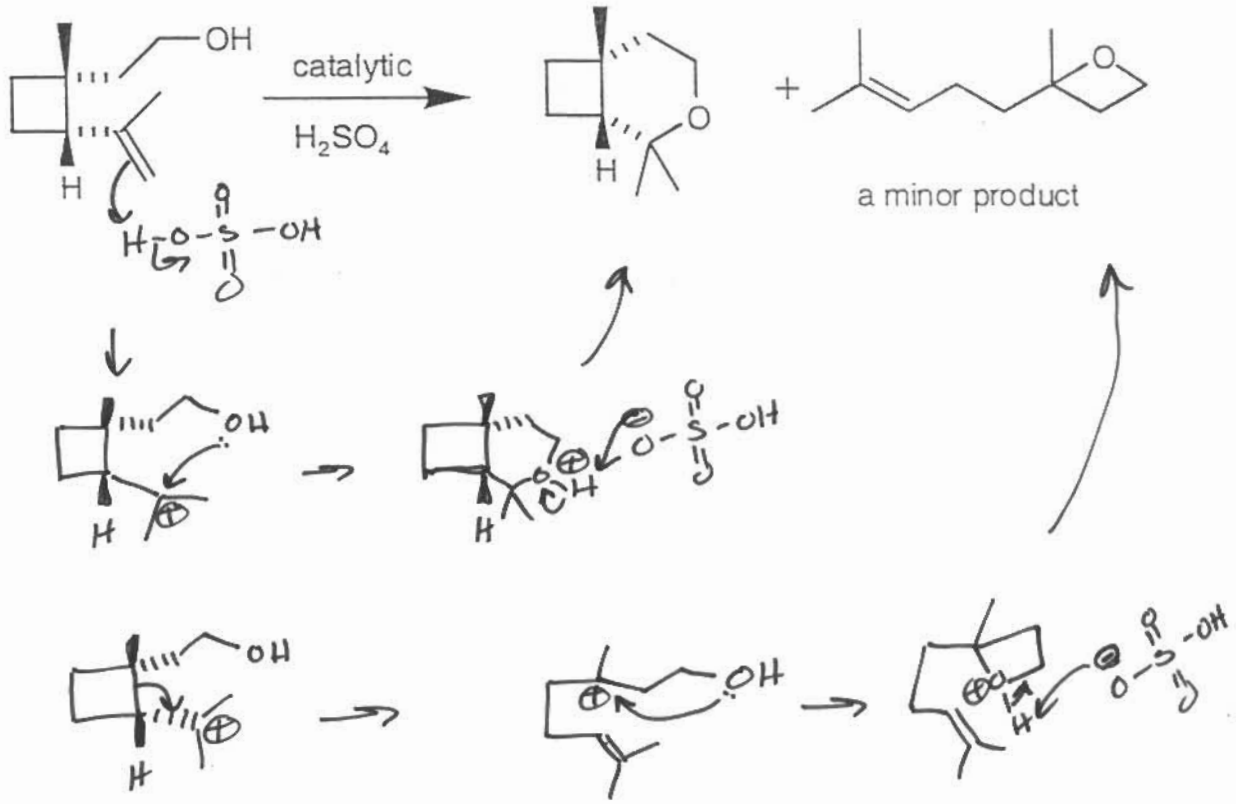
E. Dissolving grandisol in acetone would lead to several types of Van der Waals interactions between the two molecules. Clearly draw a dipole-dipole interaction between these two molecules. Indicate your interaction using a dotted line. Your drawing must be specific to receive any points.



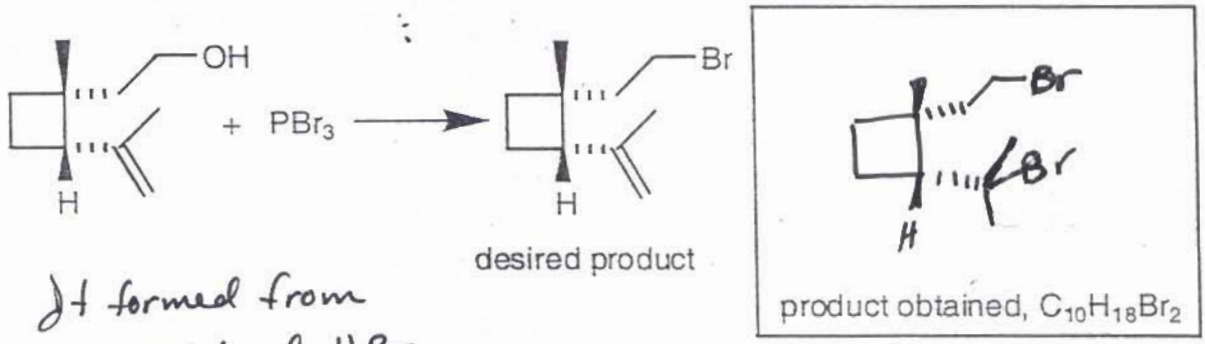
F. Predict the product.



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



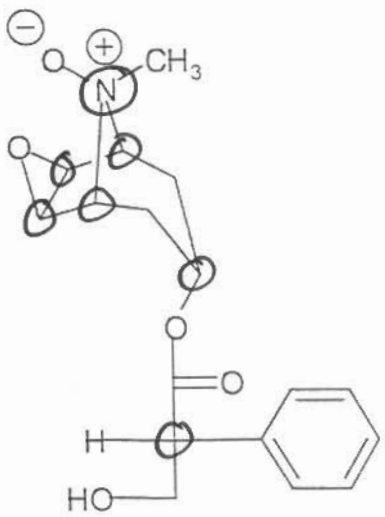
H. John T. wanted to make the bromo analog of grandisol shown below. However, after reacting grandisol with PBr_3 he obtained a different compound with the molecular formula, $C_{10}H_{18}Br_2$. What is this compound and why did it form? Words are satifactory here. You do not need to write mechanisms!



It formed from any residual HBr or Br_2P-OH (an acid).

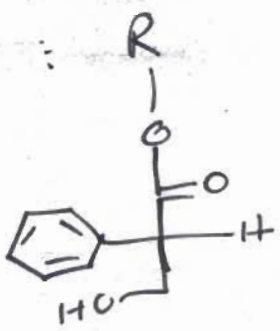
9. (40 pts)

A. Scopolamine N-oxide is a synthetic derivative of scopolamine, a naturally occuring 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.

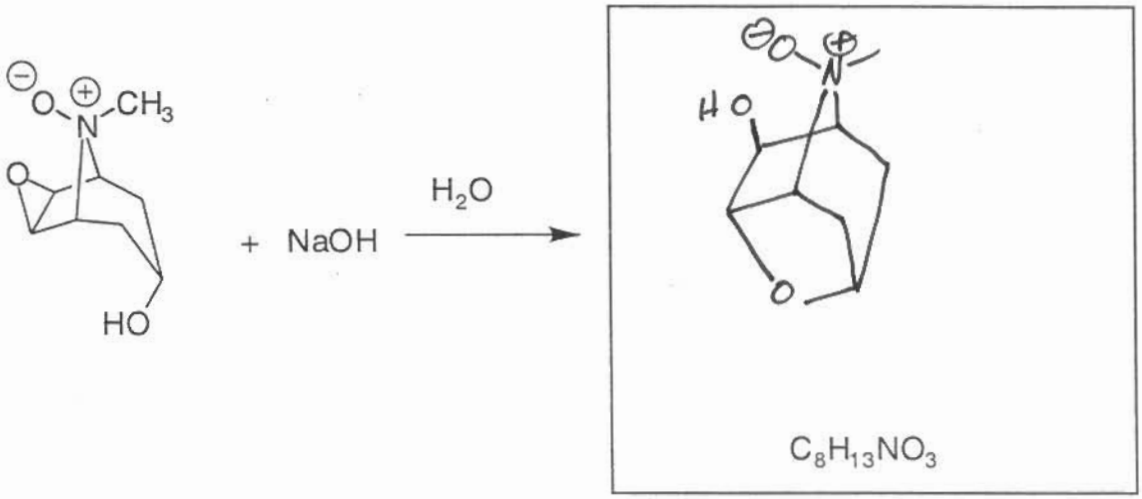


scopolamine N-oxide

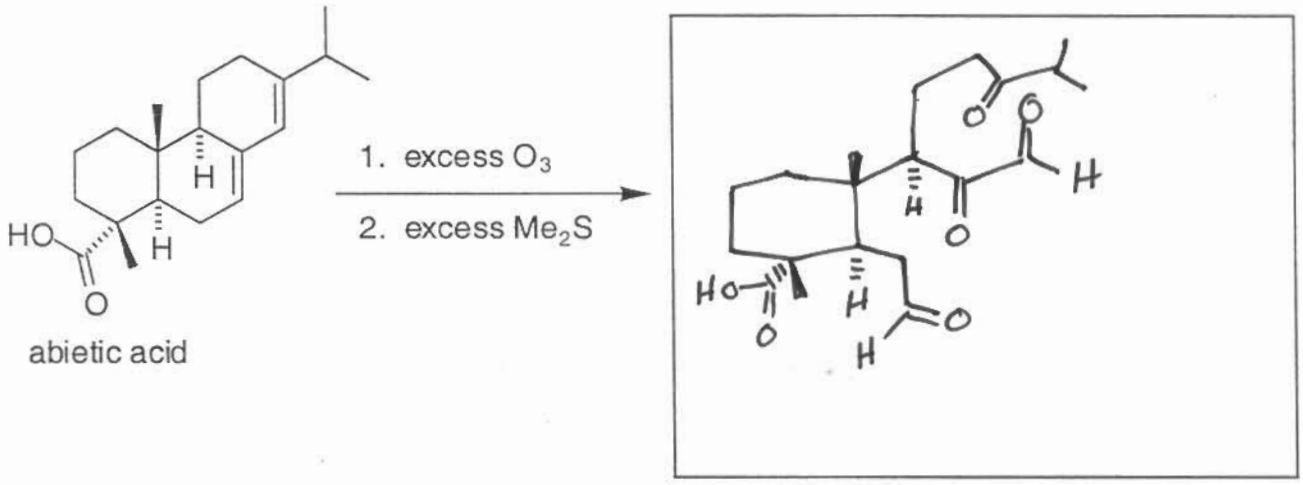
B. Draw one diastereomer of scopolamine N-oxide.



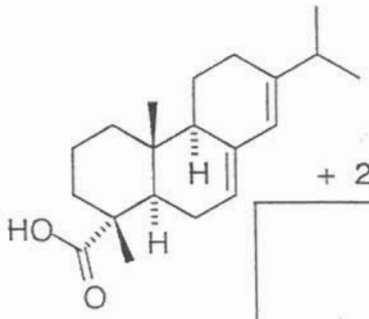
C. Predict the product.



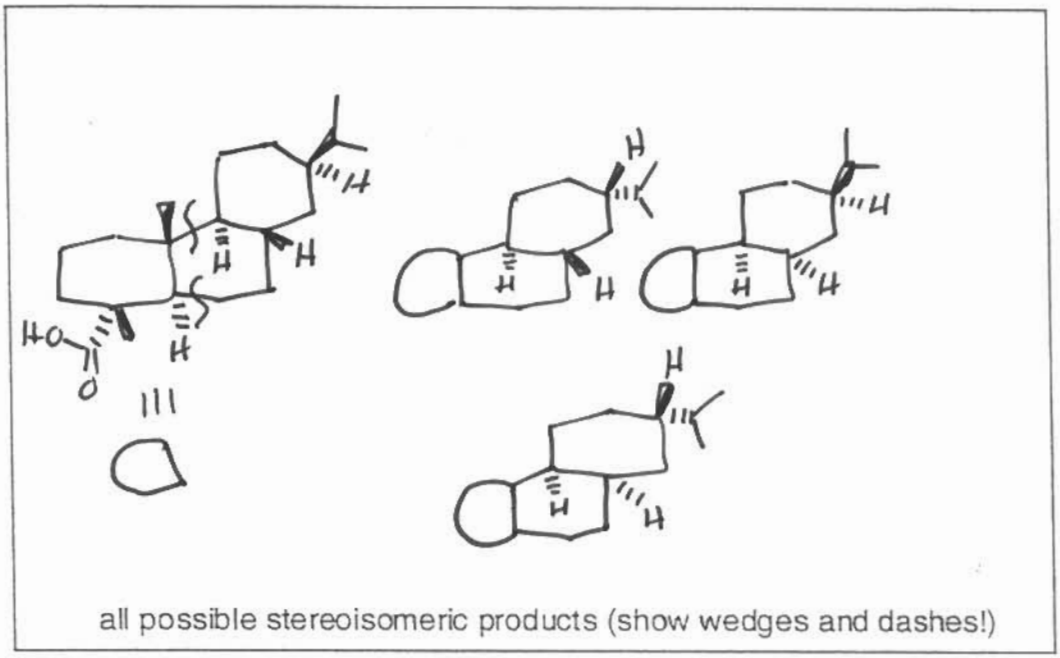
D. Show the product(s) of ozonolysis of abeitic acid.



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

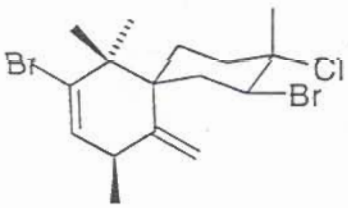


abietic acid



all possible stereoisomeric products (show wedges and dashes!)

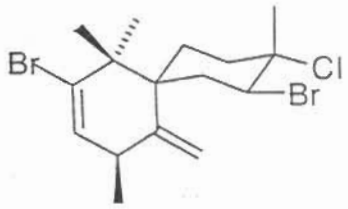
F. One of many compounds isolated from red algae is shown below. Draw the ring flipped conformer of this compound. In the small box indicate which conformer is favored using equilibrium arrows (you do not need a table of data to figure this out).



equilibrium arrows here

ring flipped conformer

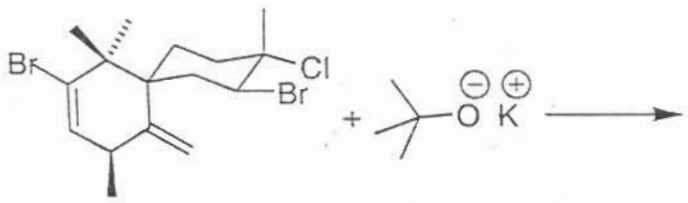
G. Which word(s) describe the relationship between the bromine and chlorine atoms in the cyclohexane ring of the compound shown below. Place an X to the left of every answer that is correct. Every wrong answer cancels a right answer.

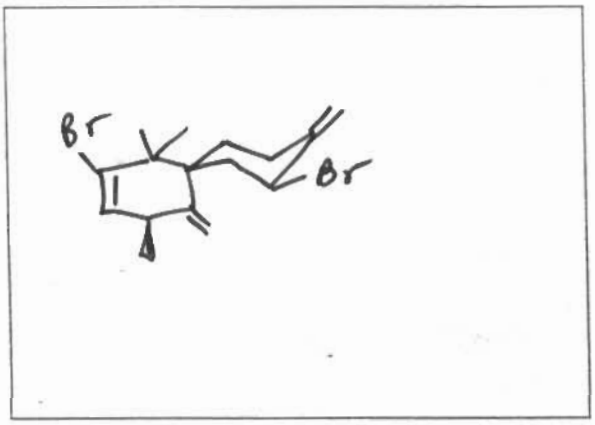


compound from red algae

- ☐ 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_3CO_2H	4.7
H_2SO_4	-5.0	HCN	9.2
HBr	-4.7	NH_4+	9.2
HCl	-2.2	CH_3SH	10.0
H_3O+	-1.7	CH_3OH	15.5
CH_3SO_3H	-1.2	H_2O	15.7
HF	3.2	NH_3	35

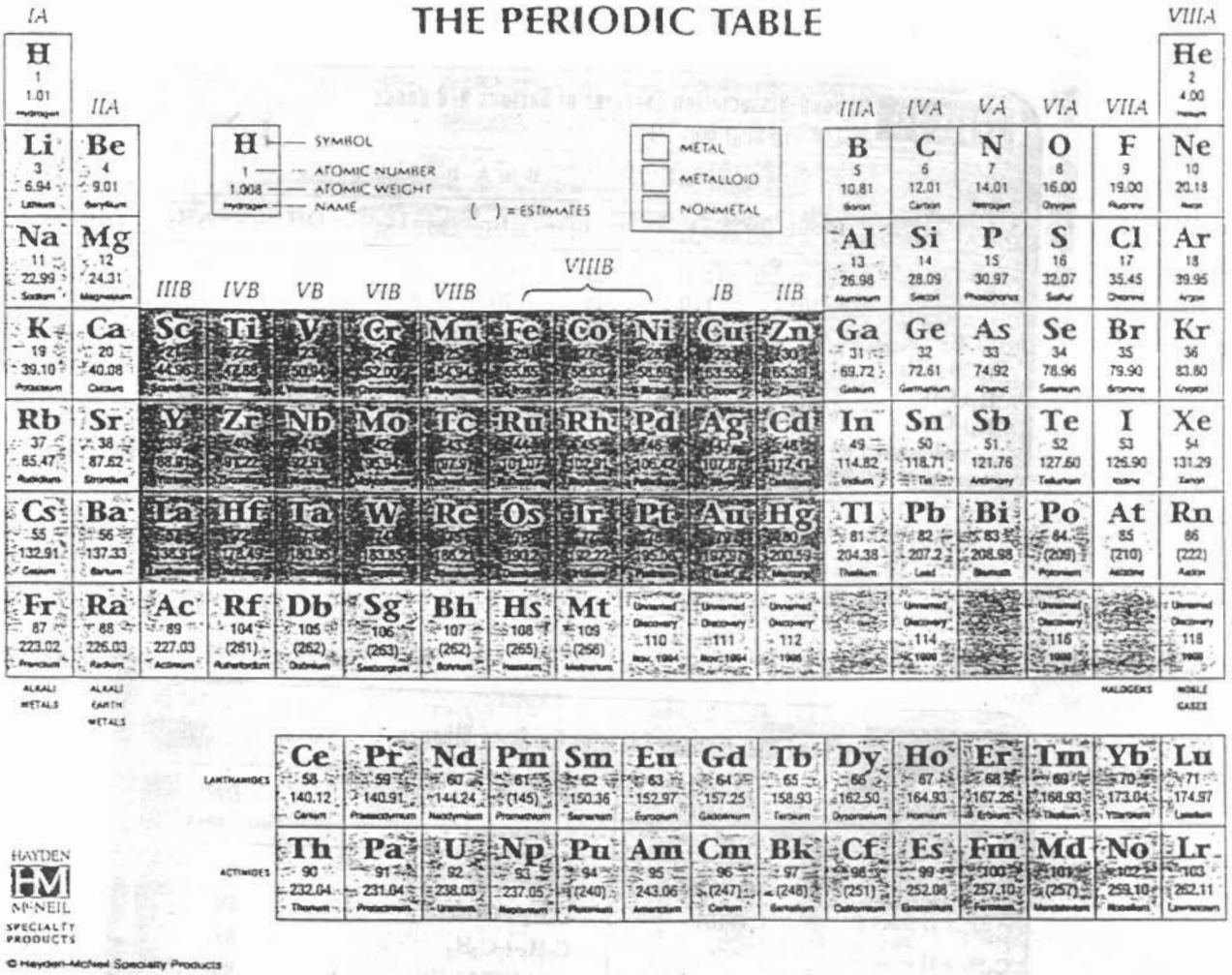


TABLE 1-2 Electronegativities of Selected Elements

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 ($DH°$ in kcal mol^{-1})

	B in A–B						
A in A–B	—H	—F	—Cl	—Br	—I	—OH	—NH_2
H—	104	136	103	87	71	119	108
CH_3—	105	110	85	70	57	93	84
CH_3CH_2—	101	111	84	70	56	94	85
$CH_3CH_2CH_2$—	101	110	85	70	56	92	84
$(CH_3)_2CH$—	98.5	111	84	71	56	96	86
$(CH_3)_3C$—	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	$DH°$ (kcal mol^{-1})	Compound	$DH°$ (kcal mol^{-1})
CH_3–H	105	CH_3–CH_3	90
C_2H_5–H	101	C_2H_5–CH_3	89
C_3H_7–H	101	C_2H_5–C_2H_5	88
$(CH_3)_2CHCH_2$–H	101	$(CH_3)_2CH$–CH_3	88
$(CH_3)_2CH$–H	98.5	$(CH_3)_3C$–CH_3	87
$(CH_3)_3C$–H	96.5	$(CH_3)_2CH$–$CH(CH_3)_2$	85.5
		$(CH_3)_3C$–$C(CH_3)_3$	78.5

Note: See footnote for Table 3-1.