Dr. Steven Pedersen December 14, 2015

Chemistry 3A

Final Exam

Student name: Answer Key

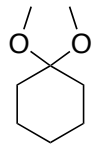
Student signature: _____

M	Problem 1	_____	(18 pts)
I	Problem 2	_____	(42 pts)
D	Problem 3	_____	(32 pts)
T	Problem 4	_____	(28 pts)
E	Problem 5	_____	(16 pts)
RM	Problem 6	_____	(14 pts)
	Problem 7	_____	(32 pts)
	Problem 8	_____	(27 pts)
	Problem 9	_____	(16 pts)
	Total Points	_____	(225 pts)

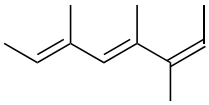
No Calculators Allowed
No Molecular Models Allowed
Be Sure Your Exam has 14 Pages
Be Sure To Try All Parts of Each Problem!

1. There will be NO partial credit for this problem. Avoid careless errors by checking over your answers. (18 pts)

A. Provide a systematic name for the following compounds (include R/S when appropriate). Use common nomenclature for any branched substituents.



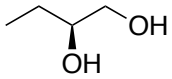
1,1-dimethoxycyclohexane



(2*Z*,4*E*,6*E*)-3,4,6-trimethyl-2,4,6-octatriene

OR

(2*E*,4*E*,6*Z*)-3,5,6-trimethyl-2,4,6-octatriene



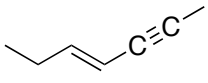
(*S*)-1,2-butanediol

OR

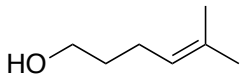
(*S*)-butane-1,2-diol

B. Draw a structure for each of the following names. For cycloalkanes use flat rings.

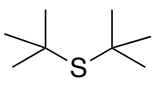
- (E) 4-hepten-2-yne



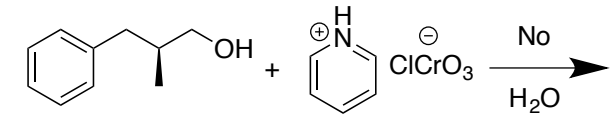
- 5-methyl-4-hexen-1-ol

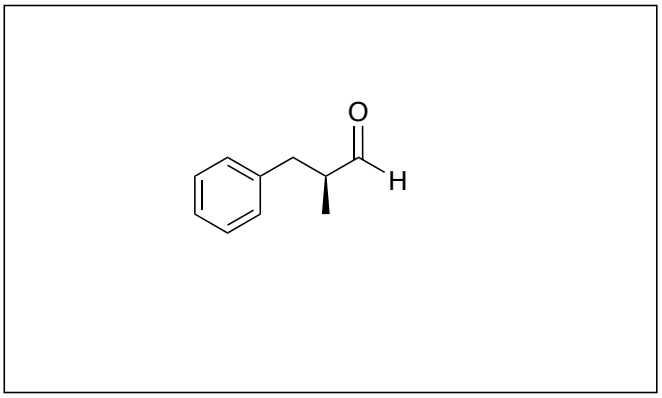


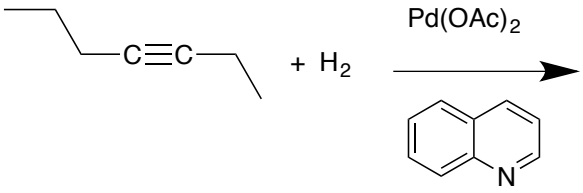
- *tert*-butylsulfide

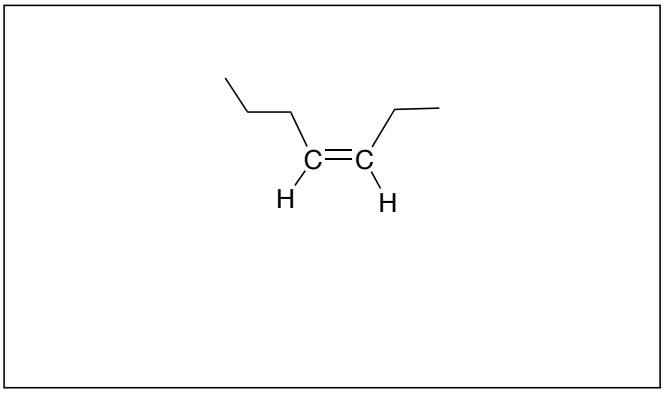


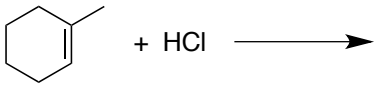
2. Predict the organic product(s) from the following reactions. Where relevant, show all stereoisomers. Pay particular attention to any information given in the product boxes. Each redundant or wrong answer cancels one correct answer. (42 pts)

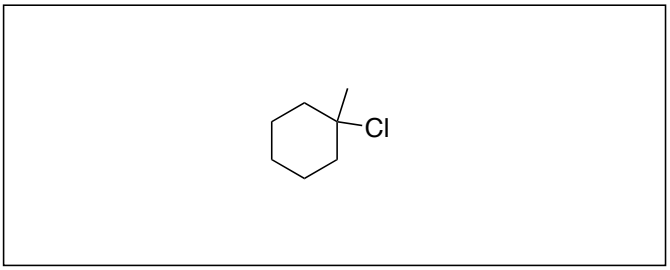


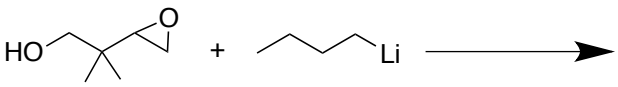


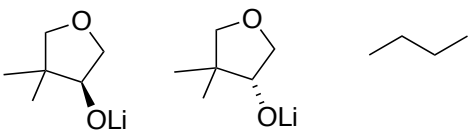












Two of the products are cyclic

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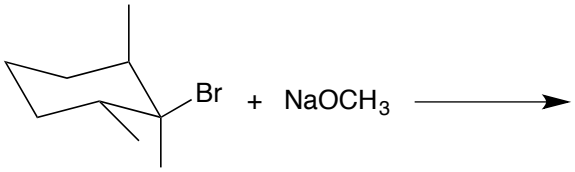
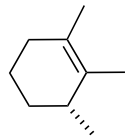
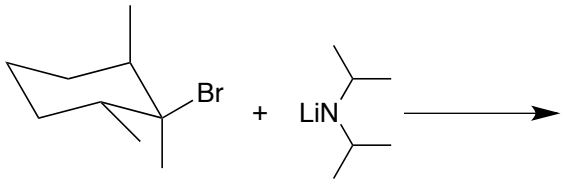
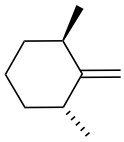




+ $HOCH_3$

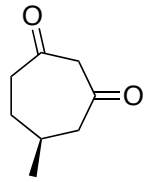
Major product only.
DO NOT show product as a chair,
only show as a flat ring.



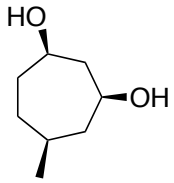


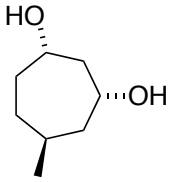
+ HN

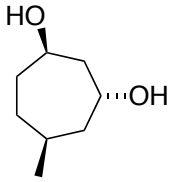
Major product only.
DO NOT show product as a chair,
only show as a flat ring.

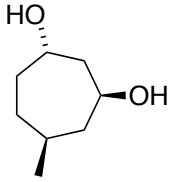


+ $NaBH_4$ MeOH

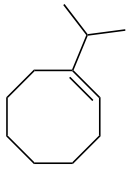






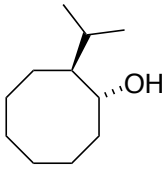


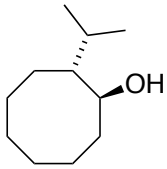
All products with the MF = $C_8H_{16}O_2$



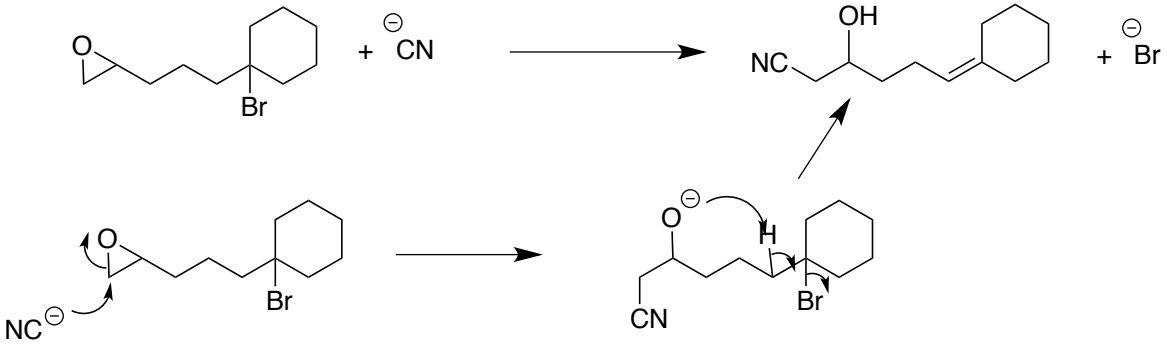
1. BH_3

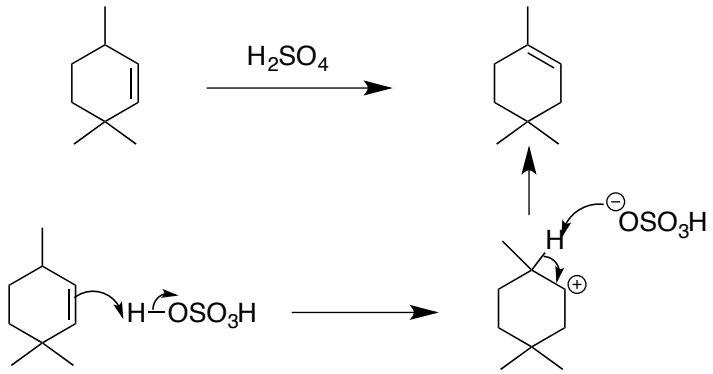
2. $HOOH, HO^{\ominus}$

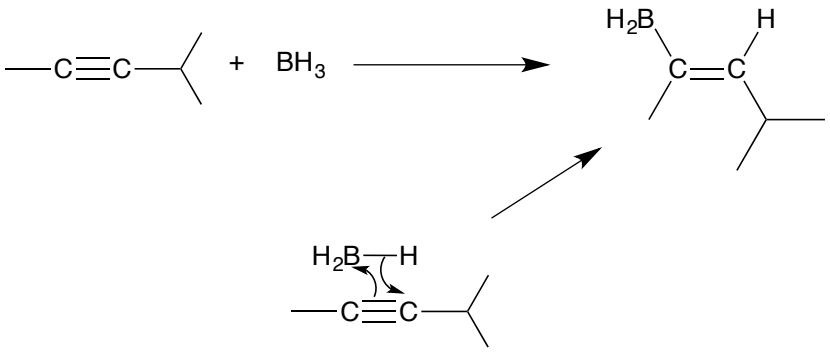


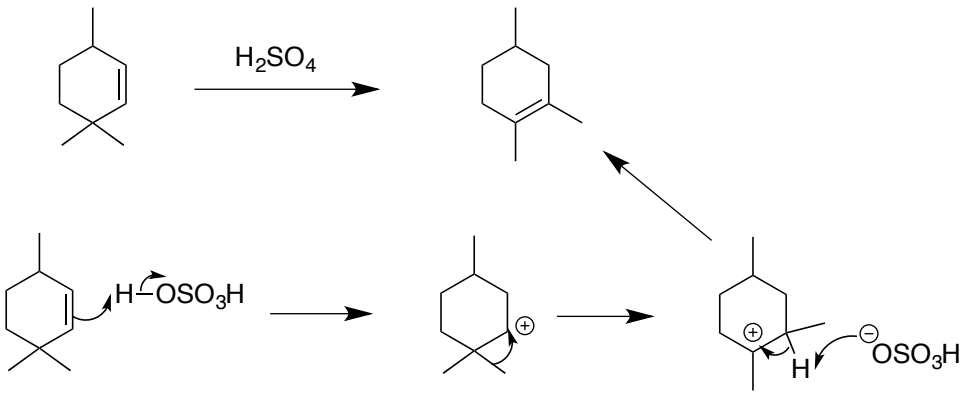


3. Write logical arrow-pushing mechanisms for the following reactions. Be sure that your mechanism accounts for all products shown. (32 pts)



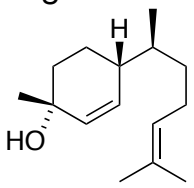



+ BH3
H2B
H
C
C
H2B
H
C
C

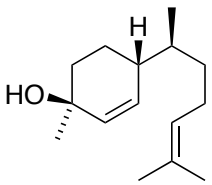

H2SO4
H
OSO3H
H
OSO3H

4. (28 pts)

The two compounds shown below have recently been isolated from ginger. They are referred to as Zingibernol's. (10.1021/acs.jnatprod.5b00638).



A



B

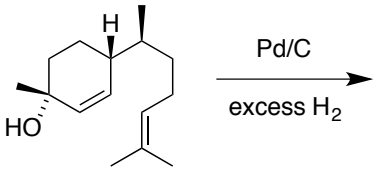
A. What is the stereochemical relationship between these two compounds? Circle one:

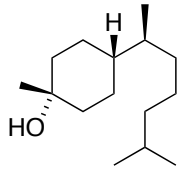
Enantiomers **Diastereomers** Atropeisomers Not Related

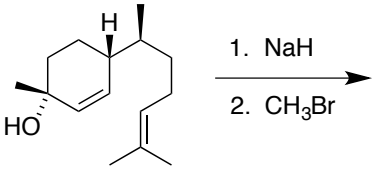
B. The alcohol group in Compound A (above) is called a: (circle one)

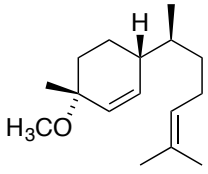
primary alcohol secondary alcohol **tertiary alcohol** quaternary alcohol

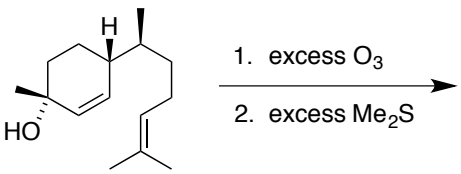
C. Predict the organic product(s) from the following reactions. Where relevant, show all stereoisomers. Each redundant or wrong answer cancels one correct answer.

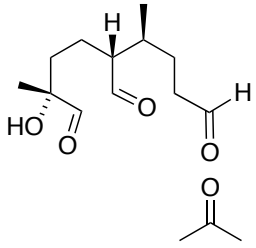






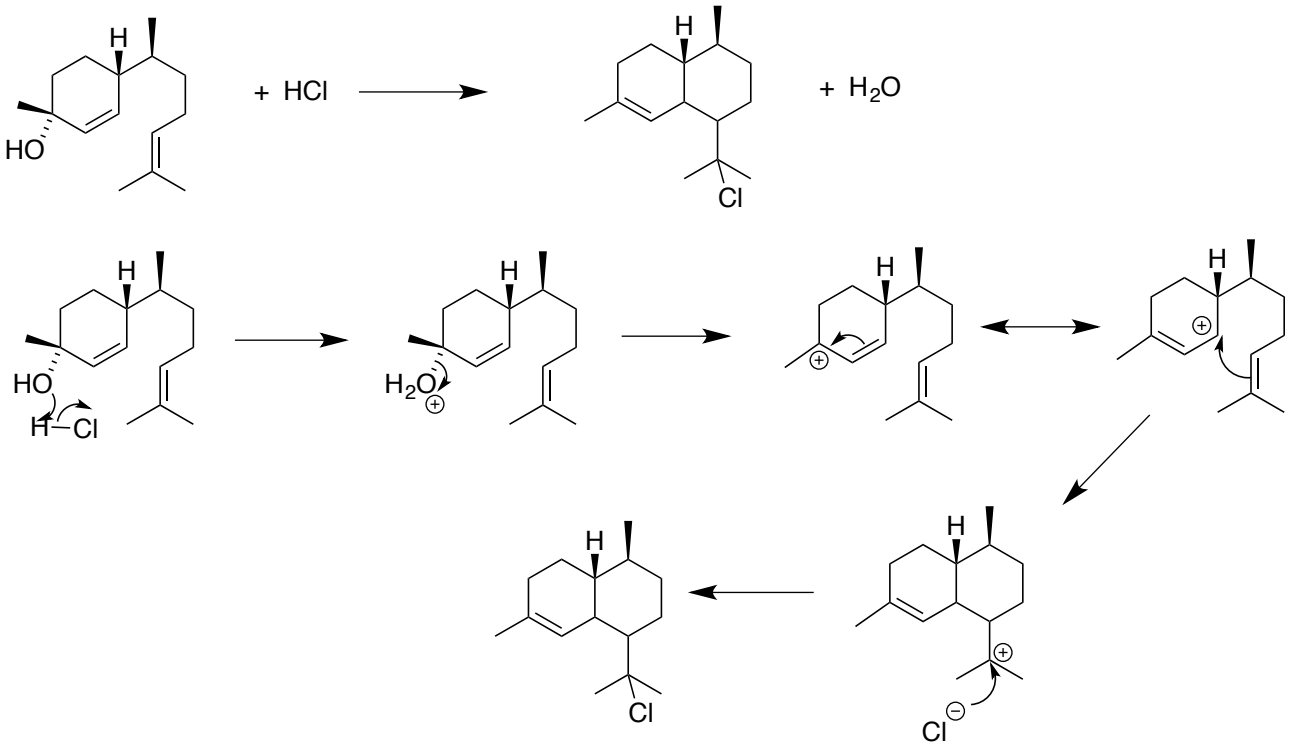


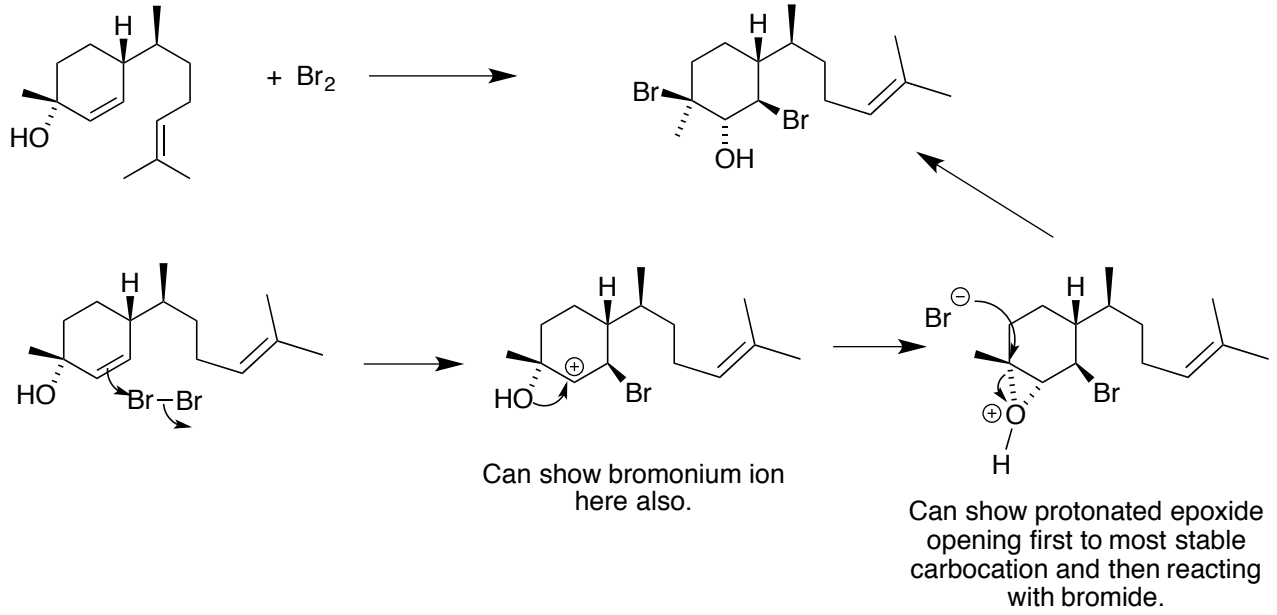




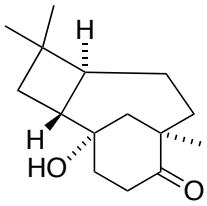
+ 2 Me_2SO

D. Write logical arrow-pushing mechanisms for the following reactions. Be sure that your mechanism accounts for all products shown.

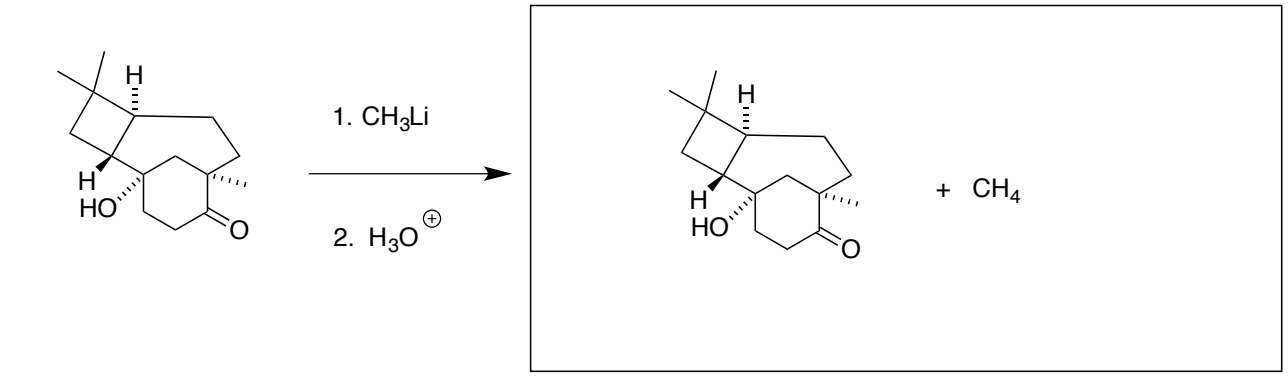


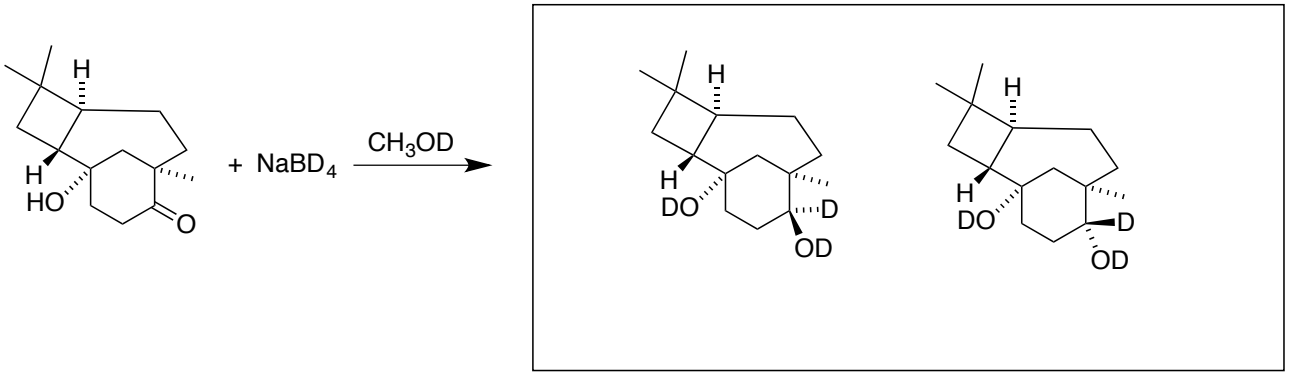


5. The compound shown below has recently been isolated from bacterial endophytes found in a species of Mangrove (DOI:10.1021/acs.jnatprod.5b00674). (16 points)

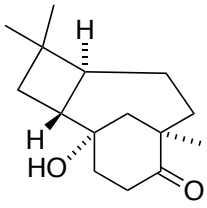


A. Predict the organic product(s) from the following reactions. Where relevant, show all stereoisomers. Each redundant or wrong answer cancels one correct answer.



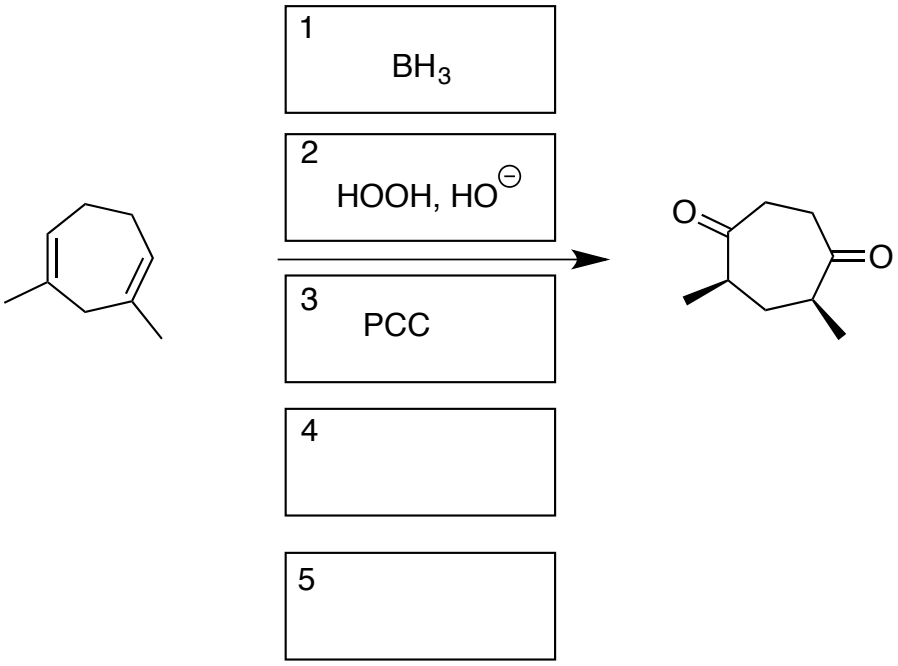


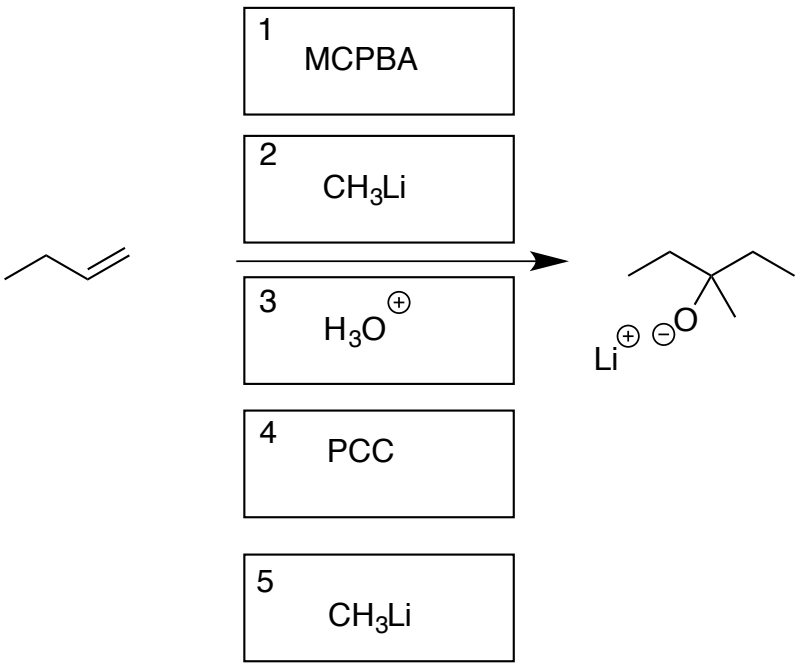
B. How many Degree's of Unsaturation are present in the molecule below?



Degrees of Unsaturation = 4

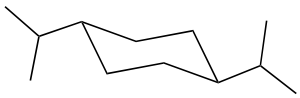
6. Provide the reagents and any other organic compounds necessary to synthesize the indicated product from the starting material shown. For each problem, five boxes are provided in which to place each step of your synthesis. **No synthesis will require more than five steps. However, some or all, may require fewer than five steps.** (14 pts)





7. (32 points)

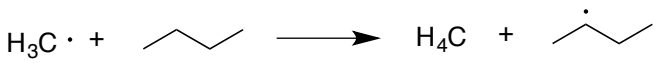
A. Draw the most stable chair conformer for *trans*-1,4-diisopropylcyclohexane.



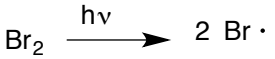
B. How many valence electrons are associated with ^{18}O?

6

C. Provide a REAL example of a radical propagation reaction.

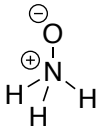


D. Provide a REAL example of a radical initiation reaction.



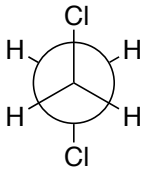
E. Draw the structure of isopropyliodide.

F. Draw the structure of amine oxide, H_3NO . Be sure to show all bonds and any relevant charges.



G. Draw a picture of the π^* orbital of ethylene.

H. Draw a Newman projection of the most stable conformer of 1,2-dichloroethane (looking down the CC bond).

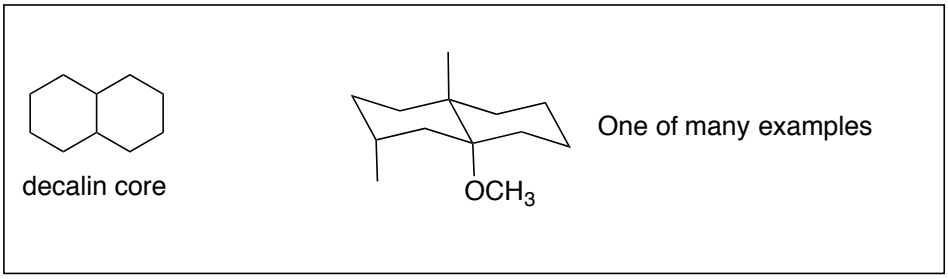


8. (27 points)

A. The Triaxial Rule For Odor Sensation is a set of rules used to develop derivatives of Ambergris, a valuable mixture of natural products used in the perfume industry. The rules are as follows:

1. You must have a *trans*-decalin core (the decalin core is shown below).
2. On this core you must have three axial substituents (i.e. not hydrogens) that exist in a 1,2,4 relationship where carbons 1 and 2 are bridgehead carbons.
3. One out of the three substituents (see rule 2) must contain an oxygen atom that is directly bonded to the *trans*-decalin core.

Based on these rules, provide ONE structure that satisifies these rules. ALL SIX MEMBERED RINGS IN YOUR STRUCTURE MUST BE DRAWN IN THEIR CHAIR FORM.



Ambrein is one of the molecules found in Ambergris. Deduce what you can about the structure of Ambrein based on the following information.

B. The molecular formula of Ambrein is shown below. Calculate the degrees of unsaturation for this compound. You must show your work to receive any credit.

MF = $C_{30}H_{52}O$

$$DOU = \frac{Hsat - Hactual}{2}$$

$$Hsat = (2 \times 30) + 2 = 62$$

$$\text{Therefore: } \frac{62 - 52}{2} = \boxed{\textbf{5}}$$

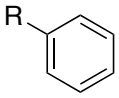
C. Reaction of Ambrein with sulfuric acid resulted in the formation of a new compound AND one equivalent of water. Furthermore, reaction of Ambrein with CrO_3 in aqueous acid gave NO REACTION. What do these results tell you about a specific functional group present in Ambrein? Briefly explain your conclusion.

What is the functional group? (Be specific) ***A tertiary alcohol.***

How did you arrive at this conclusion? Keep your answer within the space below.

The fact that Ambrein reacted with sulfuric acid to form water meant there was either a secondary or tertiary alcohol (it cannot have been a primary alcohol since that would have led to formation of a primary carbocation). Since Ambrein did not react with CrO_3, the alcohol must have been a tertiary alcohol which cannot be further oxidized. A secondary alcohol would have reacted with CrO_3 to form a ketone.

D. Reaction of Ambrein with excess ozone followed by dimethylsulfide gave three compounds (not including dimethylsulfoxide). Within these three compounds were a total of four carbonyls (two ketones and two aldehydes). It is also know (based on other results not described here) that there are NO phenyl rings present in Ambrein (an example of a phenyl ring is shown below). Based on this information, how many RINGS are found in Ambrein? You must briefly explain how you arrived at your answer. No credit unless there is a valid explanation. Before you begin your answer, restate the number of Degree's of Unsaturation (DOU) you calculated in Part B of this question (on the previous page).



a phenyl ring

Number of DOU's (from Part B): 5

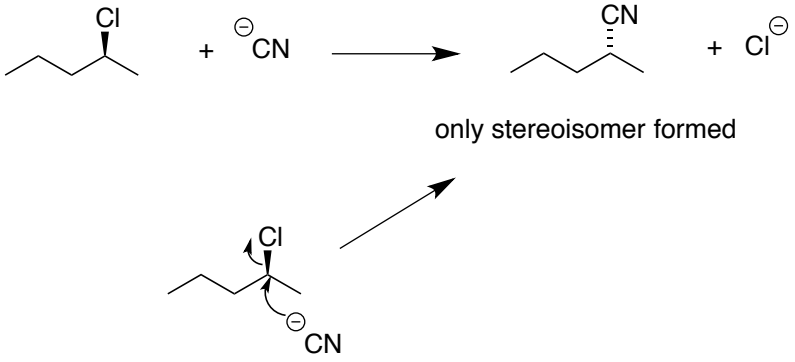
Number of Rings : ***3***

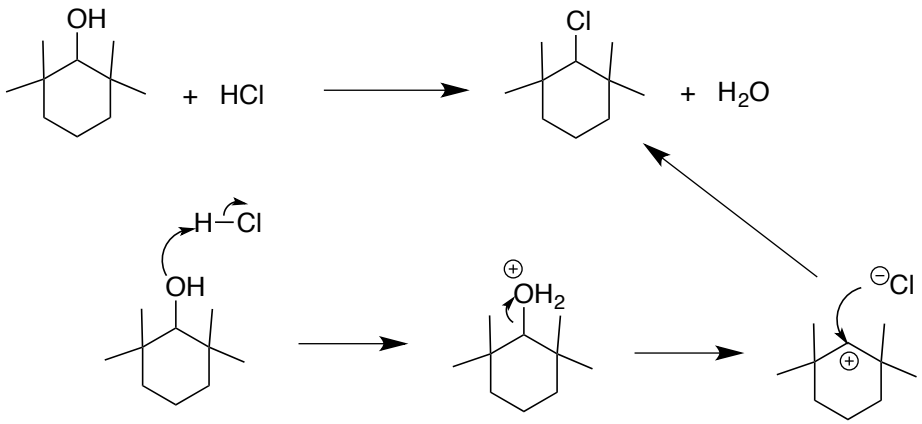
Explanation (answer must be in the space below):

Ozonolysis of Abrein yielded 4 carbonyls which means that two alkenes were present (i.e. 2 carbonyls per alkene from an ozonolysis reaction). We already know from the molecular formula that the only degrees of unsaturation had to be due to a ring or double bond (or possibly a triple bond). The double bond could not be a carbonyl since the only oxygen in the compound formed water upon reaction with sulfuric acid (Part C). Therefore, there were 5 DOU's and 2 alkenes which means there must be 3 rings (5-2 = 3).

Two Last Mechanisms!

9. Write logical arrow-pushing mechanisms for the following reactions. Be sure that your mechanism accounts for all products shown. (16 pts)





Have a Great Winter Break!!