CHEM 3311-200 (Ellison/Richardson) 2nd Exam – March 12, 2013

Your Name Key

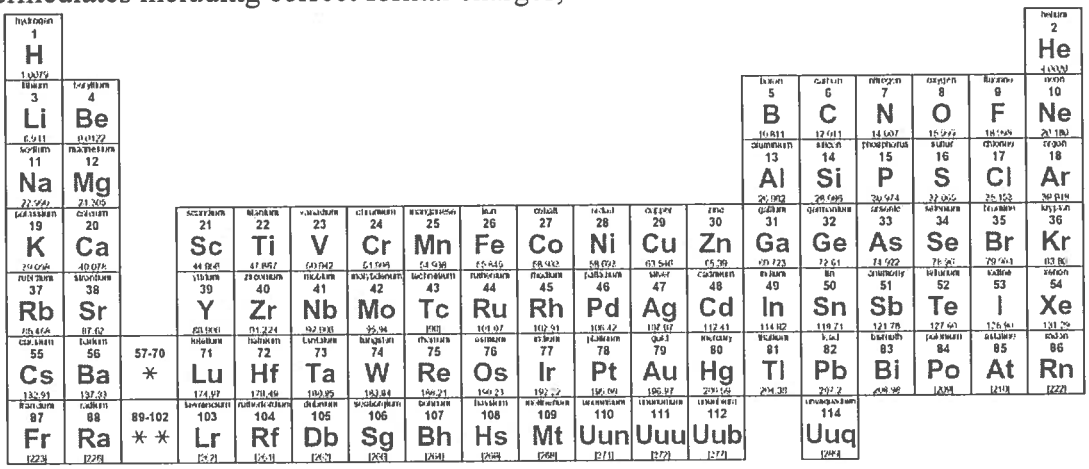
Student ID No. _____

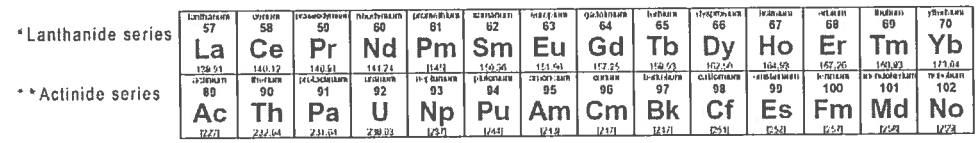
Recitation Day/Time _____

Recitation TA (circle one) Katelyn Chando, Setareh Azarnoush

Question	Score	Out of
1		15
2		8
3		10
4		10
5		12
6		10
7		10
8		15
9		10
Total		100

This is a closed-book exam. The use of notes, calculators, scratch paper, or cell phones will not be allowed during the exam. You may use models sets brought in a clear ziplock bag. Use the backs of the pages for scratch work. Please put all your final answers on the test in pen, not pencil. If your final answer is not clearly specified, you will lose points. For mechanisms, show all intermediates including correct formal charges, but do not show transition states.





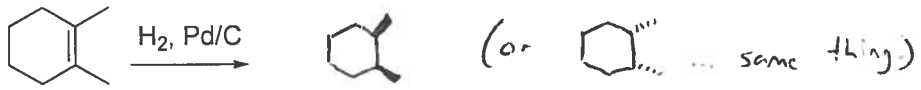
pKa Values

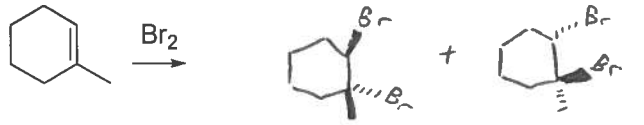
HI	-10.1	H_2O	15.7
HCl	-3.9	Alcohol (ROH)	16-18
H_3O^+	-1.7	HC≡CH	26
CH_3COOH	4.7	NH_3	36
NH_4^+	9.3	$H_2C{=}CH_2$	45
Phenol	10	CH_4	60

Average: 67.9
Median: 75.0
St Dev: ~~96~~ 22.4
Max: 96
Min: 15

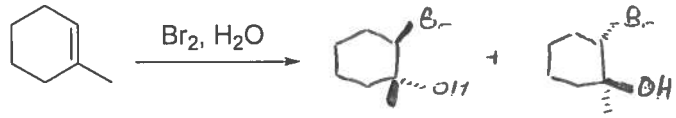
Name Key

1) For each reaction shown below, predict the product(s). If a mixture of stereoisomers is formed, show all stereoisomers using wedges and dashes to indicate configuration, and **specify whether they are enantiomers or diastereomers.** (3 pts each)

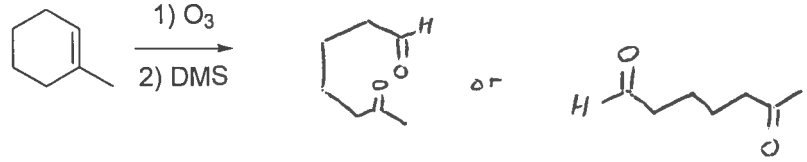
a. 

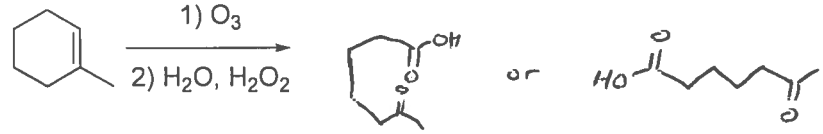
b. 

Enantiomers

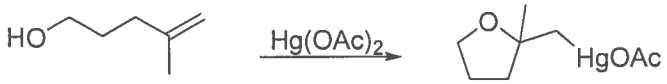
c. 

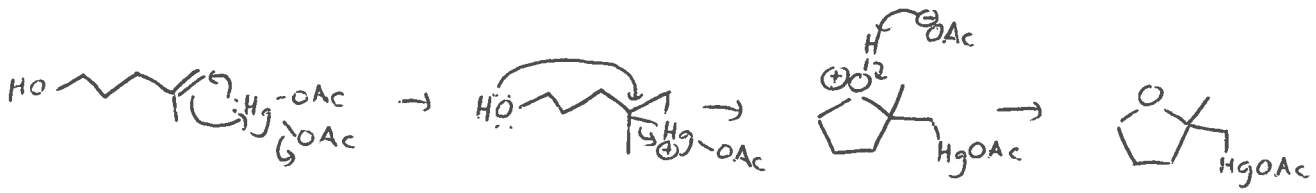
Enantiomers

d. 

e. 

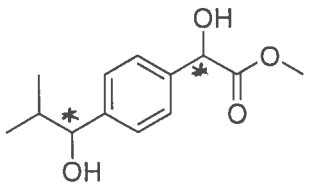
2) Suggest a reasonable mechanism for the reaction shown below. (8 pts)

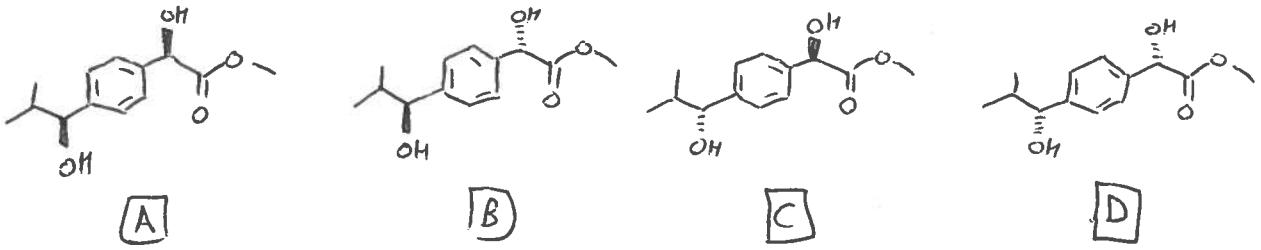




Name Key

3) Using bold and dashed bonds, show all possible stereoisomers of the structure shown below. (4 pts)





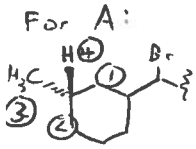
A B C D

What is the stereochemical relationship (enantiomers, diastereomers, identical) between each possible pairing of these four molecules? (Hint: there are six possible pairings). (6 pts)

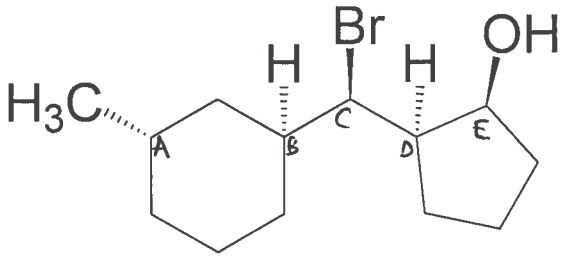
A & B: Diastereomers
A & C: Diastereomers
A & D: Enantiomers
B & C: Enantiomers
B & D: Diastereomers
C & D: Diastereomers

4) In the structure shown below, label each stereocenter as R or S. (10 pts)

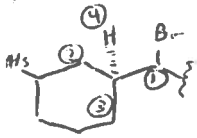
For A:



→ S.

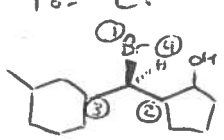


For B:



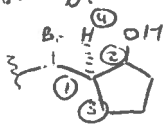
→ S.

For C:



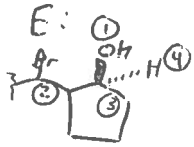
→ R.

For D:



→ R.

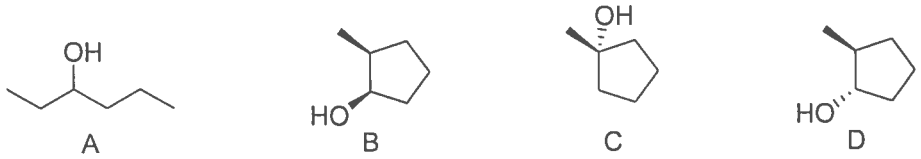
For E:



→ S.

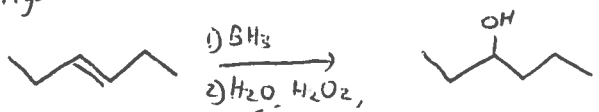
Name Key

5) Four compounds are shown below.

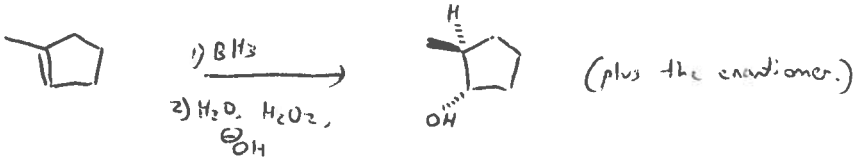


A B C D

a. Which of these compounds can be synthesized as the major product of hydroboration-oxidation? Show the precursor alkene for each alcohol that can be prepared this way. (6 pts) Hydroboration-oxidation is anti-Markovnikov syn-addition.

A: 

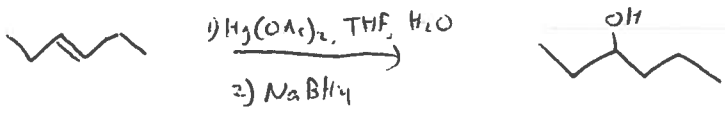
Correct letters but wrong alkene: -1
missing a letter / extra letter: -2
missing 2 letters / 2 extra letters: -3

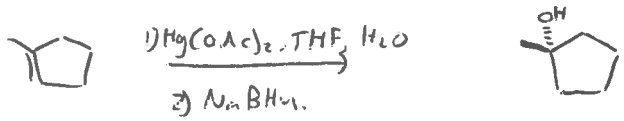
D: 

(plus the enantiomer.)

b. Which of these compounds can be synthesized as the major product of oxymercuration-reduction? (i.e., $Hg(OAc)_2$, H_2O, THF, followed by $NaBH_4$) Show the precursor alkene for each alcohol that can be prepared this way. (6 pts)

Oxymercuration-reduction is Markovnikov-style.

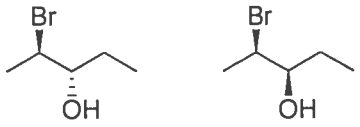
A: 

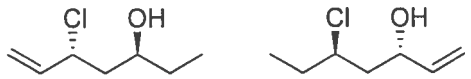
C: 

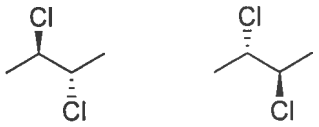
or

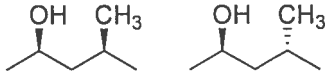
 Name Key

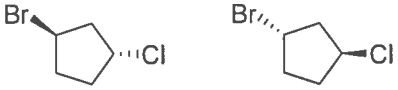
6) For each of the following pairs of molecules, are they identical, enantiomers, diastereomers, or constitutional isomers? (2 pts each)

a.  Diastereomers

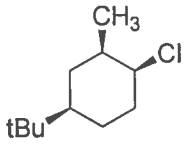
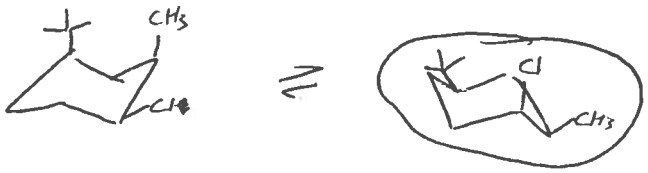
b.  Constitutional Isomers

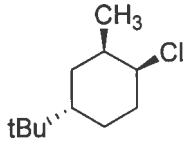
c.  Identical (both are meso: )

d.  Identical ( isn't a stereocenter)

e.  Enantiomers.

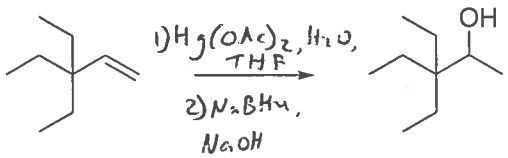
7) For each of the following structures, show both chair conformations. (Make sure your bond angles clearly indicate whether each group is equatorial or axial.) Circle the more stable ring-flip form for each molecule. (5 pts each)

a.  

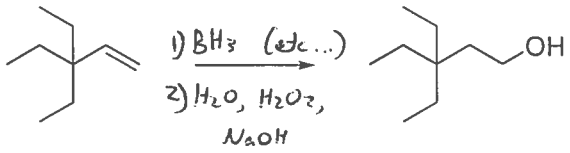
b.  

 Name Key

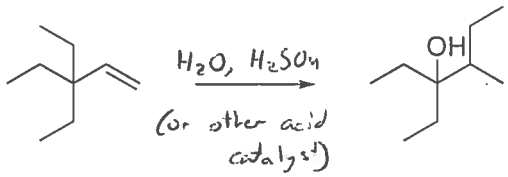
8) Fill in the reagents above the arrow to convert the starting material to each of the products. (15 pts)

a. 

Markovnikov without C+ rearrangements → Oxymercuration-reduction

b. 

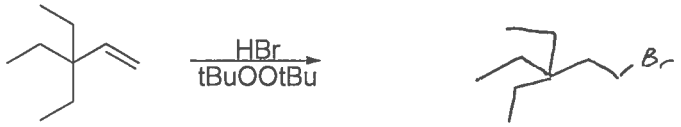
Anti-Markovnikov → Hydroboration-reduction

c. 

Markovnikov w/ C+ rearrangements → acid-catalyzed hydration.

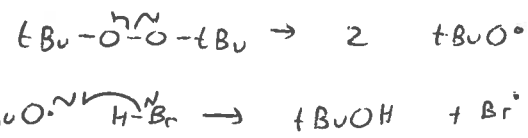
9) Radical HBr addition mechanism (10 pts)

a. Predict the major product of the reaction shown below, ignoring stereochemistry. (2 pts)

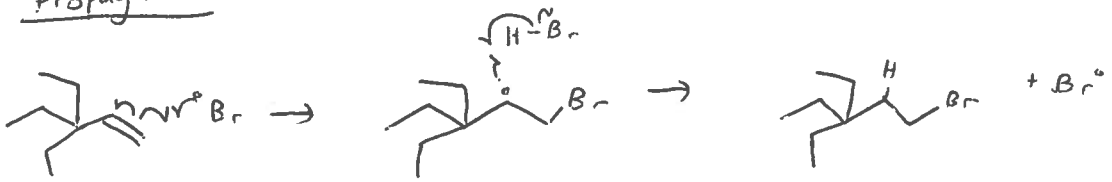


b. Write an arrow-pushing mechanism for this reaction. Clearly label the initiation, propagation, and termination steps. Show at least two examples of termination. (8 pts)

Initiation:



Propagation:



Termination: