CHEM 3311 (Richardson) Second Hour Exam – October 23, 2012

Your Name Key

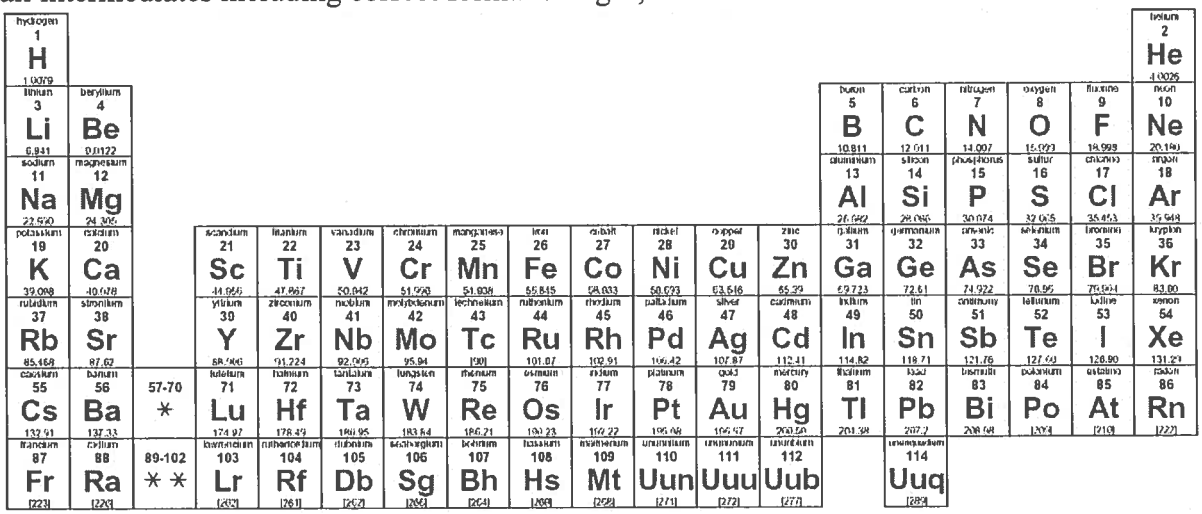
Student ID No. _____

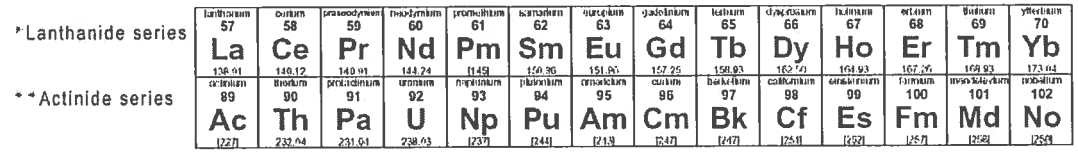
Recitation Day/Time _____

Recitation TA (circle one) Thomas Carey, Adam Csakai, Jake Greenberg, Maria Kolber, Tim Rochelle, Mike Springer

Question	Score	Out of
1		24
2		22
3		10
4		10
5		16
6		18
7		0
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.





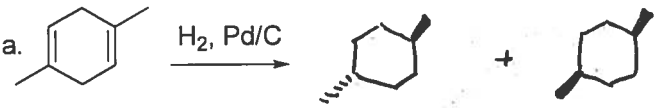
pKa Values

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

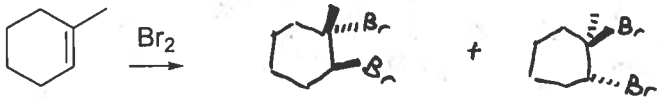
Average = 71.3
St Dev = 18.9
Max = 100
Min = 11

Name Key

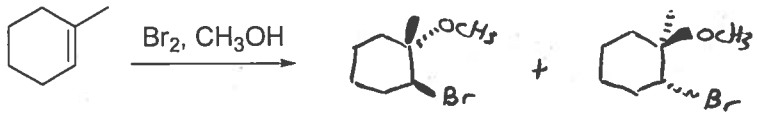
1) For each reaction shown below, predict the product(s). If a mixture of stereoisomers is formed, show all stereoisomers using wedges and dashes to indicate configuration, and **specify whether they are enantiomers or diastereomers.** If more than two products are created, you should specify the relationship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

a. 

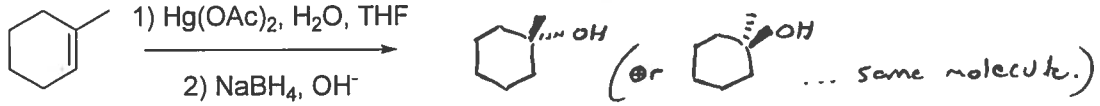
Diastereomers

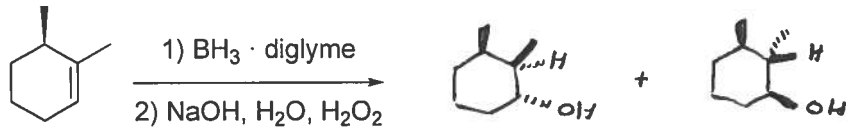
b. 

Enantiomers

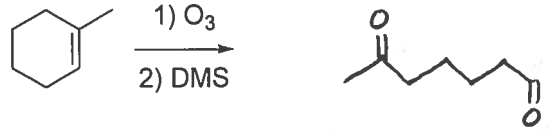
c. 

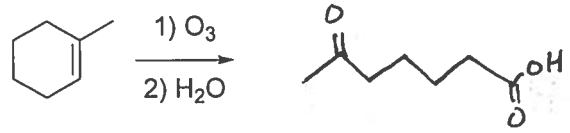
Enantiomers

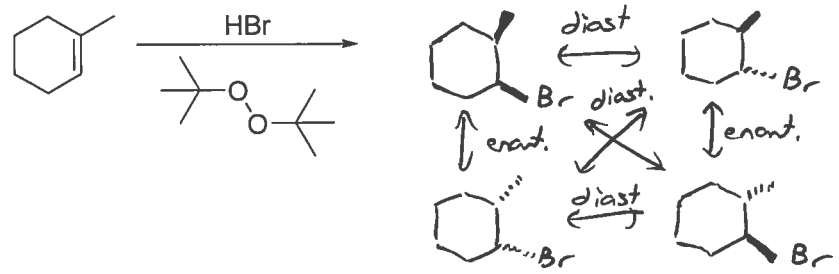
d. 

e. 

Diastereomers

f. 

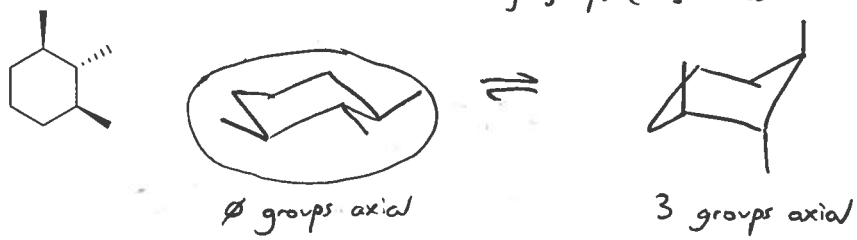
g. 

h. 

 Name Key

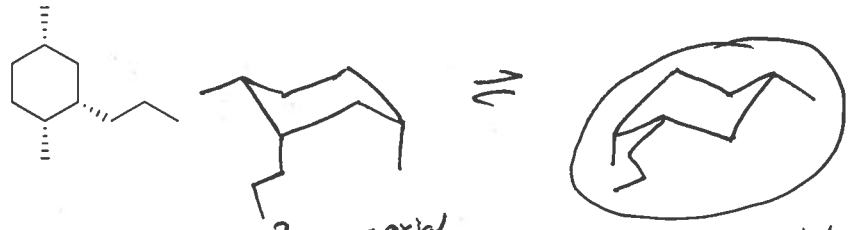
2) For each of the following structures, show **both** chair conformations. Circle the more stable of the two ring-flip forms. (5 pts each) Both structures identical = 2/5
wrong connectivity = 0/5
wrong groups (CH_3 instead of Br): 4/5

a.



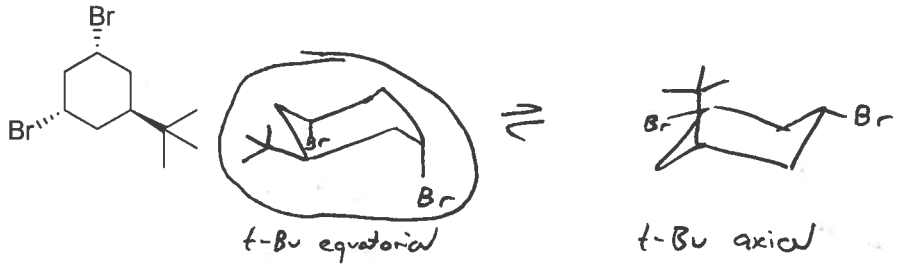
∅ groups axial 3 groups axial

b.



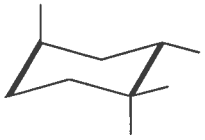
2 groups axial 1 group axial

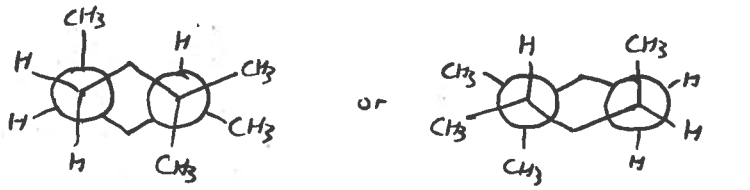
c.



t-Bu equatorial t-Bu axial

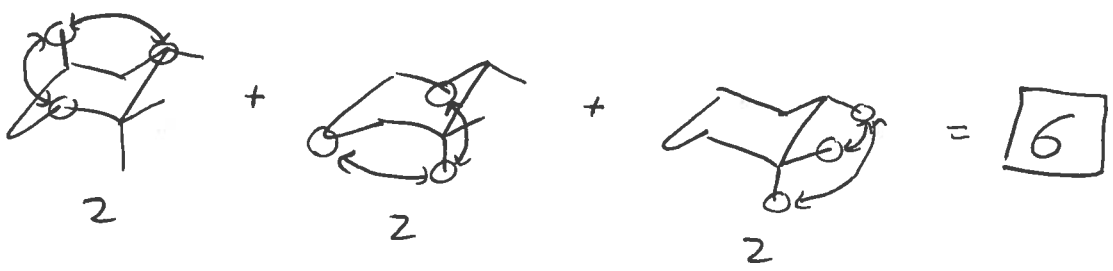
d. For the structure shown below, draw a double Newman projection, sighting along the bolded bonds. (5 pts) Projection of enantiomer = -1
Unjoined halves = -2
Hs not shown: -2





(if sighting from front) (if sighting from back)

e. How many total gauche interactions between carbons does the structure shown in part d. have? (2 pts)

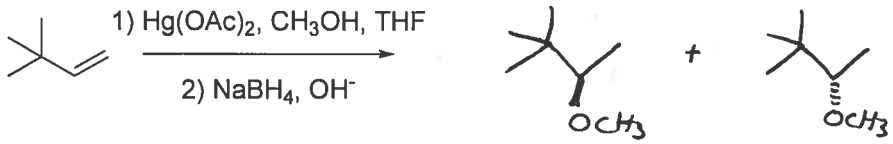


2 + 2 + 2 = 6

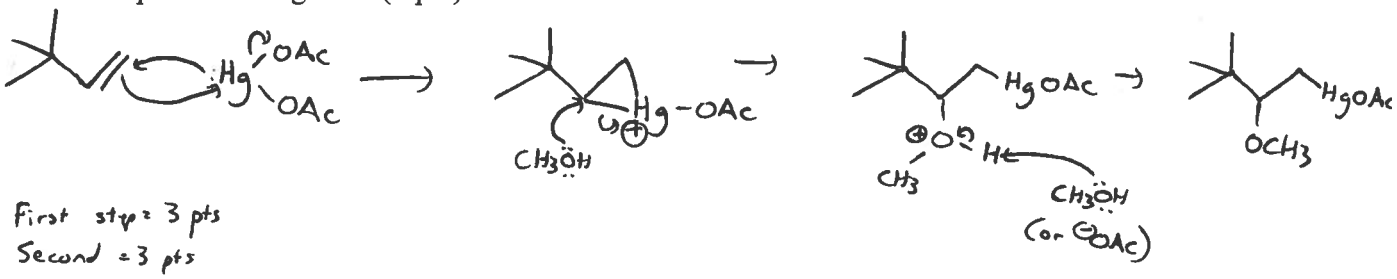
Name Key

3) Addition mechanism 1:

a. Predict the major product(s) of the reaction shown below, showing stereochemistry if necessary. Note that it uses CH_3OH instead of H_2O. Hint: we've seen other reactions where an alcohol can perform exactly the same mechanistic steps as water, such as halohydrin formation vs. haloether formation. (2 pts)



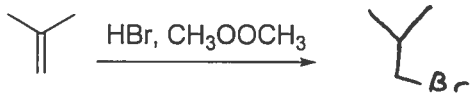
b. Write an arrow-pushing mechanism for the first half of this reaction, up until the reagents for step 2 are brought in. (8 pts)



First step = 3 pts
Second = 3 pts
Third = 2 pts

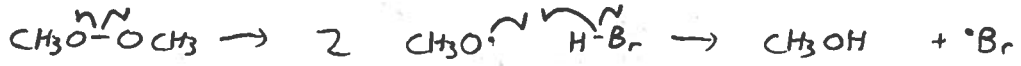
4) Addition mechanism 2:

a. Predict the major product(s) of the reaction shown below, showing stereochemistry if necessary. (2 pts)

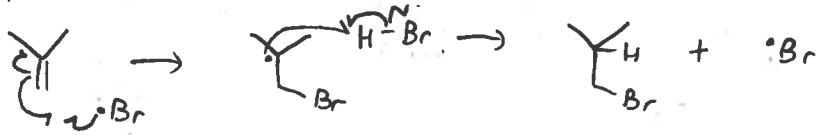


b. Write an arrow-pushing mechanism for this reaction. Clearly label your initiation, propagation and termination steps, and show at least two examples of termination. (8 pts)

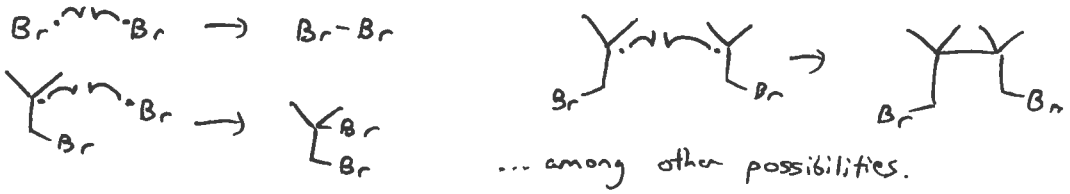
Initiation:



Propagation:

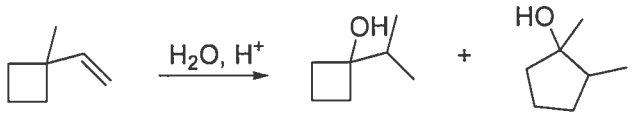


Termination:



 Name Key

5) When an acid-catalyzed hydration was performed on the molecule shown below, some unexpected products were created.

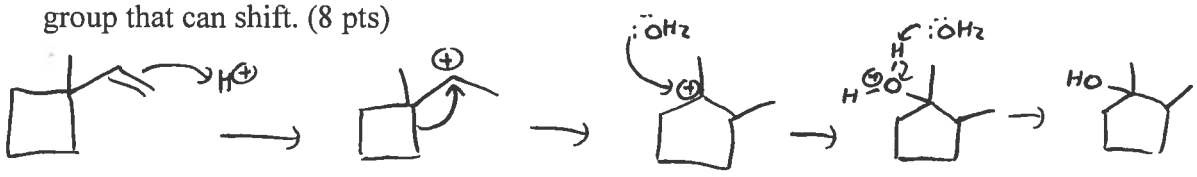


Product A Product B

a. Show the mechanism for the formation of Product A, ignoring stereochemistry. (6 pts)

No arrow for shifts: -1
missing formal charge: -½ each
Deprotonation of H_2O before attack: -1

b. Show the mechanism for the formation of Product B, ignoring stereochemistry. Hint: It's almost identical to the formation of Product A, but methyl is not the only type of alkyl group that can shift. (8 pts)

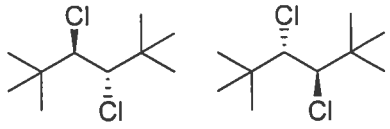


c. Based on what you know of ring size, is Product A or B more stable? (2 pts)

B - closer to six-membered ring.

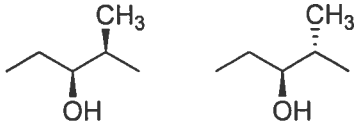
Name Key

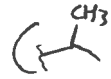
6) For each of the following pairs of molecules, are they identical, enantiomers, diastereomers, or constitutional isomers? (2 pts per pair)

a. 

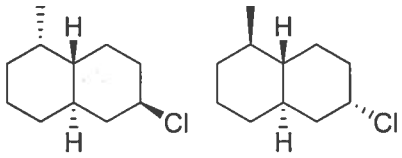
Identical – (meso)

b. 
Constitutional isomers

c. 

Identical (

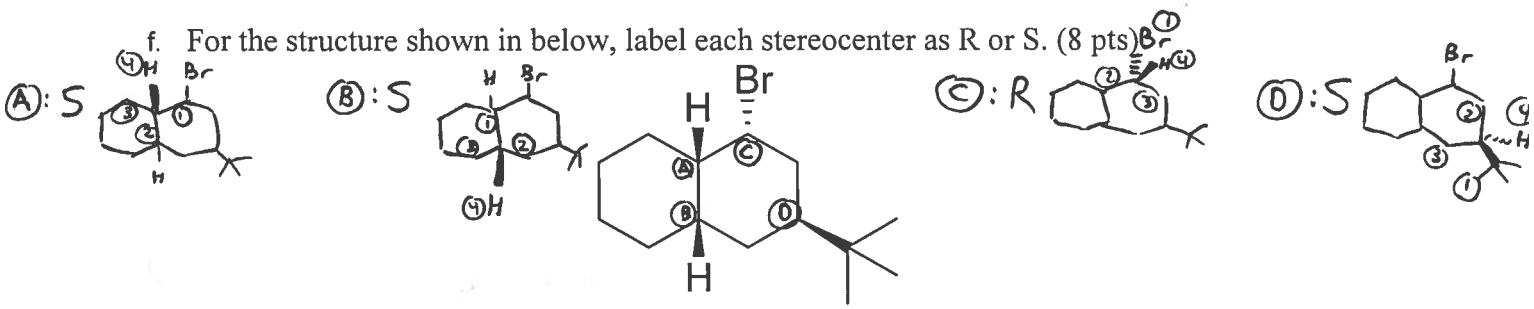
is not a stereocenter)

d. 

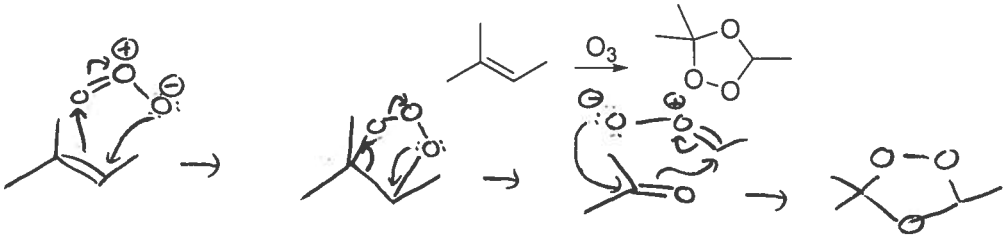
Diastereomers

e. 
Enantiomers

f. For the structure shown in below, label each stereocenter as R or S. (8 pts)



7) Extra credit! Write the mechanism for the following reaction. (5 pts extra credit)



1st step = 1 pt
2nd = 2 pts
3rd = 2 pts