

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.

Hydrogen 1 H 1.0079	Lithium 3 Li 6.941	Boron 4 Be 9.0122	Carbon 6 C 12.011	Nitrogen 7 N 14.012	Oxygen 8 O 15.999	Fluorine 9 F 18.998	Neon 10 Ne 20.183
Sodium 11 Na 22.990	Magnesium 12 Mg 24.320	Aluminum 13 Al 26.982	Silicon 14 Si 28.085	Phosphorus 15 P 30.974	Sulfur 16 S 32.065	Chlorine 17 Cl 35.453	Argon 18 Ar 39.948
Kalium 19 K 39.098	Calcium 20 Ca 40.091	Scandium 21 Sc 44.962	Titanium 22 Ti 47.907	Vanadium 23 V 50.942	Chromium 24 Cr 51.996	Manganese 25 Mn 54.938	Iron 26 Fe 55.845
Rubidium 37 Rb 84.911	Sodium 38 Sr 87.62	Tantalum 27 Ta 101.971	Rhenium 28 Ru 101.972	Ruthenium 29 Rh 102.905	Ruthenium 30 Pd 102.905	Ruthenium 31 Ni 102.905	Ruthenium 32 Cu 105.974
Ceasium 55 Cs 132.911	Barium 56 Ba 137.32	Yttrium 57-70 Lu 131.92	Zirconium 71 Hf 137.416	Nobium 72 Ta 138.95	Manganese 73 W 139.84	Rhenium 74 Re 140.921	Rhenium 75 Os 140.921
Radium 87 Fr 223	Radium 88 Ra 223	Rutherfordium 103 Lr 231.021	Rutherfordium 104 Rf 231.021	Rutherfordium 105 Db 231.021	Rutherfordium 106 Sg 231.021	Rutherfordium 107 Bh 231.021	Rutherfordium 108 Hs 231.021
Lanthanide series	Lanthanide series	Lanthanide series	Lanthanide series	Lanthanide series	Lanthanide series	Lanthanide series	Lanthanide series
Actinide series	Actinide series	Actinide series	Actinide series	Actinide series	Actinide series	Actinide series	Actinide series

Lanthanide series	La 57 138.91	Ce 58 140.12	Pr 59 141.91	Nd 60 141.71	Pm 61 141.41	Sm 62 140.98	Eu 63 141.91	Gd 64 147.25	Tb 65 147.92	Dy 66 147.92	Ho 67 146.92	Er 68 147.26	Tm 69 149.92	Yb 70 171.04
Actinide series	Ac 89 223.021	Th 90 232.64	Pa 91 231.021	U 92 231.021	Np 93 231.021	Pu 94 231.021	Am 95 231.021	Cm 96 231.021	Bk 97 231.021	Cf 98 231.021	Es 99 231.021	Fm 100 231.021	Md 101 231.021	No 102 231.021

pKa Values

HI	-10.1	H ₂ O	15.7
HCl	-3.9	Alcohol (ROH)	16-18
H ₃ O ⁺	-1.7	HC≡CH	26
CH ₃ COOH	4.7	NH ₃	36
NH ₄ ⁺	9.3	H ₂ C=CH ₂	45
Phenol	10	CH ₄	60

Average: 67.9

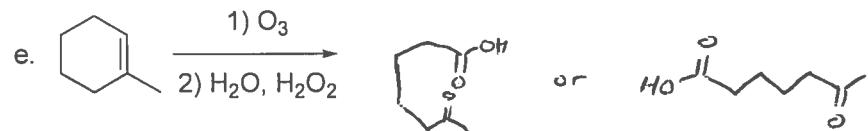
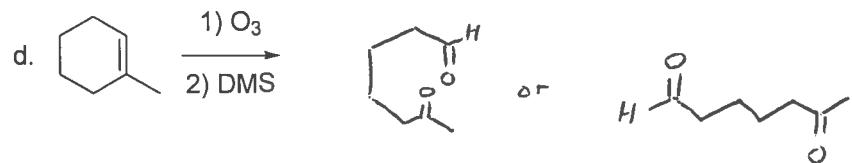
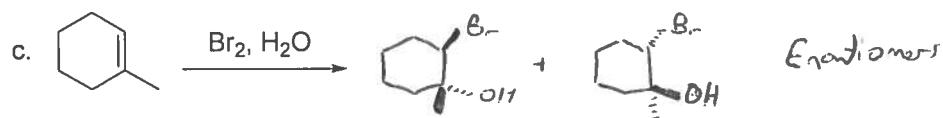
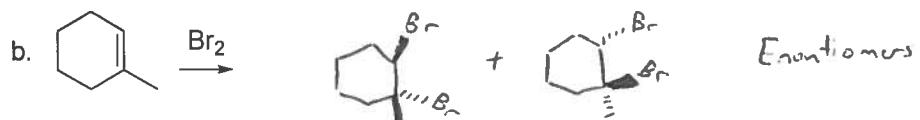
Median: 75.0

St Dev: 22.4

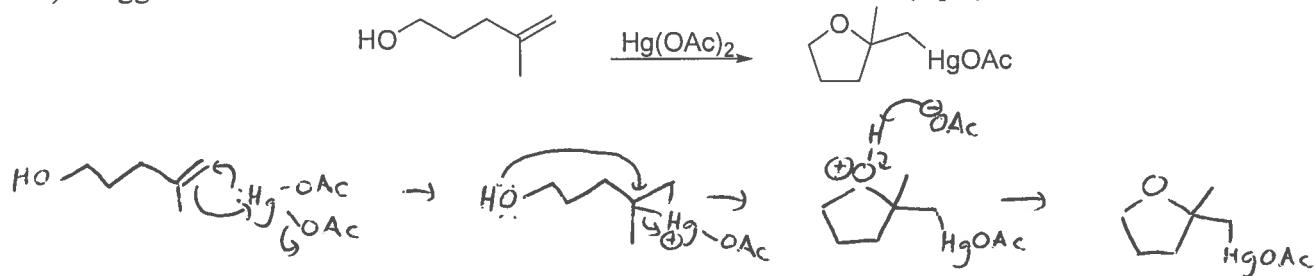
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Min: 15

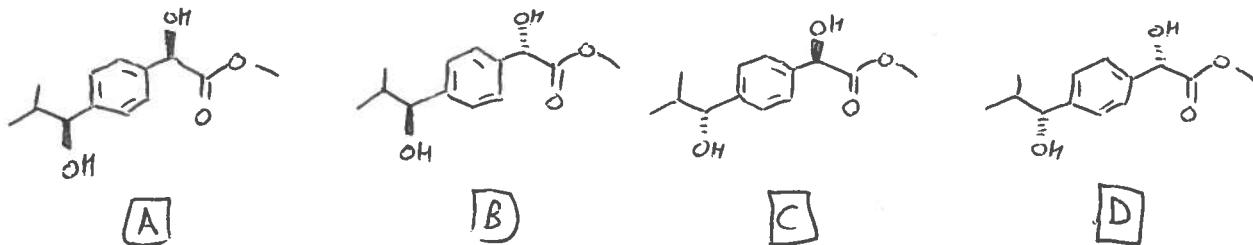
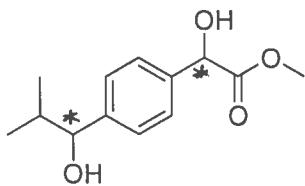
- 1) For each reaction shown below, predict the product(s). If a mixture of stereoisomers is formed, show all stereoisomers using wedges and dashes to indicate configuration, and specify whether they are enantiomers or diastereomers. (3 pts each)



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



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



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

B & C: Enantiomers

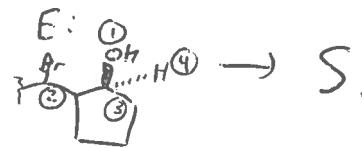
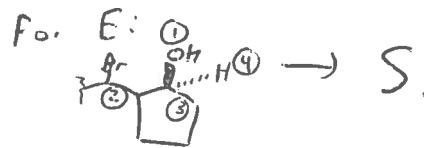
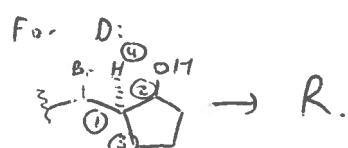
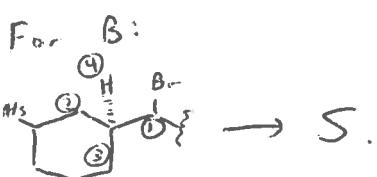
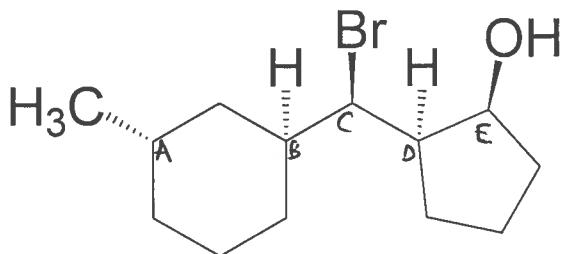
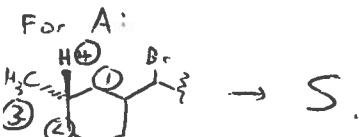
A & C: Diastereomers

B & D: Diastereomers

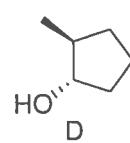
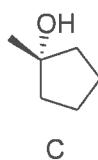
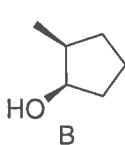
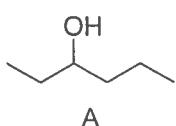
A & D: Enantiomers

C & D: Diastereomers

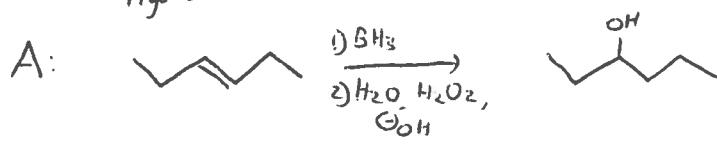
- 4) In the structure shown below, label each stereocenter as R or S. (10 pts)



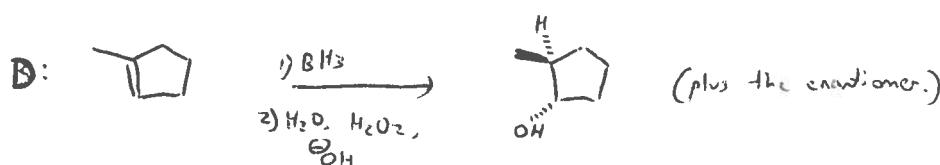
5) Four compounds are shown below.



- 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.*

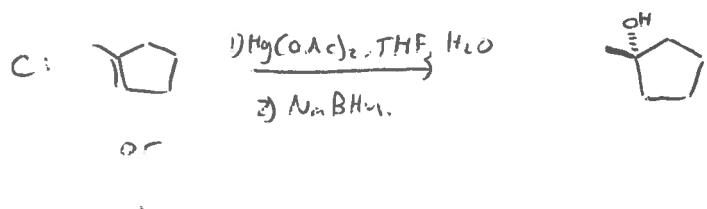
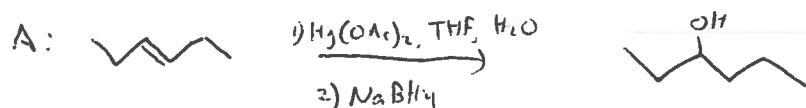


Correct letters but wrong alkene = -1
missing a letter/extraneous letter = -2
missing 2 letters/2 extraneous letters = -3

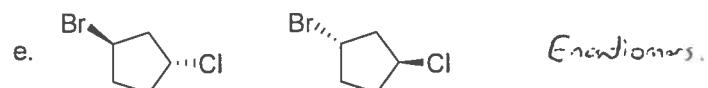
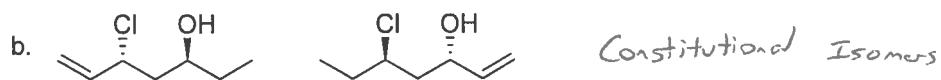
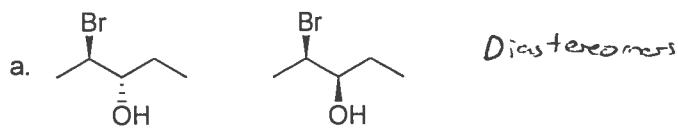


- b. Which of these compounds can be synthesized as the major product of oxymercuration-reduction? (i.e., $Hg(OAc)_2$, H_2O , THF, followed by $NaBH_4$) Show the precursor alkene for each alcohol that can be prepared this way. (6 pts)

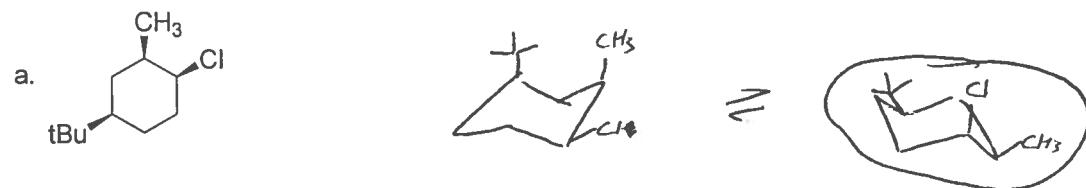
Oxymercuration-reduction is Markovnikov-style.



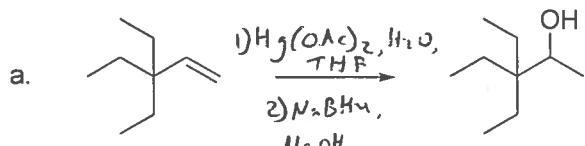
- 6) For each of the following pairs of molecules, are they identical, enantiomers, diastereomers, or constitutional isomers? (2 pts each)



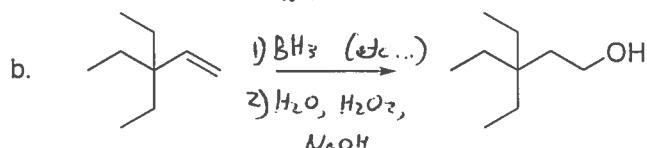
- 7) For each of the following structures, show both chair conformations. (Make sure your bond angles clearly indicate whether each group is equatorial or axial.) Circle the more stable ring-flip form for each molecule. (5 pts each)



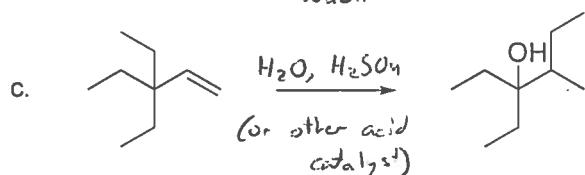
- 8) Fill in the reagents above the arrow to convert the starting material to each of the products.
(15 pts)



Markovnikov without C⁺ rearrangements →
Oxymercuration-reduction



Anti-Markovnikov → Hydroboration-reduction



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

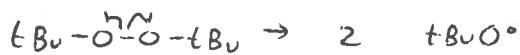
- 9) Radical HBr addition mechanism (10 pts)

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

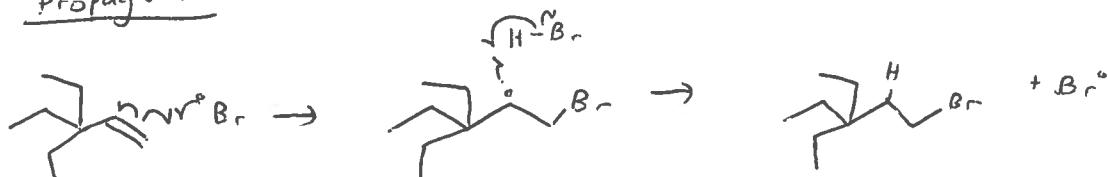


- b. Write an arrow-pushing mechanism for this reaction. Clearly label the initiation, propagation, and termination steps. Show at least two examples of termination. (8 pts)

Initiation:



Propagation:



Termination:

