CHEM 3311 (Richardson) Second Hour Exam – March 8, 2016

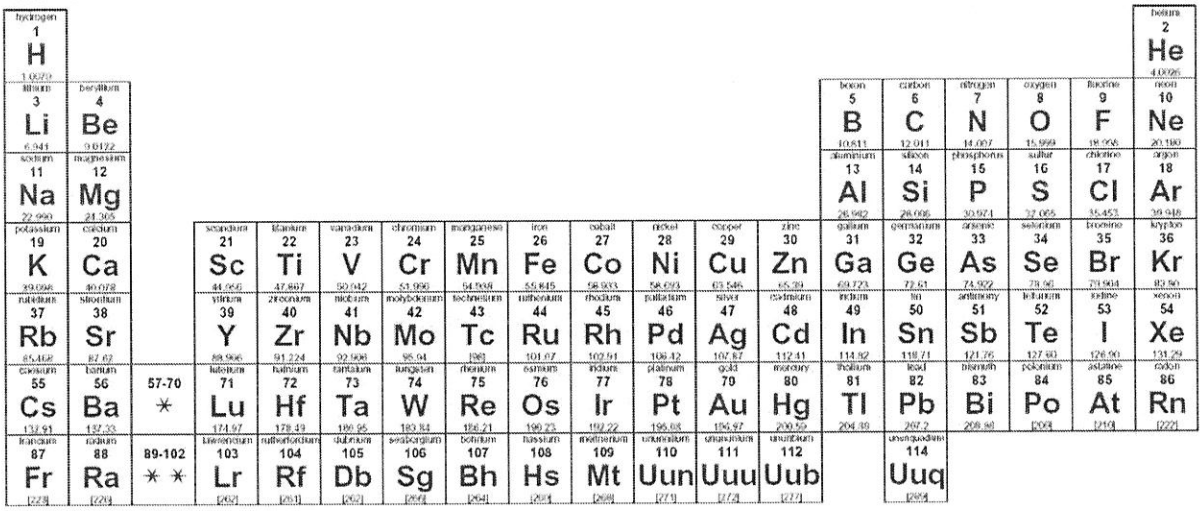
Your Name Key

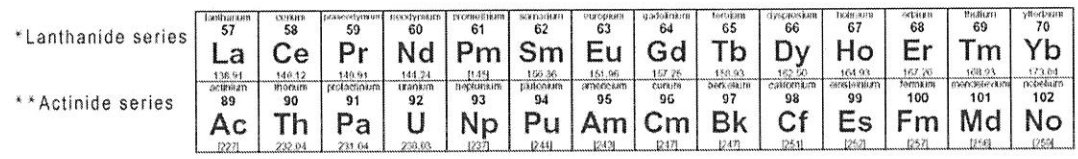
Student ID

Recitation Time (check one)
- O 3:00 Monday w/ Blaine McCarthy
- O 11:00 Tuesday w/ Thomas Carey
- O 1:00 Wednesday w/ Garrett Cairo
- O 8:00 Thursday w/ Blaine McCarthy
- O 3:00 Thursday w/ Garrett Cairo

Question	Score	Out of
1		30
2		18
3		10
4		12
5		10
6		10
7		10
8		6 e.c.
Total		100

This is a closed-book exam. The use of notes, calculators, 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. 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	CH_3COOH	4.7	Phenol	10	H_2	35
HBr	-8	HN_3	4.7	RSH	10-12	NH_3	36
HCl	-6	H_2S	7.0	H_2O	15.7	$H_2C{=}CH_2$	45
H_3O^+	-1.7	NH_4^+	9.3	Alcohol (ROH)	16-18	CH_4	60
HF	3.2	HCN	9.4	HC≡CH	26		

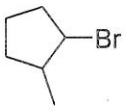
Average = 79.7
St. Dev = 15.0
Max = 104.0
Min = 42.0

 Name_____

1) Starting from any hydrocarbon with the same number of carbon atoms as the product, and using any reactions that have been covered so far in class, show how you would create the products shown **as the only major product of the reaction**. Write your hydrocarbon starting material before the arrow, and the other reagents above or below the arrow. (30 pts).

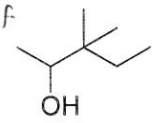
6 pts each:
3 pts alkene
3 pts other reagents

a. 

HBr, $ROOR$ (necessary for any pts) → 

(anti-Markovnikov)

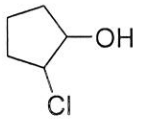
b. 

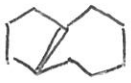
1) $Hg(OAc)_2$, H_2O, THF
2) $NaBH_4$, $^{\ominus}OH$ → 

(Markovnikov without ⊕ rearrangements)

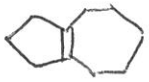
−1.5 pts for missing 1), 2).
−1.5 for missing any reagent

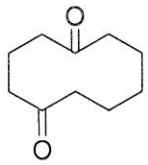
c. 

Cl_2, H_2O → 

d. 

or



1) O_3
2) DMS or H_2O, H_2O_2 → 

e. 

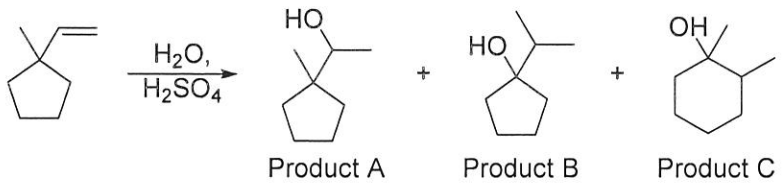
1) BH_3
2) H_2O, H_2O_2, $^{\ominus}OH$ → 

(anti-Markovnikov on 2 alkenes)

−1 pt for missing sign on $^{\ominus}OH$

 Name_____

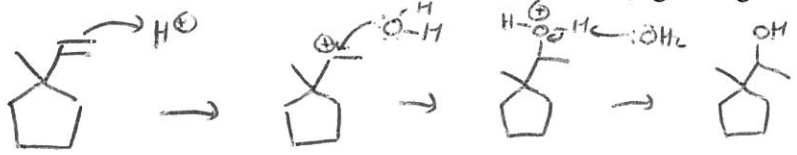
2) When an acid-catalyzed hydration was performed on the molecule shown below, some unexpected products were created.



Product A Product B Product C

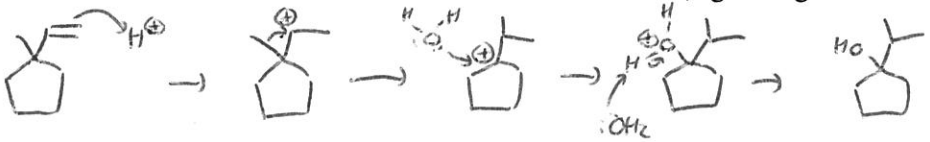
If basic conditions (⊖OH), -4 for (a), -1 for (b) & (c).

a. Show the mechanism for the formation of Product A, ignoring stereochemistry. (4 pts)



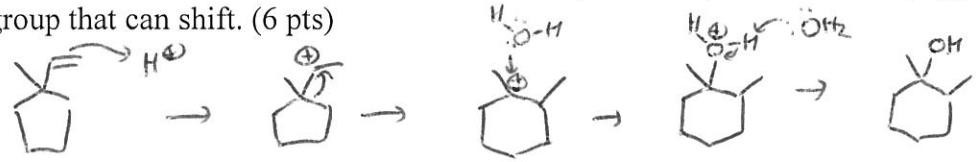
1 pt per intermediate/step
-0.5 for wrong charges

b. Show the mechanism for the formation of Product B, ignoring stereochemistry. (6 pts)



1 pt per intermediate/step
-0.5 for wrong charges

c. Show the mechanism for the formation of Product C, ignoring stereochemistry. Hint: It's almost identical to the formation of Product B, but methyl is not the only type of alkyl group that can shift. (6 pts)



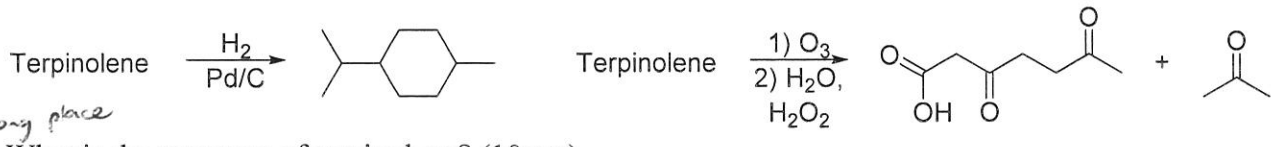
1 pt per intermediate/step
-0.5 for wrong charges
-1 for missing methyl

d. Which of these three products is likely to be produced in the smallest quantity? (2 pts)

Product A - it has a 2° ct.

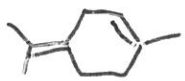
3) In your lab, you have found a mysterious bottle labeled "Terpinolene." In an attempt to discover its structure, you perform some reactions on it and observe the following results.

-3 pts for C=O or OH
-3 for one C=C in wrong place

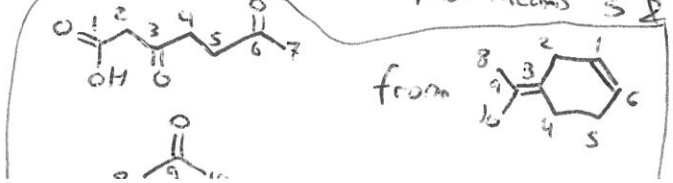


What is the structure of terpinolene? (10 pts)

4 pts for 6-mem ring
4 pts for alkene
-2 pts for too many/too few alkenes

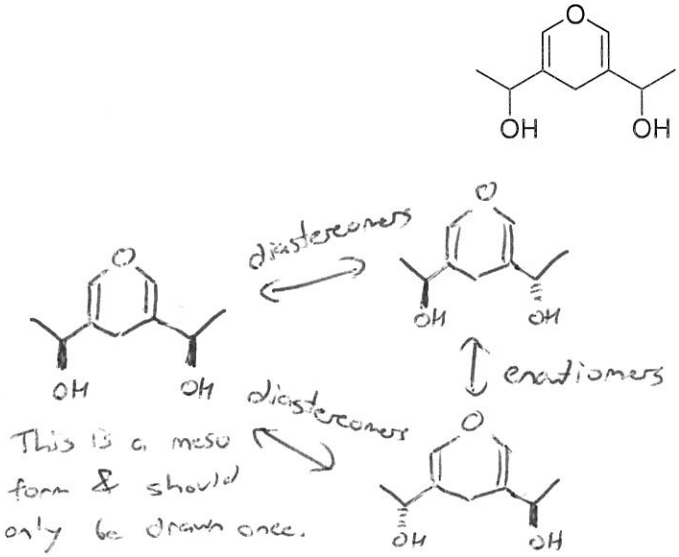


We know it has a 6-membered ring, so the only 2 carbons in ozonolysis product that could have been connected are 1 & 6. That means 3 & 9 were also connected to each other.



 Name_____

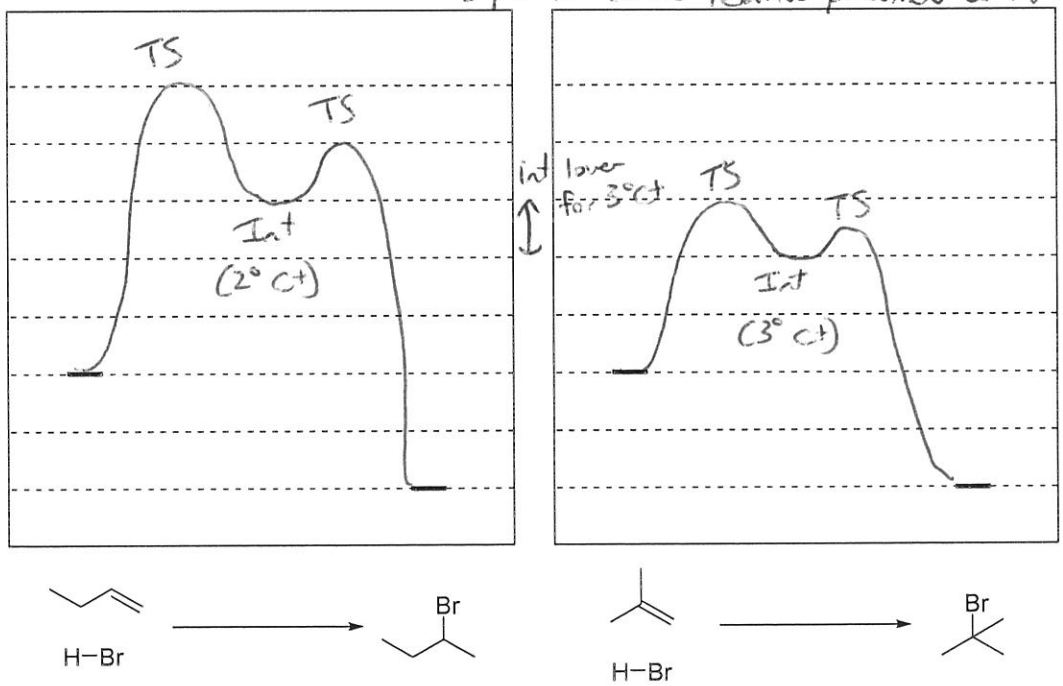
4) Using bold and dashed bonds, show all possible stereoisomers of the structure shown below. Leave all bonds in-plane (not bold or dashed) if they are part of the ring. Do not repeat any structures. What is the stereochemical relationship (enantiomers, diastereomers, identical) between each possible pairing of these molecules? (12 pts)



2 pts per structure,
2 pts per descriptor.
-1 pt for showing meso compound twice
-2 pts for structures w/ X or Y
-2 for stereochem on sp^2 carbons.

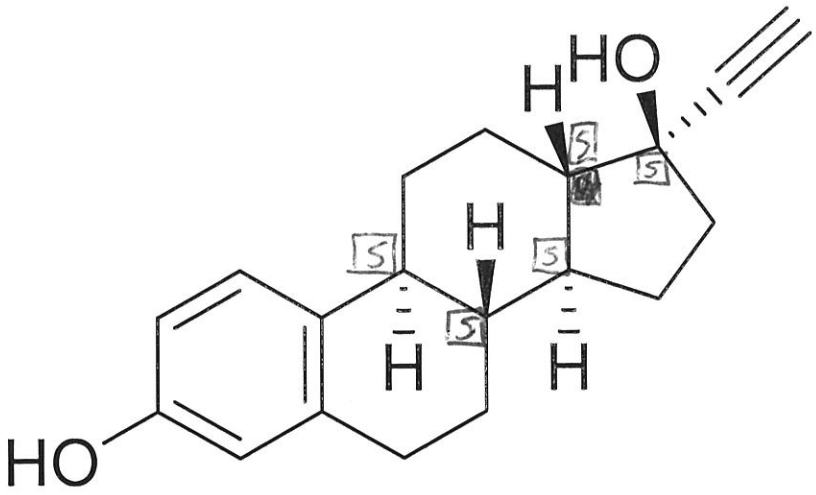
5) Two reactions are shown below. Sketch the energy diagrams for each one, starting with the levels given for reactants and products. You don't need actual numbers, but the energy levels of each state should be correct relative to each other. Clearly label the location of each intermediate and transition state on the graph, though you do not need to draw the structures. (10 pts)

for each graph: 1pt for each labeled, 1 pt for overall shape. 2 pts for correct relative placement of intermediates



 Name_____

6) The structure of ethynyl estradiol, an oral contraceptive, is shown below. Label each stereocenter as R or S. (10 pts)



2 pts each

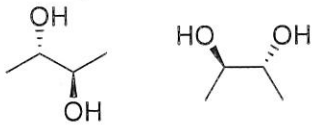
7) Put the following alkenes in order of stability, from most stable to least stable. (10 pts)
(E)-2-hexene, (E)-3-methyl-2-pentene, (Z)-2-hexene, 1-hexene, 2,3-dimethyl-2-butene

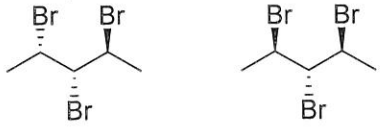
③ ② ④ ⑤ (Least stable) ① (Most stable)

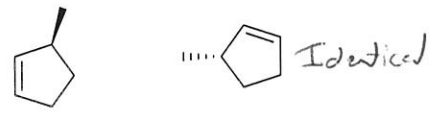
2 pts each

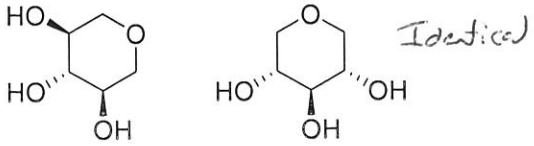
If only one is pulled out of sequence, -2 pts.

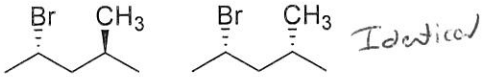
8) Extra credit! For each of the following pairs of molecules, are they identical, enantiomers, diastereomers, or constitutional isomers? (6 pts extra credit)

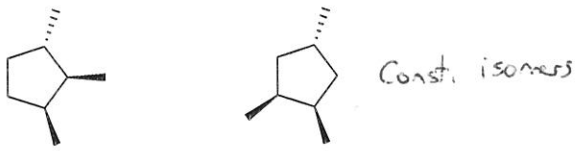
a.  Diastereomers

d.  Diastereomers

b.  Identical

e.  Identical

c.  Identical

f.  Const. isomers

1 pt each