CHEM 3311 (Richardson) Final Exam – Dec. 18, 2018

Your Name: Key

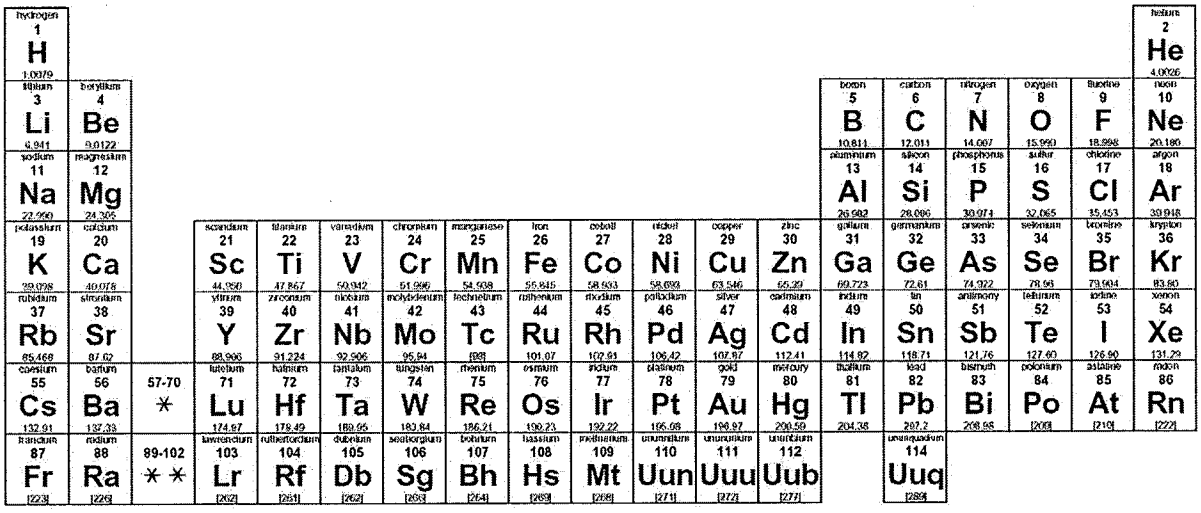
Student ID: _____

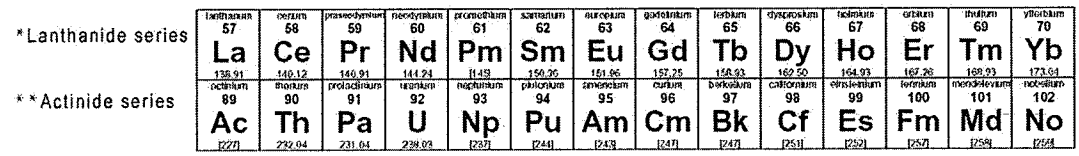
Recitation (check one)

O 11:00 Mon (Matthew Farmer)
O 2:00 Mon (Shaofeng Huang)
O 9:00 Tue (Lacey Wayment)
O 12:00 Tue (Josh Kamps)
O 3:00 Tue (Lauren Bodkin)
O 10:00 Mon (Shafer Soars)
O 1:00 Mon (Lacey Wayment)
O 3:00 Mon (Shaofeng Huang)
O 10:00 Tue (Josh Kamps)
O 2:00 Tue (Lauren Bodkin)
O 4:00 Tue (Matthew Farmer)

Question	Score	Out of
1		30
2		15
3		40
4		40
5		20
6		20
7		15
8		20
9		10 e.c.
Total		200

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	ArOH	10	HC≡CH	26
HBr	-8	HN_3	4.7	RSH	10-12	H_2	35
HCl	-6	H_2S	7.0	H_2O	15.7	NH_3	36
H_3O^+	-1.7	NH_4^+	9.3	ROH	16-18	$H_2C{=}CH_2$	45
HF	3.2	HCN	9.4	O=C-CH	9-25	CH_4	60

(28.5 pt curve)

Avg 121.5

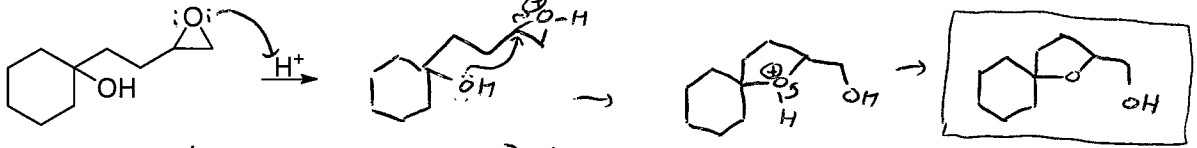
St. Dev 47

Max 204.5

Min 8

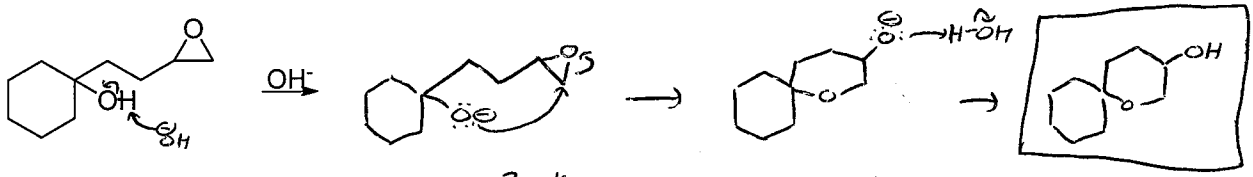
1) Each of these reactions forms a different product of formula $C_{10}H_{18}O_2$. Show a mechanism for each reaction, and draw a box around the final product. (30 pts - 15 pts each)

a.



arrow 1 pt | Structure 3 pts, arrows 2 pts | Structure 3 pts, arrow 1 pt | 5 pts

b.

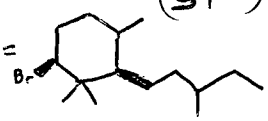


arrows 2 pts | structure 2 pts, arrows 2 pts | structure 2 pts, arrows 2 pts | 5 pts

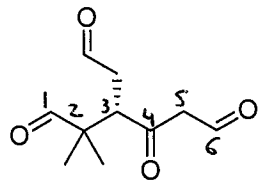
2) In your lab, you have found a mysterious bottle labeled "Luzonensin – isolated from red algae *Laurencia luzonensis*." In an attempt to discover its structure, you perform some reactions on it and observe the following results. What is the structure of luzonensin? (15 pts)

(5 pts)

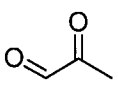
Luzonensin $\xrightarrow[Pd/C]{H_2}$ (2R,6S)-6-bromo-1,1,3-trimethyl-2-(3-methylpentyl)cyclohexane =

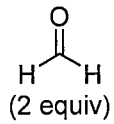


Luzonensin $\xrightarrow[tBuOH]{tBuONa}$ Alkene $C_{15}H_{22}$ $\xrightarrow[2)\ DMS]{1)\ O_3}$



(2-dimethyls)



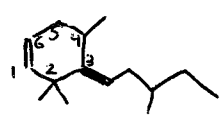


(2 equiv)

(E2 on Br)

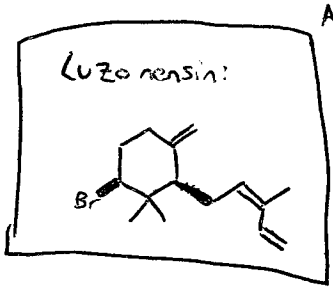
5 deg unsat w/ 1 ring = 4 alkenes

=



w/ 3 additional alkenes in it somewhere.

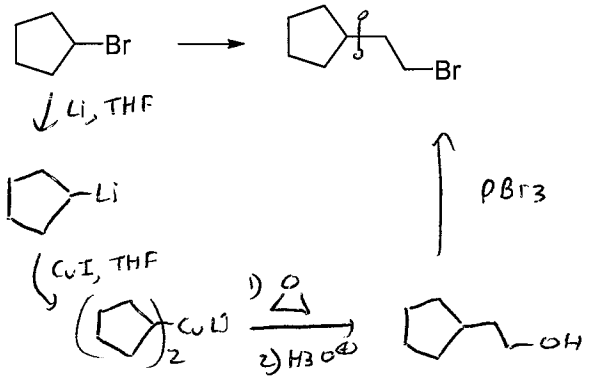
(5 pts)



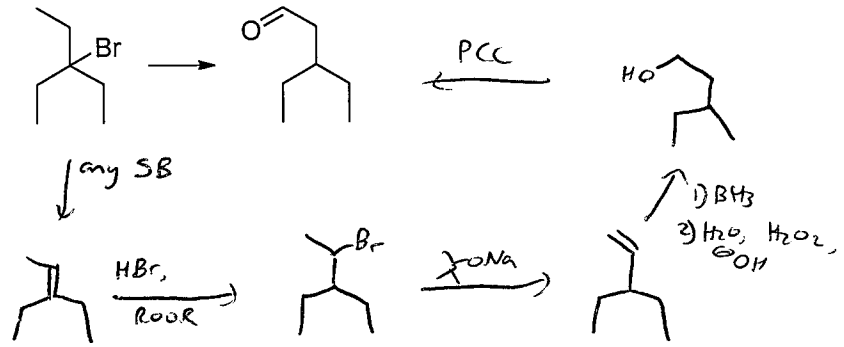
Automatic 15 pts if correct - if not, partial credit for work

3) Find a way to synthesize the desired product from the given starting material. If more than one step is necessary, show the product of each step. Do not show mechanisms. (40 pts - 10 pts each)

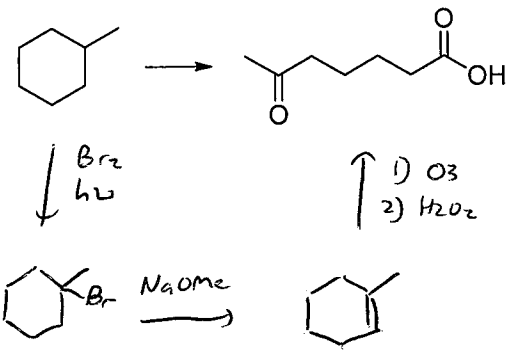
a.



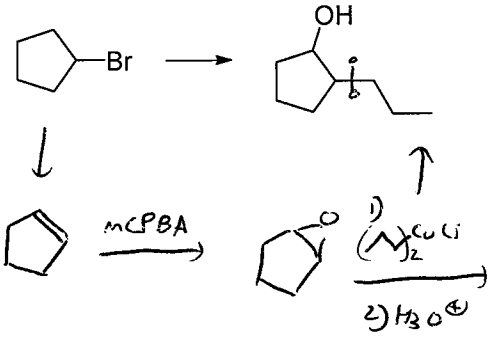
b.



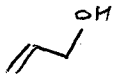
c.

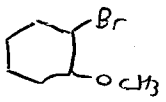


d.

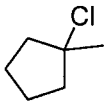


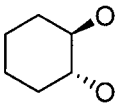
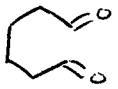
4) **Predict the product** of the following reactions, and **choose the appropriate descriptor** (reduction, oxidation, or neither) for what happens to the starting material during each reaction. You do not need to show stereochemistry. (40 pts; 4 pts each)

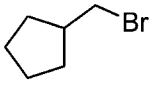
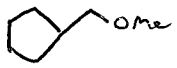
a.  1) EtMgBr, THF; 2) H_3O^+  neither

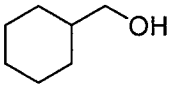
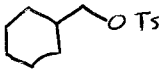
b.  Br_2, CH_3OH  oxidation

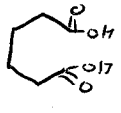
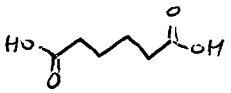
c.  1) Me_2CuLi, THF; 2) H_3O^+  reduction

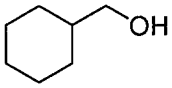
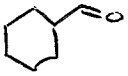
d.  ~~CH_3OH $tBuOK$~~  neither +  neither

e.  HIO_4  oxidation

f.  MeOK, MeOH  neither

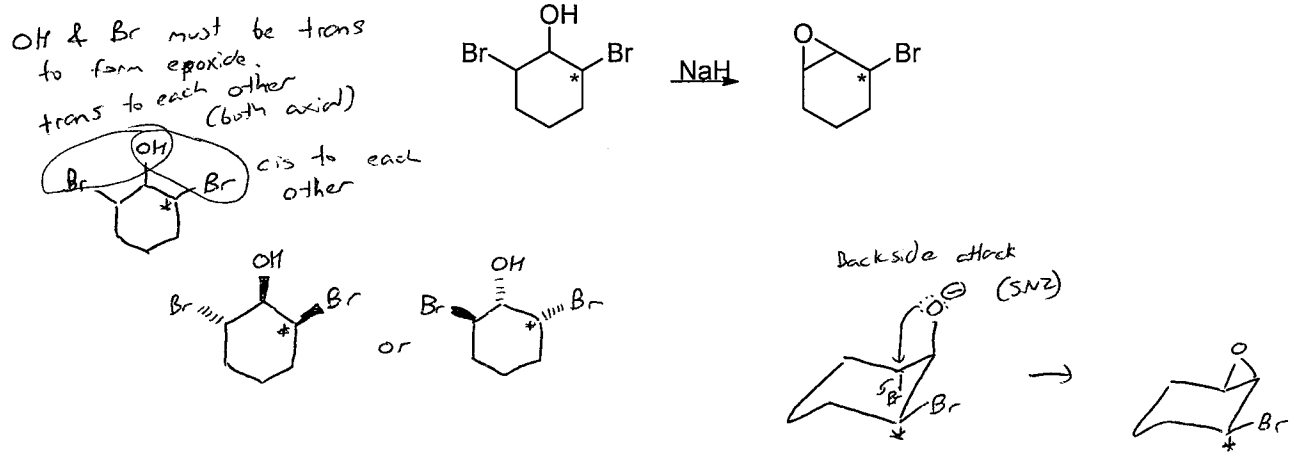
g.  TsCl, pyridine  neither

h.  1) O_3; 2) H_2O  or  oxidation

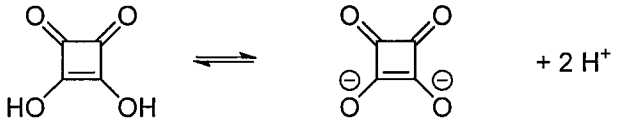
i.  PCC, CH_2Cl_2  oxidation

j.  CH_2I_2, Zn-Cu, THF  neither

5) One particular stereoisomer of 2,6-dibromocyclohexanol was labeled with a carbon isotope (indicated by an asterisk) at one of the bromine-bearing carbons. When this compound was treated with sodium hydride, it formed **only** the product shown. Draw the stereoisomer of 2,6-dibromocyclohexanol that is consistent with these results, and explain why in under 30 words, but with as many structures as you want. (20 pts)

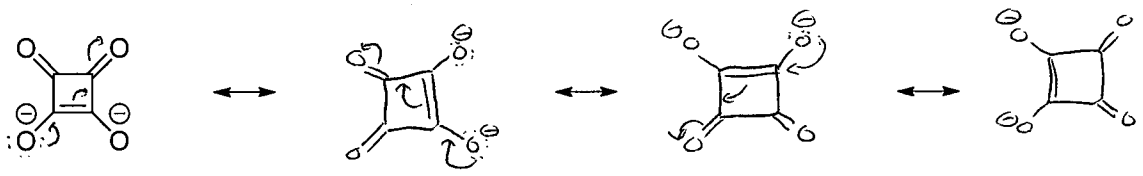


6) Squaric acid, shown below, can lose two protons to become the squarate dianion. Answer these questions about squarate. (20 pts total)



Squaric acid Squarate dianion

a. Draw three other resonance forms for the squarate dianion. Use valid arrow-pushing to show the movement of electrons. (5 pts each)



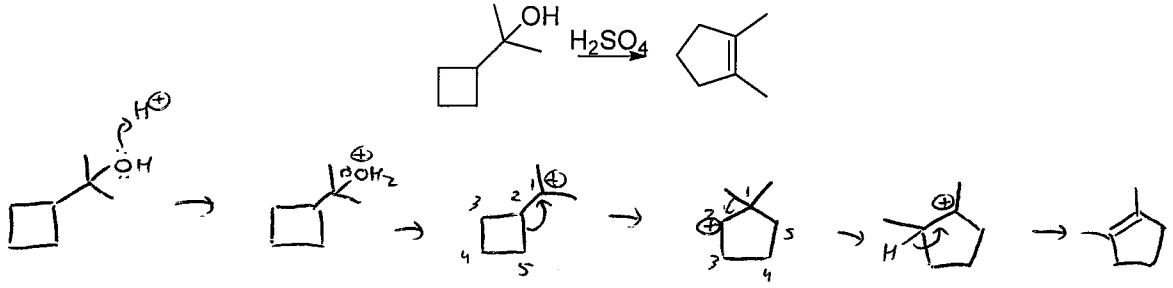
b. What is the average bond order for each C-O bond in this structure? (2 pts)

6/4 or 3/2

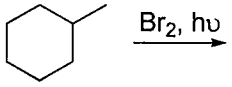
c. What is the average bond order for each C-C bond in this structure? (3 pts)

5/4

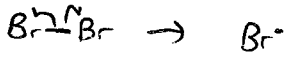
7) Show a mechanism for this reaction, and draw a box around the final product. (15 pts)



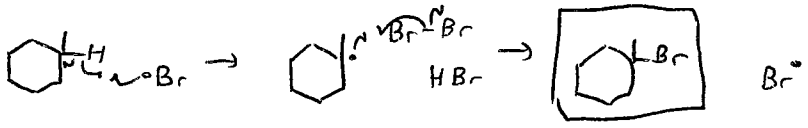
8) Show a mechanism for this reaction (ignoring stereochemistry), and draw a box around the final product. Clearly label your initiation, propagation and termination steps, and show at least two examples of termination. (20 pts)



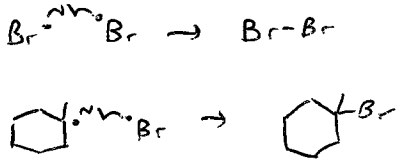
Initiation:



Propagation:



Termination:



9) Extra credit! The structure of ethynyl estradiol, an oral contraceptive, is shown below. For each of the labeled atoms, describe the hybridization as sp, sp^2, or sp^3. (10 pts extra credit)