CHEM 3311 (Richardson) Third Exam – Nov. 27, 2018

Your Name: Key

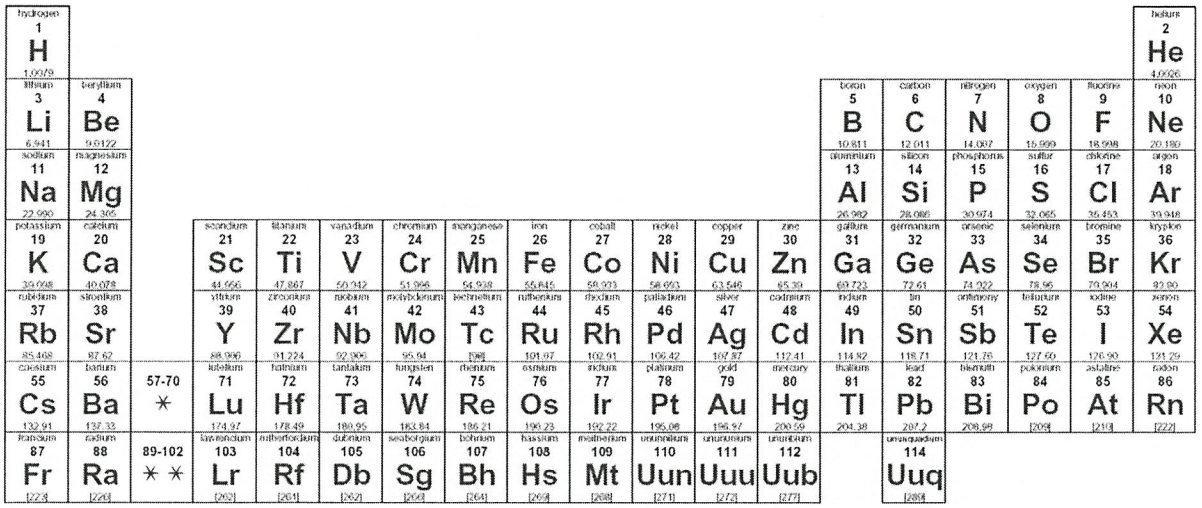
Student ID: _____

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		15
2		20
3		15
4		10
5		15
6		10
7		15
8		10 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

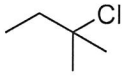
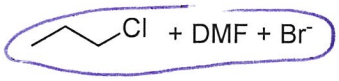
HI	-10	CH_3COOH	4.7	ArOH	10	HC≡CH	26
HBr	-8	HN_3	4.7	RSH	10-12	H_2	35
HCl	-6	H_2S	7.0	H_2O	15.7	NH_3	36
H_3O^+	-1.7	NH_4^+	9.3	ROH (R=alkyl)	16-18	$H_2C{=}CH_2$	45
HF	3.2	HCN	9.4	O=C-CH (α H)	9-25	CH_4	60

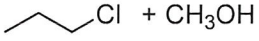
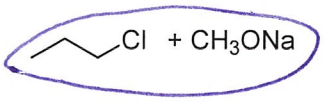
(10-pt curve)

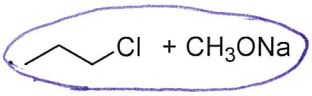
Avg 64.5
St. Dev 19.3
Max 104
Min 10

(2 pt per circle,

1) For each of the following pairs of reactions, circle the one that would be faster at S_N2 and explain why in under ten words. If both are equal, do not circle an option. (15 pts; 3 pts each) 3 pts per explanation)

a.  + DMF + Br^-  less substituted / less steric hindrance

b.  + CH_3OH  Stronger nucleophile

c.  + CH_3ONa Better leaving group

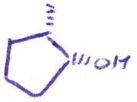
2) Structure and reactivity. For parts b. and c., if a reaction forms a racemic mixture that contains the target compound plus its enantiomer, that is an acceptable answer. (20 pts total)

a. Draw each of the following compounds. (2 pts each)

(1R,2R)-2-methylcyclopentanol 

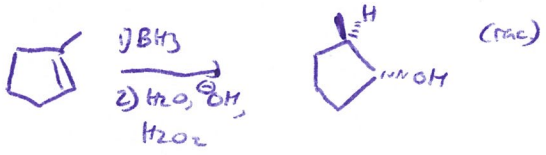
1-methylcyclopentanol 

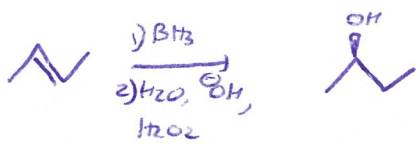
1 pt for connectivity, 1 for stereochem

(1R,2S)-2-methylcyclopentanol 

(R)-2-butanol 

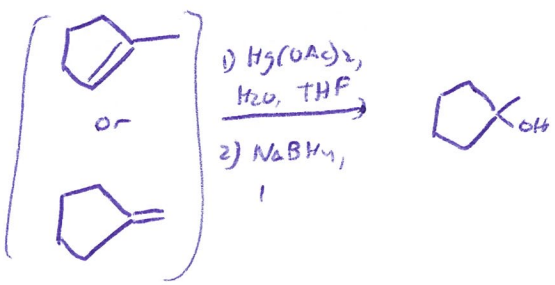
b. Which of these can be formed as the only major product of hydroboration-oxidation on any alkene of your choice? Show the overall reaction for their formation from this alkene. (6 pts)

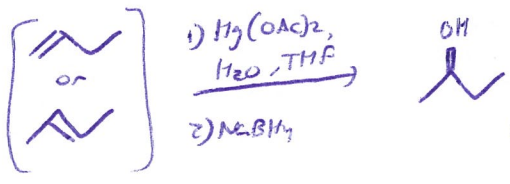




For each rxn: 2 pts for alkene, 1 for reagents

c. Which of these can be formed as the only major product of oxymercuration-reduction on any alkene of your choice? Show the overall reaction for their formation from this alkene. (6 pts)

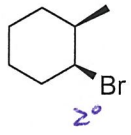




(-2 pt for a rxn w/ wrong products, No pts take for error carried forward if you draw wrong structure for a.), but b) & c) are OK.

2 pts per circled mechs, 2 pts for products

3) For each of the reactions shown below, **circle the mechanism(s)** you would expect to see, if any, and **draw the product(s)**. If a product has stereocenters, show its configuration using wedges and dashes. If two stereoisomers are formed, show both of them. If an elimination occurs, show only the major alkene product. If none of the mechanisms would take place in a reasonable time frame, write NR for No Reaction. (20 pts; 4 pts each)

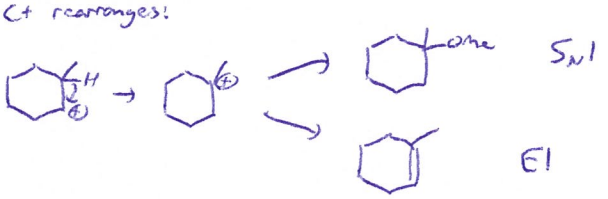
a. 

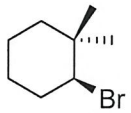
2°

MeOH
WB/PN

E2	S_N2
E1	S_N1

C+ rearranges!

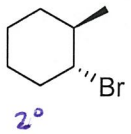


b. 

2°, neopentyl

SB/GN
PrONa
DMF

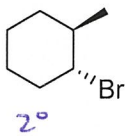
E2	S_N2
E1	S_N1

c. 

2°

WB/GN
NaCN
MeOH

E2	S_N2
E1	S_N1

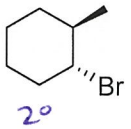
d. 

2°

SB/PN
tBuONa
THF

E2	S_N2
E1	S_N1

(anti-Zaitsev)

e. 

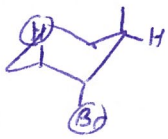
2°

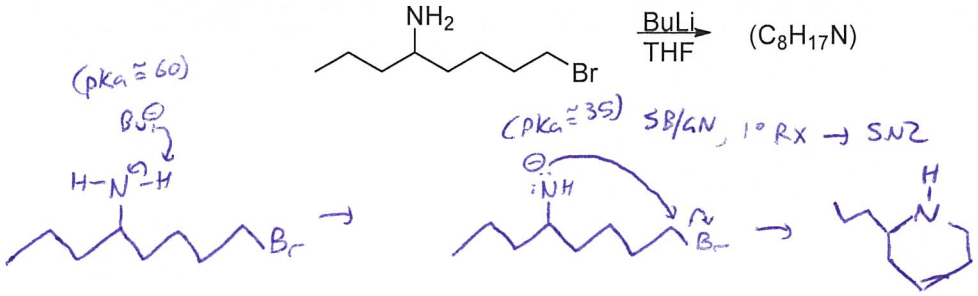
SB/GN
BuONa
THF

E2	S_N2
E1	S_N1

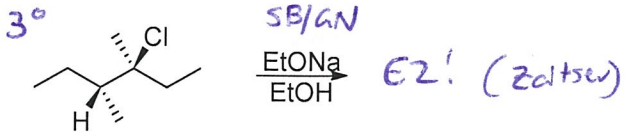
(forced to go anti-Zaitsev since Zaitsev is blocked)

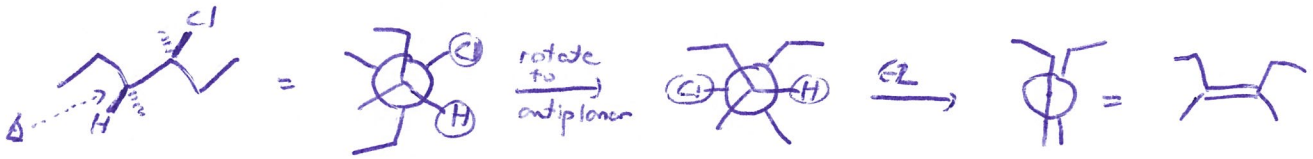
4) Show the product of this reaction and the mechanism for its formation. (10 pts)





5) Predict the product of the reaction below, including E/Z stereochemistry. Explain the stereochemical outcome in under thirty words, but with as many structures as you need. (10 pts)



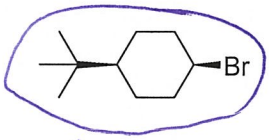


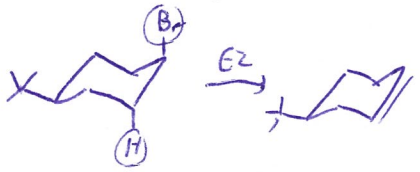
Rotating to antiplanar puts the 2 ethyl groups on same face of alkene, after E2 occurs.

E2, right stereochem, don't show E2 going antiplanar: 8/10
E2, wrong stereochem (E, not Z): 5/10
E2, wrong regiochem: 3/10
SN2 only: 3/10
SN1/E1: 2/10

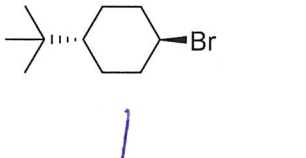
6) One of these molecules undergoes E2 elimination much faster than the other. Circle the faster molecule and explain why it is faster in under thirty words, but with as many structures as you need. (10 pts)

4 pts circle
2 pts for each chair
2 pts for explanation



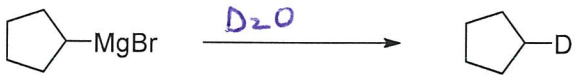


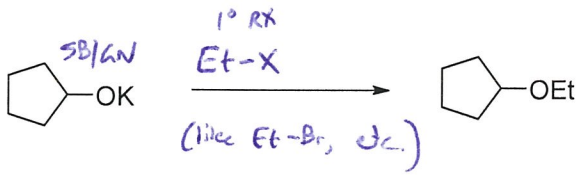
This molecule has Br locked into axial position by t-Bu group, so E2 is very easy. (always antiplanar).

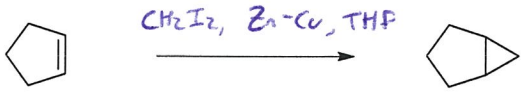


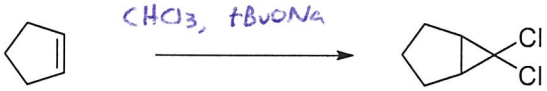
This molecule has Br locked equatorial, so it can't do E2.

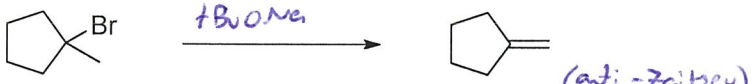
7) On each arrow, show the reagents needed to accomplish each reaction. In each case, the target product should be the major product of the reaction. (15 pts – 3 pts each)

a. 

b. 

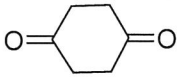
c. 

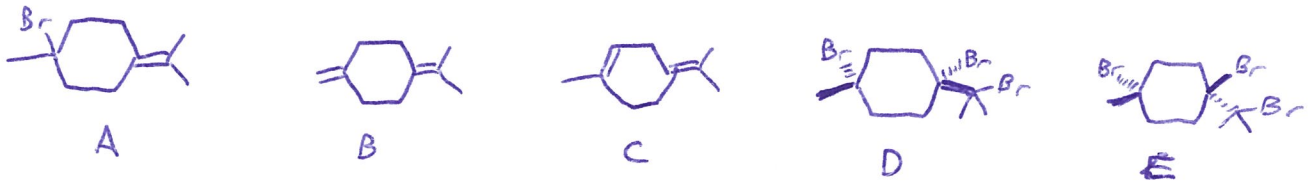
d. 

e. 

(anti-Zaitsev)

8) Extra credit! In your lab, you have found a mysterious bottle labeled "Compound **A** - achiral alkyl halide $C_{10}H_{17}Br$." In an attempt to discover its structure, you react it with KOH in ethanol and form two products (**B** and **C**), each with formula $C_{10}H_{16}$. Compound **A** rapidly undergoes solvolysis in aqueous ethanol. Ozonolysis of **A** followed by treatment with DMS gives $(CH_3)_2C{=}O$ (acetone) as one of the products plus an unidentified halogen-containing material. Catalytic hydrogenation of either **B** or **C** gives a mixture of both *trans*- and *cis*-1-isopropyl-4-methylcyclohexane. Compound **A** reacts with one equivalent of Br_2 to give a mixture of two separable compounds, **D** and **E**, both of which are achiral. Finally, ozonolysis of **B** followed by treatment with aqueous H_2O_2 gives acetone and compound **F**, shown below. Draw compounds **A** through **E**. (10 pts extra credit)





2 pts each.