CHEM 3311 (Richardson) Third Hour Exam – April 14, 2015

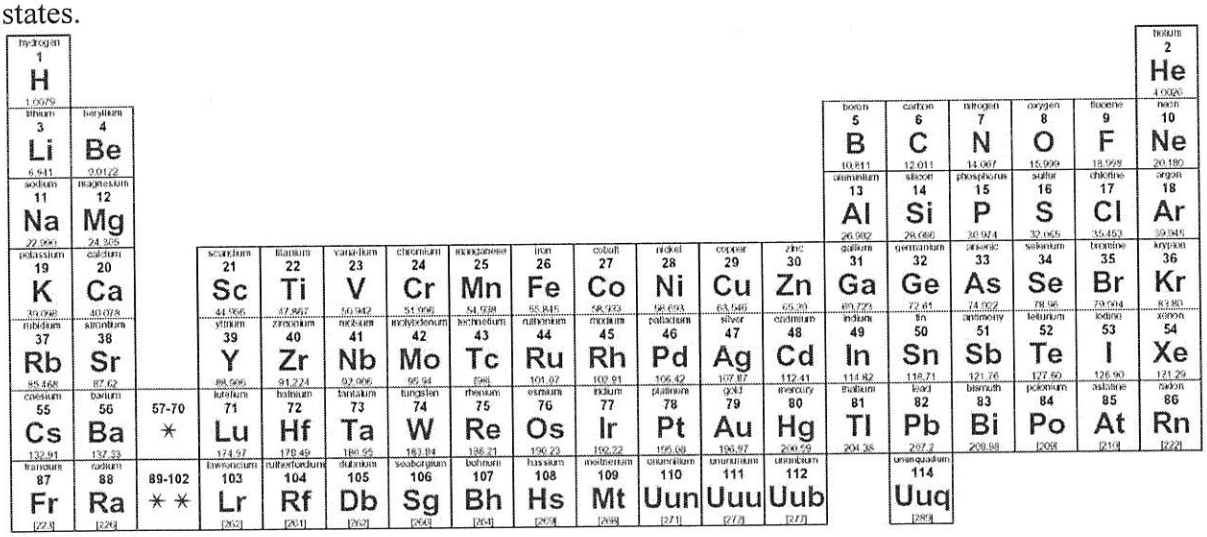
Your Name Key

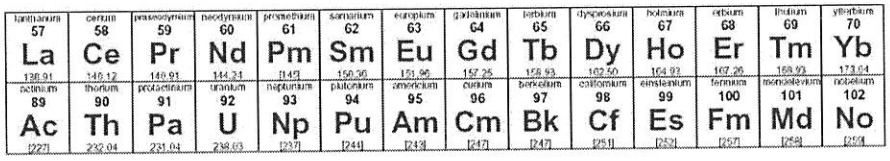
Student ID

Recitation Time 12:00 Monday, 1:00 Monday, 11:00 Tuesday, 1:00 Tuesday, 12:00 Wednesday

Question	Score	Out of
1		20
2		12
3		16
4		12
5		10
6		15
7		15
8		5 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.





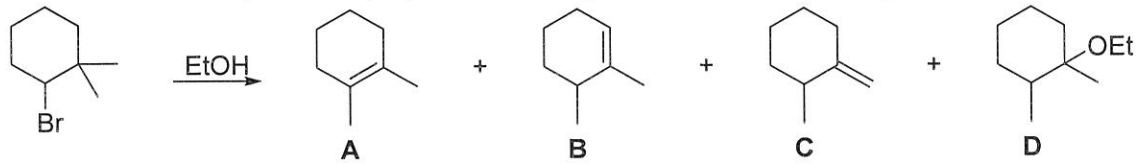
pKa Values

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		

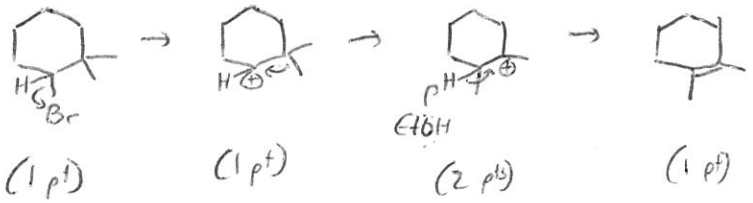
Average: 72.5
St. Dev: 16.0
Max: 98
Min: 24

 Name_____

1) When 2-bromo-1,1-dimethylcyclohexane is placed in ethanol, four products are observed.



a. Show the mechanism for the formation of product **A.** (5 pts)

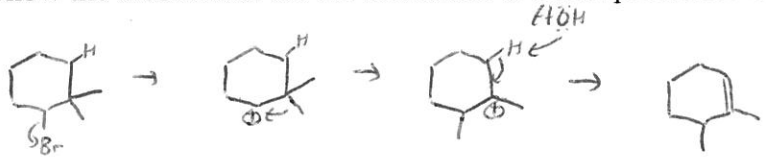


(1 pt) (1 pt) (2 pts) (1 pt)

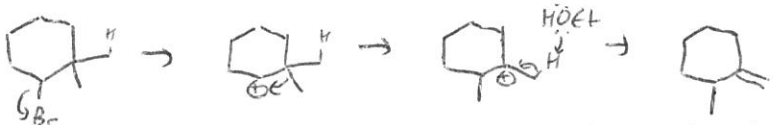
-2 pts for not using EtOH to deprotonate
-3 pts if $EtO^{\ominus}$ shows up

b. Show the mechanism for the formation of either product **B** or **C** (your choice). (5 pts)

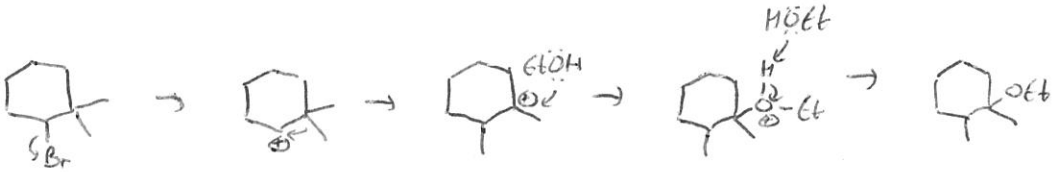
B:



C:



c. Show the mechanism for the formation of product **D.** (5 pts)

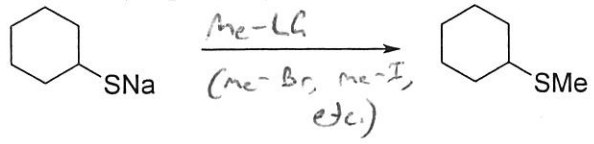


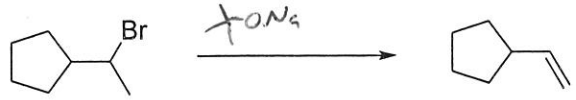
d. Rank products **A**, **B**, and **C** from greatest quantity produced to least quantity produced. Explain why this is the case in under 20 words. (5 pts)

A > B > C, because this goes from stablest (most substituted) alkene to least stable.
(most)

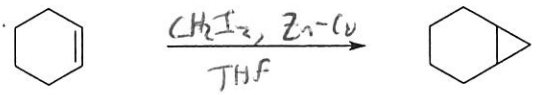
 Name_____

2) Each of these reactions can be done in a single step. On each arrow, show the reagents needed to accomplish each one. In each case, the target product should be the major product of the reaction. (12 pts – 3 pts each)

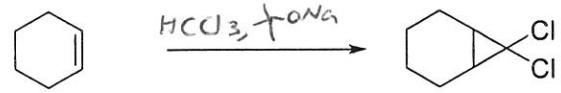
a. 

b. 

1 pt for any other alkoxide

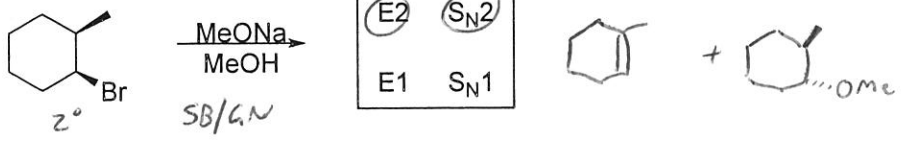
c. 

0 pts if no ZnCu

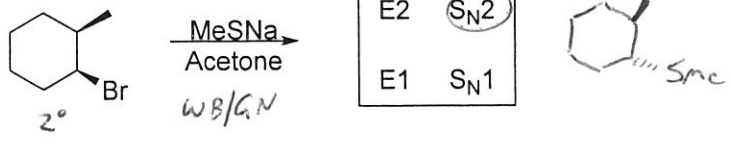
d. 

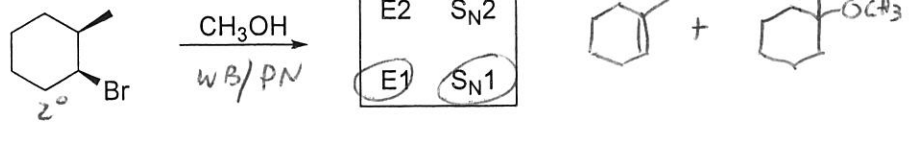
2 pts if any other alkoxide
1 pt if no alkoxide at all

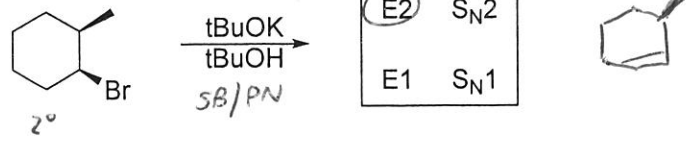
3) For each of the reactions shown below, **circle the mechanism(s)** you would expect to see, if any, and **draw the product(s)**. If a product has stereocenters, show its configuration using wedges and dashes. If two stereoisomers are formed, show both of them. If an elimination occurs, show only the major alkene product. If none of the mechanisms would take place in a reasonable time frame, write NR for No Reaction. (16 pts total - 4 pts each)

a. 

2 pts for mechanism
2 pts for products.

b. 

c. 

d. 

 Name_____

4) Arrange these compounds in order of increasing boiling point: CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$, and CH_3CH_2SH. In under ten words per compound, explain what properties of each compound are responsible for raising its boiling point. (12 pts)

$CH_3CH_2CH_3$ < CH_3OCH_3 < CH_3CH_2SH < CH_3CH_2OH

No H-bonding; van der Waals only

No H-bonding to self-dipoles only

Weak H-bonding to self

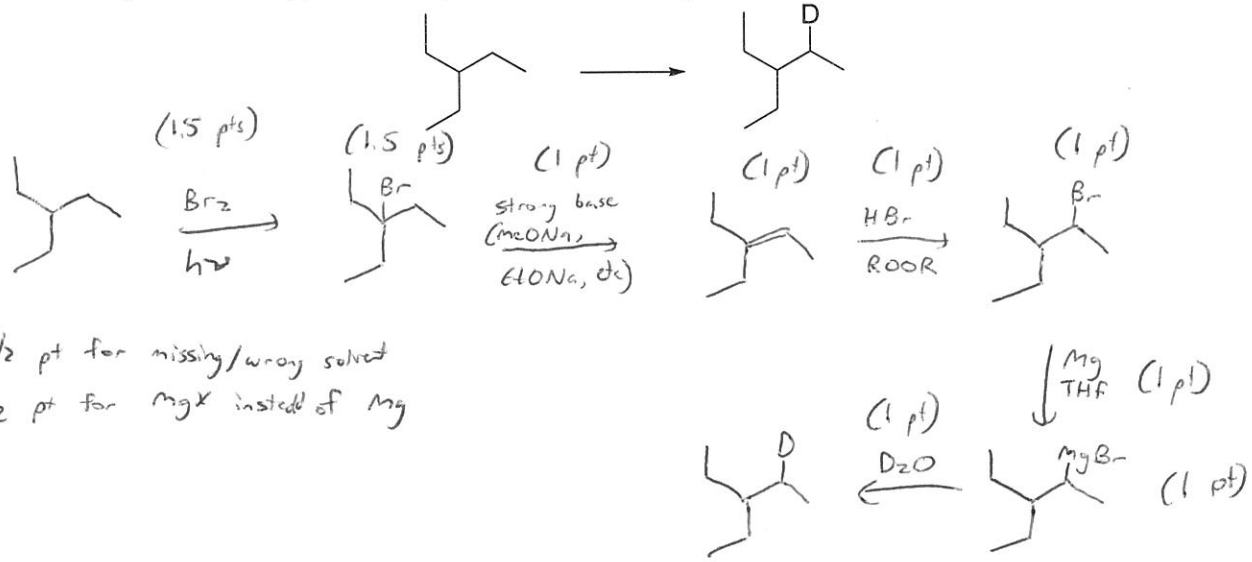
Strong H-bonding to self.

2 pts per structure in correct order

1 pt per explanation

(9 pts if EtSH & EtOH reversed)

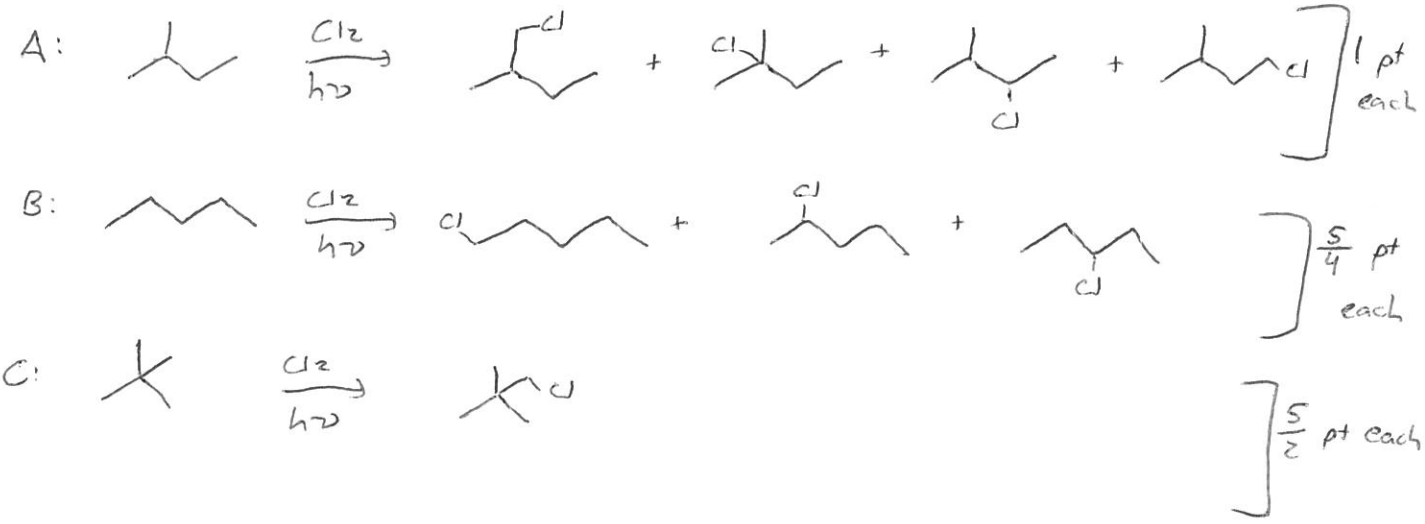
5) Find a way to synthesize the desired product from the given starting material. If more than one step is necessary, show the product of each step. Do not show mechanisms. (10 pts)



$-\frac{1}{2}$ pt for missing/wrong solvent

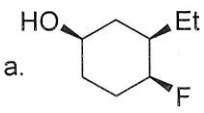
$-\frac{1}{2}$ pt for MgX instead of Mg

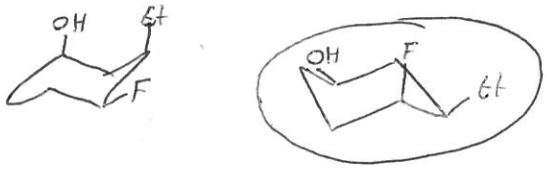
6) Three different constitutional isomers have the formula C_5H_{12}. When treated with chlorine and UV light, isomer A gives a mixture of four monochlorination products, isomer B gives a mixture of three monochlorination products, and isomer C gives a single monochlorination product. Based on this information, draw the structures of A, B, and C, and draw each of the monochlorination products that they form. (15 pts – 5 pts each)

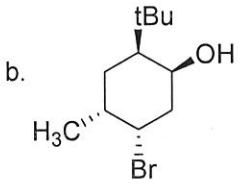


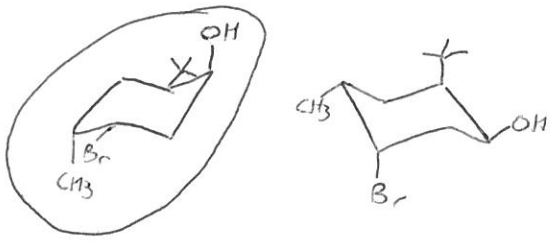
 Name_____

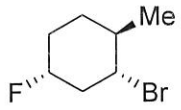
7) For each of the following structures, show both chair conformations. (Make sure your bond angles clearly indicate whether each group is equatorial or axial.) Circle the more stable ring-flip form for each molecule. (15 pts total - 5 pts each)

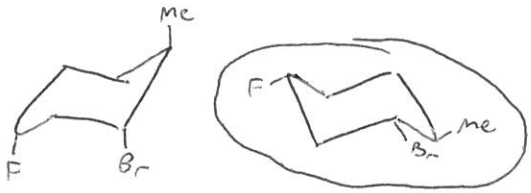
a. 



b. 



c. 



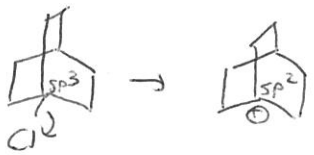
2 pts per structure,
1 pt per correct circle.

-½ pt per bond drawn at bad angle
-1 for showing enantiomer of actual molecule.

8) Extra credit! 1-chlorobicyclo[2.2.1]heptane, shown below, is virtually unreactive in the S_N1 reaction despite being tertiary. In fact, it has been estimated that it is 10^{13} times slower at S_N1 than *tert*-butyl chloride. In twenty words or less (but drawing any structures that are necessary), explain why this is the case. (Hint: what geometry does the intermediate structure have?) (5 pts extra credit)

2 pts

During S_N1, the carbocation is sp^2:



The geometry at this carbon makes it difficult to get trigonal planar geometry, due to ring strain.

0 pts for "steric hindrance" or "accessibility to nucleophile"