CHEM 3311 (Richardson) Third Hour Exam – April 18, 2017

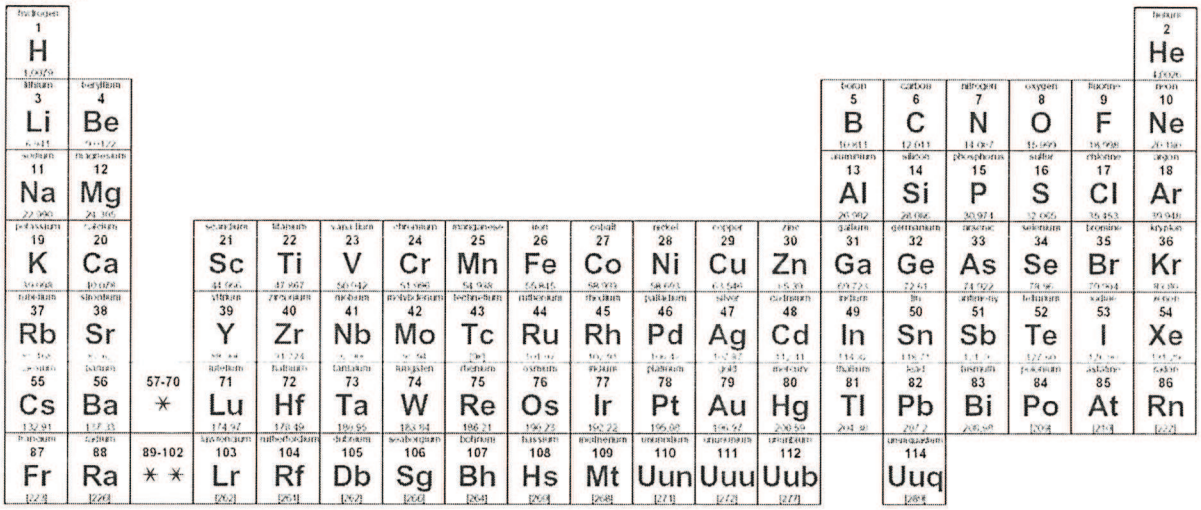
Your Name Key

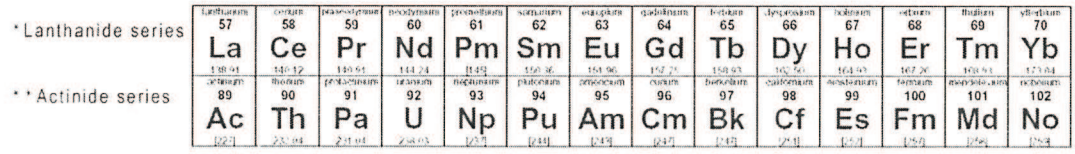
Student ID _____

Recitation Time (check one)
- O 8:00 Wednesday w/ Josh Kamps
- O 2:00 Wednesday w/ Josh Kamps
- O 10:00 Thursday w/ Brendan Griffiths
- O 11:00 Thursday w/ Brendan Griffiths
- O 12:00 Friday w/ Brendan Griffiths

Question	Score	Out of
1		15
2		15
3		9
4		16
5		25
6		20
7		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.



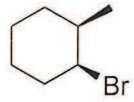


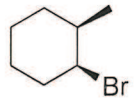
pKa Values

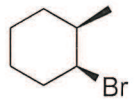
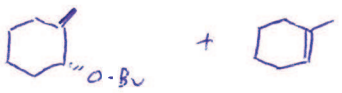
HI	-10	CH_3COOH	4.7	ArOH	10	H_2	35
HBr	-8	HN_3	4.7	RSH	10-12	NH_3	36
HCl	-6	H_2S	7.0	H_2O	15.7	$H_2C{=}CH_2$	45
H_3O^+	-1.7	NH_4^+	9.3	ROH (R=alkyl)	16-18	CH_4	60
HF	3.2	HCN	9.4	HC≡CH	26		

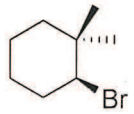
Average: 81.8
St. Devi 16.2
Max: 110
Min: 44

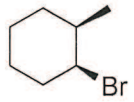
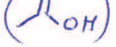
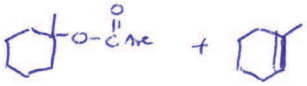
1) For each of the reactions shown below, **circle the mechanism(s)** you would expect to see, if any, and **draw the product(s)**. If a product has stereocenters, show its configuration using wedges and dashes. If two stereoisomers are formed, show both of them. If an elimination occurs, show only the major alkene product. If none of the mechanisms would take place in a reasonable time frame, write NR for No Reaction. (15 pts)

a.  tBuONa, THF → E2 S_N2 E1 S_N1 

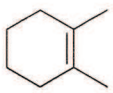
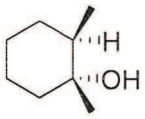
b.  NaI, MeOH → E2 S_N2 E1 S_N1 

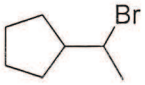
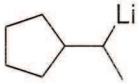
c.  BuONa, DMF → E2 S_N2 E1 S_N1 

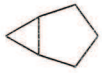
d.  PrONa, DMF → E2 S_N2 E1 S_N1 S_N2 blocked by neopentyl, though, so only E2. 

e.  $MeCO_2H$ () → E2 S_N2 E1 S_N1 

2) Each of these reactions can be done in a single-step synthesis. On each arrow, show the reagents needed to accomplish each one. In each case, the target product should be the only major product of the reaction. (15 pts)

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

b.  Li, THF → 

c.  CH_2I_2, Zn/Cu, THF → 

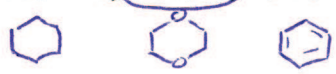
3) For each of the following groups of molecules, circle the one with the highest boiling point and explain why it is higher in under ten words. (9 pts)

a. (1,6-hexanediol); 1,4-dimethoxybutane; 3-propoxy-1-propanol

More OH groups = more H-bonding

1 pt for circle
2 pts for explanation

b. cyclohexane; (dioxane); benzene



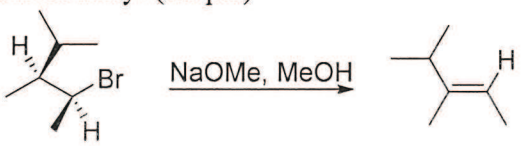
More dipoles = stronger intermolecular forces

c. 2,5-dimethylhexane; (octane); 2,2,3,3-tetramethylbutane

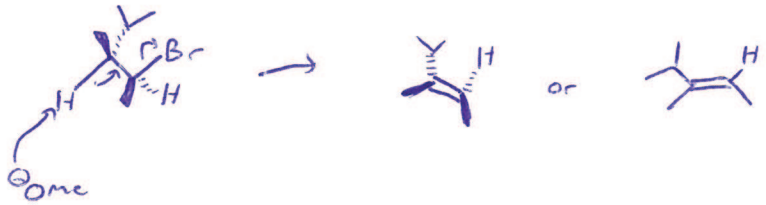
More surface area = stronger intermolecular forces

4) Show a reasonable arrow-pushing mechanism for these reactions, including stereochemistry where necessary. (16 pts)

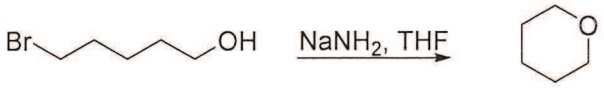
8 pts each

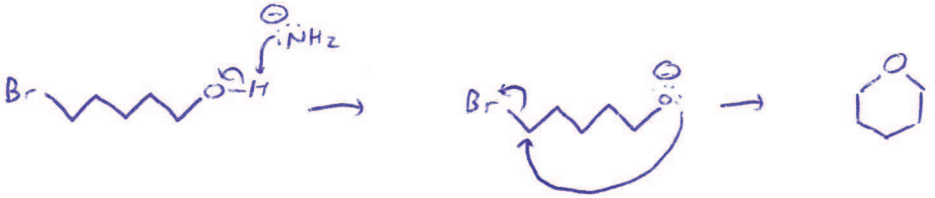
a. 

Redraw as antiplanar



-4 if stepwise

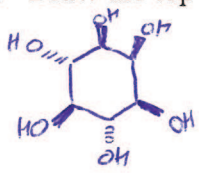
b. 



-3 if Br leaves first
-4 if one step.

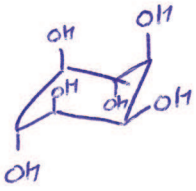
5) Inositol, or 1,2,3,4,5,6-cyclohexanehexol, is a chemical compound with formula $C_6H_{12}O_6$. Inositol has nine different possible stereoisomers. One specific stereoisomer of inositol, *myo*-inositol, is a sugar alcohol that serves several important biological purposes and is also commonly used as a stand-in for cocaine in movies. Its IUPAC name is cis-1,2,3,5-trans-4,6-cyclohexanehexol (this indicates that the OH groups on carbons 1,2,3, & 5 are all on the same face of the ring as each other, and the OH groups on carbons 4 & 6 are on the other face). Answer these questions about the molecule. (25 pts total)

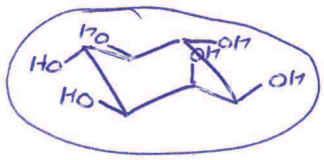
a. Draw the top-down view of *myo*-inositol, including stereochemistry. (5 pts)



b. Draw both chair conformations of *myo*-inositol and circle the more stable one. (12 pts)

Structures: 5 pts each
Stability: 2 pts

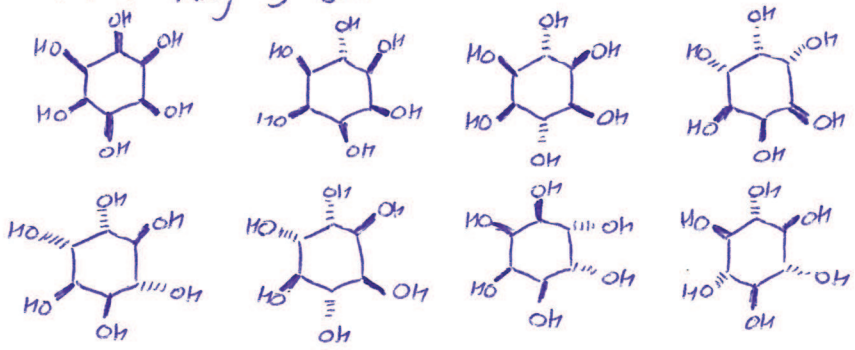




c. *myo*-Inositol is very soluble in water for an organic molecule. What intermolecular force is responsible for this property? (3 pts)

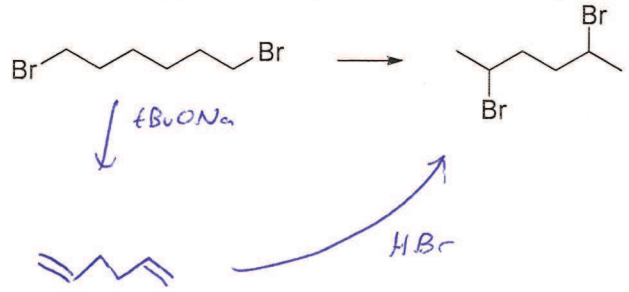
Hydrogen bonding

d. Draw five other distinct stereoisomers of inositol. Do not show any duplicate structures. (5 pts) Any 5 of:



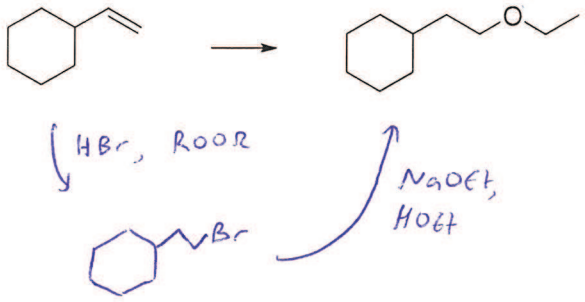
6) Find a way to synthesize the desired product from the given starting material. If more than one step is necessary, show the product of each step. Do not show mechanisms. (20 pts)

a.

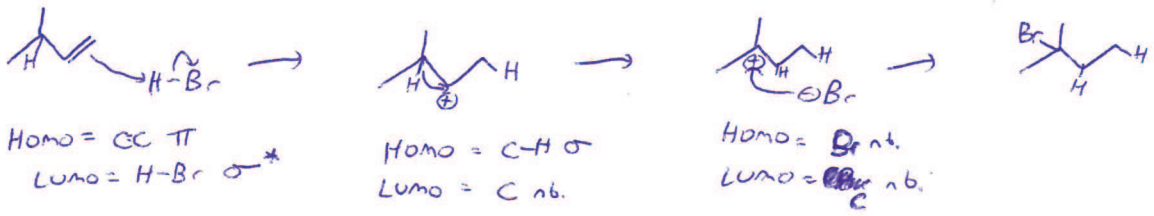


-4 for using ROOR in 2N step

b.



7) Extra credit! Draw the mechanism for the reaction of 3-methyl-1-butene with HBr (showing the major product only), and identify the HOMO and LUMO of each step. (10 pts e.c.)



HOMO = CC π
LUMO = H-Br σ*

HOMO = C-H σ
LUMO = C nb.

HOMO = Br nb.
LUMO = C nb.

For each step: 1 pt for arrows, 1 for Homo, 1 for Lumo
1 pt for correct structure.