CHEM 3311 - Luca Third Hour Exam – April 17th 2018

Your Name: _____

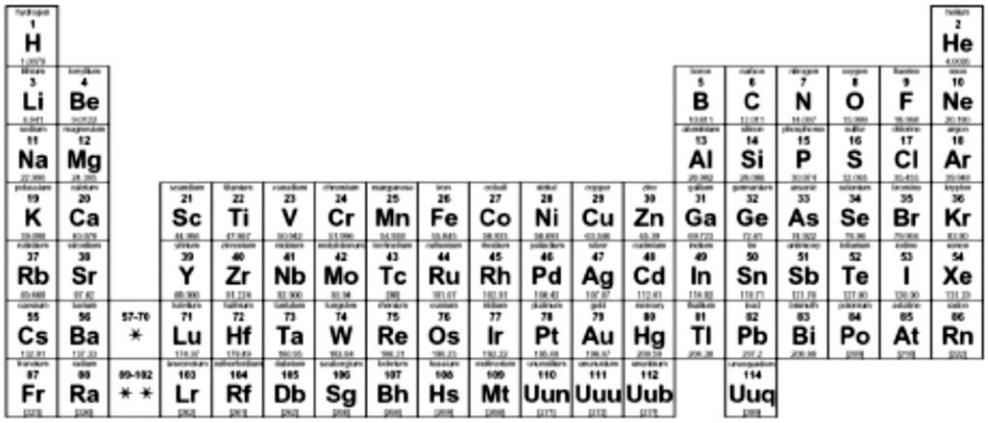
Student ID: _____

Recitation **(Check one):**

- Monday 8am - Mori
- Monday 9am - Carey
- Monday 10am - Carey
- Monday 11am - Carey
- Tue 8am - Park
- Tue 11am - Carey
- Tue 2pm - Carey

Question	Points
1	
2	
3	
4	
5	
Total	

This is a closed-book exam. The use of notes and cell phones will not be allowed during the exam. You may use models sets totally dismantled brought in a clear quart-sized ziplock bag. Use the backs of the pages for scratch work. If your final answer is not clearly specified in the given space, points will not be awarded.



pKa Values

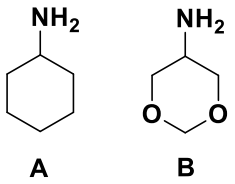
HI	-10	CH_3COOH	4.7	ArOH	10	H_2	35
HBr	-8	HN_3	4.7	RSH	10-12	NH_3	36
HCl	-6	H_2S	7.0	H_2O	15.7	$H_2C{=}CH_2$	45
H_3O^+	-1.7	NH_4^+	9.3	ROH (R=alkyl)	16-18	CH_4	60
HF	3.2	HCN	9.4	HC≡CH	26		

Name_____

1. (20 points total)

In less than 100 words, offer an explanation **for each of the following observations**. **Draw all conformations relevant to your answer.**

a. Compound A exists mostly in a chair conformation with an equatorial -NH_2 group, but compound B prefers a chair conformation with an axial -NH_2. (10 points)



A B

b. The racemic mixture of 2,2,5,5-tetramethyl-3,4-hexanediol exists with a strong intramolecular hydrogen bond, but the meso stereoisomer has no intramolecular hydrogen bond. (10 points)

Name_____

2. (20 points total)

Consider the following experiments with triphenylmethyl iodide, a very reactive tertiary alkyl halide.

a. In aqueous acetone the reaction of triphenylmethyl iodide follows a rate law that is first order in alkyl halide only. The product of this reaction is triphenylmethanol Ph_3COH. **Write the full chemical reaction out, identify the operating mechanism (E1, E2, SN1 or SN2) and sketch a reaction coordinate diagram. Label each important reaction component on this diagram as either a starting material, a product, an intermediate and or/ a transition state, where applicable.** (5 points)

b. In another reaction, triphenylmethyl iodide reacts with one equivalent of sodium azide $Na^+ N_3^-$ in aqueous acetone and the reaction rate law is identical with that of point a. The product isolated in this case is $Ph_3C\text{-}N_3$. **Write the full chemical reaction out, identify the operating mechanism (E1, E2, SN1 or SN2) and sketch a reaction coordinate diagram. Label each important reaction component on this diagram as either a starting material, a product, an intermediate and or/ a transition state, where applicable.** (5 points)

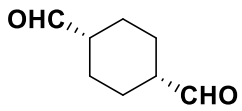
c. In a reaction mixture in which both sodium azide and water are present in equal concentrations, both triphenylmethyl alcohol and triphenylmethyl azide are formed, but the overall reaction rate remains unchanged. **Write the full chemical reactions out**, **name the operating mechanisms** and **sketch both reactions on one reaction coordinate diagram illustrating this observation**. **Label each important reaction component on this diagram as starting materials, products, intermediates and/or transition states where applicable.** (5 points)

d. Using reaction coordinate diagrams and kinetic rate laws, explain the observation described in c in three sentences or less (why are the products formed at the same rate?). (5 points)

Name_____

3. (10 points total)

An optically-active compound A has the formula $C_8H_{13}Br$. Compound A gives no reaction with Br_2 in CH_2Cl_2, but it does react with $(CH_3)_3C\text{-}O^-$ to give a single new compound B in good yield. Compound B reacts with Br_2 in CH_2Cl_2 and takes up H_2 over a catalyst. When compound B is treated with ozone followed by a Zn/DMS workup, compound C is isolated in excellent yield.



C

a. Given this information, propose structures for compounds A and B and describe your reasoning. Show your work. (5 points)

b. Write the reactions and ***all*** reaction conditions for the **A -> B** and **B -> C** reactions. Name each type of reaction. (5 points)

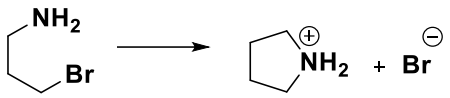
Name_____

4. (20 points total)
Reaction 1 is the reaction of benzylamine, $PhCH_2NH_2$ with benzylbromide in 60% aqueous ethanol and it follows the rate law below

Rate= k*[benzylamine]*[benzylbromide]

The product of this reaction is $(PhCH_2)_2NH_2^+Br^-$.

Reaction 2 below follows a very similar transformation but has a first order rate law:



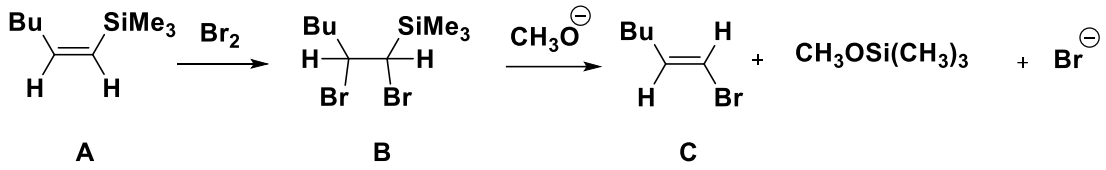
a. Show a mechanism for **Reaction 1** that is consistent with the rate law and the other facts about nucleophilic substitution reactions. (10 points)

b. Show a mechanism for **Reaction 2** that is consistent with the rate law and the other facts about nucleophilic substitution reactions. (10 points)

Name_____

5. (30 points total)

Consider the reaction sequence provided below. (Bu stands for butyl, a straight chain alkyl group with four carbons)



A B C

a. Use what you know about the stereochemistry of Br_2 additions to <u>show all stereoisomers</u> formed in the reaction of A + Br_2 -> B. Label each absolute configuration drawn, where applicable. (5 points)

b. Is the B + CH_3O^- -> C elimination antiperiplanar? **Show any conformation(s) relevant to your answer and explain.** (5 points)

c. How would the stereochemistry of the B and C products change if the (E)- stereoisomer of compound A was carried through the reaction sequence? **Show all your work and explain your answer.** (20 points)