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CHM 2123 ORGANIC CHEMISTRY LABORATORY

MIDTERM EXAM – NOVEMBER 2014

THE FINAL PAGE CONTAINS IMPORTANT INFORMATION

Verify that your exam contains 12 pages.

Professor: Alex Bush

Date: Saturday, November 1, 2014 9h30 – 11h00

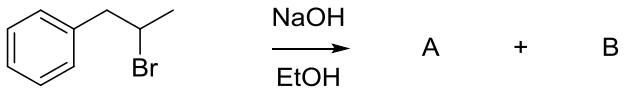
Time: 90 minutes

Name _____ Student Number _____

Lab Day _____ Name of your TA _____

QUESTION	POINTS	RÉSULTAT
1	8	
2	12	
3	8	
4	8	
5	8	
6	3	
7	13	
Points Boni	2	
TOTAL	**60**	

1. **(8 points)** Prior to throwing his 509th TD pass in the NFL, Peyton Manning completed an organic chemistry experiment on the sideline. He was asked to react 3-phenyl-2-bromopropane with KOH in ethanol, as shown in the reaction scheme below.

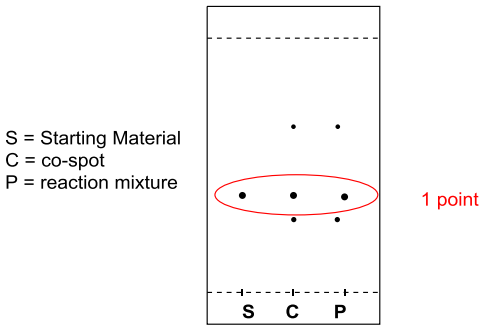


a. There are two possible organic reactions pathways for this experiment, giving products A and B. Identify the structure of each. **(2 points)**

1 point each

b. Peyton's knowledge of chemistry is as vast as his knowledge of football. He decided to follow the reaction by TLC analysis. He observes the following TLC plate. Circle which spot corresponds to the starting material and justify your decision **(2 points)**

i. Lines up with the spot in the SM lane (1 point)



1 point

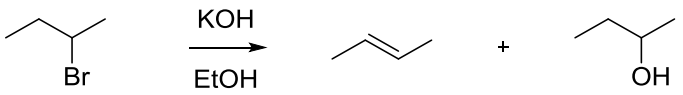
c. Identify which spot is associated with product A and which is associated with product B and justify your decision using the principles of TLC analysis. **(3 points)**

i. Alcohol is bottom, alkene is top (1 point)
ii. Alcohol has more polar interactions with silica gel, making it move least
iii. Alkene has less polar interactions with silica gel, making it move furthest

d. Upon closer inspection, he notices four spots on the TLC plate in lane P. Identify the structure of the 4th spot? **(1 point)**

1 point for the structure not included in part (a)

2. **(12 points)** Before making his way to the Superbowl, Colin Kaepernick must first complete CHM2123. In one experiment, Colin mixed 0.500 mL of 2-bromobutane with 8.00 g KOH and heated the reaction to reflux in ethanol for 30 minutes. While the reaction heated, he collected the gas produced in a eudiometer. Can you help Colin with his lab report?



a. Help Colin fill out his table of reagents. **(4 points)** **0.5 points per correct entry**

Compound	MW	Amount	Density	mol	Equivalents
2-bromobutane	137.02 g/mol	0.500 mL	1.255 g/mL	4.58 mmol (4.6×10^{-3} mol)	1
KOH	56.1 g/mol	8.00 g	Solid	142 mmol (0.142 mol)	31

b. At the end of the reaction, Colin collected 52.0 mL of gas in the eudiometer and 0.260 g of solid KBr. He measured the atmospheric pressure (755.0 mmHg) and temperature (24.5 °C). How many moles of gas was produced (use P* = 36.7 mmHg)? **(2 points)**

(1 point)

$$P = P_{atm} - P_{water} - P^*$$
$$P = 755.0 - 23 - 36.7$$
$$P = 695.3\ mmHg = 0.915\ atm$$

(1 points)

$$PV = nRT$$
$$n = \frac{PV}{RT}$$
$$n = \frac{(0.915\ atm)(0.052\ L)}{(0.08206)(297.5\ K)}$$
$$n = 0.00195\ mol\ or\ 1.95\ mmol$$

c. What ratio of S_N2:E2 did Colin obtain? **(3 points)**

(1 point)

$$n_{KBr} = \frac{mass\ of\ KBr}{molar\ mass\ KBr}$$
$$n_{KBr} = \frac{0.260\ g}{119.00\ \frac{g}{mol}}$$
$$n_{KBr} = 0.00218\ mol\ or\ 2.18\ mmol$$

(1 point)

$$n_{S_N2} = n_{KBr} - n_{E2}$$
$$n_{S_N2} = 2.18\ mmol - 1.95\ mmol$$
$$n_{S_N2} = 0.23\ mmol$$

(1 point)

$$ratio = mol\ S_N2 : mol\ E2$$
$$ratio = 0.23 : 1.95 = 1 : 8.5$$

d. Explain why substitution reactions are favoured at lower temperature and elimination reactions are favoured at higher temperature. **(3 points)**

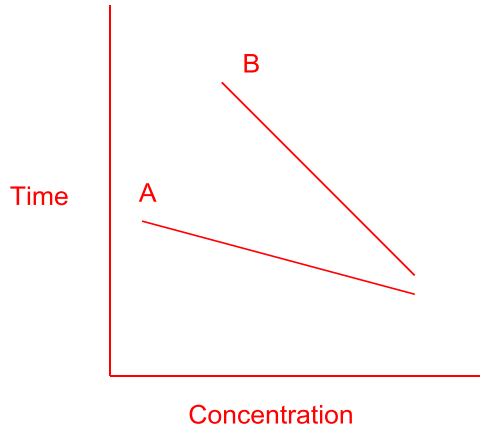
i. Energy Barrier towards substitution is lower than that of elimination
ii. At lower temperatures, fewer molecules have enough energy to overcome activation energy for elimination
iii. Higher temperatures => more molecules can overcome activation energy towards elimination => more E2 product

3. **(8 points)** Derek Carr was studying the kinetics of the hydrolysis of *t*BuCl with water under basic conditions. He used bromothymol blue as an indicator to measure the progress of the reaction. During his experiment, he performed three trials in two different solvent systems, 70:30 H_2O:acetone and 85:15 H_2O:acetone. He then averaged the times until the indicator changed color:

	[*t*BuCl] = 0.135 M	**[*t*BuCl] = 0.120 M**	**[*t*BuCl] = 0.105 M**	**[*t*BuCl] = 0.090 M**
Average time solvent A	9.0 s	26.0 s	43.8 s	60.5 s
Average time solvent B	40.0 s	112.3 s	235.7 s	345.1 s

a. Sketch a graph of time vs. concentration of [*t*BuCl] remaining in solution for each solvent system. How could Derek transform the data in order to get a linear plot? **(3 points)**

(1 point) He could get a linear plot by plotting ln[*t*BuCl] vs. time



1 point = axes labeled
1 point = two lines of different slope

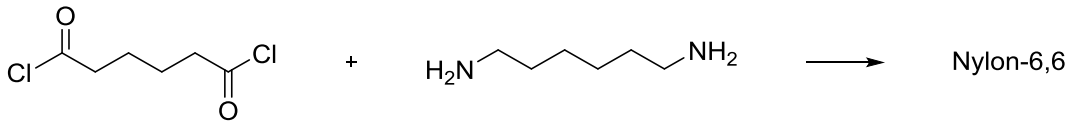
b. Derek forgot to label his data sets and did not know which times were associated with each solvent systems. Identify which solvent system (85:15 H_2O:acetone and 70:30 H_2O:acetone) goes with which trial (A or B) and justify your decision. **(3 points)**

i. A is 85:15, B is 70:30 (1 point)
ii. S_N1 reactions are faster in polar protic solvents (1 point)
iii. A has is the faster reaction, therefore it must be in the more polar protic (more water) (1 point)

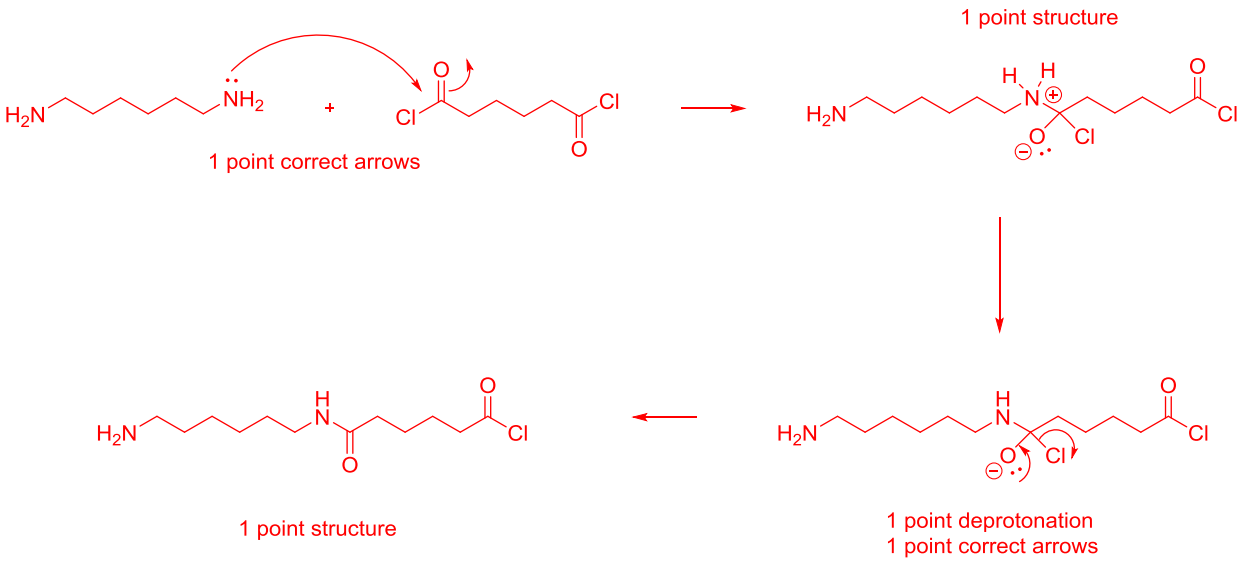
c. While running the experiment, explain why Derek kept his reaction flasks in a water bath at room temperature. **(2 points)**

i. Temperature affects the rate of the reaction (1 point)
ii. Water will maintain a more uniform temperature distribution than air (1 point)

4. **(9 points)** During his last game, Cam Newton ripped his nylon jersey while performing his trademark Superman pose after scoring a touchdown. Rather than buy a new one, Cam wants to synthesize nylon-6,6 and stitch his jersey back together.



a. Give the mechanism of the formation of one repeating unit of nylon-6,6. **(5 points)**

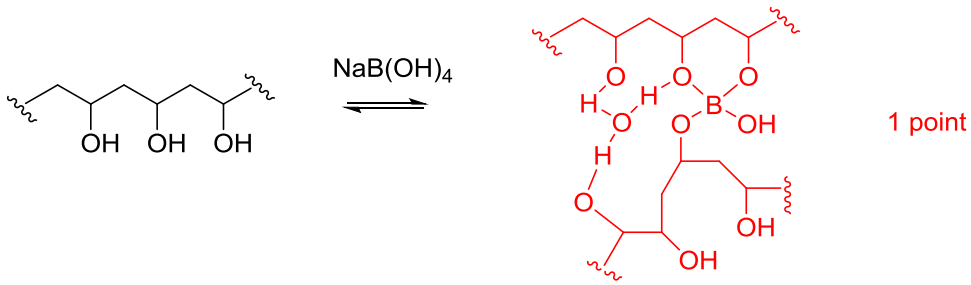


b. After letting the reaction stir for a few minutes, Cam is disappointed to see no nylon is being formed. What reagent is he missing? Why does polymerization stop? **(2 points)**

i. He is missing a base to neutralize excess acid (1 point)

ii. Without a base, the amine becomes protonated and no longer acts as a nucleophile to continue polymerization (1 point)

c. What is the role of H_2O in the cross-linking of polyvinyl alcohol and sodium borate. Draw the structure of the cross-linked polymer. **(2 points)**



i. Water increases the amount of H-bonds between polymer chains (1 point)

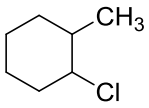
5. **(7 points)** Until getting called up into the NFL, Nick Foles was pursuing his life-long dream in organic chemistry. While studying for the midterm, he realized he didn't fully understand the difference between the purification techniques taught in his lab course. He has come to your for help.

   a. From experiment 1, he did not understand why caffeine was recrystallized. Explain why caffeine was recrystallized and the principles of recrystallization. **(4 points)**
      i. Recrystallization is a purification technique (1 point)
      ii. The product must be soluble in hot solvent and insoluble in cold solvent (1 point)
      iii. As the solution cools, the product will precipitate (or crystallize) (1 point)
      iv. The impurities remain in solution and are discarded (1 point)

   b. Nick also has difficulties with extraction. Help him by explaining the principles and goals of liquid-liquid extraction. **(2 points)**
      i. Two immiscible solvents create two phases (1 point)
      ii. Separates compounds based on their solubility in different solvents (1 point)

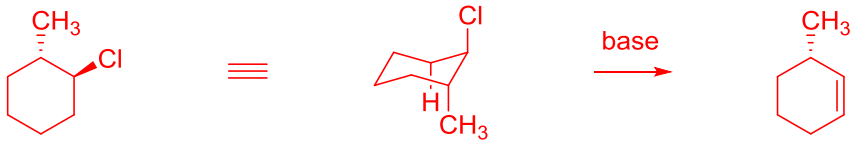
   c. Nick wants to set up a similar experiment to isolate sugar ($C_{12}H_{22}O_{11}$) from a Tim Hortons French Vanilla. Since sugar is an organic compound, he reasons he can perform a liquid-liquid extraction with an organic solvent. Do you think his experiment will be successful? If so, why? If not, why not? **(1 points)**
      i. His experiment will be unsuccessful since sugar equally soluble in water as it is in an organic solvent

6. **(3 points)** In his locker room, Andy Dalton found a bottle of 2-methyl-1-chlorocyclohexane, however, the relative stereochemistry of the methyl and chloro group was unknown.

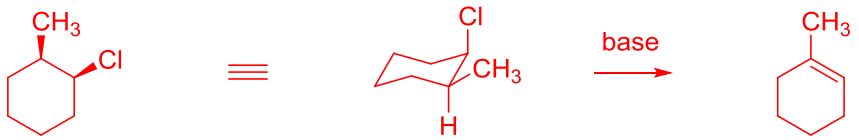


Based on the different reactivity of the isomers, what experiment could Andy perform to determine the relative stereochemistry of the molecule? Clearly explain your answer using structures. **(3 point)**

- An E2 reaction will determine the relative stereochemistry. (1 point)
- If the substituents are *trans* to each other, the only antiperiplanar hydrogen is on C6, giving the products below (1 point for words or structures)



- If the substituents are *cis* the product will be the most stable alkene, removing the antiperiplanar hydrogen on the same carbon as the methyl group (1 point for words or structures)



7. **(13 points)** The Wonderlic Test is a series of short answer questions used as a measure of football player's IQ. This year's version had only the chemistry questions listed below. (Aaron Rodgers had a perfect score!)
   a. During recrystallization, why is it important to not add all the solvent at once?
      To create a super-saturated solution

   b. Why is ethyl acetate and water not a suitable solvent combination for recrystallization?
      They are immiscible

   c. Why is it important to put the lid back on the jar containing Na_2SO_4 (or $MgSO_4$)?
      Na_2SO_4 and $MgSO_4$ are hygroscopic and absorb water from the air, ruining them for use in the lab

   d. How would the rate of reaction change if the concentration of NaOH was doubled in the hydrolysis of 1-bromobutane?
      The rate would double (since hydrolysis of 1-bromobutane is an S_N2 reaction)

   e. What type of polymer is DNA?
      Alternating co-polymer

   f. What reagent would you add to convert chlorophylls to pheophytins?
      Acid (or decay)

g. Why is water added to the bottom of a reflux condenser?
To fill the reflux condenser evenly

h. In experiment 2, the hydrolysis of *t*BuCl with water, what is the role of the bromothymol blue indicator?
Monitor the progress of the reaction by indicating when all the NaOH has been consumed

i. Why do carboxylic acids have a tendency to streak along TLC plates?
They are very polar and stick to the TLC plate

j. Explain how adding acetic acid into the already polar solvent system can prevent streaking of carboxylic acids on TLC plates.
Acetic acid protonates the silica gel which will minimize the proton exchange of the carboxylic acid, minimizing the streaking

k. Explain how a more polar solvent will move a spot further along a TLC plate?
Polar solvents interrupt the interactions between the compounds and the silica gel

l. What is the order of a unimolecular elimination reaction?
1^{st} order

m. In experiment 1, spinach was ground up with sand. What is the role of the sand?
Release chlorophyll into solution

Bonus (1 point) – PLEASE READ AND ANSWER THIS QUESTION ONLY AFTER COMPLETING ALL THE ABOVE QUESTIONS!

Every name used in a question in this exam is a current NFL quarterback. Connect each player used with their current NFL team. (In the spirit of socialism, if one student gets this correct, every student will receive the mark!)

Quarterback	Team	Running Back
A. Andy Dalton	1. Cincinnati Bengals	1. Giovanni Bernard
B. Derek Carr	2. Oakland Raiders	2. Darren McFadden
C. Nick Foles	3. Philadelphia Eagles	3. LeSean McCoy
D. Colin Kaepernick	4. San Francisco 49ers	4. Frank Gore
E. Peyton Manning	5. Denver Broncos	5. Ronny Hillman or Montée Ball
F. Cam Newton	6. Carolina Panthers	6. DeAngelo Williams
G. Aaron Rodgers	7. Green Bay Packers	7.Eddy Lacy

Double bonus (1 point): Correctly fill in the #1 running back for each team.

Useful info

$$R = 0.08206\ \frac{atm \cdot L}{mol \cdot K}$$

$$PV = nRT$$

$$P = P_{atm} - P_{water} - P^*$$

T (K)	***P_{water}* (mmHg)**	***T (K)***	***P_{water}* (mmHg)**	***T (K)***	***P_{water}* (mmHg)**
290	14.7	294	18.8	298	24.0
291	15.8	295	19.5	299	25.5
292	16.5	296	21.0	300	27.0
293	17.3	297	22.5	301	28.5