## **ANSWER KEY**

L.I.U.

Chem. 122, Sect 007,

Quiz 3, 50 pts, Spring, 2012

1. Which molecule below is more reactive to acidic hydrolysis in  $H_3O^+/H_2O$ ? Explain your choice briefly and show the hydrolysis reaction for BOTH molecules, giving all of the steps of the reaction mechanism. (12 pts)

$$\begin{array}{c|c} O & O & O \\ II & II \\ C & O & C \\ \hline & \textbf{A} & & \textbf{B} \\ \end{array} \text{NHCH}_2\text{CH}_3$$

A reacts faster than B. In B, the amide nitrogen is an excellent electron donor to the carbonyl carbon, making it less electron deficient and therefore less reactive to nucleophiles. In A, there are two carbonyl groups competing for the lone pair of the oxgyen so the carbonyl carbons are still quite electron deficient and reactive to nucleophiles.

2. Synthesize the following molecule from the starting material on the left as shown. (8 pts)

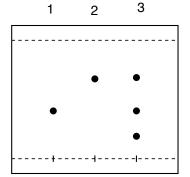
3. Show all three steps for the preparation of p-nitroaniline from aniline ( $C_6H_5NH_2$ ) and acetic anhydride [( $CH_3CO$ )<sub>2</sub>O], followed by nitration with  $H_2SO_4/HNO_3$  and final deprotection with  $H_3O^+/H_2O$  and treatment

with  $NH_4OH$ . For step one and step three you must the complete reaction mechanism, including the reaction that occurs when  $NH_4OH$  is added. (10 pts)

(2) 
$$N-C-CH_3$$
  $HNO_3$   $H_2SO_4$   $NO_2$   $H$  + ortho

(3) 
$$N - C - CH_3$$
  $H - O - H$   $N - C - CH_3$   $H - O - H$   $N - C - CH_3$   $H - O - H$   $N - C - CH_3$   $H - O - H$   $N - C - CH_3$   $N - C - CH_3$ 

4. A graduate student doing research had the following TLC plate. Lane one is starting material, lane two is the desired product and lane three is the reaction mixture that the student isolated. (a) Did the reaction go to completion? Explain briefly. (b) Was the desired product formed as desired? Explain. (c) Did the reaction produce one pure compound? Explain briefly. (10 pts)



- (a) The reaction did NOT go to completion because there is still a spot in the product (lane 3) that corresponds to the starting material.
- (b) The desired product was formed, since there is a spot in lane 3 that corresponds to the desired product in lane 2.
- (c) The product was not pure. Besides the remaining starting material, there was one other compound produced, an impurity.

5. In the unknown amine experiment, an unknown amine formed one layer when treated with benzenesulfonyl chloride ( $C_6H_5SO_2Cl$ ) in aqueous KOH solution and gave off tiny bubbles when treated with sodium nitrite and hydrochloric acid. Was the amine primary, secondary or tertiary? Explain your answer by showing all of the reactions that took place. (10 pts)

The amine was primary.

$$R-NH_2 + CI = S$$

$$R-NH_2 + CI$$

$$R-NH_2 + CI = S$$

$$R-NH_2 + CI$$

$$R-NH_2 + C$$