## Chemistry 41c SECOND QUIZ KEY April 26, 2013

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**Note:** You have 55 minutes to take this quiz. This exercise is to be worked alone and is closed book and closed notes. No electronic devices are allowed.

Acid	pK <sub>a</sub>	Acid	pK <sub>α</sub>
	5.29		16.0
H <sup>+</sup>		$C_6H_5COCH_3$	. 16
(CH <sub>3</sub> CO) <sub>3</sub> CH	5.85	(CH <sub>3</sub> ) <sub>3</sub> COH	18
<i>,</i> — <del>,</del> <del>N</del> H		CH <sub>3</sub> COCH <sub>3</sub>	20
	7.0		
H			20
$O_2N$ —OH	7.15		23
C <sub>6</sub> H₅SH	7.8	CH₃SO₂CH₃	23
(CH₃)₃ੈPH	8.65	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	24.
(CH <sub>3</sub> CO) <sub>2</sub> CH <sub>2</sub>	9	HC≡CH	H. Her Dollar
(CH <sub>3</sub> )₃NH	9.79	CH₃CN	≈25 ≈25
C <sub>6</sub> H <sub>5</sub> OH	10.00	(C <sub>6</sub> H <sub>5</sub> )₃CH	ా <sup>బ</sup> 31.5
CH <sub>3</sub> NO <sub>2</sub>	10.21	$(C_6H_5)_2CH_2$	34
CH <sub>3</sub> CH <sub>2</sub> SH	10.60	$C_2H_5NH_2$	≈35
CH₃ÑH₃	10.62	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	41
$(CH_3)_2 \overset{+}{N} H_2$	10.73		
CH <sub>3</sub> COCH <sub>2</sub> COOC <sub>2</sub> H <sub>5</sub>	11	Н	43
CH <sub>2</sub> (CN) <sub>2</sub>	. 11.2	CH <sub>2</sub> =CH <sub>2</sub>	44
CF₃CH₂OH	12.4		46
CH <sub>2</sub> (COOC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	13.3	CH <sub>4</sub>	≈49
(CH <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	14	$C_2H_6$	≈50
СН₃ОН	15.5		≈52
(CH₃) <sub>2</sub> CHCHO	15.5		
C₂H₅OH	15.9		The way

1. Write a curved-arrow mechanism for each of the following reactions. (3 pts each)

(a) 
$$\begin{array}{c} & \bigoplus \bigoplus \bigoplus \\ + & : C \equiv O : \end{array} \qquad \begin{array}{c} & H_2 S O_4 \\ & H_2 O \end{array} \qquad \begin{array}{c} & H_2 O \\ & & \\$$

(b) 
$$\begin{array}{c} H_3C \\ H_3C \\ Ph \end{array} \begin{array}{c} Mg^0 \\ THF \end{array} \begin{array}{c} H_3C \\ CO_2H \\ Ph \end{array} \begin{array}{c} H_3C \\ CO_2H \\ H \end{array} \begin{array}{c} H_3C \\ H_3C \\ O \\ Ph \end{array} \begin{array}{c} H_3C \\ O \\ Mg^0 \end{array} \begin{array}{c} H_3C \\ Mg^0 \\ O \\ Mg^0 \end{array} \begin{array}{c} H_3C \\ Mg^0 \\ O \\ Mg^0 \end{array} \begin{array}{c} H_3C \\ Mg^0 \\ O \\ Mg^0 \end{array} \begin{array}{c} H_3C \\ Mg^0 \\ O \\ Mg^0 \end{array} \begin{array}{c} H_3C \\ Mg^0 \\ O \\ Mg^0 \end{array} \begin{array}{c} H_3C \\ Mg^0 \\ O \\ Mg^0 \\ O \\ Mg^0 \end{array} \begin{array}{c} H_3C \\ Mg^0 \\ O \\ Mg$$

2. Outline a synthesis of the following compound from the indicated starting material and any other reagents. (4 pts)

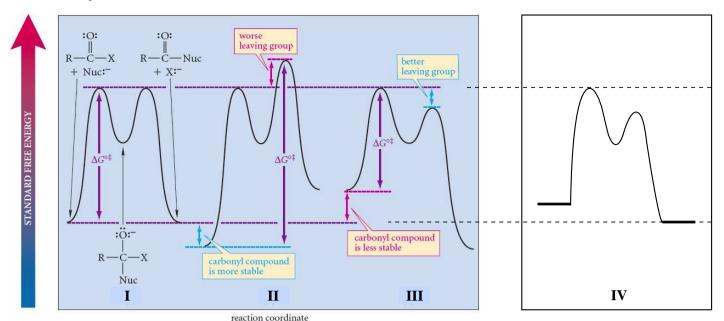
$$H_3CO$$
 $H_3CO$ 
 $H_3C$ 

3. Predict the principal products expected (if any) for the following reaction sequences. For each, draw a circle or box around the structure you want to be evaluated. (2 pts each)

a) 
$$\begin{array}{c|c} O \\ N \\ H \end{array}$$
  $\begin{array}{c} CH_3CO_2H \\ \hline 25 \, ^{\circ}C, \, 10 \, hrs \end{array}$  no reaction

d) 
$$\begin{array}{c} \oplus \ominus \\ : N \equiv N - \overrightarrow{C}H_2 \\ \hline \\ O \end{array}$$
 
$$\begin{array}{c} CO_2CH_2D \\ \hline \end{array}$$

## 4. Consider Figure 21.6 from Loudon:



(a) The reaction coordinate diagrams for II and III are meant to represent 'extreme cases.' In the boxes on the right, draw the general functional groups that Loudon is referring to in II and III. (2 pts)

R CI

(b) Loudon discusses two major factors that could affect the rate of carbonyl substitution. Use these two criteria to compare the rate of reaction of S-ethyl ethanethicate with NaOEt to the reaction of ethyl acetate with NaOEt, whose reaction coordinate diagram is shown in I of Figure 21.6. In the boxes below, explain how each factor would affect the reaction coordinate for the S-ethyl case, including annotated structures to support your arguments. Then sum up your conclusion by completing the statement below the boxes. (6 pts)

S-ethyl ethanethioate vs. 
$$O$$

OEt

NaOEt

OEt

OEt

These resonance structures require overlap of the sulfur 3p orbital with the carbon 2p orbital, which is not as strong as the overlap of the oxygen 2p orbital with the carbon 2p orbital in ethyl acetate. This loss of resonance stabilization makes S-ethyl ethanethioate is less stable than ethyl acetate.

Criterion 1: stability of the starting material

The SEt<sup>-</sup> group is a better leaving group than the OEt<sup>-</sup> group since the sulfur atom is larger than the oxygen atom and has more diffuse orbitals which can better stabilize the negative charge after the collapse of the tetrahedral intermediate as shown.

Alternatively, the  $pK_a$  of HSEt is lower than the  $pK_a$  of HOEt, the conjugate base SEt<sup>-</sup> is a weaker base than OEt<sup>-</sup>, which makes it a better leaving group.

Criterion 2: leaving group ability

<u>Circle One</u>: The reaction of S-ethyl ethanethioate with NaOEt will proceed at a <u>FASTER</u>/ SLOWER / SAME rate relative to the reaction of ethyl acetate with NaOEt.

(c) Based on your arguments in part (b), inscribe an annotated reaction coordinate diagram for the thiol ester reaction in the box labeled IV above. (2 pts)

## **BONUS QUESTIONS**

5a. Using structures and percentages, describe the sulfur-containing molecular species when ethane thiol ( $CH_3CH_2SH$ ) is dissolved in a pH 10.8 buffer solution. (bonus 3 pts)

$$\sim$$
SH  $\sim$ S B

pH - pK<sub>a</sub> = log([B]/[A])  

$$10.8 - 10.6 = log([B]/[A])$$
  
 $0.2 = log([B]/[A])$   
 $1.58 = [B]/[A]$   
[B] =  $1.58[A]$   
[A] + [B] =  $100\%$   
[A] +  $1.58[A]$  =  $100\%$ 

Note: since calculator use was not permitted on the quiz, full credit was awarded for correct set-up of the Henderson–Hasselbalch equation or for other clear demonstration of understanding how pK<sub>a</sub> relates to ionization of a species at a given pH.

5b. Which of the compounds shown below fits the following spectral data? Circle the correct structure. (bonus 2 pts)

Mass Spec: m/z 88.05 IR: 1735 cm<sup>-1</sup>

<sup>1</sup>H NMR: 4.13 ppm (quartet, 2H), 2.21 (singlet, 3H), 0.86 (triplet, 3H)

$$H_3C$$
  $O$   $CH_3$   $C$ 

$$H_3C$$
 O  $H$ 

