




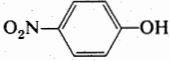
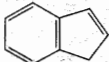
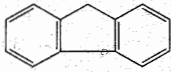



Chemistry 41c

SECOND QUIZ KEY

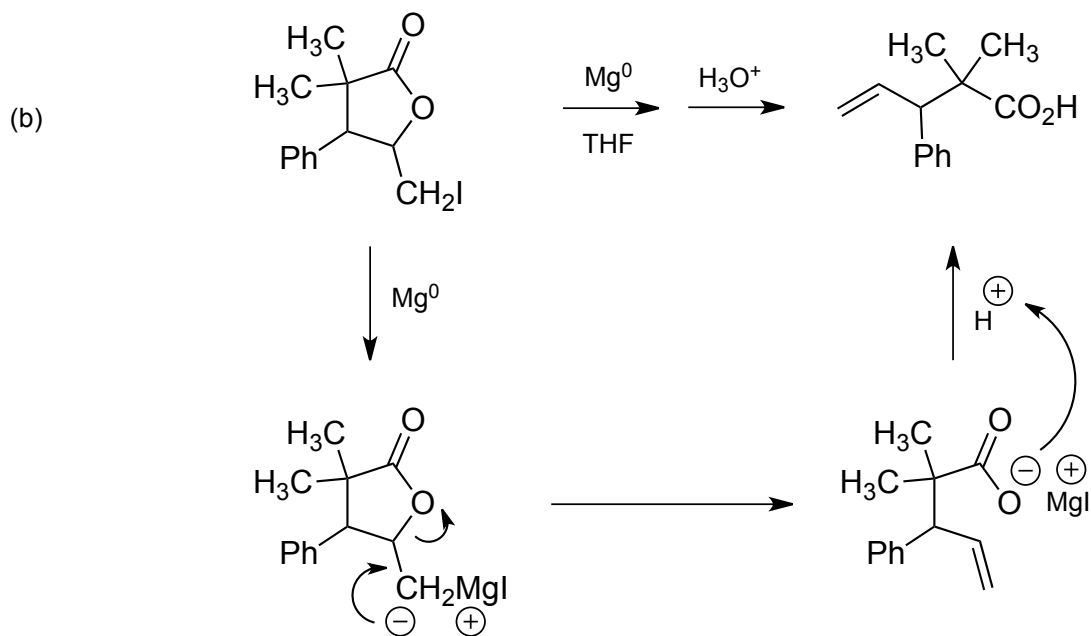
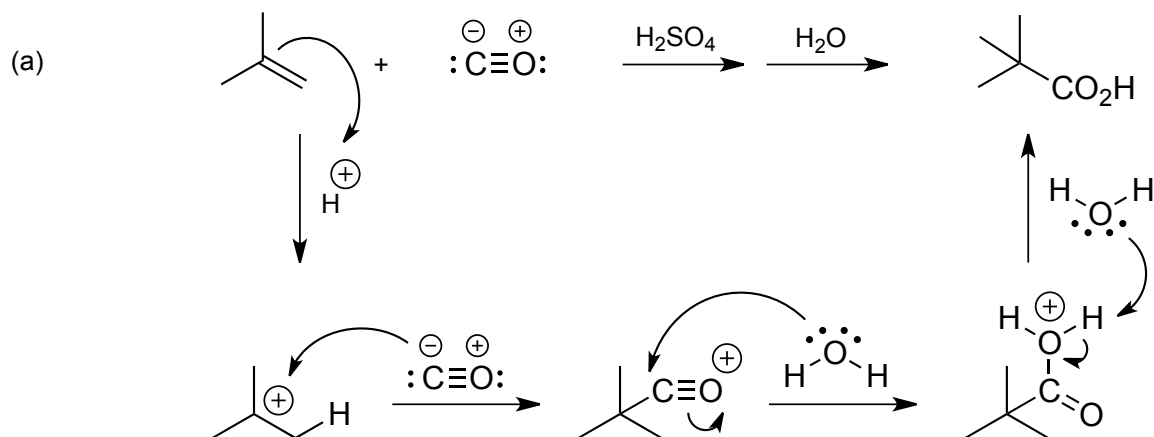
April 26, 2013

Name (print)_____Answer Key_____

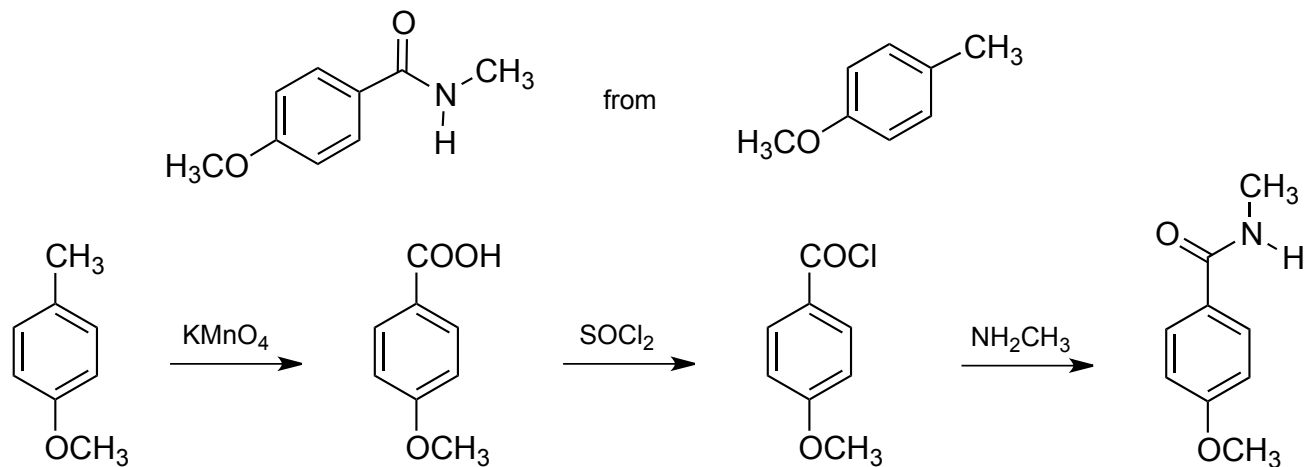
Note: You have 55 minutes to take this quiz. This exercise is to be worked alone and is closed book and closed notes. No electronic devices are allowed.

- Acidities of Organic Acids at 25°C (continued)			
Acid	pK_a	Acid	pK_a
	5.29		16.0
$(CH_3CO)_3CH$	5.85	$C_6H_5COCH_3$	16
	7.0	$(CH_3)_3COH$	18
	7.15	CH_3COCH_3	20
C_6H_5SH	7.8		20
$(CH_3)_3P^+H$	8.65		23
$(CH_3CO)_2CH_2$	9	$CH_3SO_2CH_3$	23
$(CH_3)_3N^+H$	9.79	$CH_3COOC_2H_5$	24.5
C_6H_5OH	10.00	$HC\equiv CH$	≈ 25
CH_3NO_2	10.21	CH_3CN	≈ 25
CH_3CH_2SH	10.60	$(C_6H_5)_3CH$	31.5
$CH_3N^+H_3$	10.62	$(C_6H_5)_2CH_2$	34
$(CH_3)_2N^+H_2$	10.73	$C_2H_5NH_2$	≈ 35
$CH_3COCH_2COOC_2H_5$	11	$C_6H_5CH_3$	41
$CH_2(CN)_2$	11.2		43
CF_3CH_2OH	12.4	$CH_2=CH_2$	44
$CH_2(COOC_2H_5)_2$	13.3		46
$(CH_3SO_2)_2CH_2$	14	CH_4	≈ 49
CH_3OH	15.5	C_2H_6	≈ 50
$(CH_3)_2CHCHO$	15.5		≈ 52
C_2H_5OH	15.9		

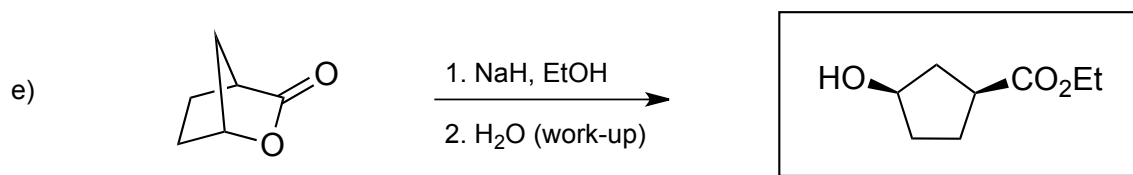
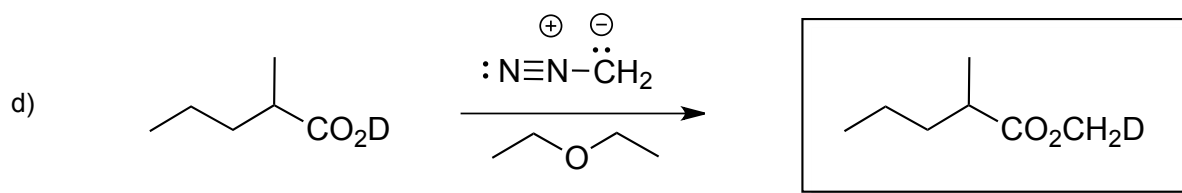
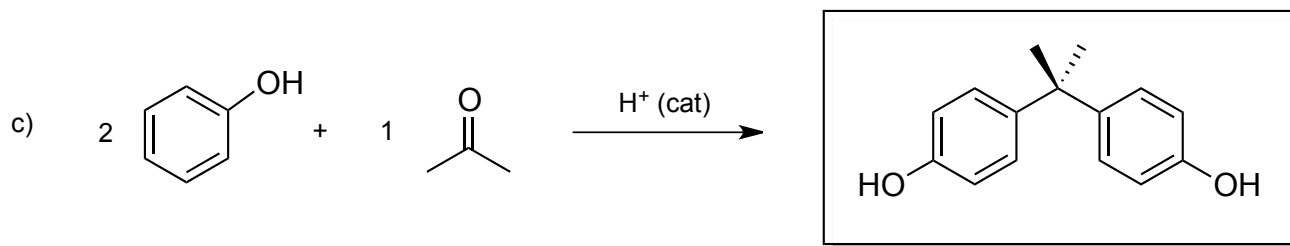
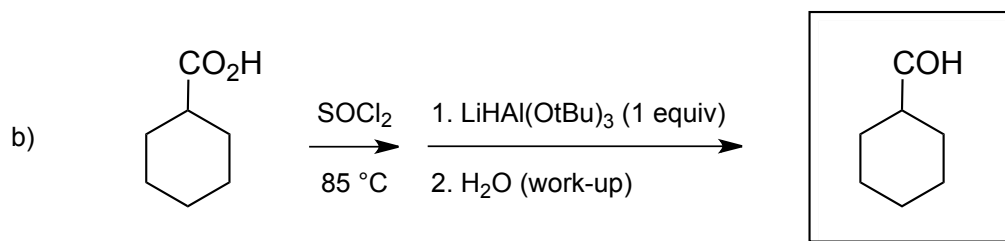
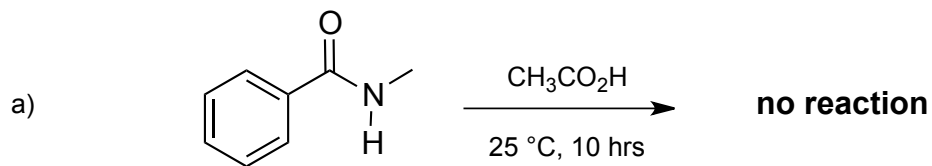
1. Write a curved-arrow mechanism for each of the following reactions. (3 pts each)



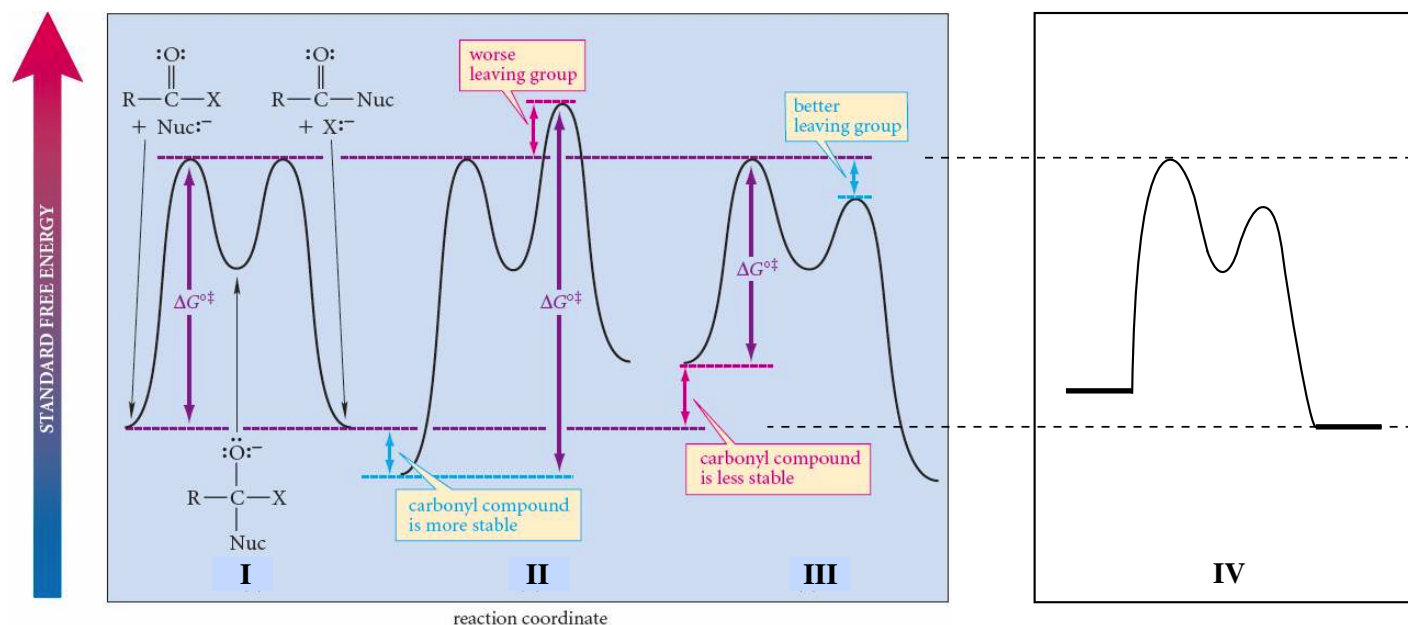
2. Outline a synthesis of the following compound from the indicated starting material and any other reagents. (4 pts)



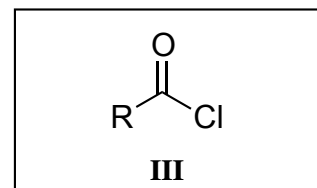
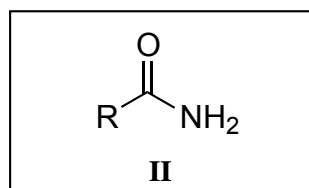
3. Predict the principal products expected (if any) for the following reaction sequences. For each, draw a circle or box around the structure you want to be evaluated. (2 pts each)



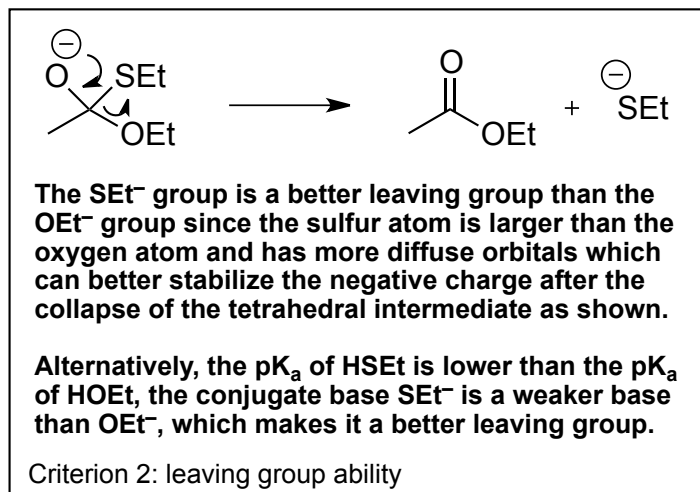
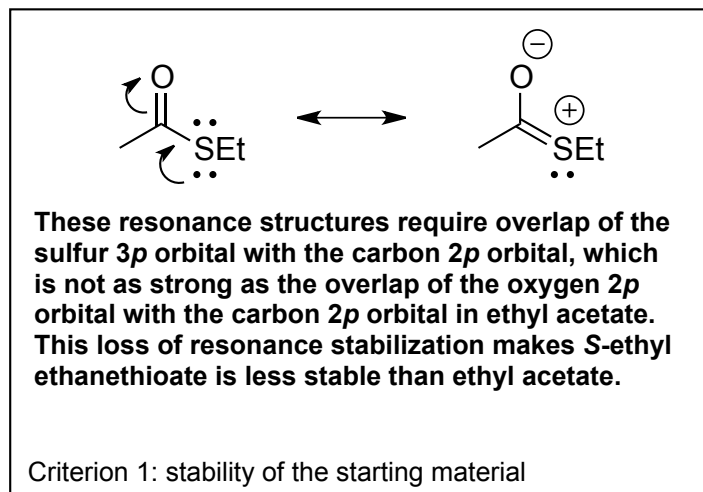
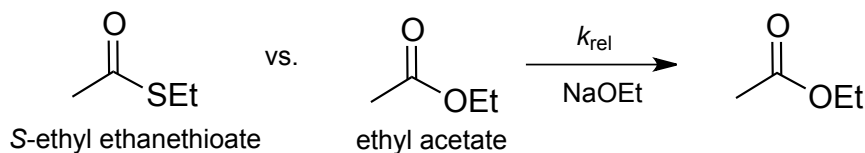
4. Consider Figure 21.6 from Loudon:



(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)



(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 ethanethioate 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)

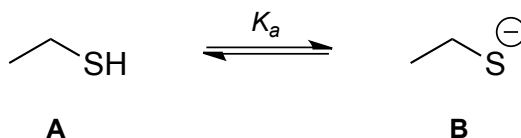


Circle One: The reaction of S-ethyl ethanethioate with NaOEt will proceed at a **FASTER** / SLOWER / SAME rate relative to the reaction of ethyl acetate with NaOEt.

(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 ($\text{CH}_3\text{CH}_2\text{SH}$) is dissolved in a pH 10.8 buffer solution. (bonus 3 pts)



$$\text{pH} - \text{pK}_a = \log\left(\frac{[\text{B}]}{[\text{A}]}\right)$$

$$10.8 - 10.6 = \log\left(\frac{[\text{B}]}{[\text{A}]}\right)$$

$$0.2 = \log\left(\frac{[\text{B}]}{[\text{A}]}\right)$$

$$1.58 = [\text{B}]/[\text{A}]$$

$$[\text{B}] = 1.58[\text{A}]$$

$$[\text{A}] + [\text{B}] = 100\%$$

$$[\text{A}] + 1.58[\text{A}] = 100\%$$

$$[\text{A}] = 38.8\%$$

$$[\text{B}] = 61.2\%$$

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_a 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^{-1}
 $^1\text{H NMR}$: 4.13 ppm (quartet, 2H), 2.21 (singlet, 3H), 0.86 (triplet, 3H)

