Name:	Ke	y

CHEMISTRY 3331, Fall 1999 Professor Walba Third Hour Exam November 18, 1999

scores:

- 1) 25
- 2) 25
- 3) 25
- 4) 25

100

This is a closed-book "open model" exam. You <u>may</u> use models, but no notes or books. Please put all your answers on the test. Use the backs of the pages for scratch.

## PLEASE read the questions carefully!

## Partial Periodic Table 8A 1A Η He 2A3A 4A 5A 6A 7A 6 8 3 9 10 $\mathbf{C}$ Li N Ne Be B O F 14 13 15 17 11 12 16 18 Na Mg Al Si P Cl Ar 35 Br 53 I

1) (20 pts) a) For each of the following pairs of compounds, circle the stronger Brønsted acid.

b) Treatment of methylacetoacetate with one molar equivalent of methoxide gives an anion (i.e. a negative ion) with formula  $C_5H_7O_3$ , as shown below. Give the three most important resonance contributors to the structure of this anion, and circle the major contributor.

$$OOO O CH_3 CH_3O^- Na^+ C_5H_7O_3^-$$

$$\begin{array}{c|c}
 & O & O \\
 & O & O \\$$

2) (25 pts) Give the single major organic product for each of the following reactions. If a racemate is formed, consider this to be one product and show only one of the enantiomers.

b) OH 
$$\frac{1) \text{ SOCl}_2}{2) \text{ CH}_3\text{CH}_2\text{NH}_2, pyridine}$$

d) 
$$CO_2H$$
  $CO_2H$   $C$ 

e) 
$$\frac{\text{CO}_2\text{CH}_3}{\text{b) H}_3\text{O}^+ \text{workup}}$$
  $\frac{\text{a) CH}_3\text{O}^- \text{Na}^+, \text{CH}_3\text{OH}}{\text{b) H}_3\text{O}^+ \text{workup}}$ 

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3) (25 pts) Propose reagents for accomplishing the following transformations. NOTE: more than one step may be required! Try to make your synthesis efficient (i.e. the desired product should be the major product).

- b) H<sub>3</sub>O<sup>+</sup> workup
  - 1) SOCl<sub>2</sub>
  - 2) NH<sub>3</sub>, pyr
  - 3) a) LiAlH<sub>4</sub>
    - b) H<sub>3</sub>O<sup>+</sup> workup

 $NH_2$ 

- b) H<sub>3</sub>O<sup>+</sup> workup
- 2) a) CH<sub>3</sub>O<sup>-</sup> Na<sup>+</sup>, CH<sub>3</sub>OH



$$H_3CO$$
 OCH<sub>3</sub>

3) a) NaOH, 
$$H_2O$$
,  $\Delta$ 

b) 
$$H_3O^+$$
,  $\Delta$ 

Name:	Key

4) (30 pts) a) Propose an arrow-pushing mechanism for the following transformation. Don't abbreviate! Show each intermediate in the mechanism, but do not show transition states.

## 4 -continued-

b) In an effort to synthesize hydroxyester  ${\bf 1}$ , a student treated the hydroxyacid  ${\bf 2}$  with methanol and  ${\bf H}^+$ . The product, however, was not the ester  ${\bf 1}$ , but a new compound  ${\bf 3}$ , with the molecular formula indicated below.

$$CH_3OH, H^+$$
OH
$$2$$
 $CH_3OH, H^+$ 
OS
$$3: C_5H_8O_2$$

Give the structure of 3, and propose a mechanism for its formation.

Ho on 
$$H_{0}$$
  $H_{0}$   $H_{0}$ 

Name: Key

4 -continued-

c) Propose a successful synthesis of hydroxyester 1 starting with hydroxyacid 2.

HO OH 
$$CH_2N_2$$
  $HO$   $OCH_3$ 

d) Propose an arrow-pushing mechanism for the following transformation.

## 4 -continued-

e) Propose a mechanism for the following famous transformation.