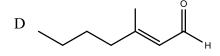
Signed

Roll Number

PART A - Scantron Scored

(44 points, 4 points each) Bubble-in the correct answer on the Scantron card. There is only one correct answer. Also circle your answer below for later review with the answer key.

- 1. Of the following compounds, the one that forms a bright yellow precipitate upon treatment with iodine in aqueous sodium hydroxide
 - A. 2-hexanone
 - B. 3-pentanone
 - C. cyclohexanone
 - D. 2-butenal
- 2. Which of the following is <u>not</u> true about keto-enol interconversion of a ketone such as 2,4-pentanedione?
 - A) A proton is removed from the methylene carbon of the ketone.
 - B) An enolate ion is formed as an intermediate in the base-catalyzed reaction.
 - C) An enolate ion is formed as an intermediate in the acid-catalyzed reaction.
 - D) A proton is donated to the oxygen atom.
- 3. The product of the aldol condensation of butanal (C_4H_8O) in base with heat is the following.



Roll Number

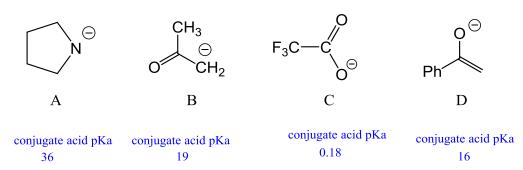
- 4. Which of the following are true about a Claisen condensation?
 - A) The reactants are two molecules of an ester and an equivalent of a base.
 - B) The base is the same as the leaving group of the ester.
 - C) The products are a beta-keto ester and an alcohol.
 - D) . Only a and c are correct.
 - E) All of the above are correct
- 5. What is the major organic product obtained from the following reaction?

- 6. The pK_a of ethyl cyanoacetate is 9. Which of the following bases will give the most ethyl cyanoacetate enolate in solution (highest concentration)? The conjugate acid pK_a 's of the bases are given.
 - A) Dimethyl amine ($(CH_3)_2NH$) [pKa conjugate acid = 11]
 - B) Acetate (CH_3CO_2) [pKa conjugate acid = 5]
 - C) t-Butoxide ((CH₃)₃CO) [pKa conjugate acid = 18]
 - D) Phenoxide (PhO) [pKa conjugate acid = 10]
 - E) Methane sulfonate (CH_3SO_3) [pKa conjugate acid = -2]

7. What is the major organic product obtained from the following sequence of reactions?

- A) A
- B) B
- C) C
- D) D
- 8. Reaction of 6,6-dimethylcyclohex-2-en-1-one with a strong base, such as Lithium diisopropyl amide in tetrahydrofuran, followed by reaction with methyl iodide results in
 - A) methyl isopropyl amine formation
 - B) amination at C4
 - C) methylation at C4
 - D) no reaction
- 9. What product is formed when 3-pentanone is dissolved in D₂O that contains some OD?
 - A) CD_3CD_2 -C(=O)- CD_2CD_3
 - B) CH₃CHD-C(=O)-CHDCH₃
 - C) CH_3CD_2 -C(=O)- CH_2CH_3
 - D) $CH_3CHD-C(=O)-CH_2CH_3$
 - $E) \ CH_3CD_2\text{-}C(=O)\text{-}CD_2CH_3$

10. Which of the following bases is \underline{not} strong enough to deprotonate CH₃SH (pKa =11)?



- A) A
- B) B
- C) C
- D) D
- E) All are strong enough to deprotonate CH₃SH
- 11. **Extra Credit:** Histidine is an amino acid. The fully protonated form has the pKa values indicated below.

$$pKa = 9.2$$
 $H_3N-CH-C-OH$ $pKa = 1.8$
 CH_2
 HN
 $PKa = 6.0$

Which one of the following is the predominant structure at pH = 7.6?

END of PART A – Scantron scored

Extra Credit (4 points): The pKa of phenol, the side chain group of the amino acid tyrosine, is close to 10. The pKa of the COOH group is 2.2 and NH_3^+ is 9.1. In the box draw the species that will predominate at a pH = **7.6**.

2. (40 points, 4 points each) Provide the structure(s)of the major organic products(s); Fill in the box for all questions.

1)
$$I_2$$
 excess /
NaOH
2) H_3O^+

$$\begin{array}{c}
O \\
D_2O / OD^{-1}
\end{array}$$

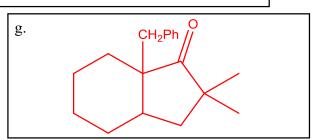
$$Ph$$
 CH_2
 CH_3

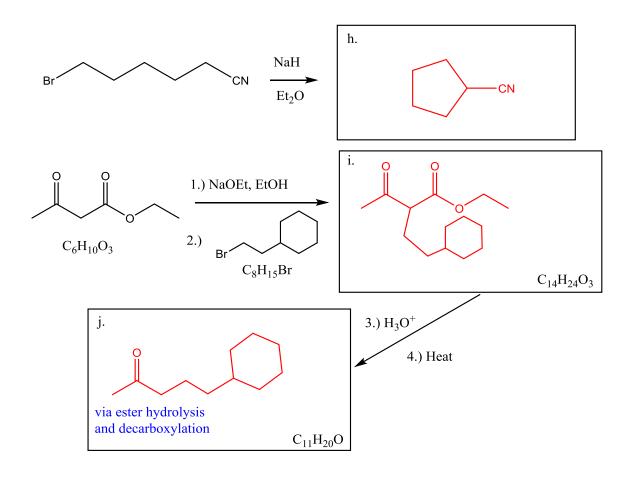
How many enolizable protons are there in the molecule on the left?

c. 3

| d. | 0 | |
|----|---|--|
| | Ĭ | |
| | | |
| | | |

$$\frac{1) \text{LDA / THF}}{2) \text{BrCH}_2 \text{Ph}}$$





End Part B

Begin Part C (next page)

3. (20 points; 10 points each)) **Mechanistic Understanding:** Provide a step wise mechanism for **BOTH** (**A and B**) of the following. Use curved arrows to show the electron movement and show all intermediates.

A.
$$\bigcap_{\text{NaOH, H}_2\text{O}} \bigcap_{\text{H-OH}} \bigcap_{\text$$

_____/ 20

| Name: | | |
|-------|--|--|
| | | |

END OF PART C

Write your class roll number on

- (1) the top of the first page and
- (2) in the box on the bottom of this page.

| | Acid | Approximate pK _a | Conjugate Base | |
|--------------------------|---|-----------------------------|--|--------------------------|
| Strongest acid | HSbF ₆ | <-12 | SbF ₆ - | Weakest base |
| | HI | -10 | [- | |
| | H ₂ SO ₄ | -9 | HSO ₄ - | |
| | HBr | -9 | Br- | |
| | HCI | -7 | CI- | |
| A | C ₆ H ₅ SQ ₃ H | -6.5 | C ₆ H ₅ SO ₃ ⁻ | |
| | (CH ₃) ₂ ŌH | -3.8 | (CH ₃) ₂ O | |
| | $(CH_3)_2C = \overset{-}{O}H$ | -2.9 | $(CH_3)_2C = O$ | |
| | CH ₃ OH ₂ | -2.5 | CH ₃ OH | |
| | H ₃ O ⁺ | -1.74 | H ₂ O | |
| | HNO ₃ | -1.4 | NO ₃ - | = |
| = | CF ₃ CO ₂ H | 0.18 | CF ₃ CO ₂ - | Cre |
| Bus | HF | 3.2 | F | asin. |
| str | CH ₃ CO ₂ H | 4.75 | CH ₃ CO ₂ - | 80 |
| acid | H ₂ CO ₃ | 6.35 | HCO ₃ - | ase |
| 50 | CH3COCH2COCH3 | 9.0 | CH ₃ COCHCOCH ₃ | stre |
| Increasing acid strength | NH ₄ ⁺ | 9.2 | NH ₃ | Increasing base strength |
| ncre | C ₆ H ₅ OH | 9.9 | C ₆ H ₅ O- | - |
| - | HCO ₃ ⁻ | 10.2 | CO ₃ ²⁻ | |
| | CH ₃ NH ₃ ⁺ | 10.6 | CH ₃ NH ₂ | |
| | H ₂ O | 15.7 | OH- | |
| | CH₃CH₂OH | 16 | CH ₃ CH ₂ O ⁻ | |
| | (CH ₃)₃COH | 18 | (CH ₃) ₃ CO ⁻ | - |
| | CH₃COCH₃ | 19.2 | -CH₂COCH₃ | |
| | HC≡CH | 25 | HC≡C⁻ | |
| | H_2 | 35 | H- | |
| | NH ₃ | 38 | NH ₂ ⁻ | |
| | $CH_2 = CH_2$ | 44 | CH ₂ =CH ⁻ | |
| Veakest acid | CH₃CH₃ | 50 | CH ₃ CH ₂ ⁻ | Strongest bas |

Note: write your Roll Number in the box

| Write your class roll number on (1) the top of the first page and (2) below. | | | | |
|--|--|--|--|--|
| Class Roll number | | | | |
| Part A Scantron scored (44 points) | | | | |
| Page 6 (20) Page 7 (12) Page 8 (12) Page 9 (20) | | | | |
| Part B only(64) | | | | |