

THE OPEN UNIVERSITY OF SRI LANKA

B. Sc DEGREE PROGRAMME / STAND ALONE COURSE 2007 / 2008

LEVEL 5 - FINAL EXAMINATION

CHU 3126 / CHE 5126 - ORGANIC CHEMISTRY

DURATION: 2 1/2 HOURS

Friday 20th June 2008

10.00 a. m. - 12.30 p. m.

Answer any FOUR (04) questions only.

If you have answered more than four questions, only the first four answers will be marked.

- 1. (a) Explain the following statements.
 - i. Thiophene undergoes electrophilic substitution at 2- position and not at 3-position.

(30 Marks)

ii. Resonance energy of thiophene and pyrrole are 122 kJ mol⁻¹ and 96 kJ mol⁻¹ respectively

(30 Marks)

(b) i. Identify the structures of the products $\mathbf{A} - \mathbf{C}$ formed in the reactions given below.

(i) 2
$$C_2H_5O_2C$$
 + $CH_3CHO + NH_3$ A B $C_2H_5O_2C$ + $CO_2C_2H_5$ (i) CH_3 (ii) $CAO/heat$ (iii) AC_2O D

ii. Give the mechanisms for the formation of product A.

(40 Marks)

2. (a) Identify the structures of compounds (E - I) in the following reactions.

$$\begin{array}{ccc}
O & O \\
II & II \\
CH_3CCH_2CH_2CCH_3 & P_2S_5
\end{array}$$
E

(iii)
$$\begin{array}{c} \text{(ii) } C_2H_5MgBr \\ \hline \text{(ii) } H+/H_2O \end{array}$$

(iv)
$$\begin{array}{c|c} & \xrightarrow{H_2O_2 \ / \ CH_3COOH} & H & \xrightarrow{fuming \ HNO_3 \ / \ Conc. \ H_2SO_4} & I \\ \hline & & heat \\ \hline \end{array}$$
 (40 Marks)

(b) Identify the product **J** in the reaction given below. Give the mechanism for the reaction involved.

$$\begin{array}{c|c}
C_2H_5 & C & BF_3 \\
N & N \\
H
\end{array}$$

(30 Marks)

4.

(c) Explain why pyrrole shows weakly acidic properties.

(30 Marks)

3. (a) Give the structures of compounds A - K in the following reactions.

i.
$$\frac{\text{MgBr}}{2. \text{ H}_3\text{O}^+} \qquad \text{A}$$
ii.
$$\frac{\text{MgCl}}{2. \text{ H}_3\text{O}^+} \qquad \text{B}$$
iii.
$$+ \text{ PhLi} \qquad \qquad \text{C} \qquad \frac{1. \text{ CO}_2}{2. \text{ H}_3\text{O}^+}$$

iv.
$$\frac{\text{1. Me}_2\text{CuLi}}{\text{2. H}_3\text{O}^+} \quad \text{E}$$

v.
$$\frac{O}{100 \, ^{\circ}\text{C}} = \frac{1. \, \text{Zn / Br} \, CO_2\text{Et}}{2. \, \text{H}_3\text{O}^+} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{H}_2\text{O}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}}{2. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C}}} = \frac{1. \, \text{DIBAL-H / -78 \, ^{\circ}\text{C$$

vi.
$$\frac{1. \text{ CHCl}_3 / \text{ alc.KOH} / 70 °C}{2. \text{ H}^+} \qquad \qquad J \qquad \frac{1. \text{ Ac}_2 \text{O} / \text{AcO} \text{ K} / 180 °C}{2. \text{ H}^+} \qquad \qquad \text{(70 Marks)}$$

(b) Consider the following reaction.



- i. Briefly giving reasons, predict the product(s) expected if NaOH is used as the base?
- ii. What would you expect if LDA is used as the base? Explain your answer in comparison with the above answer.

(30 Marks)

- 4. (a) Giving three examples explain the use of acetoacetic ester in organic synthesis. (30 Marks)
 - (b) Alkenes undergo dimerization with acids.
 - i. Predict the products formed when 2-methylpropene is reacted with 60% H₂SO₄.
 - ii. How would you obtain iso-octane from above products?

(20 Marks)

(c) During the Stobbe condensation, diethyl succinate reacts with an aldehyde or a ketone in the presence of a strong base to produce a γ -lactone, which undergoes ring opening to give the final product.

Giving the mechanism predict the product when acetophenone undergo Stobbe condensation.

(30 Marks)

(d) Give the mechanism and the expected product of the following reaction.

$$CO_2Et$$
 CO_2Et
 C

5. (a) Show how you would carry out the following conversions/syntheses.

i.
$$H$$
H
H

ii. O

iii. H
H

iii. H

ii

- (b) Consider the reaction between benzoylglycine and benzaldehyde in the presence of acetic anhydride and sodium acetate.
 - i. Give the structure of the product formed from the above reaction.
 - ii. Give the pathway of the above reaction.
 - iii. What is the use of the above reaction in organic synthesis?
 - iv. Giving reagents and conditions show how you would synthesize tyrosine using above reaction.

(c) How would you carry out the following synthesis using Wittig reaction?

(d) Give the structures of compounds P - T in the following reactions

ii.
$$\frac{2 \text{ P(OEt)}_3}{\text{heat}} \quad P$$
iii.
$$\frac{\text{CHO}}{\text{CHO}} \quad \frac{\text{Ph}_3 \text{PPh}_3}{\text{Q}} \quad Q$$
iii.
$$\frac{1. B_2 H_6}{2. \text{Na}_2 \text{Cr}_2 \text{Q}_7 / \text{H}_2 \text{SO}_4} \quad R$$
iv.
$$\frac{\text{PhC}}{\text{O-OH}} \quad \text{S} \left(\text{C}_7 \text{H}_{10} \text{O}_2\right) \quad \frac{1. \text{OH} / \text{H}_2 \text{O}}{2. \text{H}^+} \quad T$$

$$(25 \text{ Marks})$$

6. Answer any TWO (02) PARTS from PARTS A, B and C

PART A

(a) Draw the structure of dibenz[a,h]anthracene.

(05 Marks)

(b) Resonance energy of anthracene is 351.5 kJ mol⁻¹ is not equal to that of three benzene rings. (N.B. Resonance energy of benzene is 150.6 kJ mol⁻¹).

(10 Marks)

(c) Identify the structures of compounds (K - R) in the following reactions.

PART B

Identify the products (S - X) in the following reactions

(d)
$$+ Br_2 \xrightarrow{CCl_4} W$$

(e)
$$HC \equiv C - COOH + H_2NCONH_2 = \frac{H_3PO_4}{80 \, ^{\circ}C} \times \frac{1}{100 \, ^{\circ}C} \times \frac{1}{1$$

(50 Marks)

PART C

Give the structures products A - E of the following reactions.

i.
$$+$$
 CHO $100 \,^{\circ}C$ A

ii. $+$ O Me $200 \,^{\circ}C$ B

iii. CO_2Et $2. \,^{+}$ C CO_2Et CO_2Et

(50 Marks)

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