



## THE OPEN UNIVERSITY OF SRI LANKA B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2015 / 2016 LEVEL 5 - FINAL EXAMINATION CMU3120 / CME5120 - ORGANIC CHEMISTRY

DURATION: 02 HOURS

Monday 27<sup>th</sup>June 2016

1.00 - 3.00 p.m.

## Answer ALL questions.

1. Answer any **FOUR (04)** parts from (a) - (e).

(a) 'Pyrrole is more acidic and less basic than pyrrolidine'. Explain the above statement.

(25 marks)

(b) The dipole moment  $(\mu)$  of pyrrole and its saturated analogue pyrrolidine are given below. Indicate the directions of the dipole moments in each compound and account for your answer.



 $\mu = 1.81 D$ 

( ; N - H

 $\mu = 1.58 D$ 

pyrrole

pyrrolidine

(25 marks)

(c) '2-Chloropyridine undergoes nucleophillic substitution much faster than 3-Chloropyridine'.

Explain the above statement.

(25 marks)

(d) Five membered aromatic heterocycle pyrrole undergo electrophilic substitution more rapidly than benzene, while the six membered aromatic heterocycle pyridine is less reactive than benzene in these reactions'.

Explain the above statement.

(25 marks)

(e) (i) Predict the products of the following reactions.

(I) 
$$\frac{\text{(i) NaNH}_2/\triangle}{\text{(ii) H}_2\text{O}} \quad \text{A}$$

(II) 
$$\underset{N}{\bigoplus}$$
  $\underset{H}{\underbrace{CHCl_3 / NaOEt}}$  B + C

(ii) Give the mechanism of reaction (II) only.

(25 marks)

2. (a) Give the structures of the products G - J of the following reactions.

(iii) 
$$\begin{array}{c} CH_3 \\ O \\ H \end{array} \qquad \begin{array}{c} 1. \ Et_2CuLi \\ \hline 2. \ H^+ \end{array}$$

(iv) CHO 
$$CH_3$$
 +  $CO_2Et$   $C$ 

(40 Marks)

(b) Giving appropriate examples, discuss three (03) limitations of the use of Grignard reactions in organic synthesis.

(40 Marks)

(c) Illustrate the use of  $\alpha$ -acetylenic alcohol (K) in organic synthesis by stating **two (02)** different reactions with appropriate examples.

(20 Marks)

3. (a) Give the structures of the compounds P - Uof the following reaction schemes.

(i) Ph 
$$\sim$$
 CN + Ph  $\sim$  O  $\sim$  EtOH P

(ii) 
$$CO_2Et$$
  $R \xrightarrow{CO_2Et}$   $R \xrightarrow{R} R$ 

(iii) 
$$H_2C$$
  $CO_2Et + Br$   $Br$   $NaOEt$   $T$ 

(30 Marks)

(b) Write down the mechanisms of any TWO (02) of the following reactions.

(i) 
$$H_3C$$
  $H$   $NaOH$   $H_3C$   $OH$   $CH_3$ 

(ii) 
$$O$$
OEt +  $H_3C$ 
OEt  $H_3C$ 
OEt  $H_3C$ 
OOET  $O$ 
OET  $O$ 

(30 Marks)

- (c) Giving necessaryreagents and conditions show how you would carry out any **ONE(01)**of the following.
  - (i) Synthesis of CH<sub>3</sub>CH<sub>2</sub>CHO using CH<sub>3</sub>CHO as the only starting compound and employing Darzen reactions.
  - (ii) Synthesize the following compound using CH<sub>3</sub>CHO and CH<sub>3</sub>Br as the only starting compounds and employing Claisen condensation.

$$H_3C$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

(30 Marks)



(d) Give the mechanism involved in decarboxylation of a β-keto acid.

(10 Marks)

4. (a) Give the structures of the major products (A - D) in the following reaction schemes.

i) 
$$\frac{1) B_{2}H_{6}}{2) Na_{2}Cr_{2}O_{7}/H_{2}SO_{4}} \qquad A$$
ii) 
$$CHO \frac{1) HCN/NH_{3}}{2) H_{3}O^{+}} \qquad B$$
iii) 
$$C + D$$
(20 marks)

(b) Indicate how you would carry out the following synthesis using only the reagents given below. Give the mechanism of the reactions involved.

Reagents:
P(OEt)<sub>3</sub> PhLi NC Br

(40 marks)

- (c) Explain the following.
  - i) The H atom attached to the N atom of phthalimide shows significant acidity.

Phthalimide

ii) 'The activation of the acid group by preparing the acid chloride is not suitable in peptide synthesis when an amino group is protected with benzoyloxycarbonyl group'. Explain the above statement using the compound E given below.

(40 marks)