

THE OPEN UNIVERSITY OF SRI LANKA B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2014 / 2015 LEVEL 5 - FINAL EXAMINATION

CMU3120 / CME5120 - ORGANIC CHEMISTRY

DURATION: 02 HOURS

Saturday 25th April 2015

1.00 - 3.00 p.m.

Answer ALL FOUR (04) questions.

- 1. Answer any FOUR (04) parts from (a) (e).
 - (a) Explain why pyridine undergoes nucleophilic substitution readily at positions 2 and 4. (25 marks)
 - (b) Explain why electrophilic substitution takes place at the 2-position in pyrrole and 3-position in pyridine.

(25 marks)

(c) Explain why pyridine is a much stronger base than pyrrole.

(25 marks)

(d) Giving the necessary reagents and essential conditions show how you would effect the following transformation.

$$\bigcap_{N} \longrightarrow \bigcap_{N}^{NO_2}$$

(25 marks)

(e) Give the structures of major products A, B and C of the following reactions.

(i)
$$\frac{1. C_2H_5MgBr/150 \text{ °C}}{2. H_2O} \quad A$$

(ii)
$$\xrightarrow{N}$$
 HCHO/HCN B $\xrightarrow{H^+/H_2O}$ C

(25 marks)

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

(i)
$$\frac{1. \text{ MeMgBr}}{2. \text{ H}^{+}/\text{H}_{2}\text{O}} \qquad \text{G}$$

(iii)
$$CH_2I_2 \rightarrow I$$

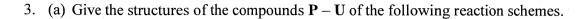
(iv) CHO + BrCH₂CO₂Et
$$\frac{1. \text{ Zn/toluene}}{2. \text{ H}^+/\text{H}_2\text{O}}$$
 J

(40 Marks)

(b) Reaction between di-isopropyl ketone and isopropylmagnesium bromide followed by acidification does not yield the desired alcohol. Giving appropriate mechanisms, explain what side reactions occur when this reaction is attempted.

(c) Giving appropriate mechanisms predict the structures of (M) and (N) of the following reaction sequence.

MgBr + EtO
$$\rightarrow$$
 OEt \rightarrow M \rightarrow N (20 Marks)



(i)
$$\frac{\text{CI} \quad \text{CO}_2\text{Et}}{\text{NaOEt}} \quad P \quad \frac{1. \text{ OH} \bar{\text{I}} \text{H}_2\text{O}}{2. \text{ H}^+} \quad Q$$

(ii)
$$CO_2Et$$
 1. LDA/THF/-78 °C R $\frac{1. OH^{-}/H_2O}{2. H^{+}}$ S $\frac{1. OH^{-}/H_2O}{3. heat}$ S

(iii)
$$CN$$
 $NaOEt$ T $1. H^+/H_2O$ $2. heat$ U

(30 Marks)

(b) Show how you would synthesize a mixture of α - and β -ionones using acetone as one of the starting material.

Giving reasons indicate the steps taken to increase the yield of the desired products during the synthesis.

$$\alpha$$
-ionone β -ionone

(30 Marks)

(c) Giving necessary starting materials, reagents, and conditions show how you would synthesize any **two** of the following compounds using the method indicated.

(i)
$$O$$
 using acetoacetic ester synthesis

(iii)
$$Ph$$
 CO_2H NH_2 using azlactone synthesis

(40 Marks)



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

(i)
$$EtO_2C$$
 $CO_2Et + HNO_2$ $\xrightarrow{H^+}$ A $\xrightarrow{Zn/HOAc}$ B $\xrightarrow{EtO^-}$ C $\xrightarrow{1. OH^-/H_2O}$ $\xrightarrow{2. H_3O^+}$ D $\xrightarrow{3. heat}$

(ii)
$$H_3CO$$
 PPh₃ E H^+/H_2O F

(30 marks)

(b) Show how you would synthesize PhCH(NH₂)COOH *via* Strecker synthesis. *Hint: Use the appropriate aldehyde as one of the starting materials.*

(20 marks)

(c) Give the route to synthesize methyl orange using aniline as the only starting material.

$$NH_2$$
 HO_3S
 $N=N$
 $N(CH_3)_2$
aniline methyl orange

(20 marks)

(d) Show how you would carry out any ONE of the following conversions.

(i)
$$H_3C$$
 O H_3CH_2C

(ii)
$$EtO_2C$$
 CO_2Et HO_2C NH_2 (30 marks)

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