MSc I - March 2013 Sem II

Organic (Paper III (Semi-Patt)

P4–RT–Exam.–Feb.–13–1–12

Con. 1886–13.

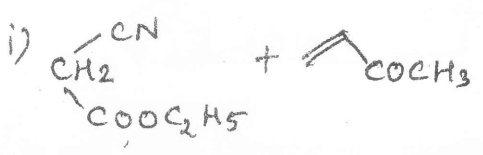
CS–5015

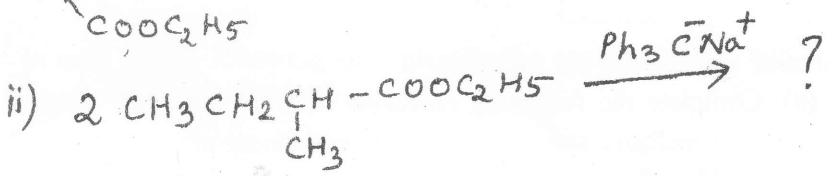
(2½ Hours) **[Total Marks : 60**

N.B. : (1) **All** questions are **compulsory**.
(2) **Figures** to the **right** indicate **full** marks.

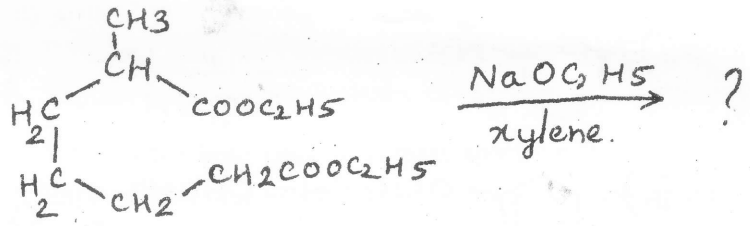
1. (A) Answer any **two** of the following :– **4**

(a) Predict the products and name the following reactions :–

i) 

ii) 

(b) Complete and name the following reaction. Explain its mechanism. **4**



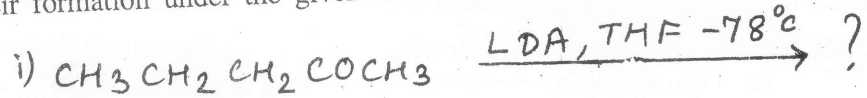
(c) What is Robinson's annulation ? Explain its mechanism. **4**

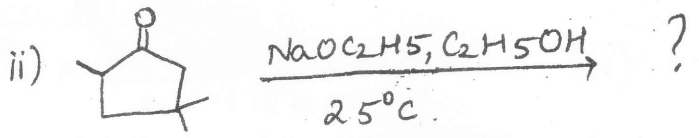
(d) Give the mechanism of the reaction of phenylacetic acid with Br_2/PBr_3 followed by hydrolysis and name the reaction. **4**

(B) Answer any **one** of the following :–

(a) What is Haloform reaction ? Explain its mechanism with a suitable example. **4**

(b) What is the major enolate formed in each of the following reactions ? Explain their formation under the given reaction conditions :– **4**

i) 

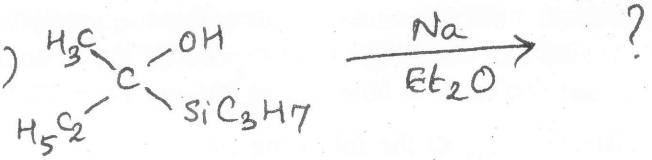
ii) 

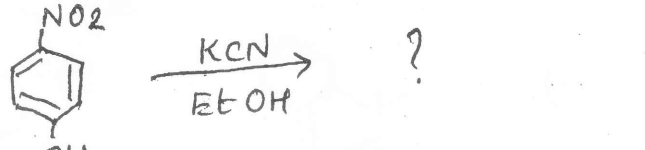
2. (A) Answer any **two** of the following :– **4**

(a) Explain the Cope and oxy-Cope rearrangements with suitable examples. **4**

(b) What is Pummerer rearrangement ? Explain its mechanism. **4**

(c) Complete the following reactions and name them –

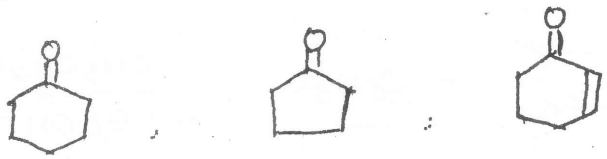
i) 

ii) 

(B) Answer any **one** of the following :–

(a) (i) What are overtone and combination bands in I. R. spectra ? 4

(ii) Arrange the following compounds in increasing order of I. R. absorption frequencies and explain.



(b) In each of the following sets, identify the compound that will absorb at a higher wave number and explain – 4

(i) p-Nitroacetophenone and p-aminoacetophenone

(ii) Benzoyl chloride and benzamide.

4. (A) Answer any **two** of the following :–

(a) (i) What are the characteristics of 'first order' NMR spectra ? 4

(ii) Explain magnetic equivalence of protons with suitable examples.

(b) (i) What is the base peak in a mass spectrum ? 4

(ii) Explain retro-Diels Alder fragmentation in mass spectrometry with an example.

(c) What is vicinal coupling in NMR spectroscopy ? Explain two factors affecting the vicinal coupling constant. 4

(d) Give the fragmentation pattern of : (i) Benzoic acid (ii) 3-Pentanone. 4

(B) Answer any **one** of the following :–

(a) An organic compound with molecular formala $C_6H_{10}O$ showed the following spectral characteristics :– 4

I.R. : 3600 – 3500 cm^{-1}, 3300 cm^{-1}, 2800 cm^{-1}, 2140 cm^{-1}

^1H–NMR : δ 1·0 (3H, t) ; δ 1·4 (3H, s) ;
δ 1·52 (2H, q) ; δ 2·84 (1H, s)
δ 3·3 (1 H, broad)

Deduce the structure of the compound and explain.

(b) (i) Explain the following terms in mass spectrometry – 4

(1) molecular ion peak (2) isotopic peak

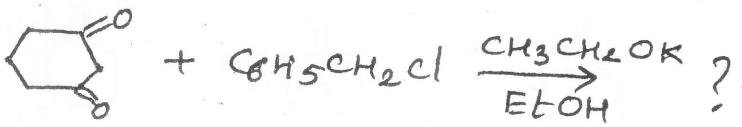
(ii) Determine the molecular formula of an organic compound based on the following mass spectral data –

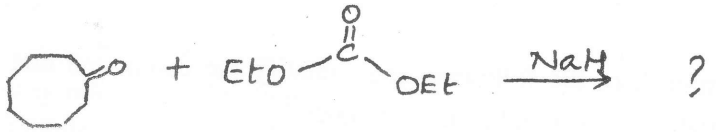
m/z = 29, 35 and 37 (3 : 1 ratio), 64 and 66 (3 : 1 ratio).

5. Answer any **four** of the following :– 12

(a) Explain the mechanism of Mannich reaction.

(b) Complete the following reactions :–

i) 

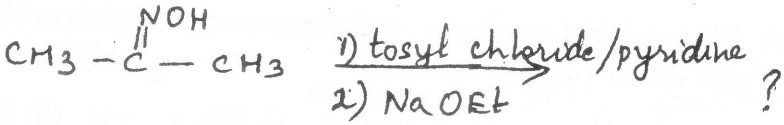
ii) 

iii) $C_6H_5COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow[ii)\ H_2O]{i)\ C_2H_5ONa}$?

(c) What is Curtius rearrangement ? Explain its mechanism.

(d) Complete the following reactions :–

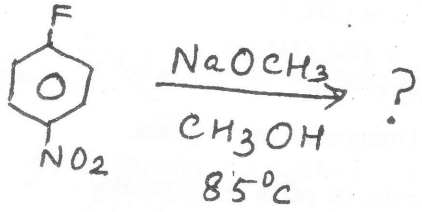
i) 

ii) 

iii) $CH_3-O-CH_2Ph \xrightarrow{PhLi}$?

(e) What is the $B_{AL}1$ mechanism of ester hydrolysis ? Give an example.

(f) Give the mechanism of the following reaction :–



(g) How is NMR spectroscopy used to distinguish between :–

(i) Inter and intra molecular hydrogen bonding.

(ii) Equatorial and axial protons in cyclohexane.

(h) Explain the following with respect to mass spectrometry :–

(i) Nitrogen rule

(ii) ortho effect.

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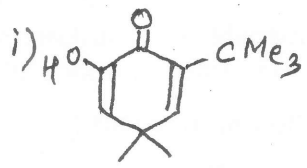
(d) Predict the products and name the following reactions :–

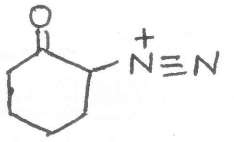
i)  $\xrightarrow[Et_2O]{Conc.\ H_2SO_4}$?

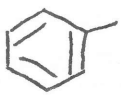
ii)  $\xrightarrow{HNO_2}$?

(B) Answer any **one** of the following :–

(a) Complete the following reactions – 4

i) $C_2H_5CH=CHCH_3 \xrightarrow[WCl_6 - EtOH]{EtAlCl_2}$?

ii)  $\xrightarrow[CH_3OH]{h\nu}$?

iii)  $\xrightarrow{\Delta}$?

iv)  $\xrightarrow[ii)\ H_2O]{i)\ \bar{O}H}$?

(b) What is Favorskii rearrangement ? Explain its mechanism. 4

3. (A) Answer any **two** of the following :–

(a) (i) Complete the following reaction with structures and stereochemistry – 4

(R) - 2 - Iodooctane $\xrightarrow{\bar{O}H}$ A $\xrightarrow{SOCl_2}$ B

(ii) Explain the S_N2' mechanism with a suitable example.

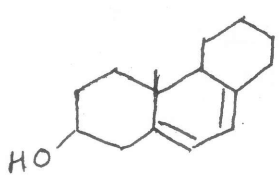
(b) (i) Explain the significance of ion pair formation on the stereochemistry of S_N1 reactions with a suitable example. 4

(ii) What are ambident nucleophiles ? Illustrate with suitable examples.

(c) (i) Explain 'cine' substitution with a suitable example. 4

(ii) Aniline absorbs at 230 nm (ϵ = 8600) but in acid solution the main absorption band is observed at 203 nm (ϵ = 7500). Explain.

(d) Calculate the λ_{max} of the following :– 4

i) 

ii)