(2½ Hours) [Total Marks : 60

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

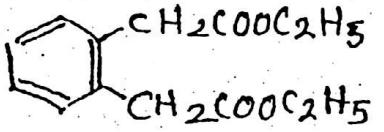
1. (A) Answer any **two** of the following :–

(a) Complete the following reaction, name it and explain the mechanism. 4

$CH_3CH_2COOH + Br_2/P \rightarrow ?$

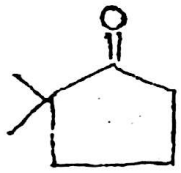
(b) Predict the products and name the following reactions 4

(i) $CH_2(COOC_2H_5)_2$ +  $\xrightarrow[2)\ H_3O^+]{1)\ NaOC_2H_5}$?

(ii)  $\xrightarrow[2)\ H_3O^+]{1)\ C_2H_5ONa}$?

(c) Discuss Robinson annulation with mechanism. 4

(d) Write the structure of the product in the following reaction and explain the mechanism of its formation. 4

 $\xrightarrow[HCl]{Me_2NH\ ,\ H_2CO}$?

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

(a) (i) Complete the following reaction and give its mechanism. 4

$CH_3CH_2COOC_2H_5 + (COOC_2H_5)_2 \xrightarrow[2)\ H_3O^+]{1)\ C_2H_5ONa}$?

(ii) Predict the product of the following reaction.

 $\xrightarrow[2)\ CH_3COCl]{1)\ NaH,\ DMF}$?

(b) Explain giving reasons which enolate is formed when 2-heptanone is treated with 4

(i) LDA, THF, –78°C

(ii) $NaOCH_3/CH_3OH$, 25°C

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

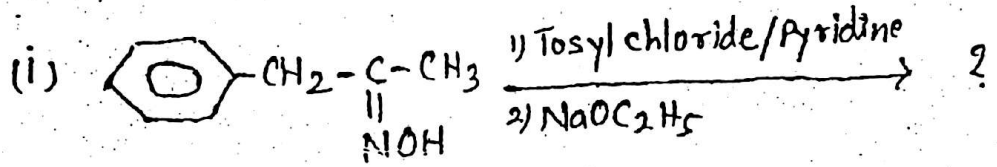
(a) Explain the following rearrangements with one example each 4

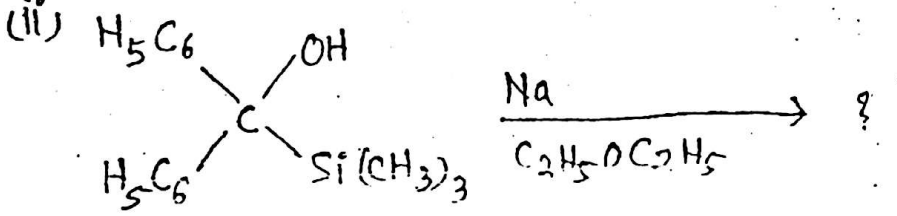
(i) oxy-Cope

(ii) olefin metathesis

(b) What products are obtained when p-chlorobenzoic acid is treated with hydrazoic acid in the presence of sulphuric acid? Name the reaction and give its mechanism. 4

(c) Complete the following reactions and name them. 4

(i) 

(ii) 

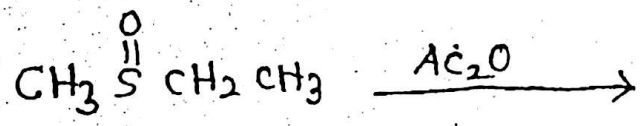
(d) Write the mechanisms of the following rearrangements. 4

(i) Curtius

(ii) Wolff

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

(a) Predict the product and give the mechanism of the following reaction 4

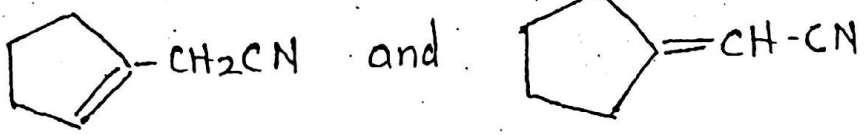


(b) What is Sommelet Hauser rearrangement? Explain its mechanism. 4

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

(a) (i) Define 'bathochromic shift'. 4

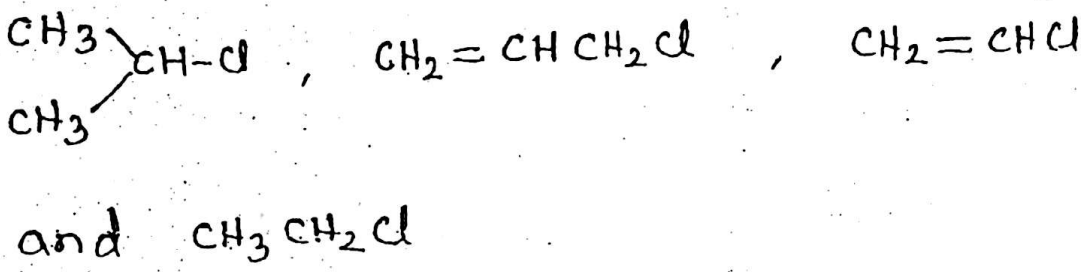
(ii) Can UV spectroscopy be used to distinguish between the following isomers? If yes, explain

I) 

II) $CH_3CO-OCH_2CH_3$ and $CH_3CH_2CO-OCH_3$

(b) Explain the following in IR spectroscopy 4
(i) Importance of finger print region.
(ii) Structure determination of compounds containing a carbonyl group

(c) Arrange the following substances in *increasing* order of reactivity to solvolysis under S_N1 reaction conditions and explain. 4



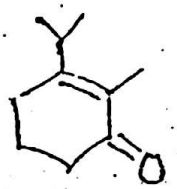
and CH_3CH_2Cl

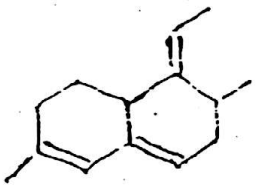
(d) Give the mechanism of the reaction of o-bromotoluene with sodamide in liquid ammonia. Identify the 'cine' and 'ipso' products of the reaction. 4

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

(a) (i) Explain neighbouring group participation of aryl rings in nucleophilic substitution reactions. 4
(ii) What are overtone and combination bands in IR spectra?

(b) Calculate the λ max of the following compounds – 4

i) 

ii) 

[Note : Increments for alkyl substituents on enone chromophore α = 10 nm
β = 12 nm, γ and higher = 18 nm]

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

(a) Explain the following in NMR spectroscopy. 4
(i) spin-spin coupling constant
(ii) Karplus curve and its significance

(b) On the basis of NMR spectroscopy how will you distinguish between 4
(i) cis and trans alkenes
(ii) axial and equatorial protons in cyclohexane

(c) Explain the fragmentation pattern of the following in mass spectrometry. 4
(i) 2, 2-dimethylbutane
(ii) ethylbenzene

(d) Explain the following in mass spectrometry 4
(i) molecular ion peak and base peak
(ii) ortho effect

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

(a) A compound has molecular formula $C_4H_5O_2N$. 4

It gave following spectral data

IR cm^{-1} : 2250 (m), 1740 (s)

PMR δ (ppm) : 3.8 (3H, singlet), 3.5 (2H, singlet)

Mass spectra m/z : 99, 73, 59

Deduce the structure of the compound.

(b) Explain the following in mass spectrometry with one example each 4

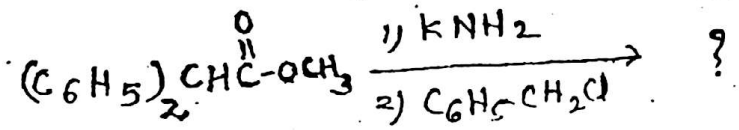
(i) Retro Diels Alder reaction

(ii) McLafferty rearrangement

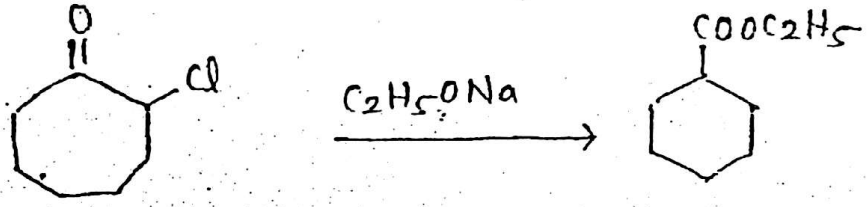
5. (A) Answer any **four** of the following :– 12

(a) Write a stepwise mechanism for the reaction between acetophenone and excess of iodine in NaOH.

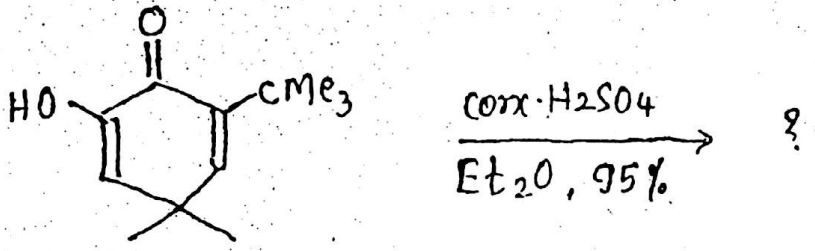
(b) Predict the product and give the mechanism of the following reaction

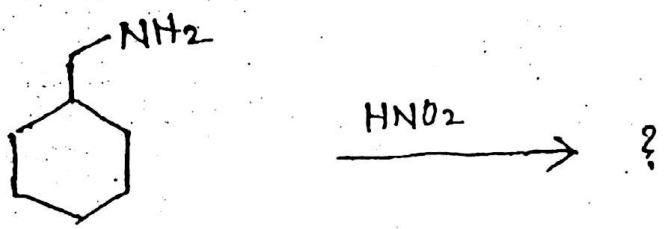


(c) Give the mechanism of the following reaction



(d) Complete the following reactions and name them





(e) Explain the following terms :–

(i) Nucleophilicity

(ii) Ambident nucleophile (with an example)

(f) Explain the $A_{AC}2$ mechanism of ester hydrolysis.

(g) Give the fragmentation pattern of benzoic acid in mass spectrometry.

(h) 'Acetylenic protons appear at around 2.8 ppm in NMR spectra'. Explain.
