BS–6667

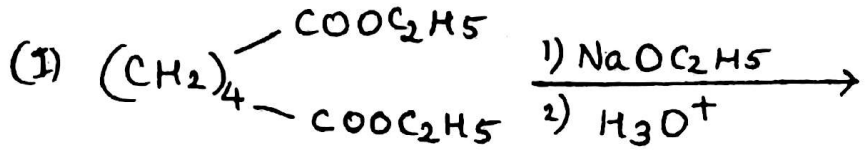
(2½ Hours) **[Total Marks : 60**

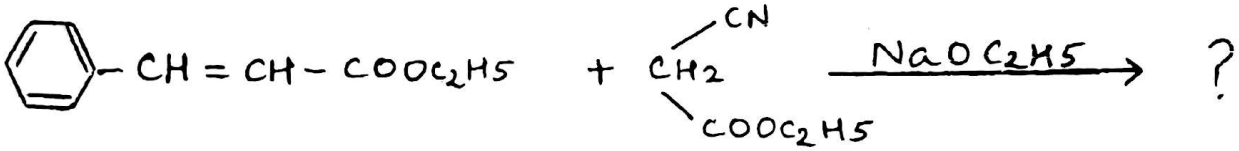
N.B. (1) **All** questions are **compulsory.**

(2) **All** questions carry **equal** marks.

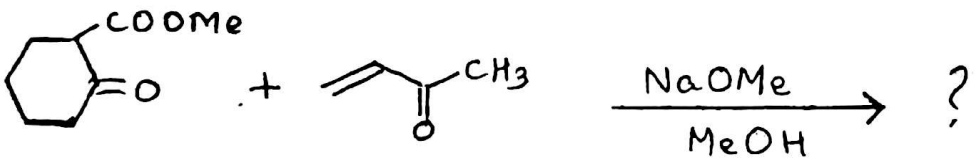
(A) Answer any **two** of the following :—

(a) Predict the products and name the following reactions :— **4**

(I) 

(II) 

(b) Complete the following reaction and give the mechanism **4**



(c) What are the products of the reaction of propanoic acid with Br_2 and PBr_3 followed by addition of water. Name the reaction and give its mechanism. **4**

(d) Discuss the mechanism of the acid catalysed reaction of acetophenone with formaldehyde and dimethylamine. **4**

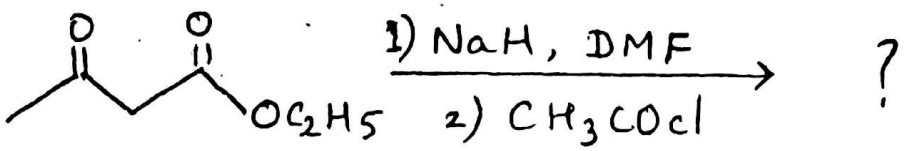
(B) Answer any **one** of the following :—

(a) Explain thermodynamic and kinetic control of enolate formation with a suitable example. **4**

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

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

(ii) What is the product of the following reaction ?



(A) Answer any **two** of the following :—

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

$$C_6H_5\underset{\displaystyle CH_3}{\underset{|}{CH}}\,CO\,NH\,O\,CO\,C_2H_5 \xrightarrow[ii)\ H_2O]{i)\ \overline{O}H} \ ?$$

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

(c) Give complete equations to represent the following rearrangements : 4

(i) Brooks

(ii) Favorskii

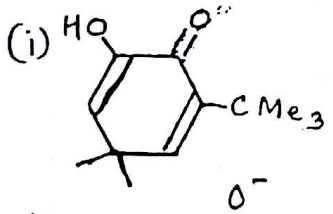
(d) Give mechanisms for the following conversions : 4

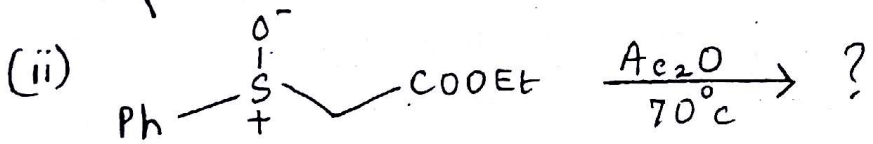
(i) α – diazoketone ⟶ ketene

(ii) acyl azide ⟶ isocyanate

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

(a) Predict the products of the following reactions and give mechanism of any **one** :— 4

(i) 

(ii) 

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

$$C_6H_5-CH_2-\underset{\displaystyle N-OH}{\underset{\|}{C}}-CH_3 \xrightarrow[ii)\ NaOC_2H_5]{i)\ \text{Tosyl chloride / pyridine}}$$

(A) Answer any **two** of the following :—

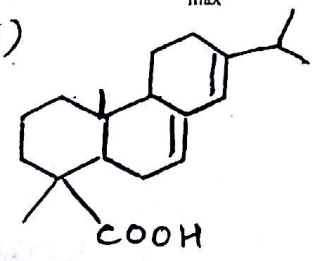
(a) (i) Explain the stereochemistry of S_Ni reactions based on the mechanism. 4

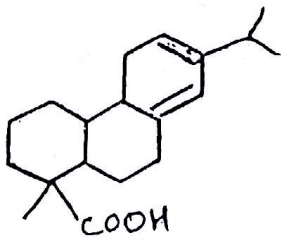
(ii) Explain the effect of NGP on stereochemistry of S_N reactions with an example.

(b) (i) 'Cyanide ion is an ambident nucleophile'. Explain with reactions. 4

(ii) Explain the lack of reactivity of vinyl chloride to S_N1 and S_N2 mechanisms.

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

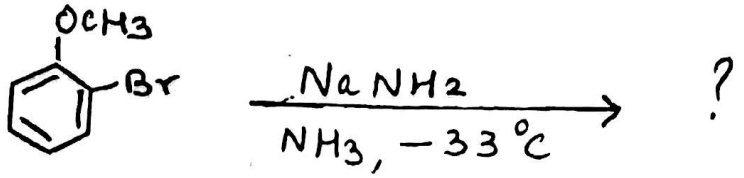
(i) 

(ii) 

(d) Explain the importance of the region 4000 – 2500 cm^{-1} in IR spectroscopy for structure elucidation in organic chemistry.

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

(a) Write and label the structures of the 'ipso' and 'cine' products of the following reaction and give the mechanism of the reaction. 4



Explain why polar protic solvents favour S_N1 but not S_N2 reactions.

(b) Write the $B_{AL}1$ mechanism for hydrolysis of t–butyl acetate. 4

(A) Answer any **two** of the following :—

(a) (i) What is McLafferty rearrangement ? 4

(ii) The various fragments in the mass spectrum of pentanal are :

m/z : 29, 44, 57 and 86

Explain the fragmentation.

(b) What is spin - spin coupling ? Explain two factors affecting the geminal coupling constant. 4

(c) (i) Explain Nitrogen rule in mass spectrometry. 4

(ii) Give the fragmentation pattern of 1-butanol in mass spectrometry.

(d) (i) Explain magnetic equivalence of protons in NMR spectroscopy with suitable examples. 4

(ii) 'Aldehydic protons appear between δ 9-10 ppm in NMR spectra'. Explain.

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

(a) An organic compound (MF $C_8H_8O_2$) showed the following spectral data : 4

IR (cm^{-1}) : 1710

NMR δ (ppm) : 3·5 (2H, s), 7·2 (5H, m) 10·8 (1H, s)

Mass m/z : 136 (M^+), 91 (base peak) and 45.

Deduce the structure of the compound and explain its fragmentation.

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

(1) metastable ion peak

(2) isotopic peaks.

(ii) What are first order spectra in NMR spectroscopy ?

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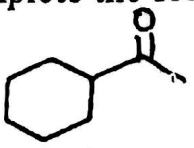
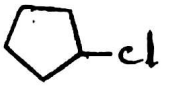
Attempt any **four** of the following :—

(a) Complete the following reaction with a stepwise mechanism.

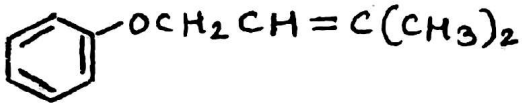


$\xrightarrow[OH^-]{I_2\ (excess)}$?

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

$CH_2(COOC_2H_5)_2$ +  $\xrightarrow{C_2H_5ONa}$?

(c) Complete the following reactions :—

(i)  $\xrightarrow{\Delta}$?

(ii) $CH_2=CH-CH_2-O-CH_2-CH=CH_2 \xrightarrow{PhLi}$?

(iii) $(C_2H_5)_2C=C(CH_3)_2 \xrightarrow[WCl_6,\ EtOH]{EtAlCl_2}$?

(d) Explain the mechanism of Schmidt reaction with a suitable example.

(e) Which of the following will absorb at longer wavelength and why ?

(i) A neutral or acid solution of aniline

(ii) Biphenyl or 2, 2', 6, 6' – tetramethylbiphenyl.

(f) What are fundamental, overtone and combination bands in IR spectroscopy ?

(g) Explain Retro-Diels-Alder reaction in mass spectrometry.

(h) What is vicinal coupling in NMR spectroscopy ? Mention the number of signals and splitting pattern expected in the NMR spectrum of $(CH_3)_3C-CH_2-CH_2-Br$.
