### **CHEMISTRY**

#### PAPER—II

Time Allowed: Three Hours

Maximum Marks: 200

### QUESTION PAPER SPECIFIC INSTRUCTIONS

# Please read each of the following instructions carefully before attempting questions

There are EIGHT questions in all, out of which FIVE are to be attempted.

Question Nos. 1 and 5 are compulsory. Out of the remaining SIX questions, THREE are to be attempted selecting at least ONE question from each of the two Sections A and B.

The number of marks carried by a question/part is indicated against it.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary, and indicate the same clearly.

Neat sketches may be drawn, wherever required.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly. Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

Answers must be written in ENGLISH only.

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### 1. Answer the following questions:

- (a) In the Cannizzaro reaction of benzaldehyde, suggest a suitable method to know the source of second hydrogen that becomes attached to benzyl alcohol, i.e., if it comes from solvent (H<sub>2</sub>O) or from a second molecule of benzaldehyde.
- (b) Neopentyl-type bromide (I) undergoes rearrangement during  $S_N1$  hydrolysis, but no such rearrangement takes place with its phenyl analogue (II). Explain:

(c) Which of the following compounds has the greater dipole moment? Justify your answer:

- (d) Methyl radical ( $\dot{C}H_3$ ) is planar, while trifluoromethyl radical ( $\dot{C}F_3$ ) is pyramidal. Justify.
- (e) Indicate what types of sigmatropic reactions are involved in the following transformations:

(f) How will you prepare the following compound by Skraup synthesis? Give mechanism for its formation:

(g) Write the product of the following reaction and predict the mechanism:

$$\begin{array}{c|c} CH_3 & CH_3 \\ \hline & N \\ CH_3 & \Delta \end{array} ?$$

(h) Give the product and mechanism of the following reaction:

$$\begin{array}{c}
 & \text{Ph} \\
 & \text{Ph} \\
 & \text{Ph} \\
 & \text{Ph} \\
 & \text{Ph}
\end{array}$$

$$\begin{array}{c}
 & \text{Ph} \\
 & \text{Ph} \\
 & \text{Ph} \\
 & \text{Ph}
\end{array}$$

$$\begin{array}{c}
 & \text{HCl} \\
 & \text{Ph}
\end{array}$$

$$\begin{array}{c}
 & \text{Ph} \\
 & \text{Ph}
\end{array}$$

2. (a) 2-Methylcyclohexanone forms an enolate mixture of varied composition when subjected to the following reaction conditions. Draw the structures of the products and identify the major/minor products:

$$\begin{array}{c}
\text{Et}_{3}\text{N/DMF} \\
\text{Or} \\
\text{NaH/DMF} \\
& \begin{array}{c}
\text{CH}_{3} \\
& \begin{array}{c}
\text{CC}_{6}\text{H}_{5}\text{)}_{3}\text{C Li} \\
\hline
& \begin{array}{c}
\text{H}_{3}\text{COCH}_{2}\text{CH}_{2}\text{OCH}_{3} \\
& \begin{array}{c}
\text{Or} \\
\text{LDA}
\end{array}
\end{array}$$
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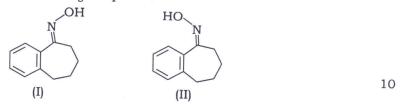
(b) 2S,3R-3-Phenyl-2-butyl tosylate (I) yielded largely racemic 3-phenyl-2-butyl acetate on heating in acetic acid solution. In contrast, the 2R,3R-diastereomer (II) was converted to optically active 3-phenyl-2-butyl acetate. Explain:

- (c) (i) When 2-fluoropentane undergoes an E1 reaction, is the major product the one predicted by Zaitsev's rule? Explain.
  - (ii) Write the structure of the major product formed in the following elimination reaction. Justify your answer:

$$CH_3 \longrightarrow P$$
?

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(d) Comment if the following two compounds will yield same product or different products on treatment with PCl<sub>5</sub>. Explain:



- 3. (a) (i) Arrange the following compounds in increasing order of their  $pK_a$  values. Justify your answer:
  - 1. CH<sub>2</sub>(COMe)<sub>2</sub>
  - 2. CH2(CO2Et)2
  - 3. MeCOCH<sub>2</sub>CO<sub>2</sub>Et 5
  - (ii) Complete the following reaction:

$$0 \longrightarrow 0$$

(b) Complete the following conversion by identifying the compounds X, Y and Z. Briefly mention the type of reaction involved in each step:

$$H_3CO$$
 $NH_2$ 
 $+$ 
 $F$ 
 $NH_2 \rightarrow X \xrightarrow{Raney} Y \xrightarrow{Raney} V$ 
 $Z$ 
 $CICO_2Et$ 
 $Z$ 
 $IO$ 

(c) Identify the products and briefly describe the steps involved :

(i) 
$$OH \longrightarrow Ph$$
  $Ph \longrightarrow Ph$  (ii)  $NH_2 \longrightarrow Ph \longrightarrow Ph$   $Ph \longrightarrow Ph$ 

(d) (i) In the following reaction, there is a possibility of formation of two isomeric products Y. However, one isomer is formed. Identify both the isomers Y and also the structure of the most likely formed product:

$$\begin{array}{ccc}
OMe & + & CN & \xrightarrow{\text{Diels-Alder}} X & \xrightarrow{\text{H}^+} Y & 5
\end{array}$$

(ii) Identify the product :

HO C=CH 
$$HgSO_4$$
,  
 $H_2SO_4$   
 $H_2O$  ?

4. (a) Formulate the product(s) and give the mechanism for the following reactions:

(i) 
$$CHCl_3 \rightarrow Ac_2O \rightarrow Ac_3O$$
Aq. NaOH  $Ac_3O \rightarrow Ac_3O \rightarrow Ac_3O$ 
(ii)  $CHCl_3 \rightarrow Ac_3O \rightarrow$ 

(b) Suggest starting materials and conditions to prepare the following molecules based on Fischer indole and Knoevenagel condensation reactions:

(c) Formulate the products and mechanism of the following reactions:

(i) 
$$CH_2$$
  $CH_2$   $CH_$ 

(d) Write the structures of the products of the following reactions:

(ii) CuBr<sub>2</sub> ?

(iii) CHO Zn-Hg
Conc. HCl ?

(iii) NH<sub>2</sub> + C-Cl 1) Aq. NaOH
2) POCl<sub>3</sub> ?

(iv) CH<sub>3</sub> 
$$\frac{CH_3}{COOEt}$$
 ?

 $\frac{CH_3}{Et_2O}$  ?

## 5. Answer the following questions:

5×8=40

- (a) A very dilute solution, 0.001 M sugar in water, is separated from pure water by an osmotic membrane. What osmotic pressure develops in atm at 25 °C?
- (b) Write the important structural and functional differences between DNA and RNA.
- (c) Calculate the molar mass of a polyisobutylene in  $CCl_4$  solutions at 30 °C. Given  $K = 2.6 \times 10^{-4}$  dL/g, a = 0.70 and intrinsic viscosity  $[\eta] = 43$  dL/g.
- (d) The following ketone-containing chiral centre undergoes racemization on photolysis. Write down the mechanism:

$$\begin{array}{ccc}
 & & & & & & hv \\
 & & & & & & hv \\
 & & & & & Norrish \\
 & & & & & Type-I
\end{array}$$
?

- (e) What is anisotropic effect? Explain this effect in aromatic protons.
- (f) Arrange the following cycloalkenes in order of their wave numbers' increasing manner and explain the importance of strain:

$$\bigcirc$$
,  $\bigcirc$ ,  $\triangle$ ,  $\square$ 

(g) How do you prepare the following compounds from cyclohexene? Explain the stereochemistry during their formation:

(h) Complete the following reaction and predict the mechanism:

$$\xrightarrow{m\text{-CPBA}} ? \xrightarrow{\text{Me}_2\text{NH}} ?$$

6. (a) (i) An unknown organic compound gave the following spectral data:

UV : 280 nm, 
$$\varepsilon_{max} = 20$$

$$IR: 1698 cm^{-1}$$

PMR (
$$\delta$$
, ppm) : 3.4 (s, 3H), 6.6 (2H, d,  $J = 8$  Hz), 7.5 (2H, d,  $J = 8$  Hz)

Find the structure and explain the data.

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(ii) A compound with molecular formula  $C_8H_8O$  gave positive iodoform test and gave the following data:

IR 
$$(v_{max}, cm^{-1})$$
: 1685

NMR ( $\delta$ , ppm) : 2·1 (s, 3H), 7·1–7·3 (m, 5H)

Mass (Rel. Abu. %): m/z 120, 105, 77 and 51

Find the structure and give its mass fragmentation.

(b) Complete the following reaction and give its mechanism:

$$C_6H_5$$
— $CH_2$ — $C$ — $CH_2$ — $C_6H_5$   $hv$ 

Norrish

Type-I

(c) Identify the products A and B of the following reactions:

(ii) 
$$hv \rightarrow CO + A + B$$
  $5 \times 2 = 10$ 

(d) (i) Which of the following molecules will show microwave rotational spectrum? Identify it and justify your answer:

$$H_2$$
,  $HCl$ ,  $NO$ ,  $N_2$ ,  $CO$ ,  $Cl_2$ 

- (ii) "DCl and HCl show different spectra." Give reason.
- 7. (a) <sup>1</sup>H <sup>35</sup>Cl has a force constant value of 483·1 N m<sup>-1</sup>. Calculate the fundamental frequency and wave number.
  - (b) Diagrammatically show different modes of vibration of H<sub>2</sub>O molecules. Justify whether these are infrared-active or not.
  - (c) Identify the product(s) in the following transformations:

(i) 
$$\xrightarrow{\text{Ph}} \xrightarrow{\text{Ph}} \xrightarrow{\text{hv}} ?$$
  $5 \times 2 = 10$ 

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- (d) (i) How will you distinguish 2-pentanone from 3-pentanone by mass spectroscopy?
  - (ii) Discuss the mass spectral fragmentation of 4-heptanone.

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**8.** (a) Show that  $\overline{M}_n = \overline{M}_w$  of the protein solution, when an equal number of protein mixtures containing—

Haemoglobin = 15.5 kg/mol Ribonuclease = 13.7 kg/mol Myoglobin = 17.2 kg/mol

are available.

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(b) (i) Predict the odd one among the following:

Terylene, Teflon, Polyethene, Styrene

Justify giving suitable explanation.

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(ii) Write the reactants with their structures to produce Nylon-66.

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(c) What are different types of electronic transitions possible when an organic compound is exposed to UV-visible radiation? Explain and calculate the  $\lambda_{max}$  values of the following compounds in nm:

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

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- (d) Discuss the following with suitable examples and give their importance in mass spectrometry:
  - (i) Metal stable peaks
  - (ii) Isotopic peaks of halogens and sulphur

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