Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Answer six questions in all.
3. Question No. 1 carries 15 marks.

1. Answer any five parts:

   (a) Cis-1, 2-Dichloroethylene shows C=C stretching absorption in its IR spectrum whereas trans-1, 2-Dichloroethylene does not show C=C stretching. Give reason.

   (b) Explain why the absorption bands in UV spectrum are generally broad when compared to the absorption bands in IR spectrum?

   (c) A 60 MHz spectrometer records the signal for a proton at a position 150 Hz downfield from TMS

      (i) Determine the chemical shift in \( \delta \)

      (ii) Predict the shift of the same proton from TMS in Hz for 100 MHz spectrometer

   (d) What are activators and antioxidants used during the process of vulcanization of rubber? Give one example of each.

   (e) What are the characteristic features of a dye?
(f) Why TMS (Tetramethyilsilane) is chosen as reference compound in NMR spectroscopy?

(g) C=O stretching in IR of acetone comes at 1720 cm\(^{-1}\) while C=O stretching in acetamide (CH\(_2\)CONH\(_2\)) comes at 1680 cm\(^{-1}\). Give reason. (5×3)

2. (a) Which of the following molecules show spin-spin coupling? Justify your answer. If splitting is observed, give the multiplicity of each kind of proton.

(i) CH\(_3\)CH\(_2\)Br

\[
\begin{align*}
&\text{H} \quad \text{C} = \text{C} \quad \text{H} \\
&\text{Br} \quad \text{Br}
\end{align*}
\]

(ii) C=O stretching in IR of acetone comes at 1720 cm\(^{-1}\) while C=O stretching in acetamide (CH\(_2\)CONH\(_2\)) comes at 1680 cm\(^{-1}\). Give reason for the difference? (3×4)

(c) Compare the PMR spectrum of ordinary (impure) ethanol and pure ethanol. Explain why the aldehydic proton appears much downfield in PMR spectrum? (3×4)

3. (a) Salicylic acid shows C=O absorption band at a lower frequency than p-Hydroxybenzoic acid in its IR spectrum? Explain and give the structures.

(b) Arrange the following compounds in increasing order of carbonyl absorption frequency. Give reason also:

(c) 1-Butene shows C=C stretching at 1650 cm\(^{-1}\) in its IR spectrum whereas 1,3-Butadiene shows C=C stretching at 1610 cm\(^{-1}\). Explain giving reason. (3×4)
4. (a) Calculate the $\lambda_{\text{max}}$ (nm) for the following compounds:

(i) ![Diagram](image)

(ii) ![Diagram](image)

*Base values for:*

Acyclic/heteroannular diene = 214 nm

Homoannular diene = 253 nm

*Addition for each substituent:*

Alkyl substituent or ring residue = 5 nm

Exocyclic double bond = 5 nm

Double bond extending conjugation = 30 nm

(b) Identify the geometric isomers of stilbene ($C_6H_5-CH=CH-C_6H_5$) from their $\lambda_{\text{max}}$ values of 294 nm and 274 nm giving reason for the assignment.

(c) Define bathochromic and hypsochromic shifts? Predict the shift in $\lambda_{\text{max}}$ value of phenol when its UV spectrum is first recorded in neutral and then in alkaline medium? Give reasons for the answer. (3×4)

5. (a) Give one synthesis of Methyl Orange? Why is it red at a pH below 3.1 and yellow above pH 4.4. Explain with the help of suitable structures.

(b) Write the three possible structures that arise out of different ways in which two Isatin units may link to form indigo (M.F. = $C_{16}H_{10}N_2O_2$). Give the reaction that establishes the correct linkage and explain.

P.T.O.
(c) Coupling of diazonium salt with phenol is favoured in mildly alkaline medium while coupling of diazonium salt with aniline is favoured in mildly acidic medium. Give reasons. 

6. (a) Give the mechanism involved when vinyl chloride is polymerised in presence of benzoyl peroxide?

(b) How is polyester synthesised. Also give the synthesis of its monomer units?

(c) List the following group of monomers in order of decreasing ability to undergo anionic polymerization. Give reason for your answer?

\[ \text{CH}_2=\text{CH}-\text{CH}_3 \quad \text{CH}_2=\text{CH}-\text{Cl} \quad \text{CH}_2=\text{CH}-\text{CN} \] 

7. (a) An organic compound A with molecular formula \( \text{C}_x\text{H}_y\text{O} \) gave following spectral data:

UV: \( \lambda_{\text{max}} \) 292 nm \( \varepsilon_{\text{max}} \) 16

IR shows important bands at 2862(w) and 1722cm\(^{-1}\) (s)

NMR: \( \delta \) 2.8 (2H, d); 7.27(5H, s); 9.78(1H, t)

Explaining the UV, IR and NMR data, derive the structure of the compound?

(b) Explain the following terms with example:

(i) Mordant dyes

(ii) Thermoplastics

8. Write short notes on the following (any three):

(a) Biodegradable polymers

(b) Synthetic rubber

(c) Edible dyes

(d) Phthalein dyes

(3\times4)

(1600)