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.

Questions no. 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.

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.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it. Answers must be written in **ENGLISH** only.

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.

SECTION A

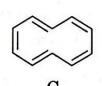
Q1. Answer the following:

5×8=40

(a) Classify the following compounds as aromatic, antiaromatic and non-aromatic. Explain your answer.



S B



D

(b) Discuss the role of crossover experiments in determining the reaction mechanism.

C-MNS-S-CHE

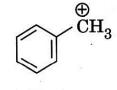
Quinuclidine reacts much faster with ethyl iodide than triethyl amine in (c) S_N2 reaction. Explain.

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Arrange the following carbocations in decreasing order of their stability. (d) Give reason in support of your answer.

5





C



A

Arrange the following in decreasing order of basicity. Give explanation (e) to justify your answer.

5



 $(\mathrm{CH_3CH_2})_3\mathrm{N}$



A

B

C

Write the products formed in the following reactions: (f)

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$$\frac{\text{KOH, 4 m}}{\text{EtOH. }\Delta}$$

(ii)

(ii)
$$CH_3 \xrightarrow{KOH} CH_3$$

(g)

Write the products formed in the following reaction sequence:

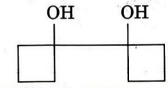
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$$\frac{\text{PhLi}}{\text{Dry ether}} \quad A \quad \xrightarrow{\text{(i)} \quad \text{Me}} \stackrel{\text{H}}{\longrightarrow} \quad B$$

(h)

Write the product and mechanism of the reaction:

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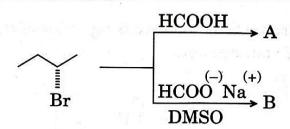
 $\stackrel{\text{H}^+}{\longrightarrow}$?

Q2. (a) (i) Write the outcome of the reaction and predict the reaction to $S_N 1$ or $S_N 2$ in each case.

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(ii) Show the products of the following reactions:

(I) OTs OAc ?

(II)
$$OAc^{(-)}$$
 ?

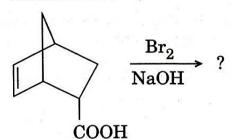
(b) On attempted E₂ reaction, A reacted much faster than B, while C reacted much faster than D. Explain with writing the product of the reaction in each case.

C-MNS-S-CHE

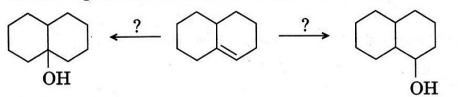
(c) (i) What product can one expect from the following reaction? Depict the stereochemical outcome at every step.

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(ii) What reagents are needed to bring the transformation?



- (d) Write a short note on aromatic character of sydnones. 10
- Q3. (a) Write the structure of the product formed.

(i)
$$\xrightarrow{\text{AgNO}_3}$$
 ?

(ii)
$$N \longrightarrow Ph \longrightarrow NaOH$$
?

(b) Complete the following pericyclic reactions: 10

(ii)
$$OH$$

$$\downarrow_{u_{n_{i}}} = \Delta ?$$
5

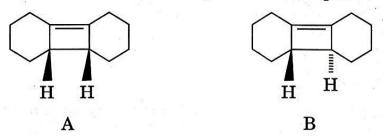
- (c) (i) Explain correlation diagrams for electrocyclic interconversion of 1,3-butadiene and cyclobutene.
 - $^{\circ}$ the $^{\circ}$

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(ii) One of the cyclobutenes on heating reacts very fast while the other reacts at extremely slow rate. Explain.



- (d) Write the products in the following reactions:
 - (i) \longrightarrow + Cl₂CH C Cl $\xrightarrow{\text{Et}_3\text{N}}$? $\xrightarrow{\text{(i)}}$ Zn, AcOH \longrightarrow ? \longrightarrow ?

(ii)
$$\overbrace{\frac{\text{p-ClC}_6\text{H}_4\text{NCO}}{\text{Et}_3\text{N, Benzene, 25°C}}}^{\text{NO}_2}?$$
 5

- **Q4.** (a) Suggest a mechanism for the following reactions:

(ii)
$$CHO$$
 OH Cl H_2O_2 , NaOH OH OH OH

- (b) Claisen-ester condensation is possible with substrates of type A but not possible with type B. Explain by writing the mechanism. 10
- (c) Discuss the mechanism of the reaction by writing the product.

$$\begin{array}{c|c}
 & \frac{\operatorname{ZnCl}_2}{\operatorname{HCl}}
\end{array}$$
?

(d) What are stabilized and unstabilized ylids? How does E-Z selectivity in Wittig reaction depend upon the nature of ylid? Explain. 10

SECTION B

Q5. Attempt the following:

5×8=40

- (a) Write the names of monomers of the following polymers and classify them as addition or condensation polymers:

5

- (i) Teflon
- (ii) Bakelite
- (b) Name the products obtained on complete hydrolysis of DNA and give their structures.
- 5

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- (c) Write the structure of X, Y and Z.
- (d) Formulate the product(s) and give the mechanism for the following reaction:
 - $Ph \xrightarrow{Ph} h\nu$
- (e) A compound contains two types of protons which exhibit signals at 139·2 Hz and 430·2 Hz downfield from TMS in a spectrometer operating at 60 MHz. What will be their relative position when measured on a 100 MHz instrument?
- 5

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- (f) Explain the following variations in λ_{max} (in nm) of CH₃Cl (173), CH₃Br (204), CH₃I (258).
- (g) Why is a bathochromic shift observed with increasing conjugation in electronic spectra? Explain.
- (h) What is McLafferty rearrangement in Mass Spectrometry? Mass spectrum of 1-phenyl butanone exhibits m/z (mass by charge) 105 as a base peak and m/z 120 as one of the major peaks. Explain.

Q6.	(a)	Calculate \overline{M}_n and \overline{M}_w for a polymer that consists of 10% by weight of a macromolecule of molecular weight 10,000 and 90% by weight of a macromolecule with molecular weight 1,00,000.
	(b)	How will you determine the molecular weight of a polymer solution using Ostwald viscometer?
	(c)	State whether <i>true</i> or <i>false</i> . If false, give the correct statement. $2 \times 5 = 10$
		(i) Polyvinyl alcohol can be prepared by polymerization of vinyl alcohol.
		(ii) CH ₄ can be polymerized.
		(iii) C ₂ H ₂ and aniline cannot be polymerized.
		(iv) Polymers have sharp melting point.
		(v) Ziegler-Natta catalyst is used for the preparation of syndiotactic polymer.
	(d)	What is an oligopeptide? How is it different from a polypeptide? What is the secondary structure of protein?
Q7 .	(a)	An organic liquid with molecular formula C ₆ H ₁₀ O gave the following
		spectral data:
		UV: v_{max} 230 nm (ϵ 12600), 329 nm (ϵ 41)
		IR: $v_{\text{max}} 2950 - 2860 \text{ (m)}, 1695 \text{ (s)}, 1620 \text{ (m)}, 1460 \text{ (m)} \text{ cm}^{-1}$
		NMR: δ 1:9 (s, 3H), 2:1 (s, 6H), 6:15 (s, 1H)
		Write the possible structure of compound with suitable justification. Predict its ¹³ C-NMR spectrum.
	(b)	How can the NMR spectrum distinguish between the isomers — p-xylene and ethyl benzene? Justify your answer.
	(c)	Give the ESR spectra of Naphthalene negative ion, Anthracene negative ion and Triphenyl methyl radical.

Q8. (a) Complete the reactions and give appropriate mechanisms of the following: $10\times3=30$

(i) Ph
$$\Delta X \xrightarrow{H_2SO_4} Y$$
NO₂ 10

(ii)
$$O \longrightarrow h \nu$$

H

(iii)
$$h\nu$$

$$O$$

$$Ph$$

$$O$$

$$Ph$$

$$O$$

$$Ph$$

(b) (i) Explain how many molecules of formaldehyde and formic acid are formed in the reaction.

(ii) Identify the X.

$$\xrightarrow{\text{m-CPBA}} X$$

