

CHEMISTRY

(Paper II)

Time Allowed : Three Hours

Maximum Marks : 250

QUESTION PAPER SPECIFIC INSTRUCTIONS

(Please read each of the following instructions carefully before attempting questions)

There are EIGHT questions divided in two Sections.

Candidate has to attempt FIVE questions in all.

Question Nos. 1 and 5 are compulsory and out of the remaining, any THREE are to be attempted choosing at least ONE question from each Section.

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

Wherever any assumptions are made for answering a question, they must be clearly indicated.

Word limit in questions, wherever specified, should be adhered to.

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.

SECTION 'A'

1. (a) Addition of bromine to ethylene in methanol gives bromomethyl methyl ether as one of the products. Formulate the reaction and give mechanistic explanation for the formation of this product. 10
- (b) The dehydrobromination of isopropylbromide requires several hours of refluxing in alc. KOH, whereas, in $t\text{-BuO}^-\text{K}^+/\text{DMSO}$, dehydrobromination can be carried out in less than a minute at room temperature. Give reason for this observation. 10
- (c)(i) Explain why the rate of the reaction: $(\text{C}_6\text{H}_5)_2\text{CHCl} + \text{F}^- \xrightarrow{\text{liq. SO}_3}$ gradually decreases with the progress of reaction. 5
- (c)(ii) Describe a simple chemical test to distinguish between aniline and benzylamine. 5
- (d) Isobutene is treated with conc. HBr in the presence of dibenzoyl peroxide in acetonitrile solution. Formulate the reaction and give explanation for the formation of the product. 10
- (e) Write the products (X) and (Y) in the following reactions:
[Figure: Reaction scheme: $\text{CH}=\text{CH}$ branching into two arrows: upper arrow labelled $\text{H}_2\text{CrO}_4 \rightarrow (\text{X})$; lower arrow labelled alk. $\text{KMnO}_4 \rightarrow (\text{Y})$] 10
2. (a) Explain why $(M + 1)$ ion peak is observed in mass spectrometry. Indicate, which electron is most likely to be lost in the ionization of following compounds and write the radical cation formed: (i) $\text{CH}_2=\text{O}$ (ii) $\text{CH}_2=\text{CH}_2$ (iii) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ (iv) CH_3Cl . 20
- (b) 1-chloromethyl cyclopropane on hydrolysis chiefly gives three products. Write a mechanism to show their formation. 15
- (c) An organic compound (X) reacts with aq. $\text{HO}^\ominus$. Write the following: (i) If (X) is dextro, comment on the optical activity of the product. (ii) If concentration of OH^- is doubled, how rate of the reaction will change? (iii) Draw energy profile diagram for the reaction. (iv) Write the mechanism of the reaction. (v) If C_2H_5 and C_6H_5 in (X) are replaced by H, comment on the optical activity of the product.
[Figure: Structure printed after the first sentence: (X) = a central C bonded to CH_3 , C_2H_5 , C_6H_5 and Cl (2-chloro-2-phenylbutane), labelled (X); no stereochemistry shown] 15
3. (a) The compound $\text{C}_2\text{H}_2\text{BrCl}$ exhibits three isomeric structures. The three isomers in proton NMR exhibit two doublets each having $J \sim 1.5, 9$ and 14 Hz respectively. Write the structures of isomers and assign J values to each one of them. 20
- (b) Describe using appropriate reagents and conditions a method to achieve the following transformations: 20

[Figure: Multistep conversion (three stacked arrows): methyl 6-oxobicyclo[2.2.1]heptane-2-carboxylate (norbornane skeleton with a ring C=O on one two-carbon bridge and a $-\text{C}(=\text{O})-\text{OCH}_3$ group on the other two-carbon bridge, both on the carbons attached to the same bridgehead) $\Rightarrow$ 6-(hydroxymethyl)bicyclo[2.2.1]heptan-2-one (same skeleton, ketone retained, the ester replaced by CH_2OH)]

- (c) Write the products of the following reactions and give the suitable mechanism:

[Figure: (i) 2-cyclopropylcyclohexanone: cyclohexanone with a cyclopropyl group on the carbon α to the $\text{C}=\text{O}$, arrow $h\nu$ over, NS-I under; (ii) cyclodecanone drawn as a ten-membered ring folded into two hexagon-like halves sharing the $\text{C}=\text{O}$ carbon (top) and the transannular carbon C-6 (bottom): the $\text{C}=\text{O}$ oxygen points into the ring towards C-6, whose two H atoms are drawn one hashed and one wedged; arrow $h\nu$ over, NS-II under]

10

4. (a) Identify [X] and [Y] in the following reactions. Explain their formation.

[Figure: (i) cis-1,2-diphenylbenzocyclobutene: benzocyclobutene (benzene ring fused to a cyclobutane ring) with a Ph on each of the two four-membered-ring sp^3 carbons, both Ph drawn with wedged bonds (cis); branching arrows: $\Delta \rightarrow [\text{X}]$, $h\nu \rightarrow [\text{Y}]$. (ii) "2" $\times$ cyclohepta-2,4,6-trien-1-one (tropone: seven-membered ring with $\text{C}=\text{O}$ and three $\text{C}=\text{C}$); branching arrows: $\Delta \rightarrow [\text{X}]$, $h\nu \rightarrow [\text{Y}]$. (iii) bicyclo[2.1.0]pent-2-ene (cyclobutene ring with a cyclopropane ring fused on the edge opposite the $\text{C}=\text{C}$; drawn as a square with a triangle on top and the double bond at the bottom edge); branching arrows: Δ , Low temp. $\rightarrow [\text{X}]$; Δ , High temp. $\rightarrow [\text{Y}]$]

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- (b) How will you prepare styrene using Wittig reaction? Write the name of reactants and explain the mechanism of the reaction.

20

- (c) Write a mechanism for the following conversion: α -pinene hydrochloride $\longrightarrow$ [structure]

[Figure: The [structure] is drawn as a cyclohexane ring with a vertical line from the top ring carbon (extending above the ring as a methyl) to the bottom ring carbon, crossed by a short horizontal line (the $\text{C}(\text{CH}_3)_2$ bridge), and Cl on the ring carbon adjacent to the top carbon, i.e. bornyl chloride (2-chloro-1,7,7-trimethylbicyclo[2.2.1]heptane); it is not named in the paper]

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SECTION 'B'

5. (a) Describe the products obtained by the treatment of cis- and trans-2-phenyl-1-cyclohexanol with H_3PO_4 .

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- (b) What is the major product of each of the following reactions? (i) $(\text{CH}_3)_3\text{COO}-\text{OH}/\text{HO}^\ominus$ and (ii) $\text{OsO}_4/\text{t-BuOH}$. Give the mechanisms of the reactions.

[Figure: Printed before "(i) ...": cyclohexene drawn with the two vinylic H atoms shown on the $\text{C}=\text{C}$ carbons –(i) and (ii) $\rightarrow$ (no product shown)]

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- (c) Identify [X] and [Y] in the following:

[Figure: 2-Pentyne with two branching arrows: upper arrow labelled $\text{Na}/\text{NH}_3 \rightarrow [\text{X}]$; lower arrow labelled Lindlar's Catalyst $\rightarrow [\text{Y}]$]

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- (d) How many NMR signals do you expect in: $\text{H}_3\text{CH}_2\text{C}-\text{C}_6\text{H}_4-\text{CH}_2\text{CH}_3$? Explain their nature.

[Figure: the compound is drawn as $\text{H}_3\text{CH}_2\text{C}-$ and $-\text{CH}_2\text{CH}_3$ attached para to each other on a benzene ring (1,4-diethylbenzene)]

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- (e) Formulate the reaction: and give a mechanism to explain the formation of the product.

[Figure: Reaction: cyclobutane ring in which two adjacent carbons each bear OH and Ph (1,2-diphenylcyclobutane-1,2-diol; OH drawn up on the upper carbon and down on the lower carbon) $-\text{H}^+ \rightarrow$?]

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6. (a) An organic compound $\text{C}_4\text{H}_8\text{O}$ gives a strong absorption band at 1710 cm^{-1} in IR spectrum. In proton NMR, it gives signal at δ 1.1 (triplet), 2.1 (singlet) and 2.3 (quartet). Write the likely structure of the compound and assign the δ values.

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- (b) Write the steps involved in the conversion of 4-bromobutanal to 4-methoxybutanal.

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- (c) Amino acids on treatment with ninhydrin give intense blue colour. What is this colouration due to?

15

7. (a) Write the name and structure of one polymer having: (i) Linear structure (ii) Network structure (iii) Three dimensional structure. Write the mechanism for the polymerization of phenol and formaldehyde in the presence of H^+ .

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- (b) Explain why free radical polymerization of 1, 3-butadiene leads to macromolecules having two different types of monomer units. 15
- (c) Write the name and structure of two purine and pyrimidine units present in DNA. Also explain why most of the genetic materials contain DNA and not RNA. 15
8. (a) Write the products of the following name reactions:
 [Figure: Ten substrates drawn as structures, each followed by an arrow carrying the reaction name (no products shown): (i) camphor (cyclohexane ring with a bridge drawn as a vertical line through the ring, extending above the top carbon, crossed by a short horizontal line; C=O on the ring carbon next to the top carbon) –Baeyer-Villiger →; (ii) 2-nitrobenzaldehyde (benzene ring with CHO and NO₂ on adjacent carbons) –Perkin reaction →; (iii) 1-tetralone, 3,4-dihydronaphthalen-1(2H)-one (benzene fused to a cyclohexanone, C=O adjacent to the ring fusion) –Reformatsky reaction →; (iv) indole (benzene fused to a pyrrole ring with N–H) –Reimer-Tiemann →; (v) diethyl adipate drawn vertically as CH₂COOC₂H₅ / (CH₂)₂ / CH₂COOC₂H₅ –Dieckmann reaction →; (vi) 1,2-diacetoxybenzene (benzene ring with two OCOCH₃ groups on adjacent carbons) –Frie’s rearrangement →; (vii) furan (five-membered ring with one O and two C=C double bonds; no substituent drawn) –Cannizaro reaction →; (viii) diethyl oxalate drawn as COOC₂H₅ over COOC₂H₅, + cyclohexanone –Claisen condensation →; (ix) 2-chlorocyclohexanone (cyclohexanone with Cl on the α-carbon) –Favorskii rearrangement →; (x) nicotinamide (pyridine with CONH₂ at C-3) –Hoffmann rearrangement →] 40
- (b) Identify (X) and (Y) in the following:
 [Figure: Reaction scheme: cyclohexene –O₃ → (X) –NaBH₄ → (Y)] 10