

CHEMISTRY

(Paper II)

Time Allowed : Three Hours

Maximum Marks : 300

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.

SECTION 'A'

1. Answer any three of the following:

20×3=60

- (a)(i)** Which of the following compounds are aromatic? Give reasons to justify your answer.
 [Figure: I = [10]annulene, all double bonds cis ("cis, cis, cis, cis, cis"); II = [10]annulene with one internal H ("trans, cis, cis, cis, cis"); III = [10]annulene with two internal H drawn as two fused-looking rings ("trans, cis, trans, cis, cis"); IV = 1,6-methano[10]annulene (bicyclic ten-carbon perimeter bridged by CH₂); V = monocyclic polyene ring containing one ring O (oxonin, ring size as drawn [?]); VI = monocyclic polyene ring containing one ring BH (boronin, ring size as drawn [?])]
- (a)(ii)** pK_a of cycloheptatriene is about 39 but that of cyclopentadiene is 16. Explain.
- (a)(iii)** The triene (A) can be readily deprotonated twice with a base to give a stable dianion (B). In contrast to this, the neutral analogue (C) is quite unstable. Explain it.
 [Figure: A = dihydropentalene (two fused five-membered rings with C=C double bonds, two sp³ CH₂ carbons) → B = pentalene dianion (same bicyclic skeleton, fully unsaturated, charge 2- marked); C = pentalene (bicyclo[3.3.0]octa-tetraene, neutral)]
- (b)** Give stereochemistry of the product that you would expect from each of the following electrocyclic reactions:
 [Figure: (i) (2E,4Z,6E)-octa-2,4,6-triene (drawn U-shaped: terminal CH₃ groups pointing outward, terminal H inward) → Heat (label below arrow illegible [?]) → ?; (ii) trans, trans-2,4-hexadiene (drawn s-cis: CH₃ at both ends pointing outward, H inward; label "trans, trans 2,4-hexadiene") → hν → ?]
- (c)** Provide mechanism for the following reactions (Use "electron pushing" arrows only, do not use words)
 [Figure: (i) cyclohexanone + CH₂N₂ → cycloheptanone (63% [?]) + 1-oxaspiro[2.5]octane (methylenecyclohexane oxide, epoxide spiro to cyclohexane) (17% [?]) + cyclooctanone (minor). (ii) cyclopentylmethylamine (cyclopentyl-CH₂NH₂) → HNO₂ → methylenecyclopentane (cyclopentane=CH₂) + cyclopentylmethanol (printed "-CH₂OH₂") + 1-methylcyclopentanol (ring carbon bearing OH and CH₃) + cyclohexanol + cyclohexene]
- (d)** Formulate a mechanism for the depletion of atmospheric ozone layer by CFC.

2. **(a)** Give mechanism of the following reactions:

(Use "electron pushing" arrows only. do not use words)

[Figure: (i) 1-acetyl-1-chlorocyclohexane (ring carbon bearing Cl and -C(=O)-CH₃) → 1. OH⁻; 2. H⁺ → 1-methylcyclohexane-1-carboxylic acid (ring carbon bearing CH₃ and COOH). (ii) 2-chlorocyclohexanone → C₂H₅O⁻ → ethyl cyclopentanecarboxylate (cyclopentyl-C(=O)-OC₂H₅). (iii) cyclohexanone → CF₃C(O)-O-OH (printed "CF₃C-O-OH") → ε-caprolactone (seven-membered ring: O-C(=O)). (iv) 1-(3-hydroxypentan-3-yl)cyclopentanol (cyclopentane C1 bearing OH and C(OH)(Et)₂) → H⁺ → 2,2-diethylcyclohexanone + 1-(1-ethylcyclopentyl)propan-1-one (cyclopentane C1 bearing Et and C(=O)-Et)]

30

- (b) Explain the following: (i) When cis-2-chlorocyclohexanol is treated with a base, the product is cyclohexanone. (ii) Why does trans-1-bromo-4-*t*-butyl cyclohexane undergo E^2 reaction in presence of OEt⁻ ion much more slowly than corresponding cis-isomer? **30**
3. (a) Predict the product(s) of the following reactions and give the mechanism of their formation
 [Figure: (i) acetaldehyde phenylhydrazone ($C_6H_5-NH-N=CH-CH_3$) $\xrightarrow{-ZnCl_2}$ A $\xrightarrow{-DMF + POCl_3}$ B. (ii) anthranilic acid (2-aminobenzoic acid) $\xrightarrow{-RONO, Et_2O}$ A $\xrightarrow{-Heat \text{ in } 1,2\text{-dichloro ethane}}$ B; B $\xrightarrow{-Dimerization}$ C; B $\xrightarrow{-I_2}$ D; B $\xrightarrow{-furan}$ E. (iii) 1-methylcyclopentene $\xrightarrow{-THF : BH_3}$ A $\xrightarrow{-Heat 160^\circ}$ B $\xrightarrow{-H_2O_2, OH^-}$ C. (iv) cyclohexanone + methyl vinyl ketone ($CH_2=CH-CO-CH_3$) $\xrightarrow{-Base}$ A $\xrightarrow{-Aldol \text{ Condensation (Base)}}$ B $\xrightarrow{-H^+}$ C] **30**
- (b) Which compound in the following pairs will hydrolyse faster
 [Figure: (i) $C_6H_5-CH_2-CH_2OTs$ OR $p-CH_3O-C_6H_4-CH_2CH_2OTs$ (OMe para). (ii) two chair cyclohexanes, each with SC_6H_5 on C1 and Cl on C2: left = SC_6H_5 axial (up) and Cl axial (down), H equatorial on both carbons (trans-diaxial); OR right = SC_6H_5 equatorial (H axial up) and Cl axial (down) (cis)] **30**
4. (a) Outline the mechanism of formation of B from A in the following reactions:
 [Figure: (i) A = cyclopentanone oxime ($C=N-OH$) $\xrightarrow{-H_2SO_4}$ B = 2-piperidinone (δ -valerolactam, $HN-C=O$ in a six-membered ring). (ii) A = 1-(chloromethyl)-1-methylcyclopentane (ring carbon bearing CH_3 and CH_2Cl) $\xrightarrow{-Aqueous AgNO_3}$ B = 1-methylcyclohexan-1-ol (ring carbon bearing CH_3 and OH)] **20**
- (b) Give the mechanism of the following reaction:
 [Figure: $2 C_6H_5CHO \xrightarrow{CN^-} C_6H_5-CO-CH(OH)-C_6H_5$ (benzoin)]
 Explain the following points about this condensation reaction: (i) Why is this condensation catalysed only by CN^- not by OH^- and OEt^- ions? (ii) Why do electron attracting substituents inhibit this condensation? (iii) Why do electron attracting substituents inhibit this condensation? **20**
- (c) In principle one of the following Diels-Alder reactions could give two products, while the other must product only one. Explain
 [Figure: (i) cyclohexa-1,3-diene + maleic anhydride $\xrightarrow{-\Delta}$ $\xrightarrow{-H_2/Pd}$; (ii) six-membered-ring 1,3-diene drawn with its double bonds on the left side of the ring (appears to be cyclohexa-1,3-diene drawn in a different orientation; exact diene unclear [?]) + maleic anhydride $\xrightarrow{-\Delta}$ $\xrightarrow{-H_2/Pd}$] **20**

SECTION 'B'

5. Answer any three of the following:

20×3=60

- (a) Give mechanism of the following transformations:
 [Figure: (i) 2-aminocyclohexanol $\xrightarrow{-HNO_2}$ cyclopentanecarbaldehyde. (ii) cyclopentanone $\xrightarrow{-Mg/Ether}$ 1,1'-bi(cyclopentyl)-1,1'-diol $\xrightarrow{-H_2SO_4}$ spiro[4.5]decan-6-one (cyclohexanone spiro-fused at C2 to cyclopentane). (iii) methyl 1,3-dioxindane-2-carboxylate (indane-1,3-dione with $COOMe$ on C2) $\xrightarrow{-CH_2N_2}$ methyl 1,4-dihydroxynaphthalene-2-carboxylate (OH at C1 and C4, $COOMe$ at C2)]
- (b) Explain the following: (i) Optically active cis-2, 3-dimethylcyclobutane on reaction with diazomethane yields an optically inactive meso product. (ii) Solvolysis of optically active 3-phenyl-4-bromobutane in hot acetic acid yields an optically inactive ester.
- (c) Give mechanism to account for the formation of the following product(s)
 [Figure: (i) dimethyl hexanedioate drawn as a chain with two $COOMe$ ends $\xrightarrow{-2 Na, Ether}$ 2-hydroxycyclohexanone (acyloin). (ii) 2-methylcyclohexanone drawn as a chair with Me axial at C2 and $C1=O$ $\xrightarrow{-LiAlH_4}$ A (Less stable) 25% [?] + B (More stable) 25% [?]; same ketone $\xrightarrow{-R_2BH}$ (R_2 = bulky group) $\rightarrow$ A 100%]
- (d) When acetone is treated with a base, a higher boiling liquid (b.p. $130^\circ C$) can be isolated from the reaction mixture. The spectral data of this compound are as follows: IR, (cm^{-1}): 1620, 1695; UV; λ_{max} : 238 nm (ϵ_{max} 11,700); ^1H NMR; δ : 1.9 (3H, S), 2.1 (6H, S), 6.15 (1H, S); MS; m/z (R.A.): 98 (49%), 83 (90%); 55 (100%); 43 (78%). Deduce the structure of the compound.
6. (a)(i) What is sigmatropic reaction? Illustrate [1, 3], [1, 5] and [3, 3] sigmatropic reactions. (ii) Why is thermal [4 + 2] cycloaddition of 1, 3-butadiene and ethylene easy but [2 + 2] addition difficult? (iii) Explain the following observations: **20**

[Figure: 1-allyl-2-(but-3-en-2-yloxy)-3-methylbenzene (aryl ether: O-CH(CH₃)-CH=CH₂ on C2, CH₃ on C3, allyl CH₂-CH=CH₂ on C1; both ortho positions blocked) -Δ → 2-allyl-4-(but-3-en-2-yl)-6-methylphenol (OH, CH₃ and allyl on the ring as before, CH₃-CH(-CH=CH₂)-para to OH) and 2-(but-2-enyl)-4-allyl-6-methylphenol (crotyl CH₂-CH=CH-CH₃ ortho to OH, allyl para to OH, CH₃ ortho)]

- (b) Draw structures of all the products which are expected to be formed in the following reactions:
[Figure: (i) cyclohex-2-en-1-one + (CH₃)₂C=CH₂ (isobutylene) -hv → ?; (ii) C₆H₅CHO + CH₃CH=CHCH₃ (2-butene drawn with the two CH₃ on the same side, cis) -hv → ?] 20
7. (a) Draw structures of the repeating units of the following polymeric materials (i) Teflon (ii) Terylene (iii) Nylon (iv) Natural rubber 12
- (b) The light catalysed reaction of nitrosyl chloride with cyclohexane gives an intermediate which has an important role in the formation of nylon 6. What is the structure of this intermediate? Outline the further steps which would be necessary for the nylon synthesis. 12
- (c)(i) What are nucleotides and nucleosides? Draw the structure of a nucleotide. (ii) When a nucleotide (3', 5'-cyclic adenylic acid) is treated with aqueous sodium hydroxide the major product that is obtained is, 3'-adenylic acid (rather than 5'-adenylic acid). Give an explanation to account for the preference to the cleavage of C₅-oxygen bond in the hydrolysis. 12
- (d) Silk consists of β-sheets whose polypeptide chains are made up of the repeating amino acid sequence: Gly-Ser-Gly-Ala-Gly-Ala. What characteristics of these amino acid side chains appear to favour the stability of β-sheet structure? 12
- (e) Predict the mechanism of the following reactions:
[Figure: (i) 2-(1-chloroethyl)-1-methylpyrrolidine (N-CH₃; ring C2 bearing CH(CH₃)Cl) -Heat → 3-chloro-1,2-dimethylpiperidine (N-CH₃, C2-CH₃, C3-Cl). (ii) partial steroid D-ring (brackets indicate the rest of the molecule; angular methyl at the ring junction) as a cyclopentanone bearing an α-oximino group (C=N-OH next to C=O) -Ac₂O, pyridine → six-membered ring (ring-expanded) containing C=O, N and C-OAc (the N in the ring between the C=O carbon and a C bearing OAc) [?]] 12
8. (a) The following dienes in ethanol have λ_{max}'s at 231 nm (ε 21,000), 236 nm (ε 12,000), 245 nm (ε 18,000), 265 nm (ε 6,400) and 282 nm (ε 11,900). Indicate which diene corresponds to which spectrum.
[Figure: Five dienes: (1) steroid (angular methyls, R at C17) with a heteroannular diene Δ^{7,9(11)} (C7=C8 and C9=C11); (2) steroid (angular methyls, R at C17) with a homoannular diene Δ^{5,7} in ring B; (3) cyclohexadiene ring with CH₃ at C1 and CH(CH₃)₂ at C4 (p-menthadiene, α-terpinene type [?]); (4) cyclohexadiene ring with CH₃ at C1 and CH₃ [?] at C4 (1,4-dimethylcyclohexa-1,3-diene type [?]); (5) 1,1'-bi(cyclohex-1-enyl) (two cyclohexene rings joined through their C1 atoms)] 15
- (b)(i) Which compound A or B is expected to show lower stretching frequency for C = O group in the IR spectrum? (ii) How do trimeric phosphonitrilic halides compare with benzene in structure and reactivity?
[Figure: A = 4'-methoxyacetophenone (CH₃-CO-C₆H₄-OCH₃, para); B = 4'-nitroacetophenone (CH₃-CO-C₆H₄-NO₂, para)] 15
- (c) A characteristic peak at m/z 58 is shown by 2-pentanone [M⁺ 86] in the mass spectrum. An isomer of this gives peaks at m/z 71 and 43, but not at m/z 58. What is the structure of this compound? Another isomer of this gives peaks at m/z 86 and 57. Identify this isomer. 15
- (d) Spectral data of a compound (molecular formula C₇H₆O₂) are given below. Suggest a structure to this compound which is consistent to the spectral data. (i) UV; λ_{max} (EtOH; (ε_{max}): 256 nm (12 600), 324 nm (3,400) (ii) IR; (cm⁻¹): 3175-3275 (broad). 1667 (strong), 1616, 1580, 1484, 1456, 1383, 1230, 1205, 1151, 1115 and 1029 (iii) ¹H NMR; (δ_{ppm}): 10.83 (1H, S) which disappears on addition of D₂O 9.59 (1H, S) 7.31-6.79 (4H, m) (iv) Ms; m/z (Relative abundance): 122 (M⁺ 100%), 121 (96%) 93 (18.5%), 29 (31%) 15