

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. (a) (i) Which molecule can follow electrophilic substitution?
 [Figure: Two structures, labelled I and II, joined by "or": I = cyclooctatetraene drawn as an eight-membered ring of CH units with four alternating C=C double bonds (each carbon bearing one H); II = [18]annulene drawn as an 18-membered ring with nine alternating C=C double bonds, twelve H atoms pointing outwards and six H atoms pointing into the ring]
 (ii) 1,5-cyclooctadiene is treated with I-Cl. What is the structure of the product? 12
- (b) (i) [structure] is exposed to $u - v$ light and compounds C and D are produced. What are the structures of C and D? (ii) 1,3-butadiene is treated with SO_2 . What product will be formed?
 [Figure: The structure in (i): 5-methylcyclopent-2-en-1-one – cyclopentenone ring with C=O, a ring C=C conjugated with it, and a Me group on the ring carbon on the other side of the C=O]
12
- (c) (i) Acetaldehyde is treated with excess formaldehyde in presence of $\text{Ba}(\text{OH})_2$ and the reaction produces a solid organic compound. What is the structure of solid organic compound? (ii) Which one of these two compounds (I and II) has aromaticity?
 [Figure: I = a 14-membered monocyclic carbon ring containing six conjugated C=C double bonds and one $\text{C}\equiv\text{C}$ triple bond (a didehydro[14]annulene: the triple bond lies in a linear $\text{C}-\text{C}\equiv\text{C}-\text{C}$ segment at the bottom of the ring); "and" II = cycl[3.3.3]azine: a central N atom common to three fused six-membered rings (tricyclic, 12 C + N), the peripheral ring carbons bearing alternating C=C double bonds]
12
- (d) (i) When compound A is treated with alkali what product is formed? Show the mechanism of the conversion.
 [Figure: A = cyclodecane-1,6-dione: ten-membered carbocyclic ring with two C=O groups on opposite carbons (1 and 6)]
 (ii) What is the structure of the compound produced from B on exposure with $u - v$ light?
 $\text{B} = \text{Ar}-\text{CH}(\text{Ar})-\text{C}(=\text{O})-\text{Ar}$, Ar = 2,4,6-trimethyl phenyl
 [Figure: B drawn as Ar – CH – C – Ar with a second Ar on the CH (bond drawn downwards) and =O on the C (drawn downwards), i.e. 1,2,2-triaryl-ethanone, Ar = mesityl]
12
- (e) (i) Isobutylene after reaction with H_2SO_4 at 80°C , is hydrogenated using Ni-catalyst. Write the structure of final product and mechanism of its formation. (ii) Camphene hydrochloride (I) on heating in polar solvent produces isobornyl chloride (II). Write the mechanism of the conversion.
 [Figure: (I) camphene hydrochloride = 2-chloro-2,3,3-trimethylbicyclo[2.2.1]heptane: norbornane skeleton with one ring carbon bearing Cl and CH_3 and the adjacent ring carbon bearing two CH_3 groups; (II) isobornyl chloride = exo-2-chloro-1,7,7-trimethylbicyclo[2.2.1]heptane: norbornane skeleton with two CH_3 groups on the one-carbon bridge (C-7), a CH_3 on bridgehead C-1 and Cl on C-2 (exo)]
12
2. (a) Phthalimide is treated with alcoholic KOH and it produces a product A. A is treated with n-butyl bromide producing B. The product B is boiled with excess NaOH producing a volatile liquid C. After removal of C, the solution on acidification gives a solid organic 20

Give structures of compounds (A), (B), (C) and (D) in the following reactions: (i) n-Octaldehyde + Ethyl bromo acetate + Zn and then $\text{H}_2\text{O} \rightarrow$ (A) ($\text{C}_{12}\text{H}_{24}\text{O}_3$) (ii) (A)+ CrO_3 in glacial acetic acid $\rightarrow$ (B) ($\text{C}_{12}\text{H}_{22}\text{O}_3$) (iii) (B)+ $\text{C}_2\text{H}_5\text{O}^-\text{Na}^+$, then benzyl chloride $\rightarrow$ (C) ($\text{C}_{19}\text{H}_{28}\text{O}_3$) (iv) (C)+ OH^- , heat, then H^+ warm $\rightarrow$ (D) ($\text{C}_{16}\text{H}_{24}\text{O}$)

β -methyl crotonaldehyde ($\text{CH}_3)_2\text{C}=\text{CH}-\text{CHO}$ on refluxing with dilute NaOH produces a product of chemical formula $\text{C}_{10}\text{H}_{14}\text{O}$. What is the structure of the product? Write mechanism of the formation.

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$$15 \times 4 = 60$$
$$\text{(b)} \quad \begin{array}{c} \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CD}_2\text{-NH}_2 \xrightarrow{\text{HONO}} \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CD}_2\text{-OH} + \text{CH}_3\text{-CH}_2\text{-CH(OH)-} \\ \text{-CHD}_2 + \text{CH}_3\text{-CH(OH)-CH}_2\text{-CHD}_2 \end{array}$$

(d) [Figure: Reaction scheme: 2-hydroxy-4-methoxybenzaldehyde (benzene ring with CHO, an OH ortho to it, and CH₃O para to the CHO) + CH₂=CH-P+Ph₃ Br⁻ + base → 7-methoxy-2H-chromene (2H-1-benzopyran: benzene ring fused to a ring -O-CH₂-CH=CH-, with CH₃O at C-7, i.e. para to C-4a and meta to C-8a which bears the ring O) + Ph₃PO]

[Figure: (I) exo-2-norbornyl tosylate (bicyclo[2.2.1]heptane with exo OTs on C-2); (II) exo-2-norbornyl acetate (exo OAc on C-2); (II) its mirror image, exo-norbornyl acetate drawn with AcO on the left-hand carbon (the enantiomer)]

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[Figure: structure 1 = cyclohex-2-en-1-yl hydroperoxide: cyclohexene ring with an $-O-OH$ group on the allylic carbon; structure 2 = an open chain of three CH_2 groups carrying a CHO group at each end, $OHC-(CH_2)_3-CHO$ (glutaraldehyde)]

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(c) Dihydropentalene (C_8H_8) is treated with two moles of n-butyl lithium and it produces a white crystalline compound A. NMR spectrum of A is as follows: a doublet δ 4.98 J = 3 Hz b triplet δ 5.73 J = 3 Hz and peak ratio of a : b = 2 : 1. What is the structure of A?

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5. (a) Tropolone [structure] has following characteristics: (i) Has high dipole moment (3.71 D). (ii) Follows Reimer – Tiemann reaction. (iii) Couples with diazonium ions. (iv) Follows nitration with dilute HNO_3 . What class of compounds does tropolone resemble? Is it stable in acid or basic medium? Explain.

[Figure: The structure after 'Tropolone': seven-membered ring with C=O and an adjacent C-OH and three ring C=C double bonds (2-hydroxycyclohepta-2,4,6-trien-1-one)]

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(b) (i) [structure 1] on heating produces trans 9,10-Dihydronaphthalene. What is the mechanism of this transformation? (ii) β -Lactone [structure 2] can be obtained by treatment of sodium maleate with Br_2 -water. Explain the mechanism of its formation.

[Figure: structure 1 = bicyclo[6.2.0]deca-2,4,6,9-tetraene: eight-membered ring with three C=C double bonds fused to a cyclobutene ring (C=C in the four-membered ring), the two ring-fusion carbons each marked with a dot (H); structure 2 = β -lactone drawn as a four-membered ring O-CH(CO₂H)-CHBr-C(=O), i.e. ring O bonded to a CH bearing CO₂H and to a C=O carbon, with CHBr between the CH and the C=O (3-bromo-4-oxooxetane-2-carboxylic acid)]

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(c) (i) Draw the rough-sketch of NMR spectra of $\text{CH}_2\text{Br}-\text{CHBr}_2$. (ii) Which bond has higher frequency in IR spectra? (1) $-\text{C}\equiv\text{N}$ (2) $-\text{C}\equiv\text{C}-$

12

- (d) (i) 1,4-butadiene carrying alkyl or aryl substitution on C-3, can photochemically rearrange to vinyl cyclopropane.
[Figure: Reaction scheme: 3,3-dialkyl-1,4-pentadiene ($\text{CH}_2=\text{CH}-\text{CR}_2-\text{CH}=\text{CH}_2$, the central carbon bearing R and R) $\xrightarrow{-h\nu}$ 1,1-di-R-2-vinylcyclopropane (cyclopropane with a vinyl group on one ring carbon and two R groups on an adjacent ring carbon)]
Explain the transformation. (ii) What are the structures of pyrimidine nucleotides present in DNA? What are the structures of their purine conjugates? 12
- (e) (i) The rate of rearrangement of hydroazobenzene to benzidine is proportional to square of concentration of H^+ in solution. Explain. (ii) Explain the mechanism of thermally allowed concerted reaction between cis-1,3-butadiene with ethylene using HOMO and LUMO. 12
6. (a) A or B when treated with $\text{KN}(\text{C}_2\text{H}_5)_2$ in diethyl amine, it produces only $\text{C}_9\text{H}_{11}\text{N}$. What is the product? Write mechanism of its formation.
[Figure: A = 1-chloro-2-[2-(methylamino)ethyl]benzene: benzene ring with $\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_3$ and Cl on adjacent (ortho) carbons; B = 1-chloro-3-[2-(methylamino)ethyl]benzene: benzene ring with $\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_3$ and Cl meta to each other] 15
- (b) Treatment of $\text{CH}_2=\text{CH}-\text{CN}$ with NH_3 produces $\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{CN}$ and $\text{NH}(\text{CH}_2-\text{CH}_2-\text{CN})_2$. Write mechanism of formation of these compounds. 15
- (c)(i) How can adiponitrile ($\text{N}\equiv\text{C}-(\text{CH}_2)_4-\text{CN}$) be produced from acrylonitrile? 8
- (c)(ii) Write the mechanism of formation of [structure] bisphenol.
[Figure: The structure (in brackets): bisphenol A, $\text{HO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{OH}$, each OH para to the central $\text{C}(\text{CH}_3)_2$] 7
- (d)(i) What are the products produced when phenyl acetate is heated with AlCl_3 ? Write the mechanism of formation. 8
- (d)(ii) What is the structural difference between Nylon-6 and Nylon 6,6? What are the raw materials of their synthesis? 7
7. (a) Resorcinol [structure] is heated with NaHCO_3 under pressure. What will be the product after acidification?
[Figure: resorcinol: benzene ring with two OH groups meta to each other (benzene-1,3-diol)] 15
- (b) Which has higher stretching frequency in IR spectra? Explain. (i) $>\text{C}-\text{Br}$ OR (ii) $>\text{C}-\text{Cl}$ 15
- (c) On treatment with aqueous HBr, both cis and trans 2-bromocyclohexanol are converted into the same product. What is the product? Explain with mechanism of conversion. 15
- (d) What are the reagents (A, B and C) used for the following conversion: (i) $\text{R}_2\text{C}(\text{OH})-\text{C}(\text{OH})\text{R}_2 \xrightarrow{\text{A}} \text{R}_2\text{C}=\text{O}$ (ii) $\text{C}_6\text{H}_5-\text{CO}-\text{CH}_3 \xrightarrow{\text{B}} \text{C}_6\text{H}_5-\text{CO}-\text{CHO}$ (iii) [structure] $\xrightarrow{\text{C}}$ [structure]
[Figure: (i) drawn as $\text{R}-\text{C}(\text{R})(\text{OH})-\text{C}(\text{R})(\text{OH})-\text{R}$ (a pinacol, each carbon bearing two R and one OH) $\xrightarrow{-\text{A}}$ $\text{R}(\text{R})\text{C}=\text{O}$; (ii) acetophenone $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{CH}_3 \xrightarrow{-\text{B}}$ in acetic acid $\rightarrow$ phenylglyoxal $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{H}$; (iii) decalin (two fused saturated six-membered rings) $\xrightarrow{-\text{C}, \text{Heat}}$ naphthalene] 15
8. (a) Write down the products of the following reactions with chemical equation: (i) $\text{R}-\text{CH}=\text{CH}_2 \xrightarrow{\text{(i)}} \text{B}_2\text{H}_6$ (ii) $\text{R}-\text{CO}-\text{H} + \text{C}_2\text{H}_5-\text{O}-\text{CO}-\text{CHN}_2 \xrightarrow{\text{H}^+ \text{(ii)}} \text{CH}_2\text{Cl}_2$ Product (iii) $\text{C}_6\text{H}_5-\text{N}_2^+\text{Cl}^- \xrightarrow{\text{(i) NaHSO}_3 \text{(ii) H}^+, \text{OH}^-}$ Product 15
- (b) Identify the product of the following reaction with mechanism: $\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4 \xrightarrow{\text{(i) C}_2\text{H}_5\text{AlCl}_2 \text{(ii) WCl}_6, \text{C}_2\text{H}_5\text{OH}}$ Product 15
- (c) Indene C_9H_8 rapidly decolourizes Br_2/CCl_4 . Only one mole of H_2 is absorbed readily to form C_9H_{10} . Vigorous oxidation of indene produces phthalic acid. What is the structure of indene? If indene is heated with strong acid, what product is formed? 15
- (d) What are the reagents used to distinguish the following pairs? (i) Primary alcohol ($\text{C}_2\text{H}_5\text{OH}$) and tertiary alcohol (t-Butyl alcohol) (ii) Cyclohexane and 1-Cyclohexene (iii) 1-hexyne and 1-hexene 15