

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) 1, 3, 5-cycloheptatriene (not an aromatic compound) reacts with a molecule of bromine to afford a compound having melting point 203°C (decomposition) and is insoluble in nonpolar organic solvents but soluble in water. Write and support the structure of the product and rationalize its formation. (ii) Account for the following observations in case of K_1 and K_2 which are the first and second dissociation constants of the dicarboxylic acids (I) and (II)

[Figure: (I) maleic acid (cis-butenedioic acid: both COOH groups on the same side of the C=C); (II) fumaric acid (trans-butenedioic acid: HOOC and COOH on opposite sides of the C=C)]

K_1 of (I) > K_1 of (II) where K_2 of (I) < K_2 of (II)

- (b) Phenanthrene is a tricyclic aromatic hydrocarbon, the structure of which is depicted below. It undergoes addition reactions at 9, 10 double bond which is not a characteristic reaction of aromatic compound. Explain the behaviour of this compound by drawing its various canonical forms.

[Figure: phenanthrene (Kekulé structure), with the C9=C10 double bond of the central ring labelled 9 and 10]

- (c) 2, 5-dimethyl-1, 1-cyclopentanedicarboxylic acid (I) can be isolated in two optically inactive compounds (A) and (B). Upon heating (A) gives two isomers of 2,5-dimethylcyclopentanedicarboxylic acid (II) whereas (B) yields only one isomer. Draw the structure of isomers of (A) and (B). What is the relationship between the isomers formed by decarboxylation of (A)?

[Figure: (I) cyclopentane C-1 bearing HOOC and COOH, C-2 and C-5 each bearing CH₃ on a wavy bond –Heat→ (II) cyclopentane C-1 bearing H and COOH, C-2 and C-5 each bearing CH₃ on a wavy bond; note under the scheme: a boxed wavy line “indicates stereochemistry not specified.”]

- (d) Propose a rational mechanism for the following transformation:

[Figure: benzofuran-2(3H)-one (five-membered lactone: ring O attached to the benzene ring, C-2 = C=O) bearing at C-3 both CH₂CH₂Br and C₆H₅ –NaOC₂H₅→ 3,4-dihydrocoumarin (chroman-2-one: six-membered lactone, ring O attached to the benzene ring, C-2 = C=O, C-3 = CH₂) bearing at C-4 both C₆H₅ and COOC₂H₅]

2. Arrange compounds in each of the following sets according to the specified order and give reasons for your choice:

15 × 4 = 60

- (a) Increasing order of reactivity toward cationic polymerization. Methyl acrylate, propene, isobutene, vinyl acetate.

- (b) Increasing order of chemical shift (NMR) is δ scale of the protons (A), (B), (C) and (D) shown in the following compound.

[Figure: 1-(2-phenylcyclopropyl)propan-1-one: $\text{CH}_3\text{CH}_2\text{C}(=\text{O})-$ attached to one cyclopropane carbon, a phenyl ring on the adjacent cyclopropane carbon; labels: (A) on the CH_3 protons, (B) on the CH_2 protons, (C) on the H of the third (CH_2) cyclopropane carbon, (D) on the aromatic H para to the cyclopropyl group]

- (c) Increasing order of stability of three main different conformations of 2-fluoroethanol.
- (d) Decreasing order of hydrolysis by aqueous KOH. $\text{p-H}_3\text{COC}_6\text{H}_4\text{CH}_2\text{Cl}$. $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ $\text{p-NCC}_6\text{H}_4\text{CH}_2\text{Cl}$. $\text{p-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$

3. Draw the structure of the predominant region/stereoisomer of the product in the following reactions. Write the mechanism of the reaction and give reasons for your choice.

[Figure: (i) oxime of 4-methoxybenzophenone, $(\text{p-OMe-C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}=\text{N-OH}$, with the OH on the same side as the $\text{p-OMe-C}_6\text{H}_4$ group (anti to C_6H_5), followed by a stray "+" $-\text{H}^+$, Heat $\rightarrow$?; (ii) 2,3-dibromo-2,3-dideuteriobutane drawn in sawhorse projection: lower (front) carbon bearing Br (up-left), D (down-left) and Me (down); upper (rear) carbon bearing Br (up), D (right) and Me (down-right); + I^- (acetone) $-\text{Heat} \rightarrow$?; (iii) $\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{Br}_2 \rightarrow \text{H}^+ \rightarrow$?; (iv) 3,4-dihydronaphthalen-2(1H)-one (2-tetralone) $-(\text{a}) \text{Na/C}_6\text{H}_6$ (b) $\text{BrCH}_2\text{OOC}_2\text{H}_5$ (as printed) $\rightarrow$?]

60

4. (a) Write the mechanism involved: (i) In the chain termination step during the cationic ring opening polymerization of hexachlorocyclotriphosphazines. (ii) In propagation step during the anionic ring opening polymerization of octamethylcycloterasiloxanes.

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- (b) Account for the following: (i) In polyamide synthesis by aminolysis of diesters with diamines, phenyl esters are preferred over alkyl esters. (ii) Anionic polymerization of acrylamide using BuLi give nylon 3.

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SECTION 'B'

5. Answer any three of the following:

$20 \times 3 = 60$

- (a) An α , β -unsaturated ketone of relative molecular mass 110 has an absorption in U.V at λ_{max} 215 ($\epsilon_{\text{max}} \sim 10,000$). A solution of this ketone showed absorbance $A = 2.0$ with 1 cm cell. Calculate concentration of ketone in the solution expressed in g/l.
- (b) U.V visible spectrum of an α , β -unsaturated carbonyl compound was recorded first in cyclohexane as solvent. What will be the effect on λ_{max} if the spectra of the same compound is taken in ethanol as solvent? Give reasons for your answer.
- (c) (i) Infra-red spectrum of (2R, 3S) 2, 3-dichloro-pentane was recorded. Do you think that this spectra will be identical with the spectra of (2S, 3R) 2, 3-dichloro-pentane & (2R,3R)2, 3-dichloro-pentane? Give reasons for your answer. (ii) The mass spectrum of ethyl phenyl ether has a prominent peak at m/z 66. Describe mode of formation of the fragment responsible for this peak.
- (d) A compound having molecular formula, $\text{C}_{10}\text{H}_{12}\text{O}_3$, exhibited following data in its ^1H NMR spectra: δ 1.3 (3H, triplet, $J = 7\text{Hz}$), 3.85 (3H, singlet), 4.3 (2H, quartet, $J = 7\text{Hz}$), 6.9 (2H, doublet, $J = 11\text{Hz}$), 7.9 (2H, doublet, $J = 11\text{Hz}$). Assign structure to the possible compound.

6. (a) Methyl chloride (A) and neomenthyl chloride (B) both react with base to lose a molecule of HCl by E_2 mechanism. The products are regioisomers (C) and (D). Identify which product is formed from which starting compound. Also mention starting compound (A) or (B) which will react faster. Give reasons for your answer.

[Figure: four cyclohexane rings: (A) methyl on the top carbon (bold wedge), isopropyl on the bottom carbon (hashed), Cl on the ring carbon adjacent to the isopropyl-bearing carbon (lower right, bold wedge); (B) same skeleton with methyl (bold wedge) and isopropyl (hashed) but Cl on the lower-right carbon on a hashed bond; (C) 1-isopropyl-4-methylcyclohexene: methyl at top, isopropyl at bottom, $\text{C}=\text{C}$ between the isopropyl-bearing carbon and the lower-right ring carbon; (D) methyl at top, isopropyl at bottom, $\text{C}=\text{C}$ in the right side of the ring between the two carbons lying between the methyl- and isopropyl-bearing carbons]

15

- (b) Account for the following: (i) Base catalysed cyclization of $\text{C}_2\text{H}_5\text{OOC}-(\text{CH}_2)_4-\text{CH}(\text{CH}_3)-\text{COOC}_2\text{H}_5$ gives 2-ethoxycarbonyl - 6 methyl

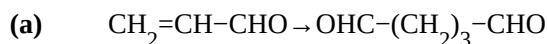
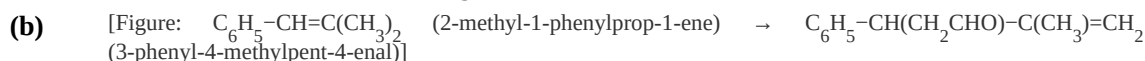
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cyclohexanone as the main product and not 2-ethoxycarbonyl - 2 methyl cyclohexanone. (ii) 3- methyl-3 - phenyl-cyclopentanone undergoes methylation with CH_3I in tetrahydrofuran using lithium di-isopropylamide at -78°C to give predominant product (A) and (B).

[Figure: (A) cyclopentanone with C-2 bearing CH_3 (bold wedge) and C-3 bearing C_6H_5 (hashed) and CH_3 (bold wedge), i.e. 2,3-dimethyl-3-phenylcyclopentanone with the 2- CH_3 trans to the phenyl; (B) cyclopentanone with H_3C on C-2 (= C-5 side of the carbonyl, away from the quaternary carbon) and C-4 bearing C_6H_5 and CH_3 (no stereochemistry shown), i.e. 2,4-dimethyl-4-phenylcyclopentanone]

7. Accomplish the following transformations:

15 × 4 = 60



8. (a) Write the mechanism of the following reactions: (i) [see figure] (ii) [see figure] (iii) Dehydrobromination of meso and racemic 1, 2-dibromo-1, 2-diphenylethane given cis and trans 1-bromo-1, 2-diphenylethane respectively.

[Figure: (i) a trimethylcycloheptatriene with a gem-dimethyl (H_3C , CH_3) on the sp^3 ring carbon and a further H_3C on a ring double-bond carbon $\rightarrow$ an isomeric trimethylcycloheptatriene (one CH_3 on the top sp^2 carbon, the adjacent sp^3 carbon bearing H and CH_3 , H_3C on the left ring carbon) + a bicyclo[3.2.0]heptadiene bearing a gem-dimethyl (H_3C , CH_3) and a further CH_3 [?]; the first product $\rightarrow$ (downward arrow) $\rightarrow$ another trimethylcycloheptatriene (sp^3 carbon bearing H_3C and H, CH_3 on the adjacent sp^2 carbon, H_3C on the left ring carbon) [?] (drawing poorly reproduced; exact positions of the methyl groups uncertain); (ii) a 4a-methyl-octahydronaphthalene (angular CH_3) with a ring $\text{C}=\text{C}$ next to the ring junction, bearing on a ring carbon an OH and a 1-hydroxyethyl group (HO , HO , H_3C) $\rightarrow$ (i) $\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$, pyridine (ii) CaCO_3 [?] $\rightarrow$ ring-expanded bicyclic ketone: a cycloheptenone fused to a cyclohexane, with angular CH_3 at the ring junction, the ring $\text{C}=\text{O}$ and a H_3C on the carbon alpha to the $\text{C}=\text{O}$, and a $\text{C}=\text{C}$ next to the ring junction [?] (drawing poorly reproduced)]

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(b) Explain the effect of Lewis acid on the cycloaddition of 1, 3-butadiene and methyl acrylate using 'Frontier Molecular Orbitals' method

15