

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) Identify the compound from each of the following pairs, which exhibits aromatic character:
 [Figure: Pair I: cyclopentadienyl anion (five-membered ring with two C=C and a negative charge on the fifth carbon) & cyclopentadienyl cation (same ring with a positive charge on the fifth carbon); Pair II: cycloheptatrienyl anion (seven-membered ring with three C=C and a negative charge on the seventh carbon) & cycloheptatrienyl (tropylium) cation (same ring with a positive charge on the seventh carbon)] 10
- (b) Enumerate the reasons for different rates of acetolysis for the following compounds:
 [Figure: Three bicyclo[2.2.1] brosylates with their relative rates printed below: (1) 7-norbornyl brosylate (saturated bicyclo[2.2.1]heptane, OBs on the one-carbon bridge C7), rate 10^1 ; (2) syn-7-norbornenyl brosylate (bicyclo[2.2.1]hept-2-ene, BsO on C7 drawn pointing towards the side of the C2=C3 double bond), rate 10^7 ; (3) anti-7-norbornenyl brosylate (bicyclo[2.2.1]hept-2-ene, OBs on C7 drawn pointing away from the double bond), rate 10^{11}] 10
- (c) Name the following reaction and give suitable reagent and mechanism:
 [Figure: Reaction: bicyclo[2.2.1]heptan-2-one (norcamphor) $\xrightarrow{?}$ 2-oxabicyclo[3.2.1]octan-3-one (bicyclic lactone in which a ring O has been inserted between the bridgehead carbon and the C=O carbon; the C=O is now an ester carbonyl, $-\text{O}-\text{C}(=\text{O})-$)] 10
- (d) Design a suitable experiment to establish the presence of possible intermediate in the following reaction: Identify the non-isolable intermediate.
 [Figure: Reaction: benzenediazonium-2-carboxylate (benzene ring bearing N_2^+ and, ortho to it, COO^-) + cyclopentadiene $\xrightarrow{-\Delta}$ 1,4-dihydro-1,4-methanonaphthalene (benzonorbornadiene: benzene ring fused to a bicyclo[2.2.1]heptadiene, with a CH₂ bridge and a C=C in the other two-carbon bridge)] 10
- (e) Account for the stereochemical outcome in the following reaction by proposing appropriate transition state:
 [Figure: Reaction: meso-3,4-dimethyl-1,5-hexadiene (drawn as $\text{H}_3\text{C}-\text{CH}(\text{CH}=\text{CH}_2)-\text{CH}(\text{CH}=\text{CH}_2)-\text{CH}_3$ with both CH₃ groups on bold wedges; label printed "Meso-3,4-dimethyl-1,5-pentadiene") $\xrightarrow{-\Delta}$ octa-2,6-diene drawn curled in a six-carbon "ring-like" outline (open between the two terminal alkene carbons on the left): CH₂-CH₂ on the right, C=C upper and lower; the upper terminal alkene carbon bears H₃C; the lower terminal alkene carbon bears H₃C and H drawn overlapping, plus an H drawn below it; label printed "cis-trans-2,6-octadiene"] 10
2. (a) 2-methylcyclohexanone gives different enolates under kinetic and thermodynamic conditions. While 2-tetralone gives only one (same) enolate under kinetic and thermodynamic conditions. Predict the structures of enolates in each case and account for the same.
 [Figure: 2-methylcyclohexanone (cyclohexanone with CH₃ on the α -carbon) and 2-tetralone (3,4-dihydronaphthalen-2(1H)-one: benzene ring fused to a cyclohexanone ring, C=O at C2 so that C1 is a benzylic CH₂ between the ring and the carbonyl)] 10
- (b) Which of the carbo-cations will be more stable in each of the following pairs? Give reasons. 10

[Figure: Pair 1: $C_6H_5CH_2-C^+(OCH_3)(CH_3)$ (1-methoxy-1-methyl-2-phenylethyl cation) and $C_6H_5CH_2-C^+(CN)(CH_3)$ (1-cyano-1-methyl-2-phenylethyl cation); Pair 2: 2-norbornyl cation (bicyclo[2.2.1]hept-2-yl cation, + on C2 of a two-carbon bridge) and 1-norbornyl cation (bicyclo[2.2.1]hept-1-yl cation, + on the bridgehead carbon)]

- (c) Addition of hydrogen iodide to 3,3-dimethyl-1-butene (A) yields mixture of 3-iodo-2,2-dimethylbutane and 2-iodo-2,3-dimethylbutane. Offer a mechanism to account for the formation of the products.

[Figure: (A) $(CH_3)_3C-CH=CH_2$ drawn as $H_3C-C(CH_3)_2-CH=CH_2$]

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- (d) Identify the reaction and predict the product/s in the following transformations:

[Figure: (i) 7-cyano-7-(trifluoromethyl)bicyclo[4.1.0]hepta-2,4-diene (norcaradiene: cyclohexadiene ring fused to a cyclopropane whose third carbon bears CF_3 and CN) $\Rightarrow \Delta$?; (ii) 1-methoxycyclohexa-1,3-diene (OCH_3 on a terminal diene carbon) + vinyl p-tolyl sulfone ($CH_2=CH-SO_2C_6H_4CH_3$) $-\Delta \rightarrow$?; (iii) allyl vinyl ether: $CH_3CH_2-CH(O-R)-C(CH_3)=CH_2$ where $R = -C(=CH_2)-C(CH_3)=CH_2$ (i.e. 2-methylpent-1-en-3-yl 3-methylbuta-1,3-dien-2-yl ether) $-\Delta \rightarrow$?]

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3. (a) Briefly explain the important methods of generation of carbenes. Explain what are singlet and triplet carbenes. Predict the product/s in the reaction of cis-2-butene with singlet and triplet carbenes.

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- (b) Predict the products and offer the mechanisms for the following chemical transformations:

[Figure: (i) 2-benzyl-2-methyl-1,2,3,4,5,6-hexahydro-2-benzazocinium ion (benzene ring fused to an eight-membered ring: ring sequence benzo $C-CH_2-N^+(CH_3)(CH_2Ph)-CH_2-CH_2-CH_2-CH_2$ -benzo C) $-NaNH_2$, liq. $NH_3 \rightarrow$?; (ii) 1-(2-hydroxypropan-2-yl)cyclohexan-1-ol (cyclohexane C1 bearing OH and $C(CH_3)_2OH$) $-H^+ \rightarrow$?]

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- (c) Write the products expected in the reactions shown below. Sketch the mechanisms involved in each case.

[Figure: Benzaldehyde (C_6H_5-CHO) in the centre: to the left $-KCN \rightarrow$?; to the right $-(i) NH_2NH_2$; (ii) KOH ; (iii) $\Delta \rightarrow$?]

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- (d) Write the mechanism involved in the formation of the following compound by Fischer-Indole protocol:

[Figure: 2,3,4,9-tetrahydro-1H-carbazole (benzene ring fused to a pyrrole ring $N-H$, which is fused to a cyclohexene ring)]

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- (e) Account for the stereoselectivity and propose a suitable mechanism for the following reaction:

[Figure: Reaction: threo isomer of 3-(4-methoxyphenyl)butan-2-yl brosylate drawn in sawhorse projection: rear carbon bears H , CH_3 and OBs ; front carbon bears H , CH_3 and the para-substituted benzene ring (the para substituent printed only as "O") $-\text{Acetolysis} \rightarrow$ threo isomer of 3-(4-methoxyphenyl)butan-2-yl acetate in the same sawhorse projection (rear carbon H , CH_3 , OAc ; front carbon H , CH_3 and $4-CH_3O-C_6H_4$)]

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4. (a) Explain with the help of FMO approach, why stereochemical outcome for 1,5-suprafacial carbon migration and 1,5-antarafacial carbon migration are different.

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- (b) What frontier molecular orbitals are involved in the reaction of (E, Z)-2,4-hexadiene via thermal and photochemical pathways? Account for the formation of the different stereoisomeric products.

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- (c) Prove the existence of intramolecular mechanism, when allyl phenyl ether on heating yields o-allyl phenol.

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- (d) Predict the products and give the mechanisms involved in the following chemical transformations:

[Figure: (i) α -bromo cage ketone: homocubaneone (a cube-shaped cage in which one top edge is expanded by an extra carbon carrying $C=O$, i.e. pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one) with Br on the cage carbon next to the $C=O$ $-KOH \rightarrow$?; (ii) p-cresol (4-methylphenol: OH at top, CH_3 para) $-CHCl_3$, $KOH \rightarrow$?]

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SECTION 'B'

5. (a) Write the mechanism of radical polymerization of ethylene leading to branching in the resultant polymer.

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- (b) Predict the major product and explain the origin of the regioselectivity and stereoselectivity observed in the following hydroboration-oxidation reaction:
[Figure: Reaction: 1-methylcyclopentene $\xrightarrow{(i) B_2H_6; (ii) H_2O_2, ^-OH \rightarrow ?}$] 10
- (c) Show Norrish type-II fragmentation for the following compound:
[Figure: 5-(furan-2-yl)-1-phenylpentan-1-one: $C_6H_5-CO-CH_2-CH_2-CH_2-CH_2-(furan-2-yl)$] 10
- (d) Briefly explain why C = O bond stretch frequency occurs at 1740 cm^{-1} for the carbonyl compound of an aliphatic ester and at 1850 cm^{-1} for the carbonyl group of acid chloride. 10
- (e) Distinguish between the following compounds using proton NMR spectra: (i) 1-bromopropane and 2-bromopropane (ii) Propanal and propanone 10
6. (a) Given below are two isomeric compounds with molecular formula $C_5H_{10}O$. Predict the base peaks for each of the following: Show McLafferty fragmentation peak wherever applicable.
[Figure: pentan-2-one ($CH_3COCH_2CH_2CH_3$) and pentan-3-one ($CH_3CH_2COCH_2CH_3$)] 10
- (b) An unknown compound, $C_9H_{10}O_2$, did not dissolve in aqueous NaOH. The IR spectrum exhibited strong absorption at 1730 cm^{-1} . The ^1H NMR spectrum had signals at δ 7.2 (multiplet), 4.1 (quartet) and 1.3 (triplet). Elucidate the structure of the unknown compound. 10
- (c) What are the factors responsible for the stability of the double helix structures of DNA? Show the structures of hydrogen bonding between complementary bases between two DNA strands. 15
- (d) Give the mechanism for reduction of a ketone by $LiAlH_4$ and predict the products in the following reactions:
[Figure: (i) 1,2-epoxydecane ($CH_2-CH(CH_2)_7CH_3$ with an O bridging the two carbons) $\xrightarrow{-LiAlH_4} ?$; (ii) hexa-2,4-dienoic acid (sorbic acid, $CH_3CH=CH-CH=CH-COOH$, drawn as a zigzag) $\xrightarrow{-LiAlH_4} ?$; (iii) $H_3C-C_6H_4-CH_2CN$ (p-tolylacetonitrile) $\xrightarrow{-LiAlH_4} ?$] 15
7. (a) Give the mechanisms involved in the epoxidation of an alkene and Baeyer-Villiger oxidation of a ketone using MCPBA. 10
- (b) What is the advantage of anionic polymerization process in the formation of polystyrene? Enumerate the steps involved in the polymerization of styrene using butyl lithium as an initiator. 10
- (c) Draw the possible structures for the compounds that meet the following descriptions: (i) C_2H_6O ; one singlet (ii) C_3H_7Cl ; one doublet and one septet (iii) $C_4H_8Cl_2O$; two triplets (iv) $C_4H_8O_2$; one singlet, one triplet and one quartet 10
- (d) Complete the following reactions and suggest a suitable reaction mechanism for each:
[Figure: (i) 1-(hydroxymethyl)cyclopentan-1-ol (cyclopentane C1 bearing OH and CH_2OH) $\xrightarrow{-HIO_4} ?$; (ii) 3-nitrobenzaldehyde (O₂N and CHO meta on a benzene ring) $\xrightarrow{-NaBH_4, \text{methanol}} ?$; (iii) methyl phenyl sulfoxide ($C_6H_5-S(=O)-CH_3$) $\xrightarrow{-LiAlH_4} ?$; (iv) cyclohexanone $\xrightarrow{-CrO_3} ?$] 20
8. (a) Predict the McLafferty rearrangement ion (m/c) peak for the following compound:
[Figure: 2-propyl-3,4-dihydronaphthalen-1(2H)-one (1-tetralone with an n-propyl group on C2, the carbon α to the C=O)] 10
- (b) Suggest the product and offer the mechanism in the following reaction:
[Figure: Reaction: cyclohex-2-en-1-one $\xrightarrow{-h\nu} ?$] 10
- (c) Propose the mechanism for the following chemical conversion:
[Figure: Reaction: benzoic acid (C_6H_5-COOH) $\xrightarrow{-Na, \text{liq. } NH_3} \text{cyclohexa-2,5-diene-1-carboxylic acid (ring carbon bearing H and COOH, the para } CH_2 \text{ drawn with two H, two } C=C \text{ between them)}$] 10
- (d) Give the structures of all the bases which occur in both RNA and DNA. Also give the structures of the bases which occur in RNA alone or in DNA alone. 10
- (e) One of the five compounds shown below was analysed by IR spectroscopy. Peaks were observed at 1639 cm^{-1} (weak) and 1714 cm^{-1} (strong). There was no signal between 3100 cm^{-1} to 3500 cm^{-1} . Which compound was analysed?
[Figure: Five compounds: 1 cyclohexanol; 2 cyclohexa-1,4-diene; 3 cyclohexanone; 4 cyclohex-3-en-1-one (C=O not conjugated with the ring C=C); 5 cyclohex-3-en-1-ol] 10