

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 the following:

10×6=60

- (a) Which one of the following compounds is more basic? Explain with reason.
[Figure: (I) a fulvene: cyclopenta-1,3-diene ring whose C5 carries an exocyclic C=C to a carbon bearing $(\text{CH}_3)_2\text{N}$ and Ph, i.e. 6-(dimethylamino)-6-phenylfulvene; (II) the seven-membered analogue: cyclohepta-1,3,5-triene ring whose C7 carries an exocyclic C=C to a carbon bearing $(\text{CH}_3)_2\text{N}$ and Ph, i.e. 8-(dimethylamino)-8-phenylheptafulvene]
- (b) Write the structures of the reaction products from succinimide with bromine and aq. KOH.
- (c) Acetolysis of compound (A) is 10^{11} times faster than that of (B) with retention of configuration. Account for this observation.
[Figure: (A) anti-7-norbornenyl tosylate: bicyclo[2.2.1]hept-2-ene with OTs and H on the C7 bridge carbon, TsO drawn on the side away from the C2=C3 double bond (anti) and H on the side of the double bond; (B) 7-norbornyl tosylate: bicyclo[2.2.1]heptane with TsO and H on C7]
- (d) How would you synthesise the following compound using aldol condensation? Give the structure of starting material (A) and the mechanism of the reaction.
[Figure: (A) $\rightarrow$ 1H-indene-3-carbaldehyde (indene with CHO on the C3 carbon of the five-membered-ring C2=C3 double bond, C1 being the CH2)]
- (e) How will you synthesise 1,3-pentadiene starting from piperidine?
- (f) How would you synthesise (A) shown below using Beckmann rearrangement reaction? Show the proper geometry of the intermediate.
[Figure: (A) $\text{C}_6\text{H}_5\text{-CONH-C}_6\text{H}_4\text{-OCH}_3$ (para-substituted: N-(4-methoxyphenyl)benzamide)]

2. (a) Azulene possesses dipole moment 1.0 D and electrophilic substitution in it occurs at the position-1 of the five membered ring. Provide explanation. **20**
- (b) One of the following hydrocarbons is much more acidic than the other two. Justify your answer considering the stability of their conjugate bases.
[Figure: three five-membered-ring hydrocarbons. (A) a fulvene: ring C1 carries an isopropyl group (single bond to $\text{CH}(\text{CH}_3)_2$), ring double bonds C1=C2 and C3=C4, ring C5 carries an exocyclic $=\text{CH}_2$ (1-isopropyl-5-methylenecyclopenta-1,3-diene). (B) ring C1 carries an exocyclic $=\text{C}(\text{CH}_3)_2$ (isopropylidene), ring double bond C2=C3, C4 carries an exocyclic $=\text{CH}_2$, C5 is a ring CH2 (3-methylene-5-isopropylidenecyclopentene). (C) 6,6-dimethylfulvene: ring C1 carries an exocyclic $=\text{C}(\text{CH}_3)_2$, ring double bonds C2=C3 and C4=C5] **20**
- (c) Explain the following with reasons: (i) Electrophilic substitution of pyrrole is easier than benzene. (ii) Furan undergoes Diels – Alder reaction more readily than pyrrole. **20**

3. (a) Why is $\text{CN}^\ominus$ (cyanide ion) a highly specific catalyst for the benzoin condensation? Formulate the product(s) in the following reaction with mechanism:
[Figure: $\text{C}_6\text{H}_5\text{-CHO} + (\text{CH}_3)_2\text{N-C}_6\text{H}_4\text{-CHO} \xrightarrow{\text{KCN}}$? (the second aldehyde drawn as a benzene ring with $(\text{CH}_3)_2\text{N}$ and CHO para: 4-(dimethylamino)benzaldehyde)] 20
- (b) Give the mechanisms for the following transformations:
[Figure: (i) 1-bromo-4-nitrobenzene $\xrightarrow{(\text{CN}^\ominus)}$ 3-bromobenzoic acid (COOH and Br meta to each other); (ii) $\text{C}_6\text{H}_5\text{-CH}_2\text{-N}^\oplus(\text{CH}_3)_3 \xrightarrow{(\text{NaNH}_2)}$ benzene ring bearing CH_3 and, ortho to it, $\text{CH}_2\text{-N}(\text{CH}_3)_2$] 20
- (c) The compound (A) shown below can be synthesised from (B) as well as (C) using alkoxide. Name the reaction and propose the mechanisms. $\text{C}_6\text{H}_5\text{-CH}_2\text{-CH}_2\text{-COOR}$ (A) $\text{C}_6\text{H}_5\text{-CH}_2\text{-CO-CH}_2\text{-Cl}$ (B) $\text{C}_6\text{H}_5\text{-CH}(\text{Cl})\text{-CO-CH}_3$ (C) 20
4. (a) "dl-pair of threo-3-bromo-2-butanol when treated with HBr furnished dl-pair of 2,3-dibromobutane whereas the dl-pair of erythro compound gave the meso isomer." Explain with mechanism. 20
- (b) How would you carry out the following transformations? Indicate the reagents used and show the mechanisms involved. (i) Aniline + Acrylaldehyde $\rightarrow$ (ii) $\text{C}_6\text{H}_5\text{-NH-NH}_2 + \text{C}_6\text{H}_5\text{-CH}_2\text{-CO-CH}_3 \rightarrow$
[Figure: (i) product drawn: quinoline; (ii) product drawn: 1H-indole with CH_3 at C2 and C_6H_5 at C3 (N-H shown), i.e. 2-methyl-3-phenylindole] 30
- (c) Alkaline hydrolysis of $(\text{C}_2\text{H}_5)_2\text{N-CH}_2\text{-CH}(\text{Cl})\text{-C}_2\text{H}_5$ produces $(\text{C}_2\text{H}_5)_2\text{N-CH}(\text{C}_2\text{H}_5)\text{-CH}_2\text{OH}$ easily. Account for the observation. 10

SECTION 'B'

5. Answer the following: 10×6=60
- (a) Give the structure of (A) and its conversion to (B) with mechanism for the following transformation:
[Figure: bicyclo[2.2.1]hepta-2,5-dien-7-one (norbornadienone; C7 bridge carbon is C=O) [labelled (A) under the drawing] $\xrightarrow{-(\text{h}\nu)}$ (A) $\rightarrow$ (B) tropone (cyclohepta-2,4,6-trien-1-one)]
- (b) How Malaprade oxidation is used to determine cis-glycolic units in sugars? Illustrate with one example showing mechanism.
- (c) An organic compound of molecular formula $\text{C}_4\text{H}_9\text{NO}$ showed the following PMR data in δ (ppm) scale: 2.9 (t, 4H), 3.8 (t, 4H) and 1.8 (broad singlet, exchanged with D_2O , 1H). Suggest the structure of the compound assigning the reasons for the peaks.
- (d) How will you differentiate the following pairs by IR spectra? (i) R-COOCH_3 and R-CO-O-COR (ii) $\text{CH}_3\text{-CHO}$ and
[Figure: (ii) second compound: oxirane (ethylene oxide), $\text{CH}_2\text{-CH}_2$ bridged by O]
- (e) Give the purpose of the following compounds in polymer chemistry: (i) Benzoyl peroxide (ii) Hydroquinone (iii) CCl_4 (iv) Ethyl mercaptan (v) Hydrogen peroxide
- (f) The base peak (m/e) appears at 105 for one of the following compounds (A, B and C) and at m/e = 119 for the other two. Match the compounds with appropriate m/e values for their base peaks.
[Figure: (A) 1-ethyl-3,5-dimethylbenzene; (B) 1-methyl-3-propylbenzene (n-propyl and methyl meta); (C) 1-isopropyl-3-methylbenzene (methyl and isopropyl meta)]
6. (a) Thermal cyclisation of cis, trans-2,4-hexadiene gives cis-3,4-dimethyl cyclobutene whereas trans, trans-2,4-hexadiene gives trans-3,4-dimethyl cyclobutene by the conrotatory process. Explain using Woodward – Hoffmann rule. 20
- (b) How would you explain the transformation of butadiene to (A) and (B) by one route but (C), (D) and (E) as shown by a different route? Give the mechanism for the transformation. 20

[Figure: 1,3-butadiene $\xrightarrow{-(h\nu, \text{ sens.})}$ (C) trans-1,2-divinylcyclobutane + (D) cis-1,2-divinylcyclobutane + (E) 4-vinylcyclohexene; 1,3-butadiene $\xrightarrow{-(h\nu, \text{ direct, downward arrow})}$ (A) bicyclo[1.1.0]butane + (B) cyclobutene]

- (c) A peptide was synthesised from phenylalanine, tyrosine and lysine in the sequential order by protecting first the amino group of phenylalanine. Write the structure of the peptide showing the reagents used in various steps. Will the newly formed peptide be acidic or basic? Give the reason.

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7. (a) Explain why (2 + 2) thermal cycloaddition of two molecules of ethylene to cyclobutene is forbidden but photochemically allowed. Explain this result by using HOMO-LUMO concept.

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- (b)(i) The exo-norborene (A) as shown below when heated gives (B) with complete retention of configuration of the migrating group. Explain showing the mechanism.

[Figure: (A) bicyclo[3.2.0]hept-2-ene drawn as a cyclopentene ring (one C=C) fused at a ring carbon to a two-carbon unit: from one ring-fusion carbon a solid bond down to a carbon bearing D and H, which is bonded to a carbon bearing OAc and H; that OAc-bearing carbon is joined to the other ring-fusion carbon by a dashed (breaking) bond. $\xrightarrow{-(\Delta)}$ (B) bicyclo[2.2.1]hept-2-ene (norbornene) with OAc on C5 and D on C6, both drawn on the exo face]

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- (b)(ii) "Photo reaction of acetone with (A) by $S_1 (n \rightarrow \pi^*)$ process gives cis and trans products, but with (B) gives only one isomer." Explain.

[Figure: $(\text{CH}_3)_2\text{C}=\text{O} + (\text{A}) \text{ cis-1,2-dicyanoethylene } (\text{NC}-\text{CH}=\text{CH}-\text{CN}, \text{ cis}) \rightarrow 2,2\text{-dimethyloxetane-3,4-dicarbonitrile}$ drawn twice: one isomer with plain bonds to both CN groups + one isomer with CN on C4 wedged and CN on C3 hashed; $(\text{CH}_3)_2\text{C}=\text{O} + (\text{B}) \text{ CH}_2=\text{C}(\text{CH}_3)\text{CN}$ (methacrylonitrile), downward arrow $\rightarrow$ single oxetane: ring O bonded to a carbon bearing CH_3 and CN and to a carbon bearing two CH_3 , the fourth ring atom a CH_2 (2,4,4-trimethyloxetane-2-carbonitrile)]

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- (c) Predict the structure of the products in the following reactions. Give the mechanism. (i) $\xrightarrow{\text{mCPBA}}$? (ii) $\xrightarrow{\text{SeO}_2}$? (iii) $\text{C}_3\text{H}_7-\text{C}\equiv\text{C}-\text{Et} \xrightarrow{\text{Li liq. NH}_3}$? (iv) $\text{CH}_2=\text{C}(\text{CH}_3)(\text{Et}) \xrightarrow{\text{BH}_3, \text{H}_2\text{O}_2, \text{NaOH}}$?

[Figure: (i) substrate: partial structure: cyclopentanone ring whose α -carbon is a quaternary ring-fusion carbon carrying an angular methyl group, the next ring carbon a ring-fusion CH; the bonds to the rest of the fused ring system are shown as wavy lines (as in a steroid D-ring 17-ketone); (ii) substrate: 2-methylcyclohexanone]

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8. (a) When acetone is heated with NaOH (aq.) a product (A) is obtained which showed the following spectral features: IR (cm^{-1}): 1695, 1620; ^1H NMR (δ): 1.90 (s, 3H), 2.10 (s, 6H), 6.00 (s, 1H); Mass (m/e): 98, 83, 55 (100%), 53, 43, 39. Deduce the structure of A and interpret the spectral data.

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- (b) Calculate the λ_{max} for the following compounds using Woodward – Fieser rule:

[Figure: (i) 6-acetoxy-6-methylcyclohexa-2,4-dien-1-one (ring C=O at C1; C6 sp^3 bearing CH_3 and OCOCH_3 ; ring double bonds C2=C3 and C4=C5); (ii) bicyclic enone: cyclopentenone fused to a cyclohexane — five-membered ring with C=O, the carbon next to it bearing CH_3 and attached to a ring-fusion CH, the other side of the C=O a ring CH= double-bonded to the other ring-fusion carbon (1-methyl-1,4,5,6,7,7a-hexahydro-2H-inden-2-one); (iii) 3,4,5-trihydroxybenzoic acid (gallic acid); (iv) 1-tetralone (3,4-dihydronaphthalen-1(2H)-one)]

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- (c) How would you explain the carbonyl stretching frequencies given below the structure of the following compounds?

[Figure: cyclohexanone, ν_{max} 1727 cm^{-1} ; cyclopentanone, 1754; cyclobutanone, 1802; cyclopropanone, 1825]

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