

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) Whether the following compound is aromatic, non-aromatic or antiaromatic. Justify.
[Figure: 1,6-methano[10]annulene (bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene): a naphthalene-shaped ten-carbon perimeter with alternating double bonds, the two central (bridgehead) carbons spanned by a one-carbon CH₂ bridge drawn above the ring]
- (b) In the reaction sequence $C_6H_5N^*HNH_2 + CH_3(C_2H_5)CO \rightarrow (P) \xrightarrow{BF_3} (Q)$ identify (P) and (Q) and clearly show isotopically labelled ^{*}N.
[Figure: phenylhydrazine drawn as a benzene ring bearing N^{*}HNH₂, the asterisk on the N attached to the ring; + CH₃(C₂H₅)CO (butan-2-one) $\rightarrow$ (P) $\xrightarrow{-(BF_3)}$ (Q)]
- (c) Write the major product (X) of the reaction $CH_3(CH_2)_3CH(F)CH_3 \xrightarrow{CH_3ONa / C_2H_5OH} (X)$
- (d) Write the major product formed on treatment of urea with NaOBr. Also write the name of the reaction involved.
- (e) Identify intermediate (P) and product (Q) in the reaction
[Figure: cis-9,10-dihydronaphthalene (two fused six-membered rings, each with two C=C double bonds, the two ring-fusion carbons sp³ with their H atoms shown as dots on the same side) $\xrightarrow{-(hv)}$ [P] $\rightarrow$ [Q]]
- (f) A mixture of formaldehyde and p-methoxybenzaldehyde is treated with conc. KOH. Write the products of reaction.

2. (a) Identify (P) to (S) in the reaction sequence

[Figure: $C_6H_5-CH(I)-CH_3 \xrightarrow{-(KOH (alc.), \Delta)} (P) \xrightarrow{-(H_2/Ni, 2-3 \text{ atm}, 293 \text{ K})} (Q); (Q) \xrightarrow{-(H_2O_2, HCOOH)} (R); (R) \xrightarrow{-(H_2/Ni, 10 \text{ atm}, 400 \text{ K})} (S)$]

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- (b) 2-Methyl-3-phenyl-2,3-butanediol on treatment with H₂SO₄ gives a major product (X). Identify (X) and write a mechanism to explain its formation. Also write the name of reaction involved.

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- (c) Draw resonating structures for the attack of SO₃H⁺ at different positions of Indole, using curved arrows. At which position attack occurs preferentially? Draw an energy profile diagram for the position of preferential attack.

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3. (a) Answer the following: (i) A student carried out reaction of aniline with concentrated HNO₃/H₂SO₄. Write the structure of product/s he is likely to obtain. (ii) Write a mechanism to explain the formation of major product in (i). (iii) If the reaction in (i) is carried out only in nitric acid, write an equation for the formation of NO₂⁺.

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- (b) Identify (P) to (R) in the following:

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[Figure: (P) $-(i) ^-OCH_3$; (ii) $H_2O/H^+ \rightarrow C_6H_5(CH_2)_2COOCH_3$; 4-hydroxy-2-methylacetophenone (benzene ring with OH at C1, CH_3 at C3 and $COCH_3$ at C4, i.e. OH para to $COCH_3$ and CH_3 ortho to $COCH_3$) $-(anh. AlCl_3, \Delta) \rightarrow$ (Q); $H_3COOC(CH_2)_4COOCH_3-(^-(OH) \rightarrow$ (R)]

- (c) Write the resonance structures of the following: Explain its aromaticity in nitration reaction.

[Figure: 3-phenylsydnone drawn as a five-membered ring: $H_5C_6-N^+$ bonded to CH and double-bonded to N; $CH=C$; the C bears O^- (exocyclic) and is bonded to ring O; ring O bonded to the N (sequence $N^+(C_6H_5)-CH=C(O^-)-O-N=$ back to N^+)]

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- (d) Write the products of the reaction (i) $CH_3-CH=C(CH_3)_2 \xrightarrow{HCl}$ (P) (ii) $CH_3-CH=CH_2 \xrightarrow{CCl_4}$ (Q) (iii) trans-2-butene $\xrightarrow{Br_2}$ [R] $\rightarrow$ (S) and (T) (branching arrow from [R] to (S) and (T))

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4. (a) Sketch the mechanism of following reactions:

[Figure: (i) 2,3-bis(bromomethyl)-1,4-dimethylbenzene (ring bearing CH_3 , CH_2Br , CH_2Br , CH_3 on four consecutive carbons) $-(\Delta, Zn/Ag) \rightarrow$ A $-(CH_2=CH-COCH_3) \rightarrow$ B; (ii) allyl 2,6-dimethylphenyl ether ($OCH_2CH=CH_2$ on the ring carbon flanked by two CH_3 groups) $-(\Delta) \rightarrow$; (iii) tetraphenylcyclopentadienone (cyclopenta-2,4-dien-1-one with Ph on C2, C3, C4 and C5) + $Ph-C\equiv C-Ph-(\Delta) \rightarrow$]

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- (b) Draw the structures of [6], [10], [12] and [14] annulenes and discuss their aromaticity.

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SECTION 'B'

5. Answer the following:

10×6=60

- (a) Draw the structure of purine nucleotides present in DNA.
- (b) Benzoic acid on reduction with Na in liq NH_3 gives 1,2-dihydroproduct, whereas, anisole gives 2,5-dihydroproduct. Explain.
- (c) Predict the products and explain their formation
[Figure: norbornene (bicyclo[2.2.1]hept-2-ene) in the centre; to the left: $-(C_6H_5COC_6H_5, hv) \rightarrow$ B; to the right: $-(CH_3COCH_3, hv) \rightarrow$ A]
- (d) What changes do you expect in the electronic spectrum of acetoacetic ester in hexane and ether.
- (e) ^1H NMR spectrum recorded for $CH_3-CH=CH_2$ at 90 MHz gave coupling constant (J) of 5 Hz for vinyl protons. If spectrum is recorded at 500 MHz, write the expected value of coupling constant.
- (f) What is the range of fingerprint region in infrared spectrum. Write the range in which carbonyl group normally absorbs.

6. (a) (i) Define thermoplast and thermosets. Which are thermoplast among the following? PVC, Phenolics, Aminoresins, Polypropylene, Teflon, Nylan, Polyster, Polystyrene, Alkyd resin, Polyethylene (ii) Differentiate between LDPE and HDPE.

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- (b) Give the synthetic route of epoxy resin based on bisphenol-A. Mention the principal fields of applications of epoxy resins.

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- (c) Write the product formed in the oxidation of quinoline by CrO_3 .

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- (d) Identify A and B and discuss the selectivity of the reagents

[Figure: methyl 4-oxocyclohexane-1-carboxylate (cyclohexanone with $COOCH_3$ at C4) $-(NaBH_4; H_2O) \rightarrow$ A; same compound $-(LiAlH_4; H_2O) \rightarrow$ B]

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7. (a) Write the structures of possible products of following photochemical reactions and mention the type of Norrish process (I or II) in each.

[Figure: (i) 2-methylcyclohexanone $-(hv) \rightarrow$; (ii) $CH_3CH_2-CO-CH_2CH_2CH(CH_3)CH_3$ (drawn as $CH_3CH_2-C(=O)-CH_2CH_2CHCH_3$ with a CH_3 hanging from the CH , i.e. 6-methylheptan-3-one) $-(hv) \rightarrow$]

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- (b) Photochemical (2 + 2) addition of benzophenone with cis- and trans-2-butene yield a mixture of same products. Explain their formation with the mechanism.

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- (c) Which among the following (A or B) is formed when Pent-2-ene is oxidised by OsO_4 and $NaHSO_3$? Explain its formation with the mechanism.

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[Figure: two Fischer projections of pentane-2,3-diol with CH_2CH_3 at top and CH_3 at bottom. (A) upper carbon H left, OH right; lower carbon H left, OH right (both OH on the same side: erythro). (B) upper carbon H left, OH right; lower carbon HO left, H right (OH on opposite sides: threo)]

- (d) Identify the compound susceptible for HIO_4 oxidation and justify (i) $\text{CH}_3-\text{CHNH}_2-\text{CH}_2\text{OH}$ (ii) $\text{CH}_2\text{NH}_2-\text{CH}_2-\text{CH}_2\text{OH}$ 10

- (e) Write the reagents required for the following conversions.

[Figure: (i) indane-1,3-dione (benzene ring fused to a five-membered ring with $\text{C}=\text{O}$ at C1 and C3, C2 a CH_2) $\rightarrow$ five-membered ring with three $\text{C}=\text{O}$ groups (C1, C2, C3) fused to a six-membered ring drawn without any double bonds or aromatic circle (as printed); (ii) p-xylene (1,4-dimethylbenzene) $\rightarrow$ terephthalaldehyde (benzene-1,4-dicarbaldehyde)] 10

8. (a) An organic compound with molecular formula C_9H_{10} gives following spectral characteristics.

Electronic spectrum	λ_{max} at 235 nm
Infrared spectrum	3035, 3000, 2925, 1640, 990, 915, 740 and 615 cm^{-1}
NMR spectrum	δ at 3.1(2H), 4.8(1H), 5.1(1H), 5.8(1H), 7.1(5H)
Mass spectrum	m/e at 117

Suggest a possible structure with probable justification for each spectral feature. 30

- (b) What characteristic bands will be observed in the ir spectrum of 1-phenylethanone? 10
- (c) Room temperature NMR spectrum of acetylacetone exhibits two close by peaks at $\delta = 1.97$ and 2.14 ppm . Explain the reason for their origin. What other peaks will be observed. 10
- (d) How would you determine molecular wt of acetone on the basis of its mass spectrum? Suggest possible fragmentation pattern. 10