

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) Predict which of the following compounds would be aromatic? Explain the basis of your prediction in minimum possible words.

[Figure: Eight structures numbered 1–8 (drawing of low quality): 1 = cyclopropene with an exocyclic C=CH₂ (methylenecyclopropene); 2 = two cyclopropene rings joined by an exocyclic C=C double bond (trifulvalene, bi(cyclopropenylidene)); 3 = cyclopentadiene with exocyclic =CH₂ (fulvene); 4 = cyclopropene ring joined by an exocyclic C=C to a cyclopentadiene ring (calicene, triapentafulvalene); 5 = two cyclopentadiene rings sharing one sp³ spiro carbon (spiro[4.4]nona-1,3,6,8-tetraene); 6 = cycloheptatriene with exocyclic =CH₂ (heptafulvene); 7 = cyclopentadiene ring joined by an exocyclic C=C to a cycloheptatriene ring (sesquifulvalene, pentaheptafulvalene); 8 = cycloheptatriene ring joined by an exocyclic C=C to a second ring drawn as a cyclic polyene (heptafulvalene) [?]]

- (a)(ii) The value of the barrier of rotation for the marked bond in A is only about 14 Kcal/mole. What could be the reason for this low value of barrier of rotation in this molecule?

[Figure: Molecule A (drawing almost illegible in the source): a cyclic polyene ring (cyclopentadiene or cycloheptatriene ring [?]) joined through the marked exocyclic C=C double bond to a six-membered cross-conjugated ring bearing a para C=O group (a quinone-methide/fulvene-type push–pull system) [?]]

- (b)(i) An adduct A is formed by the Diels-Alder reaction of cyclopentadiene with ethyne. When A is treated with hexachlorocyclopentadiene (B), it forms the well known pesticide Aldrin (C). Epoxidation of C with per acid produces another pesticide. Dieldrin (D). Draw structures of A, B, C, D and explain how these products are formed.

- (b)(ii) Compound A is photochromic (it becomes coloured on exposure to light). The process is reversible giving back the starting material in the dark. Propose a structure for the coloured photoisomer B.

[Figure: A ⇌ B (forward arrow labelled hν, reverse arrow labelled “dark”). A = a xanthone-derived tricyclic: benzene ring fused to a pyran-4-one (C=O at the top, ring O at the bottom), which is fused to a third six-membered ring carrying, going round from the carbonyl side: C(Ph)(OH), C(CN)₂, C(CN)= and =C(Ph) next to the ring-O side (i.e. a ring C=C bearing CN and Ph)]

- (c) Illustrate the following terms: (i) Carbocation (ii) Non-classical carbocation (iii) Carbonium ion (iv) Carbenium ion (v) Carbenes

- (d) Decomposition of a diazocompound A in methanol gives an alkene B(C₈H₁₄O), whose ¹H NMR spectrum shows following signals: δppm. = 3.50 (3H, s) 5.50 (1H, dd, J = 17.9 and 7.9 Hz), 5.80 (1H, ddd, J = 17.9, 9.2 and 4.3 Hz) 4.20 (1H, m) and 1.3–2.7 (8H, m). What is its structure? (i) B is unstable and isomerises at room temperature to another compound C. (ii) When the diazocompound A is decomposed in presence of a diene (D) it is trapped as an adduct E. Explain the reactions which give the products B, C and E.

[Figure: A = 7-diazobicyclo[4.1.0]heptane (cyclohexane fused to a cyclopropane whose free carbon bears =N₂) –MeOH → B [C₈H₁₄O] –Δ → C = 3-methoxycycloheptene (cycloheptene with OMe on the allylic carbon). A –MeOH, in presence of D (2,3-dimethylbuta-1,3-diene) → E = bicyclic adduct: a cyclohexene ring bearing two methyls on its C=C, fused to a cycloheptane ring; the two ring-fusion H atoms drawn one up (wedge) and one down (hashed), i.e. trans-fused; OMe on the cycloheptane carbon adjacent to the upper ring-fusion carbon]

2. (a) Following two mechanisms are among those which have been postulated for the decomposition of aryl diazonium salts in aqueous solutions containing nucleophilic anion A[–]
 [Figure: Mechanism A: C₆H₅–N⁺≡N + A[–] → transition state in which the ipso carbon carries both N^{δ+}≡N and A^{δ–} → C₆H₅–A + N₂. Mechanism B: C₆H₅–N⁺≡N → ^{slow}C₆H₅⁺ + N₂; C₆H₅⁺ + A[–] → ^{fast}C₆H₅–A]
 Indicate how the following method might be applied to distinguish between the two mechanisms: (i) Kinetic studies (ii) Study of rate & product composition as a function of [A[–]]^{–1} (iii) Solvent isotope studies (iv) Study of isotope effect resulting from substitution of D from H at ortho position (v) Substituent effect studies 20
- (b)(i) Among the norbornane derivatives the acetolysis of the anti-tosylate (III) is 10¹¹ times faster than I while the acetolysis of the syn-isomer (II) is only 10⁴ times faster than I. Explain.
 [Figure: I = 7-norbornyl tosylate (bicyclo[2.2.1]heptane with OTs on C7); II = syn-7-norbornenyl tosylate (bicyclo[2.2.1]hept-2-ene with OTs on C7 on the side of the C=C, drawn TsO); III = anti-7-norbornenyl tosylate (OTs on C7 away from the C=C)] 0
- (b)(ii) 3-bromocyclohexene reacts with NaOH more rapidly than 4-bromocyclohexene, which in turn reacts more rapidly than bromocyclohexane. Explain. 20
- (c) Outline mechanism for the formation of B from A:
 [Figure: (i) A = cyclohexanone –1. R₂NH; 2. EtOOC–C≡C–COOEt → B = cyclooctenone ring; C=O, adjacent ring carbon C(COOEt)=C(COOEt) (diethyl 8-oxocyclooct-1-ene-1,2-dicarboxylate). (ii) A = oxime (C=N–OH) of 6,6-dimethyl-6,7,8,9-tetrahydro-5H-benzocyclohepten-5-one (benzene fused to a seven-membered ring; C=NOH at the benzylic carbon, gem-dimethyl carbon next to it) –H⁺ → B = 1,2,3,4-tetrahydronaphthalene carrying CN on the aromatic carbon peri to the saturated ring and gem-dimethyl on the benzylic carbon at the other end of the saturated ring (5,5-dimethyl-5,6,7,8-tetrahydronaphthalene-1-carbonitrile)] 20
3. (a) Predict the products of the following reactions and outline the mechanism involved in their transformation:
 [Figure: (i) 4-R-nitrobenzene (NO₂ at C1, R [?] at C4) –NaCN, H₂O → A. (ii) aniline + methyl vinyl ketone (CH₂=CH–CO–CH₃) –FeCl₃, ZnCl₂ (Nitrobenzene) → A. (iii) 1,1'-bi(cyclobutyl)-1,1'-diol (two cyclobutane rings joined C1–C1', each C1 bearing OH) –H⁺ → A –NaBH₄ → B; B –H⁺ [?] → C = bicyclo[3.3.0]oct-1(5)-ene (two fused cyclopentane rings with the C=C at the ring fusion). (iv) cholesterol (3-HO, Δ⁵, C₈H₁₇ side chain at C17) –1. B₂H₆; 2. H₂O₂, OH[–] → A] 13
- (b)(i) In cyclohexane series it is observed that with chromic acid it is the axial hydroxyl group that is oxidised more rapidly than equatorial hydroxyl group by a factor of about 3, but the saponification of the esters of related compounds however shows a reverse order of reactivities i.e., axial ester group hydrolyses very slowly than the equatorial ester group. Explain. 13
- (b)(ii) The N-benzoyl methyl ester derivatives of the amino acids glycine, alanine and valine react with N-bromosuccinimide to give monobromination products containing bromine at the α-carbon atom of amino acids. The order of reactivity is glycine > alanine > valine (23 : 8 : 1) Account for this trend of reactivity. 20
- (c) Provide plausible mechanisms for the following transformations
 [Figure: (i) A = CH₃(CH₂)₄–C≡CH –CCl₄, ROOR, 77 °C → B = Cl(CH₃–(CH₂)₄)C=CHCCl₃ (1,1,1,3-tetrachlorooct-2-ene) + C = cyclopentane carrying CH₃ and =CCl₂ (dichloromethylene) on adjacent carbons [?]. (ii) A = α-santonin (cross-conjugated cyclohexadienone ring with angular CH₃ and a ring CH₃ next to C=O, fused to a ring bearing a γ-lactone with CH₃ on the α-carbon) –H⁺ → B = desmotroposantonin (the dienone ring now an aromatic phenol: HO on the aromatic ring, two aromatic CH₃ groups; the lactone ring with CH₃ retained)] 13
4. (a) Explain how the following products could be formed in these reactions: 20

[Figure: (i) A = bicyclo[2.2.1]heptane bearing H and CH₂NH₂ on C2 –HNO₂, H⁺, H₂O → B (bicyclic alcohol, HO and H shown; yield %[?]) + C (bicyclic alcohol, H and OH; %[?]) + D (bicyclic tertiary alcohol, H and OH; %[?]) – the structures and percentages are illegible in the source [?]. (ii) A = styrene –MCPBA → B = styrene oxide (phenyloxirane) –BF₃ → C = phenylacetaldehyde (C₆H₅–CH₂–CHO). (iii) A = cyclohexanecarbonyl chloride (C₆H₁₁–COCl) –Et₃N → B = dispiro 1,3-cyclobutanedione (two cyclohexane rings spiro-fused at the 2- and 4-positions of a cyclobutane-1,3-dione; ketene dimer). (iv) A = cis-cyclooctene (H, H shown on the C=C) –(i) CHBr₃, Pot. t-butoxide; (ii) [reagent illegible] [?] → B = nine-membered ring product with two H shown (cyclononene/cyclonona-1,2-diene [?])]

- (b) Explain the following: (i) o-deuteriofluorobenzene reacts with sodium amide in liquid ammonia to yield aniline more slowly than does o-deuteriobromobenzene. When the reaction of the fluorocompound is stopped at 50% conversion to aniline the starting material is found to be largely devoid of deuterium. When the reaction of the bromo-compound is stopped at 50% conversion to aniline, the starting material still contains large amount of deuterium. (ii) Hexylbenzenesulphonate reacts with sodium methoxide to give hexylmethylether in over 90% yield with only a trace of 1-hexene being formed. With potassium-t-butoxide however, the yield of t-butylhexylether is 69% and 20% of 1-hexene is formed.

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- (c) Predict mechanism for the following transformations:

[Figure: (i) 1 = N-methyl-1,2,3,4,5,6,7,8-octahydroquinoline (enamine: C₄a=C₈a double bond, N–Me) with a gem-dimethyl group on C5 (next to C₄a) –Br₂ + NaOH (HOBr) → 2 = spiro compound: N-methylpyrrolidine whose C2 is the spiro carbon of a cyclohexanone; the cyclohexanone C=O is adjacent to the spiro carbon on one side and the gem-dimethyl carbon on the other side of the ring [?]. (ii) I = 3-chloro-octahydroquinolin-2(1H)-one (cyclohexane cis-fused, H at both fusion carbons, to a δ-lactam ring: NH, C=O, CCl) –Ba(OH)₂ → 2 = octahydroindole-2-carboxylic acid (cyclohexane fused to a pyrrolidine, H at both ring-fusion carbons, NH, COOH on C2 with wavy bond)]

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SECTION 'B'

5. Answer any three of the following:

20×3=60

- (a) Rationalize the products formed in the following reactions:

[Figure: Four amino alcohols (2-amino-4-tert-butylcyclohexan-1-ols) drawn as chairs with the tert-butyl equatorial: 1 = C1 OH equatorial (H axial up), C2 NH₂ equatorial (H axial down); 2 = C1 OH axial (up), C2 NH₂ equatorial; 4 = C1 OH equatorial, C2 NH₂ axial (down); 6 = C1 OH axial (up), C2 NH₂ axial (down). 1 –NaNO₂ + HCl → 3 and 2 –NaNO₂ + HCl → 3, where 3 = 3-tert-butylcyclopentanecarbaldehyde; 4 –NaNO₂ + HCl → 5 = 4-tert-butylcyclohexanone; 6 –NaNO₂ + HCl → 7 = 4-tert-butyl-1,2-epoxycyclohexane (7-oxabicyclo[4.1.0]heptane with t-Bu)]

- (b)(i) Claisen rearrangement of allyl ether A often gives a product B (instead of the expected product). How is this unwanted product formed? Addition of a small amount of a weak base such as PhNMe₂ helps to prevent the unwanted reaction. What could be the role of the base? Explain.

[Figure: A = phenyl 2-methylallyl ether (C₆H₅–O–CH₂–C(CH₃)=CH₂) [?] –Heat → B = 2,2-dimethyl-2,3-dihydrobenzofuran]

- (b)(ii) Why does the acetolysis of threo-3-phenyl-2-butyl tosylate give the threo racemic products, while that of erythro isomer gives the product with the retention of configuration? Explain.

- (c) Outline mechanism for the following transformation (Show the mechanism by electron pushing arrows only. words not required):

[Figure: (i) furfuryl chloride (2-(chloromethyl)furan) –NaCN → 5-methylfuran-2-carbonitrile (furan with CH₃ at C5 and CN at C2). (ii) pyridine –SOCl₂ → 1-(4-pyridyl)pyridinium chloride (Cl[–], N⁺ bonded to C4 of a second pyridine) –H–C(=O)–NMe₂, 140–60° → 4-(dimethylamino)pyridine + CO + HCl. (iii) indole –CHCl₃, KOH → indole-3-carbaldehyde + 3-chloroquinoline. (iv) 3-benzylindole (CH₂Ph at C3) –CH₂=CH–CH₂–Br, Lewis acid → 3-allyl-2-benzylindole]

- (d) Treatment of phthalimide 1 with bromine in aqueous sodium hydroxide followed by acidification with acetic acid affords compound 2. Spectral data of 2 are summarised below. Deduce the structure of 2 and provide a mechanism for its formation. Compound 2 reacts with HNO₂ to give an unstable product 3. When 3 is treated with

trans-trans-2,4-hexadiene (4), it forms an adduct 5. Identify 3 and explain how 5 is formed from 3.

[Figure: phthalimide (1) –(i) Br₂ + KOH; (ii) AcOH → 2 –HNO₂ → 3 –4 → 5]

Compound 2: M/S, m/z: = 137 (59%), 119 (100%) 93 (79%), 92 (59%); IR (KBr) = 3940 (m), 3380 (m) 3300–2400 (br), 1665 (s), 1245 (s), 765 (m) cm⁻¹; ¹H NMR (δ_{ppm}) = 6.52 (1H, t, J = 8.0 Hz), 6.77 (1H, d, J = 8.0 Hz), 7.23 (1H, t, J = 8.0 Hz), 7.72 (1H, d, J = 8.0 Hz), 8.60 (3H, br.s, disappears on addition of D₂O)

6. (a) Identify the products of the following sequence of reactions and explain how these are formed:

[Figure: (i) cyclohexanone [ring size uncertain, ?] –(i) LiAlH₄; (ii) H₃O⁺ → A –(i) NaH, Ether; (ii) CS₂; (iii) CH₃I → B –Heat → C. (ii) α-pinene –BH₃ → [(pinanyl)2BH] (diisopinocampheylborane) –cis-2-butene (CH₃, CH₃ on one side, H, H on the other) → A –H₂O₂, OH⁻ → B. (iii) benzophenone (C₆H₅)₂C=O + benzyl bromide (Br–CH₂–C₆H₅) –(i) Ph₃P; (ii) n-BuLi → A –N-bromosuccinimide → B. (iv) cyclohexanone –NaBH₄ → A –H₂SO₄ → B –Pb(OAc)₄ → C + D + E]

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- (b)(i) When compound A is heated at 150°, It is transformed to compound C and D. via a cyclic tetraene (B). Propose a structure for B and describe the process involved in the conversion of A → B, B → C and C → D.

[Figure: A = cis-bicyclo[6.2.0]deca-2,4,6,9-tetraene (cyclooctatriene ring fused to a cyclobutene; H, H at the ring fusion) –160° C → B → C = trans-9,10-dihydronaphthalene (H at the two ring-fusion carbons, one up, one down) –Δ → D = 1,2-dihydronaphthalene]

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- (b)(ii) Provide mechanism for the following transformations:

[Figure: 2,2-dimethylcyclohexanone –hv → B = 6-methylhept-5-enal (OHC–CH₂–CH₂–CH₂–CH=C(Me)Me). A = cis,cis-cycloocta-1,3-diene –hv → B = bicyclo[4.2.0]oct-7-ene (cyclobutene fused to cyclohexane); A –hv, Sensitizer → C = (E,Z)-cycloocta-1,3-diene (one trans double bond) –Δ → B]

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7. (a) Identify the products A and B in the reaction given below:

[Figure: B-vinylborazine (borazine ring B₃N₃ with H on each N and on two B atoms, a vinyl group CH=CH₂ on the third B) –Borazine, 125° C → A –1000° C, NH₃ → B]

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- (b) Explain the following: (i) Polyethylene cannot be prepared by cationic polymerization whereas polystyrene can. (ii) Anion polymerization is a good method for the preparation of n-polyacrylonitrile but not for polyisobutylene. (iii) Why radicals prefer to add at carbon 1 of isoprene rather than carbon 2, 3 and 4. (iv) Both the polymers, poly (vinyl chloride) and poly (vinylidene chloride) are prepared by free radical processes, but the former is amorphous and the latter is highly crystalline. (v) In SBR (styrene-butadiene rubber) why do most double bonds have a trans configuration?

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- (c) Give mechanism of the following transformations:

[Figure: (i) A = 3-phenylbutan-2-one (Ph and Me on the chiral carbon, Me on wedge) –Per acid → B = 1-phenylethyl acetate, Ph(Me)CH–O–C(=O)–Me, configuration retained (87%) + C = methyl 2-phenylpropanoate, Ph(Me)CH–C(=O)–O–Me (13%). (ii) A = CH₃–CO–C(=CH₂)–CH₂–CHR₂ (an α-methylene ketone with a CHR₂ group at the γ-position) [?] –hv → B = cyclobutanol: C1 bearing OH and CH₃, C2 bearing =CH₂, the carbon across bearing R, R [?] + C = cyclobutane bearing CH₃–C(=O)– on one carbon and R, R on the opposite carbon [?]. (iii) A = cyclobutanecarbonyl azide (C₄H₇–C(=O)N₃) –hv, H₂O → B = cyclobutylamine. (iv) A = ten-membered ring (cyclodecane) bearing at one carbon HO and CH₃ and at a transannular carbon HO and O [?] –H₂O/H₃O⁺ → B = ten-membered ring bearing O and CH₃ at one carbon and C=O at the transannular carbon [?] (drawing poorly legible)]

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- (d)(i) Formaldehyde reacts with ammonia to give A [C₆H₁₂N₄]. A reacts with HNO₃ to give a well known explosive B [C₃H₆N₆O₆]. Predict the structure of B and show how B is formed from A.

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- (d)(ii) When bromoketone (A) is treated with potassium-t-butoxide in t-butyl alcohol at room temperature it gives B. But when A is treated with LDA in THF at –72°C followed by heating it gives C. Explain why different reaction conditions give different products.

[Figure: A = 1-[2-(3-bromopropyl)cyclopentyl]ethan-1-one (cyclopentane with –C(=O)CH₃ on C1 and –CH₂CH₂CH₂Br on C2) –1. (CH₃)₃COK, (CH₃)₃COH, 25° C; 2. H₂O → B = 1-acetylbicyclo[3.3.0]octane (acetyl, C(=O)CH₃, on a ring-fusion carbon of two fused cyclopentanes); A –1. LDA/THF, –72° C [?]; 2. Δ; 3. H₂O → C = bicyclo[5.3.0]decan-2-one (cyclopentane fused to cycloheptanone, C=O adjacent to a ring-fusion carbon)]

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8. (a) Predict the position of absorption bands for the carbonyl group in the IR spectra of the following compounds:
 [Figure: 1 = methyl benzoate ($\text{C}_6\text{H}_5\text{--CO--OCH}_3$); 2 = 5,6-dihydro-2H-pyran-2-one (α,β -unsaturated six-membered lactone); 3 = benzoic acid; 4 = cyclohex-2-en-1-one; 5 = cyclopentanone; 6 = (E)-but-2-enal (crotonaldehyde, $\text{CH}_3\text{--CH=CH--CHO}$)] 15
- (b)(i) p-nitroaniline exhibits a pronounced red shift in the K-band, which is not observed in o or m-isomer. Explain. 5
- (b)(ii) Calculate the λ_{max} for the triene (A) which contains both a heteroannular and homoannular diene. Your calculation should be based on the homoannular diene.
 [Figure: A = steroid triene (cholestane skeleton, C_8H_{17} at C17, angular methyls): two conjugated C=C in ring A and one C=C in ring B ($\text{C}_6=\text{C}_7$) conjugated with them, so that ring A holds a homoannular diene and rings A/B a heteroannular diene [?]] 15
- (c)(i) Predict the structure of a fragment ion which is responsible for the appearance of a strong characteristic peak at $m/z = 149$ in the mass spectra of the esters of the phthalic acid. Give the mechanism of its formation from diethyl phthalate. 5
- (c)(ii) Treatment of A with KOH gives a compound B($\text{C}_7\text{H}_{10}\text{O}$). Spectral data of B are given below. What is its structure and how is it formed? Explain.
 [Figure: A = 2,2-dimethyl-4-oxopentanal ($\text{CH}_3\text{--CO--CH}_2\text{--C}(\text{CH}_3)_2\text{--CHO}$) $\xrightarrow{\text{KOH, H}_2\text{O}}$ B [$\text{C}_7\text{H}_{10}\text{O}$]]
 IR; = 1710 cm^{-1} ; $^1\text{H NMR}$, $\delta_{\text{ppm}} = 1.15$ (6H, s), 2.1 (2H, s), 6.8 (1H, d), 7.3 (1H, d) 15
- (d) Deduce the structure of a compound on the basis of the spectral data given below: (i) Molecular formula: $\text{C}_{12}\text{H}_{15}\text{NO}_3$ (ii) UV, $\lambda_{\text{max}}: < 210\text{ nm}$ ($\epsilon > 10,000$), 280 nm ($\epsilon = 900$) (iii) IR, cm^{-1} : 3300, 1710, 1670 cm^{-1} (iv) $^1\text{H NMR}$, δ_{ppm} : 2.21 (3H, s), 3.37 (2H, s), 3.76 (3H, s), 4.34 (2H, d), 6.80–7.18 (4H, dd) (One proton does not show, it exchanges with D_2O) 5