

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) Which one of following ions is expected to be aromatic? Explain the reason. Draw additional resonance structures for the aromatic ion.
 [Figure: Two ions: (1) cycloheptatrienyl cation (tropylium): seven-membered ring with three C=C double bonds and $\oplus$ on the remaining carbon; (2) cycloheptatrienyl anion: seven-membered ring with three C=C double bonds and $\ominus$ with a lone pair (two dots) on the remaining carbon] 10
- (b) 2-Methylcyclohexanone can be converted to two different enolates by appropriate choice of reaction conditions. These on further treatment with methyl iodide can yield 2, 6-dimethylcyclohexanone and 2, 2-dimethylcyclohexanone. Account for the formation of these products. 10
- (c) Give the geometry and the hybridization state involved in singlet and triplet carbenes. Predict the product in the following reaction:
 [Figure: Reaction scheme: norbornene (bicyclo[2.2.1]hept-2-ene) + $\text{N}_2\text{CHCOOC}_2\text{H}_5$ -0.5 equiv. $\text{CuCN} \rightarrow ?$] 10
- (d) How do you account for the fact that Dieckmann cyclization of diethyl 3-methylheptanedioate gives a mixture of two β -keto ester products. What are their structures, and why is a mixture formed? 10
- (e) Predict and account for the formation of stereoisomers in the following reactions:
 [Figure: Reaction scheme: a conjugated triene in which the first C=C lies in a cyclohexene ring (left ring; its upper alkene carbon bears CH_3), the middle C=C is a $\text{CH}=\text{CH}$ linking unit, and the third C=C lies in a second cyclohexene ring (upper right; its terminal alkene carbon is a ring CH lying next to the CH_3), i.e. $\text{CH}_3\text{-C}(\text{ring})=\text{C}(\text{ring})\text{-CH}=\text{CH}\text{-C}(\text{ring})=\text{CH}(\text{ring})$, drawn s-cis/s-cis so the CH_3 -bearing carbon and the terminal ring CH face each other; branching arrows: upper arrow labelled $h\nu \rightarrow ?$; lower arrow labelled $\Delta \rightarrow \Delta$ (the product is printed as " Δ ")] 10
2. (a) How do you account for the fact that 3-bromo-1-butene and 1-bromo-2-butene undergo $\text{S}_{\text{N}}1$ reaction at the same rate although one is a secondary halide and the other is primary? 10
- (b) Give two important methods of generation of free radicals and explain why allylic and benzylic radicals are both more stable than non-allylic radicals. 10
- (c) Predict the product and identify the product/s in the following reactions:
 [Figure: (i) $\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{CH}=\text{CH}_2$ (6-methyleneocta-1,7-dien-3-one, drawn as a zig-zag chain: a 1,3-diene unit tethered by two CH_2 groups to a vinyl ketone) $-\Delta \rightarrow ?$; (ii) 1-[(E)-but-2-enyloxy]-4-methoxybenzene (benzene ring with $\text{O}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$, drawn trans, and OCH_3 para to it) $-\Delta \rightarrow ? \rightleftharpoons ?$; (iii) 5-vinylbicyclo[2.2.2]oct-2-ene (bicyclo[2.2.2]octene: one two-carbon bridge contains the C=C, one is CH_2-CH_2 , the third is CH_2-CH bearing a vinyl group $\text{CH}=\text{CH}_2$) $-\Delta \rightarrow ?$] 15
- (d) The reaction of 1, 3-butadiene with HCl produces a mixture of products. Write those products. Among the products which one is formed preferentially in the early stages of 15

the reaction? What does this indicate? What will happen to the product mixture as a function of time?

3. (a) In NGP reactions enhancement of rate and retention of configuration is observed. Explain why. Also predict the product/s in the following reactions with justification.
[Figure: Two reactions: (1) 2-norbornyl brosylate with OBs exo and H endo (H drawn pointing down) –Acetolysis → ?; (2) 2-norbornyl brosylate with OBs endo (drawn pointing down) and H exo –Acetolysis → ?; [Bs = SO₂-C₆H₄-Br, Br para]] 20
- (b) Predict and account for the different regioisomers formed in the reactions given below:
[Figure: Two reactions on menthane chairs (cyclohexane chair carrying an isopropyl group and a CH₃ group 1,4 to each other, both equatorial, with the leaving group on the carbon next to the isopropyl-bearing carbon, drawn axial, and its H equatorial; the H on the isopropyl-bearing carbon is axial and drawn up; the H on the CH₃-bearing carbon is axial and drawn down): (1) Neo-menthyl chloride (axial Cl) –Base → ?; (2) Neo-menthyl xanthate (axial O-C(=S)-SCH₃) –Δ → ?] 15
- (c) What product would you expect from Hofmann elimination of a cyclic amine such as piperidine? Write all the steps involved in the elimination.
[Figure: Reaction scheme: piperidine (six-membered ring with NH) –1. CH₃I (excess); 2. Ag₂O, H₂O; 3. Δ → ?] 15
4. (a) Diels-Alder reaction of cyclopentadiene with maleic anhydride is much faster than the reaction of cyclopentadiene with cis-2-butene. Account for the same on the basis of HOMO-LUMO energies involved. 10
- (b) Explain the origin of regioselectivities observed in Diels-Alder reaction. Predict the major regioisomer formed in the following reaction:
[Figure: Reaction scheme: penta-1,3-diene drawn s-cis with the CH₃ on a terminal diene carbon (C-1) + methyl acrylate (CH₂=CH-COOCH₃) –Δ → ?] 10
- (c) Suggest suitable experiment/technique to establish the following with suitable example: (i) Detection of suspected intermediate (ii) Differentiate between intramolecular and intermolecular mechanisms. 15
- (d) Give mechanism involved in Wittig reaction. Comment on the effect of stabilized and non-stabilized ylids on outcome of stereochemistry in the reaction. Predict the product in the following reaction:
[Figure: Reaction scheme: benzofuran (benzene ring fused to a furan ring, O at the lower left) carrying CHO and OCH₃ on adjacent carbons of the benzene ring (CHO at C-5 and OCH₃ at C-6 as drawn) + Ph₃P=CHCOOCH₂CH₃ –EtOH → ?] 15

SECTION 'B'

5. (a) (i) Draw the structure of repeating unit of following polymers: Neoprene rubber, Gatta Percha and Polystyrene. (ii) Sketch the synthetic route for monomers of Nylon-6 and Kevlar fibres. 10
- (b) What is cis-trans photoisomerization? Give mechanism involved in the isomerizations of alkenes. Predict the equilibrium product in the following reaction:
[Figure: Reaction: cis-cyclononene drawn as a nine-membered ring with atoms numbered 1–9 and the C=C between C-1 and C-2 –hv (equilibrium arrows ⇌) → ?] 10
- (c) Explain why hydroboration-oxidation protocol gives anti-Markonikoff's alcohol from unsymmetrical alkene. Complete the following reaction giving predominant stereoisomer and regioisomer.
[Figure: Reaction scheme: 2-methylbicyclo[2.2.1]hept-2-ene (norbornene with CH₃ on one alkene carbon) –(i) B₂H₆; (ii) H₂O₂, NaOH → ?] 10
- (d) Which of the following two pairs of stereoisomers can be distinguished with the help of coupling constants in PMR spectroscopy? Account for your choice:
[Figure: (i) (Z)-stilbene, Ph(H)C=C(H)Ph with both Ph on the same side, and (E)-stilbene, Ph(H)C=C(H)Ph with Ph trans; (ii) (Z)-1-phenylpropene, Ph(H)C=C(H)CH₃ with Ph and CH₃ on the same side, and (E)-1-phenylpropene, Ph and CH₃ trans] 10
- (e) Classify the proteins. Give a note on their 1°, 2° and 3° structures. 10

6. (a)(i) Give major m/e peaks for 1-phenyl-1-butanone. Give mechanism involved in the formation of McLafferty rearrangement product for the same. 10
- (a)(ii) Account for the different carbonyl absorptions [ν C = O] for the following compounds:
[Figure: acetophenone $\text{C}_6\text{H}_5\text{--CO--CH}_3$, 1683 cm^{-1} ; benzoyl bromide $\text{C}_6\text{H}_5\text{--CO--Br}$, 1812 cm^{-1} ; ethyl benzoate $\text{C}_6\text{H}_5\text{--CO--OC}_2\text{H}_5$, 1720 cm^{-1}] 10
- (b) Draw the structures of DNA and RNA with all four bases. 15
- (c) Suggest appropriate reagents/conditions, with justification, for the desired chemical transformations shown below:
[Figure: 1-methylcyclohexene at the centre with four arrows, each labelled “?”, to: (1, left) cis-1-methylcyclohexane-1,2-diol (C-2 bears H and a hashed OH; C-1 bears CH_3 and a hashed OH); (2, right) trans-2-methylcyclohexan-1-ol (C-1 bears H and a hashed OH; C-2 bears a wedged CH_3 and a hashed H); (3, lower left) trans-1-methylcyclohexane-1,2-diol (C-2 bears a wedged OH and a hashed H; C-1 bears CH_3 and a hashed OH); (4, lower right) 1-methylcyclohexan-1-ol (C-1 bears a wedged CH_3 and a hashed OH)] 15
7. (a) Assign structure to the compound with mol. formula $\text{C}_9\text{H}_{10}\text{O}_2$, on the basis of the following spectral data: (i) UV (EtOH): λ_{max} 268, 264, 257, 243 nm (ii) IR: 1745 cm^{-1} , 1225 cm^{-1} , 749 cm^{-1} , 697 cm^{-1} (iii) ^1H NMR: δ 7.1 – 7.3 (m, 5H), 5.0 (s, 2H), 1.96 (s, 3H) (iv) Mass: m/e ions: 150, 108, 91, 43. 15
- (b) (i) Draw the structure of repeating unit of PVC, PET and SBR. (ii) Sketch the synthetic route for monomers of Nylon-6, 6. 15
- (c) Suggest suitable reagents and provide mechanism for the following chemical conversions:
[Figure: (i) octahydro-2H-chromene-4a,8a-diol (two fused six-membered rings, one containing a ring O next to the lower ring-fusion carbon; an OH on each ring-fusion carbon) $\rightarrow$ the same bicyclic outline (the bond between the two former ring-fusion carbons is still drawn) with a C=O in place of each OH (the lower one next to the ring O, i.e. a lactone C=O), intended as the ten-membered keto-lactone from cleavage of the fusion bond; (ii) 7-(methoxymethyl)bicyclo[2.2.1]heptan-2-one ($\text{H}_3\text{COH}_2\text{C--}$ on the one-carbon bridge) $\rightarrow$ the corresponding bicyclic lactone with O inserted between the C=O and the bridgehead (2-oxabicyclo[3.2.1]octan-3-one carrying $\text{H}_3\text{COH}_2\text{C--}$ on the one-carbon bridge); (iii) bicyclo[2.2.1]heptan-2-one (norcamphor) $\rightarrow$ bicyclo[2.2.1]heptane-2,3-dione; (iv) norbornene $\rightarrow$? $\rightarrow$ cis-exo-bicyclo[2.2.1]heptane-2,3-diol (both OH exo, drawn up; both H endo, drawn down)] 20
8. (a) Predict ^1H NMR spectra for the following compounds: (i) 1-propene (ii) 1-phenyl-1-propanone. 10
- (b) Predict the base peaks for the following compounds in mass spectroscopy:
[Figure: 4-ethylanisole (benzene ring with $\text{CH}_2\text{--CH}_3$ and H_3CO para to each other) and benzophenone (O=C bonded to two phenyl rings)] 10
- (c) Give mechanism involved in Norrish type II reaction and predict the products in the following reactions:
[Figure: Reaction: 2-(2-phenylethyl)-3,4-dihydronaphthalen-1(2H)-one (1-tetralone with a $\text{CH}_2\text{CH}_2\text{Ph}$ group on C-2, the carbon α to the C=O) $\xrightarrow{-h\nu}$?] 10
- (d) Provide mechanism for the following conversion:
[Figure: 4-tert-butylcyclohexanone drawn as a chair with the t-butyl group equatorial and the ring H on that carbon axial $\xrightarrow{-\text{Na/liq. NH}_3}$? followed by the product drawn as a chair: trans-4-tert-butylcyclohexanol with t-butyl equatorial, OH equatorial and the H on the carbinol carbon axial (drawn up)] 5
- (e) What is condensation polymerization? Give structure of repeating units in terylene and show how terylene is obtained. 5
- (f) Illustrate the difference between thermoplastics and thermosetts. 5
- (g) Calculate λ_{max} for the following compounds:
[Figure: (1) bicyclic (decalin-skeleton) heteroannular diene: one C=C in the left ring and a second C=C from the ring-fusion carbon into the right ring, conjugated with the first (transoid), with a CH_3 on the left-ring alkene carbon adjacent to the ring fusion; (2) bicyclic homoannular diene: both C=C in the left ring, one of them ending at the ring-fusion carbon ($\text{C}_4=\text{C}_{4a}$) and the other at $\text{C}_2=\text{C}_3$, with an angular CH_3 on the other ring-fusion carbon ($\text{C}-8a$)] 5