

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.

All questions carry equal marks.

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:
 - (a) State the criteria of aromaticity. Decide whether each of the following compounds is aromatic. (i) Pyrrole (ii) 1,3,5-Hexatriene (iii) 1,3,5-Cyclo-heptatriene (iv) 18-Annulene
 - (b) Predict the product from each of the reactions. Give mechanisms in support of your answer.
[Figure: (i) α -chloroketone $R-CH_2-C(=O)-CH(Cl)-R'-(OCH_3) \rightarrow ?$ (ii) ketoxime $R-C(=NOH)-R'-(p-TsCl \text{ over arrow; pyridine under arrow}) \rightarrow ?$]
 - (c) Explain Wittig reaction. Give its mechanism. How would you synthesize $C_6H_5CH=CH-CH_3$?
 - (d) (i) What are sigmatropic rearrangements? Give their stereochemistry. Say whether 5-methyl cyclopentadiene can offer such a rearrangement. (ii) Depict Cope and Claisen rearrangements as examples of sigmatropic shift.
2. (a) Account for the fact that treatment of p-bromotoluene with NaOH at 300° yields a mixture of two products but treatment of m-bromotoluene with NaOH yields a mixture of three products. Give mechanism of the reaction and also give evidences in support of your answer.
 - (b) Predict the product(s) in the following reactions. Give their mechanisms.
[Figure: (i) 2-bromo-2-methylpentane, $(CH_3)_2C(Br)-CH_2-CH_2-CH_3-(t-BuO^-K^+ \text{ over arrow; } \Delta \text{ under arrow}) \rightarrow ?$ (ii) quaternary ammonium hydroxide $CH_3-CH_2-N^+(CH_3)_2-CH_2-CH_2-CH_3-OH$ (ethyl-dimethyl-n-propylammonium hydroxide; the lower N-methyl is printed as "CH₂") $-(\Delta) \rightarrow ?$ (iii) amine oxide $CH_3-CH_2-N^+(O^-)(CH_3)_2$ (N,N-dimethylethylamine N-oxide) $-(\Delta) \rightarrow ?$]
 - (c) Predict the products from the following reactions. Give their mechanisms.
[Figure: (i) 1-methylcyclohexene (cyclohexene ring with CH_3 on a double-bond carbon) $-(HBr \text{ over arrow; ether under arrow}) \rightarrow ?$ (ii) 1-octyne, $CH_3-(CH_2)_5-C\equiv CH-(R_2BH \text{ over arrow; THF under arrow}) \rightarrow ?$ (iii) ketone $R-C(=O)-R' + R''-NH_2-(H^+) \rightarrow ?$]
 - (d) Predict the product from the following reactions. Discuss their mechanisms.
[Figure: (i) 2-chloro-1,3,5-trinitrobenzene (picryl chloride: benzene ring with Cl at C1, NO₂ groups at both ortho positions and at the para position) $-(OH^-) \rightarrow ?$ (ii) pyrrole (five-membered ring with N-H) $-(HNO_3-H_2SO_4) \rightarrow ?$ (iii) 2,3,4,6-tetra-O-acetyl-glucopyranosyl bromide drawn as a chair (ring O at the back right; CH_2OAc on C5; OAc groups (printed "ACO", "OAC") on C4, C3 and C2; Br on C1 drawn as an equatorial-type bond to the right) $-(MeOH, Ag_2O) \rightarrow ?$]
3. (a) Explain the aromatic properties of tropolones. Give one synthesis of β -tropolone.
 - (b) (i) In theory, trans-3,4-dimethyl cyclobutene can open by two conrotatory paths to give either (2E,4E)-hexadiene or (2Z,4Z)-hexadiene. Explain why both products are symmetry allowed and then account for the fact that only the 2E,4E isomer is obtained in practice. (ii)

What products would you expect to obtain from the photochemical cyclizations of (2E,4Z,6E)-octatriene and of (2E,4Z,6Z)-octatriene?

- (c) (i) What stereochemistry would you expect for the product of the Diels-Alder reaction between (2E,4E)-hexadiene and ethylene? What stereochemistry would you expect if (2E,4Z)-hexadiene were used instead? (ii) (2E,4Z,6Z,8E)-Decatetraene has been cyclised to 7,8-dimethyl-1,3,5-cyclo-octatriene. Predict the manner of ring closure conrotatory or disrotatory-for both thermal and photochemical reactions and predict the stereochemistry of the product in each case.
- (d) (i) What stereochemistry would you expect to observe in these reactions? (a) A photochemical [1, 5] sigmatropic rearrangement (b) A thermal [4, 6] cyclo addition (c) A thermal [1, 7] sigmatropic rearrangement (ii) A photochemical [2, 6] cyclo addition Predict the product you would expect to obtain from the following reaction. Should this shift be a suprafacial or an antarafacial process?

[Figure: Phenyl 2,4-hexadienyl ether, $\text{C}_6\text{H}_5\text{-O-CH}_2\text{-CH=CH-CH=CH-CH}_3$ (benzene ring bonded to O; zigzag chain from O with double bonds at the second and fourth bonds, ending in CH_3) $\rightarrow$ ((5, 5) over arrow; Δ under arrow) $\rightarrow$?]

4. (a) What are the products formed by Dieckmann Cyclization of diethyl-3 methyl-heptane-dioate? Give its mechanism.
- (b) What is Reformatsky reaction? Show how it is used for preparing β -hydroxyesters. Give its mechanism.
- (c) Predict the product in the following reaction. Propose its mechanism.
[Figure: Diethyl succinate, $\text{CH}_2\text{CO}_2\text{Et-CH}_2\text{CO}_2\text{Et}$ (printed "CO₂Es") + benzophenone, $\text{Ph}_2\text{C=O}$ $\rightarrow$ (1. $\text{t-BuO}^-\text{K}^+\text{-t-BuOH}$; 2. Δ ; 3. H_3O^+) $\rightarrow$ (product not shown)]
- (d) Predict the products in the following reactions. Give their mechanisms.
[Figure: (i) $\text{PhNHNH}_2 + \text{Ph-C(=O)-CH}_3$ (acetophenone) $\rightarrow$ (ZnCl_2) $\rightarrow$? (ii) phenol (benzene ring with OH) + $\text{CHCl}_3 + \text{NaOH}$ $\rightarrow$ (Δ) $\rightarrow$?]

SECTION 'B'

5. Answer any three of the following:
- (a) Propose a structure for the compound with the following data: M/S (m/z) = 55 (base peak), 90 and 92 (peaks about 1/3 the size of 90) IR (cm^{-1}) 1642, 990 and 930 $^1\text{H NMR}$ (δ) = 1.6 (d), 4.5 (quint), 4.9 6.3 (m) in 17.5 6 19.5 integral ratios Unsaturation number = 1
- (b) Suggest the reaction product(s) and explain its mechanism:
[Figure: (i) methylenecyclohexane (cyclohexane ring with exocyclic $=\text{CH}_2$) $\rightarrow$ (NBS over arrow; CCl_4 , Δ under arrow) $\rightarrow$? (ii) trans-alkenyl iodide $\text{n-C}_7\text{H}_{15}\text{-CH=CH-I}$ ($\text{n-C}_7\text{H}_{15}$ and H on one carbon, H and I on the other, $\text{n-C}_7\text{H}_{15}$ and I trans; the I label is faint) $\rightarrow$ (n-Bu Li over arrow; CuI , ether under arrow) $\rightarrow$? (iii) $\text{C}_6\text{H}_5\text{-CH(OCH}_3\text{)-CH}_2\text{-Hg-O}_2\text{CCF}_3$ (benzene ring bearing a $\text{CH(OCH}_3\text{)}$ group whose other carbon is $\text{CH}_2\text{-Hg-O}_2\text{CCF}_3$) $\rightarrow$ (1. NaBH_4 ; 2. H_2O) $\rightarrow$?]
- (c) Explain the general structure of DNA including the H-bonding.
- (d) Predict the products in the following reactions and suggest their mechanisms.
[Figure: (i) 2-ethylbenzophenone (benzene ring with CH_2CH_3 and, ortho to it, C(=O)Ph) $\rightarrow$ (hv , 2-propanol) $\rightarrow$ (product not shown) (ii) $\text{R-C(=O)-(CH}_2\text{)}_2\text{-CH}_2\text{-R'}$ $\rightarrow$ (hv) $\rightarrow$ (product not shown) (iii) α,β -unsaturated ketone drawn skeletally: C=O carbon bearing a short vertical stub (CH_3) and attached to CH=C , the β -carbon carrying R and a second R (printed "R", possibly R' [?]) $\rightarrow$ (hv) $\rightarrow$ (product not shown)]
6. (a) Discuss the basic chemical bonding in α -Keratin including the H-bonding.
- (b) Describe the determination of mol. wt. of polymer by end group analysis method.
- (c) Give the synthesis, properties and use of terylene.

- (d) Predict the major products in the photochemical reactions and propose mechanisms.

[Figure: (i) $\text{C}_6\text{H}_5\text{--C(=O)--CH}_2\text{--CH}_2\text{--CH}_3$ (butyrophenone) $\xrightarrow{h\nu}$ (ii) bicyclic β -lactone drawn as two fused squares: in the right-hand four-membered ring the top-right corner carbon carries =O and the bottom-right corner is a ring O (2-oxabicyclo[2.2.0]hexan-3-one skeleton; no double bond visible in the left ring) $\xrightarrow{77\text{ K under arrow}}$]

7. (a) Which types of compounds are oxidised by the periodate? Give an example in each case. Mention the product formed by the periodate oxidation of the following compound.

[Figure: Two fused six-membered rings (decalin-type) with OH on each ring-fusion carbon (one drawn up, one drawn down); the left ring has a ring O attached to the lower ring-fusion carbon (octahydro-2H-chromene-4a,8a-diol)]

- (b) Describe the reduction of acid chlorides with lithium aluminium hydride and give its mechanism. What happens when 3 equivalents of t-butyl alcohol and LAH are used in this reaction?

- (c) How is SeO_2 used in organic chemistry? Give two examples and discuss their mechanisms.

- (d) Predict the major product of the photochemical reaction and give their mechanisms. (i) Methyl butyrate (ii)

[Figure: Cyclic ketone drawn as a seven-membered ring [?]: C=O at the top; going round, the ring carbon left of the carbonyl's neighbour bears two Ph groups and the corresponding carbon on the right bears two Ph groups, with a two-carbon bottom edge (3,3,6,6-tetraphenylcycloheptanone as drawn [?]); no reagent or arrow printed]

8. (a) Compound 'A' $\text{C}_5\text{H}_{10}\text{O}$ is one of the basic building blocks of nature. $^1\text{H NMR}$ of the compound shows the following data: 1.63 δ (3 H singlet) 1.70 δ (3 H singlet) 3.83 δ (1 H broad singlet which disappears on adding D_2O) 4.15 δ (2 H doublet, $J = 7\text{ Hz}$) 5.70 δ (1 H triplet, $J = 7\text{ Hz}$) Prepare a structure for A.

- (b) (i) Show the benzene radical anion ESR spectrum. (ii) How would you distinguish by MS between 3-heptanone and 4-heptanone?

- (c) (i) Phenol is a weak acid with $\text{pK}_a = 10.0$. It has $\lambda_{\text{max}} = 210\text{ nm}$ in ethanol. When dil NaOH is added to the solution, the absorption increases to $\lambda_{\text{max}} = 235\text{ nm}$. How do you account for this shift. (ii) Calculate λ_{max} for the following:

[Figure: (A) 6,7,8,8a-tetrahydronaphthalen-2(1H)-one: bicyclic dienone, ketone C=O at C2 of the left ring, C3=C4 double bond in the left ring conjugated with a C4a=C5 double bond exocyclic to the left ring (in the right ring); (B) 2,4-dihydroxy-3,5-dimethylacetophenone: benzene ring with C(=O)CH_3 at C1, OH at C2, Me at C3, OH (printed HO) at C4, Me at C5, H at C6]

- (d) (i) How could you use IR spectroscopy to tell if preparation of 5-cholesten-3-one from cholesterol by Jones oxidation is complete?

[Figure: Partial steroid skeleton (rings A and B with angular CH_3 at C10, C5=C6 double bond, rest of the molecule shown by a wavy bracket): 3-OH compound (cholesterol) $\xrightarrow{\text{(Jones Oxid.)}}$ the corresponding 3-ketone (5-cholesten-3-one, C3=O)]

- (ii) Distinguish between the following pairs by IR. (A) CH_3CN and $\text{CH}_3\text{--C(=O)--NH}_2$ (B) $\text{CH}_2\text{=CH--OCH}_3$ and $\text{CH}_3\text{--CH}_2\text{--CHO}$