

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) Indicate which of the following compounds is aromatic, non-aromatic and anti-aromatic in character and give explanation for your answer

[Figure: (i) a benzene ring fused on two adjacent sides to two cyclopentane rings (hexahydro-as-indacene); (ii) cyclopentadienone (five-membered ring with C=O and two C=C; the ring bond between the two upper carbons is not visible in the print); (iii) cyclopropenyl anion (three-membered ring with one C=C and a $\ominus$ charge on the third carbon); (iv) pentalene (two fused five-membered rings with C=C bonds); (v) 2,7-dihydroxytropone (seven-membered ring with C=O, the two ring carbons flanking the carbonyl bearing OH, and three ring C=C)]

- (b)(i) Explain why 1-hydroxybenzene exists entirely in the enolic form whereas 2-hydroxypyridine exists very largely in the ketonic form i.e., the lactam form,

- (b)(ii) Explain the difference between kinetic control and thermodynamic control of a reaction with the help of a potential energy diagram.

- (c) Formulate the following sequence of reactions and give mechanism for the formation of product in each step

[Figure: Reaction scheme: $\text{Ph}-\text{CO}-\text{CH}_3-\text{Cl}_2/\text{AcOH}/\text{RT} \rightarrow \text{A} \rightarrow \text{Ethylene glycol}/\text{p-TSA}/\Delta/\text{H}_2\text{O} \rightarrow \text{B} \rightarrow \text{KCN} \rightarrow \text{C} \rightarrow \text{H}_3\text{O}^+ \rightarrow \text{Ph}-\text{CO}-\text{CH}_2\text{COOH}$]

What is the role of ethylene glycol in the above sequence of reactions?

- (d)(i) Using suitable reagents, how will you convert toluene into ethyl p-aminobenzoate?

- (d)(ii) Give mechanistic explanation for the following observed fact:
 $\text{CH}_3\text{CHO} + 4\text{HCHO} \rightarrow \text{C}(\text{CH}_2\text{OH})_4 + \text{HCOOH}$.

2. (a) Give explanations for the following observations (i) In the reaction of 3-phenyl-1-propene with HI, the major product formed is 1-phenyl-1-iodopropane. (ii) Treatment of o-chlorotoluene with sodamide in liquid ammonia yields a mixture of o- and m-toluidines. (iii) Pyrrole is a much weaker base compared to pyridine (by several powers of 10).

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- (b) Give mechanisms for the following conversions:

[Figure: (i) 4-methylbenzaldehyde (H_3C para to CHO) –reagent printed illegibly as “Al?/RT” [?]→ 4-methylbenzoic acid (H_3C para to COOH ; the ring is only partly printed); (ii) phenyl 1-ethylallyl ether, $\text{C}_6\text{H}_5-\text{O}-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}=\text{CH}_2 \xrightarrow{\Delta/200^\circ\text{C}}$ 2-substituted phenol: OH on C-1 and $\text{CH}_2-\text{CH}=\text{CH}(\text{C}_2\text{H}_5)$ on C-2 of the benzene ring; (iii) indene $-\text{CHCl}_3/\text{t-BuO}^-\text{K}^+/\text{RT} \rightarrow$ 2-chloronaphthalene]

What evidence you can present in support of your mechanism for the above reactions?

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3. Formulate the reactions and give mechanistic explanation for each step of the following:

- (a) Treatment of cinnamic acid with bromine in refluxing CCl_4 gives dibromocinnamic acid which with excess aq. NaOH gives (in two stages) phenyl propiolic acid. **30**
- (b) Reaction of (R)-2-Butanol with thionyl chloride yields (R)-2-chlorobutane which with sodium azide under $\text{S}_{\text{N}}2$ conditions gives an azido derivative. The latter on catalytic hydrogenation leads to (S)-2-aminobutane which with excess MeI and subsequent Hofmann elimination gives 1-butene. **30**
4. (a)(i) Nitration of pyrrole with nitronium acetate gives 2-nitropyrrole whereas nitration of indole with the same reagent gives 3-nitroindole. Explain. **15**
- (a)(ii) Using appropriate reagents, how will you transform thiophene into 5-nitrothiophene-2-aldehyde? Explain giving the mechanisms. **15**
- (b)(i) Heating a mixture of m-chloroaniline with glycerol in the presence of an acid catalyst gives a mixture of isomeric products i.e., chloroquinolines. What are these products and how are they formed? **15**
- (b)(ii) Treatment of phthalic anhydride with urea yields phthalimide which with bromine in aq. NaOH gives anthranilic acid. Explain the reactions giving mechanisms. **15**

SECTION 'B'

5. Answer any THREE of the following:
- (a) (i) Write the structures of all-trans and all-cis polyisoprene. (ii) Explain the difference between silicones and silicates. (iii) Using the technique of mass spectrometry, indicate how will you distinguish between the three identical-mass-compounds (Mol. wt. 58) i.e. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{N}=\text{N}-\text{CH}_3$ and $\text{CH}_3\text{CH}_2-\text{CHO}$? (iv) In the mass spectrum of acetophenone, a meta-stable peak was observed at 56.5 [?]. Explain what is it due to. **20**
- (b) (i) Write the structures of the product/s formed in the Birch reduction of anisole and benzaldehyde and explain their formation. (ii) Describe a method for the conversion of 1-methyl-cyclohexene to 2-methylcyclohexanone and explain the mechanism. **20**
- (c) (i) Grade the following transitions according to the amount of energy required and give explanation for your grading on the basis of Molecular Orbital Theory in a qualitative manner:- $\pi \rightarrow \pi^*$; $n \rightarrow \pi^*$; $\sigma \rightarrow \sigma^*$. (ii) The IR spectrum of p-nitrobenzyl alcohol, when recorded in the KBr phase, shows a medium, broad absorption at around 3200 cm^{-1} . The same absorption shifts to 3450 cm^{-1} as medium, sharp absorption when recorded in CHCl_3 solution. Explain. **20**
- (d) (i) Explain why TMS is used as a reference standard in ^1H NMR spectroscopy. (ii) What is hyperfine splitting in ESR spectroscopy and what is its significance? (iii) Write the structures of the two isomeric alcohols corresponding to a molecular formula of $\text{C}_3\text{H}_8\text{O}$ and explain their proton NMR spectra. (iv) What is the difference between a "sensitizer" and a quencher" in photochemistry? Explain your answer with one example for each. **20**
6. (a) Using FMO approach, give explanation for the following reactions:
[Figure: (Trans-3, trans-3, 5-octadiene) [as printed; i.e. (3E,5E)-octa-3,5-diene drawn s-cis with the two terminal C_2H_5 groups outward and the two inner H] $-\Delta \rightarrow$ (Trans-3, 4-diethylcyclobutene): cyclobutene with H_5C_2 and H on C-3, H and C_2H_5 on C-4, the ethyl groups on opposite faces; and $-\text{h}\nu \rightarrow$ (Cis-3, 4-diethylcyclobutene): both C_2H_5 groups on the same face, both H on the other face] **20**
- (b)(i) Write the structure of the product formed by condensation polymerisation of terephthalic acid and ethylenediamine and explain its formation. **5**
- (b)(ii) The glass transition temperature of a polymer is 0°C . What will be its behaviour (in terms of its mechanical properties) at (+) 25°C and at (-) 25°C ? **5**
- (b)(iii) What are the products formed by free-radical polymerisation of difluoroacetylene? **10**
- (c) Explain the following transformations: **20**

[Figure: (i) cyclohexene $\xrightarrow{-\text{OsO}_4}$ cis-cyclohexane-1,2-diol (both OH on wedged bonds); (ii) indoline (2,3-dihydro-1H-indole, N-H) $\xrightarrow{-\text{Pb}(\text{OAc})_4}$ indole (N-H); (iii) 2-methylbut-2-ene $\xrightarrow{-\text{B}_2\text{H}_6}$ and then $\text{HO}^\ominus \rightarrow$ 3-methylbutan-2-ol $((\text{CH}_3)_2\text{CH}-\text{CH}(\text{OH})-\text{CH}_3)$; (iv) cyclohexanone $\xrightarrow{-\text{NBS}}$ and then $\text{HO}^\ominus \rightarrow$ cyclohex-2-en-1-one]

7. (a) (i) Explain the difference between singlet and triplet states of 1, 3-butadiene. (ii) Photolysis of ethyl methyl ketone gives biacetyl and n-butane whereas that of butyrophenone gives acetophenone and ethylene as products Explain. 20
- (b) Predict which of the following pairs of compounds will have higher λ_{max} values and why? (i) $\text{CH}_3-\text{CH}_2-\text{OH}$ and CH_3CHO (ii) [?] and aniline (iii) Trans $\text{Ph}-\text{CH}=\text{CH}-\text{CH}_3$ and $\text{Ph}-\text{CH}_2\text{CH}=\text{CH}_2$ (iv) Piperidine and [?] (v) [?] and [?]
 [Figure: (ii) a cyclohexane ring bearing a substituent drawn as “—O” (label garbled; apparently cyclohexylamine [?]); (iv) 1-(cyclohex-1-en-1-yl)piperidine (the enamine: piperidine N bonded to the double-bond carbon of a cyclohexene ring); (v) cyclohexa-1,4-diene and cyclohexa-1,3-diene] 20
- (c) Using IR spectroscopy, indicate how will you differentiate between the following pairs of compounds? (i) Benzyl chloride and Benzyl Cyanide (ii) Aniline and N-methylaniline (iii) Cyclohexanone and Cyclohexanol (iv) Benzoic acid and Benzaldehyde (v) Styrene and Phenylacetylene 20
8. (a) Indicate how you can identify the products of the following reaction using ^1H NMR spectroscopy?
 [Figure: 2-bromo-4-ethylanisole (benzene ring with OCH_3 at C-1, Br at C-2, C_2H_5 at C-4) $\xrightarrow{-\text{Cl}_2/\text{FeCl}_3}$ Mixture of three isomers (Chlorobromoethylmethoxy-benzenes) $\rightarrow$ Individual isomers.] 10
- (b) Explain how can you use ^1H NMR to identify the following isomers?
 [Figure: two cinnamic acids: $\text{PhHC}=\text{CHCOOH}$ with Ph and COOH on the same side (cis) “and” $\text{PhHC}=\text{CHCOOH}$ with Ph and COOH on opposite sides (trans)] 5
- (c)(i) What is meant by rotational degrees of freedom for a molecule? Explain the selection rules for rotational spectra of molecules. 10
- (c)(ii) How do you assay bulk drugs using UV-visible spectroscopy? 10
- (c)(iii) The molecular formula of a compound was found to be $\text{C}_3\text{H}_3\text{Cl}_5$. In its ^1H NMR spectrum, it showed signals at δ 4.52 [?] (t) and 6.07 (d). The ratio of integrals was found to be 2 cms: 4 cms. What is the structure of this compounds? 10
- (c)(iv) The mass spectrum of a compound showed its M^+ at 177. Its IR spectrum showed peaks at 3000 cm^{-1} (medium, sharp), 2700 cm^{-1} (medium, sharp), 1660 cm^{-1} (strong, sharp) and no other diagnostic absorptions. Its ^1H NMR spectrum showed signals at δ 1.25 (t, 6H), 3.4 (q, 4H), 6.6-7.4 (A_2B_2 , 4H) and 9.7 (s, 1H). The compound analyzed for C 74.6%, H 8.6% [?] and N 8.1%. No evidence for the presence of S or halogens could be found. Deduce the structure of this compound. 15