

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) Alcohols react with thionyl chloride to yield the unstable chlorosulfite (A) which reacts further to give the alkyl chlorides and SO₂. In dioxane, the product B with retention of configuration is formed but if pyridinium hydrochloride is present, the configuration is inverted to give C in this reaction. Explain the observations.

[Figure: Scheme: R₁R₂R₃C-OH (stereocentre with R₁ on a plain bond up, R₂ hashed, R₃ wedged, OH to the right) → SOCl₂ → A = R₁R₂R₃C-O-SOCl (same configuration) → B = R₁R₂R₃C-Cl with Cl to the right in the same spatial arrangement (retention) and C = R₁R₂R₃C-Cl drawn as the configurational alternative (inversion); the labels on B and C are partly hidden by the watermark]

- (b) Identify an aromatic compound from amongst the following. Enumerate the properties of the compound selected by you that would suggest aromatic character. What makes a compound anti-aromatic?

[Figure: (i) cyclooctatetraene; (ii) cyclopropenyl anion (three-membered ring with one C=C and a $\ominus$ charge on the apex carbon); (iii) 4H-pyran (six-membered ring with ring O and two C=C, the carbon opposite O saturated); (iv) thiophene]

- (c) Suggest an explanation for the fact that the order of reactivity of the halides towards n-butyl brosylate in acetone of $\text{Cl}^- > \text{Br}^- > \text{I}^-$ when $(\text{C}_4\text{H}_9)_4\text{N}^+$ is the cation of the halide but the order is $\text{I}^- > \text{Br}^- > \text{Cl}^-$ when Li^+ is the cation.

- (d) Explain the observed pK_a of the following compounds:

Compound	pK _a
CH ₃ -C(=O ⁺ H)-CH ₃	-2.85
CH ₃ -S(=O ⁺ H)-CH ₃	-1.54
C ₆ H ₅ -C(=O ⁺ H)-CH ₃	-4.02 [?]
CH ₃ -S ⁺ H-CH ₃	-6.99

2. (a) Explain the relative magnitudes of the following pairs of β-deuterium isotope effects (per deuterium) for solvolysis:

[Figure: two vinyl triflates: (H₂)D₂C=C(Ph)(OTf), $k_H/k_D=1.20$; and (H₂)D₂C=C(C₆H₄NO₂-p)(OTf) (4-nitrophenyl), $k_H/k_D=1.31$]

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- (b) Explain why treatment of 1-chloronaphthalene with ethoxide ion gives no reaction but treatment with A, it gives B:

[Figure: A = 5-chloroacenaphthylene (Cl on the naphthalene ring carbon para to the five-membered-ring junction; five-membered ring with a C=C); B = the corresponding ethoxy compound with OC₂H₅ in place of Cl; also drawn: 1-Chloronaphthalene]

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- (c) Propose a mechanism for the following transformation, explaining the migration of carboethoxy group in preference to phenyl group despite having a lower migratory aptitude:

[Figure: 4-phenyl-4-(ethoxycarbonyl)cyclohexa-2,5-dien-1-one (C-4 bearing Ph and CO₂Et) $\xrightarrow{H^+}$ phenol bearing CO₂Et meta to OH (C-3) and Ph para to OH (C-4), i.e. ethyl 5-hydroxy-2-phenylbenzoate]

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- (d) Explain why carbene (A) does not react with cyclohexene in a manner of ordinary carbenes but does react with dimethyl fumarate (B) and maleate (C) to yield spiropentanes (D)

[Figure: A = diphenylcyclopropenylidene (three-membered ring with C=C bearing two Ph groups, the third carbon the carbene centre); B = dimethyl fumarate (MeO₂C and CO₂Me trans); C = dimethyl maleate (both CO₂Me cis); D = spiro compound: diphenylcyclopropene ring (Ph, Ph on the C=C) spiro-fused to a cyclopropane bearing two CO₂Me groups]

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3. (a) Identify the major product in each of the following reactions. Give mechanisms of the reactions involved and stereostructure, if any:

[Figure: (i) 3,5-dimethoxybenzoic acid (CO₂H at C-1, MeO at C-3 and C-5) $\xrightarrow{1) Na/NH_3, 2) C_5H_{11}Br, 3) Pb(OAc)_4}$?; (ii) 1,1'-bi(cyclobutyl)-1,1'-diol (two cyclobutane rings joined at carbons each bearing OH) $\xrightarrow{-H^+}$?; (iii) cyclohexane bearing on adjacent carbons: HO (wedge, top), CH₂OH (HO-CH₂ on a hashed/wedged bond) and OH (at the next carbon, plain bond down) $\xrightarrow{-PhCHO, H_3O^+}$?; (iv) 2-methoxybuta-1,3-diene [?] (drawn as a diene with OMe on C-2) + CH₂=CH-CN $\xrightarrow{-\Delta}$?]

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- (b) What is a symmetry forbidden reaction? Explain the process by taking one example of an alkene.

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4. (a) How will you carry out the following transformations in good yields? Indicate the reagents used, conditions employed & reasons thereof:

[Figure: (i) cyclohex-2-en-1-ol $\rightarrow$ cyclohexane-1,2,3-triol (C-1 OH plain, C-2 OH hashed, C-3 OH on a wedged/bold bond); (ii) CH₃CH₂COCH₃ $\rightarrow$ PhCH(OH)-CH(CH₃)-CO-CH₃ (aldol: OH on hashed bond, CH₃ wedged; 4-hydroxy-3-methyl-4-phenylbutan-2-one); (iii) 1-chloro-3-phenylpropan-2-one (PhCH₂COCH₂Cl) $\rightarrow$ phenyl cyclopropanone [as drawn: benzene ring attached to a cyclopropanone ring carbon]; (iv) phenyl 3-methylbut-2-enyl ether (PhOCH₂CH=C(CH₃)₂) $\rightarrow$ 2-(1,1-dimethylprop-2-enyl)phenol (OH at C-1, C(CH₃)₂CH=CH₂ at C-2)]

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- (b) What are sigmatropic shifts? Give one example each of 3, 3- and 1, 5- sigmatropic shifts in organic reactions while explaining the logic behind such migrations.

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SECTION 'B'

5. Answer any three of the following:

20 × 3 = 60

- (a) Compound given below dissolves in acetone to form a brightly coloured solution whereas in ether, it remains colourless. The proton NMR at room temperature shows a broad signal at δ 1.88 which on cooling to -50 °C resolves into two signals at δ 2.07 (6H) and δ 1.29 (3H). Explain.

[Figure: 2,3-dimethylcycloprop-2-en-1-yl group (H₃C on each double-bond carbon) attached through its sp³ carbon to a carbon bearing two CN groups and a 4-nitrophenyl group: (CH₃)₂C₃H-C(CN)₂-C₆H₄NO₂-p]

- (b) How many vibrational degrees of freedom will be observed for gaseous acetylene (C₂H₂) and which of these will be infrared active?
- (c) Calculate the probability of a polymer formed by condensation of monomers consisting of 25 monomers when the reaction is 75% complete. What is the value of number average degree of polymerization under these conditions? Determine the extent of reaction in order for the number of degrees of polymerization to exceed 25.
- (d) Explain why on heating cis-3, 4- dimethylcyclobutene gives (E, Z)-hexa-2, 4-diene while its trans-isomer gives only the (E, E)-hexa-2, 4-diene. What happens when the same substrates are irradiated with UV light?

6. (a) Indicate in each of the following pairs as to which compound would undergo the mentioned rearrangement faster and why. Write main products of the rearrangement reactions:

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[Figure: (i) oxime of 4-methoxybenzophenone (Ph and $4\text{-CH}_3\text{OC}_6\text{H}_4$ on $\text{C}=\text{N}-\text{OH}$) and oxime of 4-nitrobenzophenone (Ph and $4\text{-NO}_2\text{C}_6\text{H}_4$ on $\text{C}=\text{N}-\text{OH}$) (Beckmann Rearrangement); (ii) benzamide ($\text{C}_6\text{H}_5\text{CONH}_2$) and phenylacetamide ($\text{C}_6\text{H}_5\text{CH}_2\text{CONH}_2$) (Hofmann Rearrangement); (iii) p-tolyl 1,3-dimethylbut-2-enyl ether ($4\text{-Me-C}_6\text{H}_4\text{-O-CH(Me)-CH=C(CH}_3)_2$) and allyl p-tolyl ether ($4\text{-Me-C}_6\text{H}_4\text{-OCH}_2\text{CH=CH}_2$) (Claisen Rearrangement); (iv) phenyl acetate ($\text{C}_6\text{H}_5\text{OCOCH}_3$) and phenyl acrylate ($\text{C}_6\text{H}_5\text{OCOCH=CH}_2$) (Fries Rearrangement)]

(b) How will you use IR and NMR spectroscopy to distinguish o- and p-hydroxyacetophenones? 12

7. (a) Explain the formation of citral through the following reaction sequence via sigmatropic shifts:

[Figure: 3-methylbut-3-enal [as drawn: $\text{CH}_2=\text{C(CH}_3)_2\text{-CH}_2\text{-CHO}$] + 3-methylbut-2-en-1-ol (prenyl alcohol, $(\text{CH}_3)_2\text{C=CH-CH}_2\text{OH}$) $\rightarrow$ dienyl ether: $(\text{CH}_3)_2\text{C=CH-CH}_2\text{-O-CH=CH-C(CH}_3)_2\text{CH}_2$ [as drawn] $-\Delta \rightarrow$ Citral ($(\text{CH}_3)_2\text{C=CH-CH}_2\text{-CH}_2\text{-C(CH}_3)_2\text{CH=CHO}$)] 15

(b) Arrange the following in order of increasing magnitude of coupling constant between H_A and H_B in the NMR spectrum. Give reasons for your answer.

[Figure: (i) $\text{RCH}=\text{CH}_\text{A}\text{H}_\text{B}$ (geminal H_A , H_B on the terminal alkene carbon); (ii) $\text{R-CH}_\text{A}-\text{CH}_\text{B}-\text{R}$ (vicinal, sp³); (iii) $\text{RCH}_\text{A}=\text{CH}_\text{B}\text{R}$ with H_A and H_B cis; (iv) $\text{RCH}_\text{A}=\text{CH}_\text{B}\text{R}$ with H_A and H_B trans] 15

(c) Experimental attempts to prepare the acid chloride of A by treatment with thionyl chloride gave B instead. Explain what might have happened:

[Figure: A = 1-tert-butylaziridine-2-carboxylic acid (t-Bu-N in a three-membered ring, CO_2H on a ring carbon); B = 1-tert-butyl-3-chloroazetidin-2-one (four-membered β -lactam: N bearing t-Bu, $\text{C}=\text{O}$ next to N, Cl on the adjacent ring carbon)] 15

(d) Identify major products A and B that might be formed in the following reaction sequence:

[Figure: p-cresyl acetate (benzene ring with OCOCH_3 and CH_3 para) $-\text{AlCl}_3, \Delta \rightarrow \text{A} -\text{PhCO}_3\text{H} \rightarrow \text{B}$]

Give mechanisms of the reactions involved. 15

8. (a)(i) How would mass spectral studies help you to distinguish the following? If mass spectrum is not appropriate, can the job be accomplished by IR, UV or NMR? How? 10

[Figure: pentan-2-one, pentan-3-one and 3-methylbutan-2-one (skeletal formulae)]

(a)(ii) How can NMR/IR be used to estimate enol content of the following? (1) $\text{CH}_3\text{-CO-CO-CH}_3$ (2) $\text{CH}_3\text{-CO-CH}_2\text{-CO-CH}_3$ (3) [?] 10

[Figure: (3) bicyclo[2.2.1]heptane-2,3-dione (norbornane-2,3-dione, two adjacent $\text{C}=\text{O}$ on the two-carbon bridge)]

(b) Using the indicated spectral determination, how the following pairs of isomeric compounds can be differentiated? (i) $\text{PhCOCH}_2\text{CH}_3$ and $\text{PhCH}_2\text{COCH}_3$ UV spectrum (ii) $\text{PhCH}_2\text{C}\equiv\text{CH}$ and $\text{PhCH}=\text{C}=\text{CH}_2$ IR spectrum (iii) $\text{PhOCH}_2\text{CH}_3$ and $\text{PhCH}_2\text{OCH}_3$ NMR spectrum (iv) [?] Any spectral method (v) $\text{CH}_3\text{-CH}_2\text{-C(CH}_3)_2\text{-CHO}$ and $(\text{CH}_3)_3\text{CCH}_2\text{CHO}$ NMR spectrum

[Figure: (iv) 4-(chloromethyl)benzonitrile (CN and CH_2Cl para) and 3-chloro-5-methylbenzonitrile (CN at C-1, Cl at C-3, CH_3 at C-5)] 20

(c)(i) 2, 4, 6-Trimethyl benzoic acid (mesitoic acid) undergoes acid catalysed esterification very slowly. However when it is dissolved in concentrated H_2SO_4 and the solution is poured into excess of alcohol, good yields of mesitoic esters are obtained. Explain. 10

(c)(ii) Identify A and B in the following reaction. Give reasons for your identification 10

[Figure: iodobenzene $-\text{Cl}_2/\text{CHCl}_3 \rightarrow \text{A} -\text{Na}_2\text{CO}_3 \rightarrow \text{B}$]