

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:
 - (a)(i) HNO_2 is treated with [?] and [?] separately in acidic medium. What are the products?
 [Figure: The two substrates are garbled in the source: the first is drawn only as a ">" bond fragment (labels CH_3 , NH , CH_3 displaced to the page margin, i.e. apparently dimethylamine, $(\text{CH}_3)_2\text{NH}$ [?]); the second is a benzene ring carrying one substituent drawn as a plain vertical bond whose label is lost (apparently N,N-dimethylaniline [?])] 20
 - (a)(ii) If [?] undergoes nucleophilic substitution reaction, what are the favoured positions? Explain mechanistically.
 [Figure: a six-membered aromatic ring drawn as a hexagon with an inner circle; the heteroatom label is lost (a stray "N" appears at the foot of the page, so apparently pyridine [?])] 20
 - (b)(i) How the aromaticity of a molecule can be judged from ^1H NMR spectrum? Which thermodynamic data is concrete evidence? 20
 - (b)(ii) Pyrrole with acid (strong) makes a red coloured compound. What is its chemical nature? 20
 - (c)(i) Potential Energy (PE) changes during rotation about C(2) - C(3) bond of n-butane. Present the variation semi-quantitatively with rotation of the bond. 20
 - (c)(ii) What are the products formed when $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ reacts with CHCl_3 and NaOH ? 20
 - (d) Identify A-C in the following:
 [Figure: Reaction scheme: 3-bromobenzamide (benzene ring with $\text{C}(=\text{O})\text{NH}_2$ and Br meta to each other) $\xrightarrow{\text{(i) KOBr}}$ (ii) reflux, (iii) Extract with ether $\rightarrow$ A $\xrightarrow{-\text{HNO}_2/\text{HCl}}$ B $\xrightarrow{-\text{NaBH}_4}$ C] 20
2. (a) Ozonolysis of $\text{A}_2\text{C}=\text{CB}_2$ and $\text{E}_2\text{C}=\text{CD}_2$ (Where B & D are stronger electron donor than A and E) produces four ozonides. Explain mechanistically.
 [Figure: the two alkenes drawn structurally: $\text{C}=\text{C}$ with two A groups on one carbon and two B groups on the other; $\text{C}=\text{C}$ with two E groups on one carbon and two D groups on the other] 20
 - (b) Butadiene on reaction with Br-F (mole ratio = 1 : 1) produces two products. Explain. 10
 - (c) $\text{C}_6\text{H}_5\text{-Cl}$ on reaction with NaOH in an autoclave produces phenol (major), diphenyl ether and p-phenyl phenol. Explain the mechanism of formation. 20
 - (d) Why p-nitro benzaldehyde does not follow benzoin condensation? Explain. 5
 - (e) $\text{C}_6\text{H}_5\text{CHO}$ is refluxed in the presence of NaOH and excess HCHO . Write the major aromatic product. 5
3. Identify the intermediates and products:
 - (a) [Figure: (i) $\text{C}_6\text{H}_5\text{-CHO} + \text{CH}_3\text{C}(=\text{O})\text{-CH}_3 \xrightarrow{\text{base}}$ A $\xrightarrow{-\text{CH}_2(\text{CO}_2\text{Et})_2}$ Base $\rightarrow$ B $\xrightarrow{\text{Acid hydrolysis}}$ C. (ii) 1, 3-butadiene (excess) + p-benzoquinone $\xrightarrow{\text{heat at } 50^\circ\text{C}}$ A $\xrightarrow{\text{heated with Se}}$ B $\xrightarrow{-\text{Zn} + \text{acid}}$ C] 20

- (b) [Figure: naphthalene + COCl_2 - AlCl_3 , Room temp. $\rightarrow$ A - NH_2OH $\rightarrow$ B - PCl_5 , mild heat $\rightarrow$ C - (a) Reflux with HCl, (b) Filtered, filtrate is treated with NH_3 $\rightarrow$ D - $\text{CH}_2=\text{CH}-\text{CHO}$, H_2SO_4 , H_3AsO_4 $\rightarrow$ E] 20
- (c) [Figure: cyclopentane ring bearing at C-1 a CH_3 (wedged) and a CO_2H , and at C-3 an H (wedged) and a C(=O)NH_2 group (3-carbamoyl-1-methylcyclopentane-1-carboxylic acid) - OBr^- $\rightarrow$ A - heat $\rightarrow$ B] 10
- (d) [Figure: $\text{C}_6\text{H}_5-\text{C(=O)-OEt} + \text{CH}_3-\text{C(=O)-OEt}$ - (a) $^- \text{OC}_2\text{H}_5$, (b) HCl $\rightarrow$ A - (a) $^- \text{OC}_2\text{H}_5$, (b) $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ $\rightarrow$ B - (a) acid hydrolysis, (c) Acid (as printed) $\rightarrow$ C] 10
4. Identify the products in the following reactions:
- (a) [Figure: diethyl adipate drawn as $\text{CH}_2-\text{CH}_2-\text{C(=O)-OEt}$ over $\text{CH}_2-\text{CH}_2-\text{C(=O)-OEt}$ (the two CH_2 ends joined) - OEt^- , reflux & acidify $\rightarrow$ A - Acid hydrolysis $\rightarrow$ B - $\text{NC}-\text{CH}_2\text{CO}_2\text{Et}$, $\text{CH}_3-\text{CO}_2\text{NH}_4$ $\rightarrow$ C] 15
- (b) [Figure: 4-nitrobenzaldehyde (O_2N para to CHO) + 4-methoxybenzaldehyde (CH_3O para to CHO) - CN^- , Catalyst $\rightarrow$ A + B] 10
- (c) [Figure: 1-chloro-2-nitrobenzene (Cl and NO_2 ortho) - $^- \text{OCH}_3$ $\rightarrow$ A - (i) Zn , HCl , (ii) HNO_2 , HCl , (iii) Boiled in water $\rightarrow$ B - (i) CHCl_3 + KOH , (ii) acidify $\rightarrow$ C] 15
- (d)(i) [Figure: $\text{CH}_3-\text{CO}_2\text{C}_2\text{H}_5$ - $^- \text{C}_2\text{H}_5$ (as printed), reflux and acidify $\rightarrow$ A - (a) $^- \text{OC}_2\text{H}_5$, (b) I_2 $\rightarrow$ B - P_2S_5 , heat $\rightarrow$ C] 15
- (d)(ii) [Figure: thiophene + succinic anhydride (two CH_2 groups each bonded to a C=O , the two C=O joined through a ring O) $\rightarrow$ A] 5

SECTION 'B'

5. Answer any THREE of the following:
- (a)(i) Using Woodward-Fieser rule predict the λ_{max} for the following in their electronic spectra:
[Figure: (A) six-membered ring with CH_3 at C-1 and C-4 (opposite corners) and a ring C=C at the lower right; the remaining ring bonds are obscured by the watermark (apparently 1,4-dimethylcyclohexa-1,3-diene [?]); (B) bicyclic hexahydronaphthalene with a C=C at the ring fusion (C-8a=C-1), C-1 bearing a vinyl group printed " $\text{CH}=\text{H}_2$ " (i.e. $\text{CH}=\text{CH}_2$ [?]), and a second C=C in the other ring adjacent to the ring fusion] 20
- (a)(ii) What are Norrish type I and II photo-cleavages? 20
- (b)(i) The ^1H NMR spectrum of molecule $\text{C}_2\text{H}_2\text{BrCl}$ has two doublets with $J = 16$ Hz. Write its structure with reason. 20
- (b)(ii) For synthesis of polyester, glycol is treated with dimethyl terphthalate but not phthalic acid. Explain. 20
- (c)(i) Explain the appearance of $m/z = 44$ peak in the mass spectrum of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$. 20
- (c)(ii) The dehydration of 1, 2-dimethyl cyclohexanol (cis or trans) gives three alkenes. How can you distinguish them on the basis of their IR spectra? 20
- (d)(i) The geometric isomers of stilbene show λ_{max} at 278 and 294 nm. Assign each value to appropriate isomer and sketch them. 20
- (d)(ii) Write reagent(s) for the following conversion:
[Figure: cyclopentene $\rightarrow$ cyclopentane-1,2-diol (both OH drawn on plain bonds on adjacent carbons)] 20
6. Identify A-D in the following
- (a) [Figure: Scheme: cyclopentanone (five-membered ring $=\text{O}$) - $h\nu$ $\rightarrow$ [A] - $(-\text{CO})$ $\rightarrow$ B $\rightarrow$ C, with B also giving $2\text{CH}_2=\text{CH}_2$ (vertical line from B to " $2\text{CH}_2=\text{CH}_2$ "); [A] - $\gamma\text{-H}$ abstraction (downward arrow) $\rightarrow$ D] 20
- (b) What are products formed by photodimerization of cyclopent-2-en-1-one? 10
- (c) How adipic acid can be produced from phenol (only two steps)? 10
- (d) 2, 3-dimethyl-2-chlorobutane on E2 dehydrohalogenation gives how many products? Can they be distinguished by IR spectroscopy? Justify your answer. 20
7. (a) Explain the mechanism of following transformation:
[Figure: indene-1-d equilibria: 1-deuterioindene (C-1 bearing H and D) $\rightleftharpoons$ 2-deuterioindene (D on C-2) $\rightleftharpoons$ 3-deuterioindene (D on C-3); benzene ring drawn with inner circle, five-membered ring C=C between C-2 and C-3] 15
- (b) $4 + 2$ cycloaddition is thermally allowed. Explain through HOMO and LUMO. 15

	(c)(i)	What is the hybridization of DNA?	10
	(c)(ii)	Mechanical strength of Nylon is better than polyester. Explain.	10
	(c)(iii)	Why does B_2H_6 follow anti-Markovnikovs addition to $R_2C=CH_2$?	10
8.	(a)	How $H_2C=C=CH_2$ and $H_3C-C\equiv CH$ are distinguished by IR spectroscopy and proton NMR spectroscopy? Give method for chemical separation of the two compounds.	20
	(b)	How is azelaic acid obtained from oleic acid? Azelaic acid $HOOC(CH_2)_7COOH$ Oleic acid = $CH_3(CH_2)_7-CHCH(CH_2)_7COOH$.	10
	(c)	A cyclonitrile can be polymerized by base catalyzed reaction but not by acid catalyzed reaction. Explain.	15
	(d)	In the mass spectrum of $CH_3CH_2C(=O)-OCH_3$ the peaks at $m/z = 57, 59, 88$ appear. Explain.	15