C–HENT–N–BGDLB

CHEMISTRY

PAPER—II

Time Allowed : Three Hours	Maximum Marks : 200

QUESTION PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions

There are EIGHT questions in all, out of which FIVE are to be attempted.

Question Nos. **1** and **5** are compulsory. Out of the remaining SIX questions, THREE are to be attempted selecting at least ONE question from each of the two Sections A and B.

Attempts of questions shall be counted in chronological 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.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it.

Answers must be written in ENGLISH only.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary and indicate the same clearly.

Neat sketches may be drawn, wherever required.

SECTION—A

1. Answer briefly the following : 5×8=40

(a) Indicate the type of bonding in ferrocene while commenting on its aromatic character.

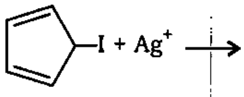
(b) Dipole moments of pyrrole and furan are in opposite direction. Explain.

(c) Predict the site of protonation for each of the following molecules :

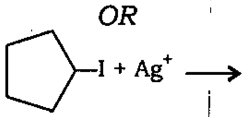
$PhCH{=}N{-}Ph$, CH_3CONH_2, Pyrrole, 2-Aminopyridine

Explain the basis of your answer.

(d) Explain which of the following reactions would be faster :

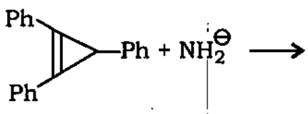
(i) 

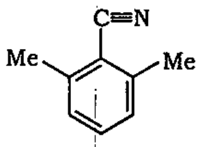
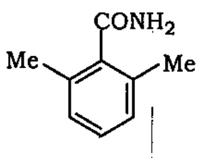
OR



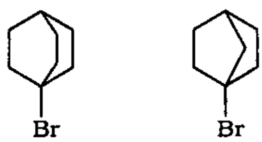
(ii) $Ph_3CH + NH_2^{\ominus} \longrightarrow$

OR



(e) The nitrile,  can be hydrolysed very readily to corresponding amide,  which is extremely difficult to hydrolyse further. Discuss.

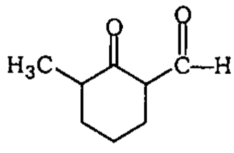
(f) Explain why (*A*) reacts faster than (*B*) when treated with aqueous silver nitrate :



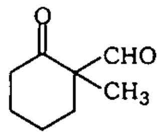
(*A*) (*B*)

(g) The rate of solvolysis of benzyl bromide in aqueous media is decreased in the presence of lithium bromide but not in the presence of lithium nitrate. However, none of these salts affects the rate of solvolysis of methyl bromide. Explain.

(h) Explain why ethyl formate condenses with 2-methyl cyclohexanone in the presence of a base to yield (*A*) and not (*B*) :

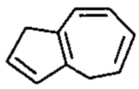


(*A*)



(*B*)

2. *(a)* Azulene (*X*) has a dipole moment despite the fact that there is no functional group attached to it. Explain. 10



(*X*)

(b) If aldol condensation of acetone in the presence of D_2O is stopped before completion, the unreacted acetone is found to be deuterated. Offer an explanation for this observation. 10

(c) Kinetic observations on the following reaction give the rate constant *k* to be proportional to concentration of acetaldehyde and also to the concentration of hydroxide ion. How is this information helpful in deducing a possible reaction mechanism for it? 10

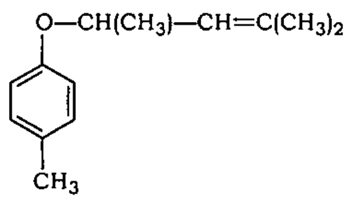
$$2CH_3CHO \xrightarrow{OH^-} CH_3CH(OH)CH_2CHO$$

(d) Explain formation of the major product in the thermal decomposition of the tetra-alkyl ammonium salt

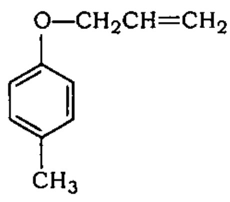
$$\left[\begin{array}{c} \text{Me} \\ | \\ \text{Et—N—}t\text{-Bu} \\ | \\ \text{Me} \end{array} \right]^+ OH^-$$

10

3. *(a)* Which of the following [(*A*) or (*B*)] would undergo Claisen rearrangement faster? Give reasons in support of your answer : 10



(*A*)

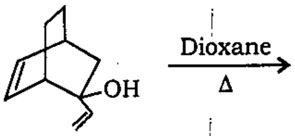


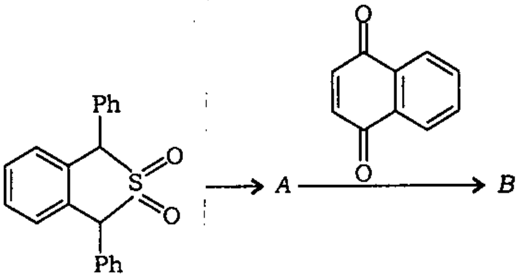
(*B*)

(b) *(i)* Explain why iodine is often used as a catalyst in aromatic bromination reactions.

(ii) Discuss the mechanism of the reaction of *N*-bromosuccinimide with toluene. 10

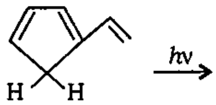
(c) Complete the following sigmatropic reactions : 10

(i) 

(ii) 

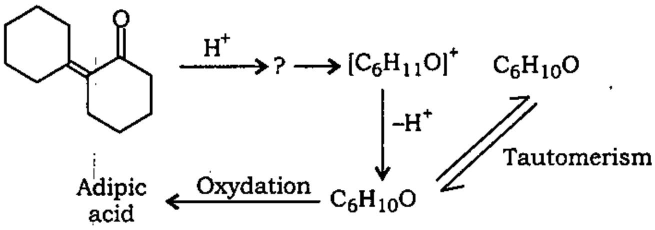
(d) (i) Apply Woodward-Hoffmann rules to predict the reaction between ethene and allyl cation.

(ii) Write the product of the following reaction and give mechanism for it :



10

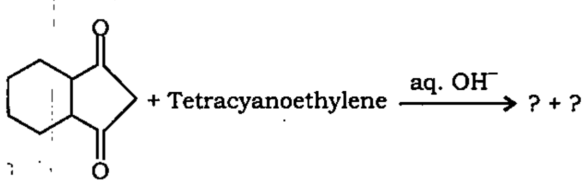
4. (a) Outline the steps in the following transformation with corresponding structures : 10



(b) Give the products in the reaction of $\overset{\ominus}{C}H_2—N=\overset{+}{N}$ with ethyl methyl ketone. 10

(c) 8-Quinolinol yields 5 and 7 substituted isomers on Reimer-Tiemann reaction. Explain the reaction mechanism. 10

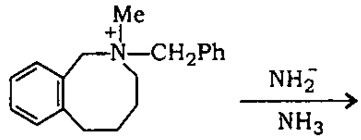
(d) Complete the following reaction with structures and products : 10



SECTION—B

5. Answer the following : 5×8=40

(a) Give the major product of the reaction



and possible mechanism involved.

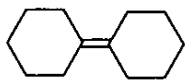
(b) Predict the order of rates of S_N1 and S_N2 reactions in the following solvents with dielectric constants given in the parentheses :

C_2H_5OH (25·0), CH_3OH (31·0), Hexane (1·9), Water (78·0), Benzene (2·3)

(c) The reaction between an alcohol and $SOCl_2$ to give alkyl chloride is accompanied by inversion of configuration when pyridine is used as the solvent. In the absence of pyridine, the same reaction leads to retention of configuration. Explain.

(d) *(i)* Explain why the presence of cesium(III) or Zn(II) modifies the stereochemistry of borohydride reduction of cyclohex-2-enone.

(ii) How will you obtain the following in the laboratory?



(e) The rotational spectrum of CO shows a series of lines placed 3·84235 cm^{-1} apart. Calculate the moment of inertia of C = O bond.
($h = 6 \cdot 626 \times 10^{-27}$ erg-sec)

(f) Explain the ESR spectrum of isopropyl alcohol radical.

(g) *(i)* Given green, blue and yellow dyes. Which dye absorbs the shortest wavelength and which the longest?

(ii) List all the electronic transitions possible for CCl_4, CH_2O, cyclopentane and CH_3OH.

(h) Illustrate McLafferty rearrangement with a suitable example.

6. *(a)* Give the significance of two types of molecular weights in polymers. 10

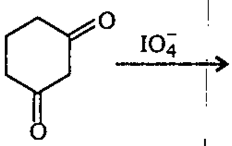
(b) How do secondary and tertiary structures of proteins differ from each other in terms of nature of bonding and interactions? What happens in quaternary structures? 10

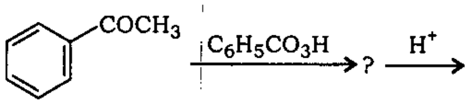
(c) What is cross-linking in the context of polymers? Give one method for obtaining polyvinyl alcohol. 10

(d) Give the major product of the following reactions : 10

(i) $Ph_2C(OH)CH_2OH \xrightarrow{H^+}$

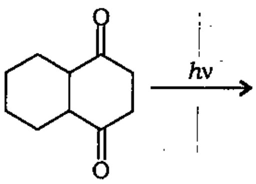
(ii) $PhNHN{=}\overset{\displaystyle R \atop |}{C}{-}CH_2R' \xrightarrow{ZnCl_2}$

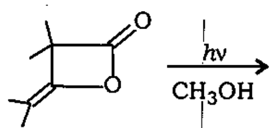
(iii) 

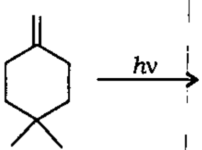
(iv) 

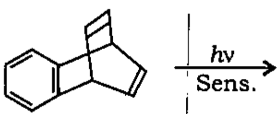
(v) *cis*-2-Butene + Singlet and triplet carbenes ⟶

7. *(a)* Complete the following reactions giving their mechanism : 5×4=20

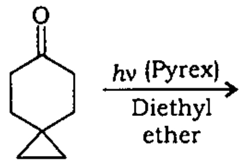
(i) 

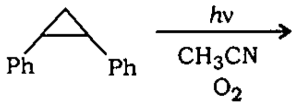
(ii) 

(iii) 

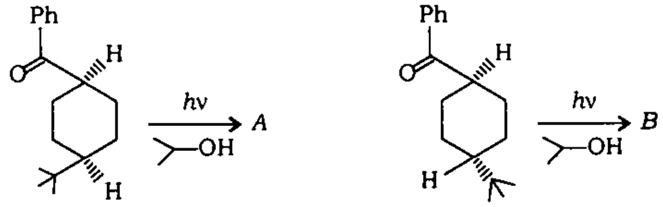
(iv) 

(b) Predict the products of the following reactions. Justify : 5×2=10

(i) 

(ii) 

(c) Identify the products A and B in the given transformations, and explain the difference : 5×2=10



8. (a) (i) Explain why a polar solvent usually shifts the $\pi \rightarrow \pi^*$ transition to longer wavelength and $n \rightarrow \pi^*$ transition to shorter wavelength.

(ii) How many fundamental vibrational frequencies would you expect to observe in the IR spectrum of CO_2? Discuss. 5+5=10

(b) (i) Assign the molecular structures for C_5H_8 and C_6H_2 when both give only one singlet in their ^{1}H-NMR spectra.

(ii) Predict the molecular ion peak which occurs at m/z = 76 in the mass spectrum of phthalic anhydride. 5+5=10

(c) An organic compound [X] gave the following spectral data :

(i) Mass (m/z) : 73, 91, 149, 164

(ii) IR $\nu = 1730\ \text{cm}^{-1}$

(iii) ^{1}H-NMR = δ : 2·0 ppm (3H, s)
δ : 2·93 ppm [2H, t (J = 7 Hz)]
δ : 4·30 ppm [2H, t (J = 7 Hz)]
δ : 7·3 ppm (5H, s)

Deduce the structure of the compound. 7+3+10=20

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