

CHEMISTRY

19

PAPER—II

Time Allowed : Three hours

Maximum Marks : 300

The figures in the margin indicate full marks for the questions

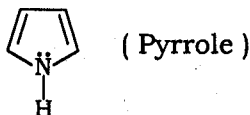
Candidates should answer Question Nos. 1 and 5 which are compulsory and other **three** of the remaining questions, selecting at least **one** from each Section

SECTION—A

1. Answer any *three* of the following :

20×3=60

(a) Pyrrole behaves as an aromatic compound




Explain it in the light of Hückel's rule.

(b) Explain the observed pK_a values of the following three hydrocarbons :

(i) $\text{HC}\equiv\text{CH}$ ($pK_a = 25$)

(ii) $\text{CH}_2=\text{CH}_2$ ($pK_a = 50$)

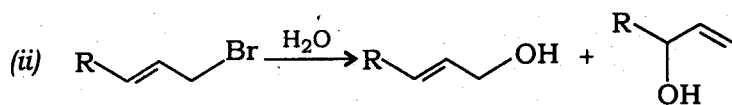
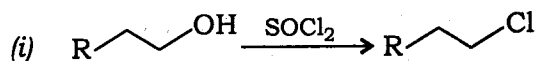
(iii)  ($pK_a = 15$)

(c) Propose a general mechanism of electrophilic substitution reaction of benzene. How can Lewis-proposed mechanism be supported by isotopic labelling technique?

(d) Write two methods of generating carbenes by photolytic α -elimination reactions. How can ketenes be obtained by skeletal rearrangement of carbenes?

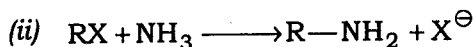
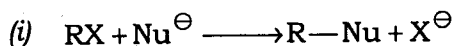
2. (a) Write the mechanism of the following reactions :

10×2=20



(b) Discuss the effect of solvent polarity on the rates of the following S_N reactions :

10×2=20



(c) Answer the following :

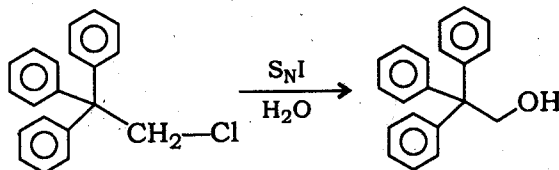
10×2=20

(i) Write a method of synthesis of indole ring. Which position of indole is attacked by E^+ ? Give reasons.

(ii) Why does furan undergo cycloaddition reaction with acetylene dicarboxylic acid? Write a general mechanism of electrophilic substitution of pyrrole explaining the regioselectivity of the reaction.

3. (a) What are non-classical carbocations? In the light of this, explain why the following 1°-alkyl halide undergoes $\text{S}_\text{N}1$ reaction readily :

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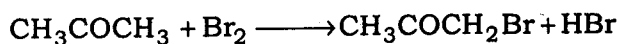


(b) Give an example of cationotropic 1,2-shift involving a carbanion intermediate and write the mechanism of the reaction.

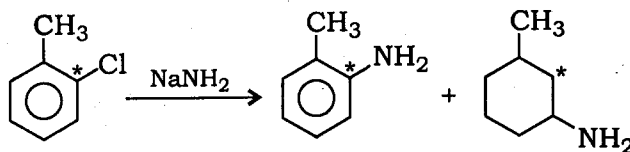
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(c) What is primary kinetic isotope effect? Using this method, establish the mechanism of the following bromination reaction :

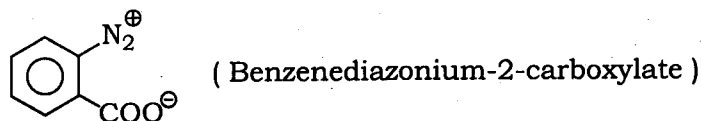
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- (d) The following labelled chlorobenzene (* shows the labelled atom) derivative on heating with sodamide gives a mixture of aniline derivatives. Propose a mechanism of the reaction to explain the formation of products : 15



- (e) How will you explain that benzenediazonium-2-carboxylate spontaneously decomposes with violence? 15



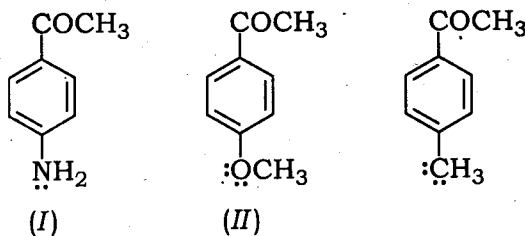
What products will be obtained if the above decomposed mixture is treated with (i) NH_3 and (ii) H_2S ? 15

4. (a) Propose a mechanism of Von Richter reaction to explain the formation of product and N_2 molecule. 20
- (b) Write how benzoin condensation is carried out. Why it may be regarded as a carbonyl umpolung reaction? 20
- (c) (i) How can catenanes be synthesized by acyloin condensation reaction? Write the mechanism of the reaction. 15
- (ii) Discuss the choice of the solvent and the base in the formation of enolate ion for C—C bond formation by aldol condensation. 5

SECTION—B

5. Answer any *three* of the following : 20×3=60

- (a) (i) State the IR frequency of the group $\text{C}=\text{O}$ and explain the change of frequencies in the following compounds : 15



(ii) Explain why alkene *trans*-4 octene does not show any infrared absorption for its carbon—carbon double bond.

5

(b) Answer the following :

5×4=20

(i) Generally a polar solvent shifts the $\pi \rightarrow \pi^*$ to longer wavelengths, whereas it shifts the $n \rightarrow \pi^*$ transition to shorter wavelengths. Explain.

(ii) β -carotene present in carrot absorbs in the visible region. Explain.

(iii) The O—H infrared absorption is more intense than the C—H infrared absorption. Explain.

(iv) Which one of the following pair is expected to show higher C=O stretching frequency? Give reasons of it :

Acetic acid and acetone

(c) (i) The $J = 0 \rightarrow J = 1$ rotational absorption line occurs at 1.153×10^{11} Hz in $C^{12}O^{16}$ and at 1.102×10^{11} Hz in C^xO^{16} . Find the mass number of unknown carbon isotope.

10

(ii) A very dilute solution of ethyl alcohol in carbontetrachloride shows a sharp infrared band at 3600 cm^{-1} . As the solution is made more concentrated, a new rather broadband appears at 3200 cm^{-1} – 3600 cm^{-1} . The sharp band disappears and is replaced entirely by broadband. Explain.

10

(d) How can the members of each pair of the following compounds be distinguished by a glance at their IR spectra?

20

(i) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

(ii) $(\text{CH}_3)_3\text{N}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

(iii) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ and $\text{CH}_3\text{CH}_2\text{CH}_2=\text{CH}_2$

(iv) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{CH}_2\text{COOCH}_3$

6. (a) Write a step-by-step mechanism for the polymerization of vinyl chloride in presence of organic peroxide. 20

(b) (i) Discuss how you can distinguish the three (*ortho*, *meta* and *para*) dibromobenzenes by their NMR spectra. 10

(ii) Suggest a structure consistent with the following NMR data : 10

Molecular formula = C_9H_{12}

Singlet at $\delta 6.78$, 3H

Singlet at $\delta 2.25$, 9H

(c) Discuss the secondary and tertiary structure of proteins. Explain interactions of different forces present in the tertiary structures. 20

7. (a) How can the following be distinguished from their mass spectra? 20

(i) 3-methyl-2 hexanone from 4-methyl-2 hexanone

(ii) 3-pentanone and 2-pentanone

(b) Explain the following with reference to mass spectrometry : 20

(i) The molecular ion for a tertiary alcohol is not detectable

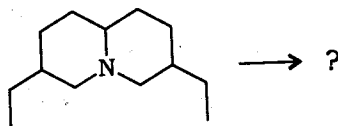
(ii) A primary alcohol can be easily identified by the presence of a strong peak at $m/z = 31$

(iii) Some alcohols show a peak at $m/z = M-18$

(iv) The mass spectrum of 1-chloropropane contains two peaks at $m/z = 78$ and 80, in addition to other peak

(c) (i) Compare the stereoselectivity of Saytzeff and pyrolytic eliminations. 5

(ii) How many Hoffmann eliminations will be needed to expel the N-atom from the following compound? Write the steps of the reaction and the structure of the final product : 15



8. (a) An organic compound with molecular formula C_8H_7Br yields a primary alcohol on hydroboration. The spectral data of the compound is given below :

(i) UV λ_{max} 282 m μ ϵ_{max} 450

(ii) IR : 3033 (m), 1646 (m), 1602 (m), 1582 (v), 820 (s) and 761 cm^{-1} (m)

(iii) NMR : 2.62–2.74 τ (asymmetrical pattern, 18.9 squares)
4.30 τ (double doublet, 4.7 squares)
3.30 τ (double doublet, 4.9 squares)
4.86 τ (double doublet, 5.0 squares)

Determine the structure of the compound.

20

(b) Discuss the ESR spectra of—

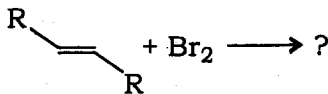
(i) $[Fe(CN)_5NO]^{3-}$ ion;

(ii) bis-salicylaldimine Cu(II).

5+15=20

(c) (i) Why do alkenes undergo Ad_E reaction but carbonyl compounds undergo Ad_{Nu} reactions? Discuss the regio- and stereo-selectivity of the following Ad_E reaction :

15



(ii) Discuss the advantages of $Si(CH_3)_4$ over other substances in using it as a standard in NMR spectroscopy.

5
