CC/M/EXAM. 2020

CHEMISTRY

PAPER—II

Time : 3 hours] [Full Marks : 250

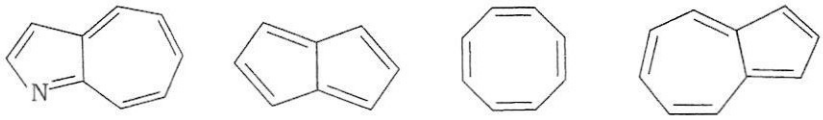
Note : Question Nos. **1** and **5** are compulsory and out of the remaining, any **three** are to be attempted choosing at least ONE question from each Section. The number of marks carried by a question/part is indicated against it.

SECTION—A

1. Answer *any* **five** of the following questions : 10×5=50

(a) What is antiaromaticity? Illustrate with two examples.

(b) Define Hückel's rule of aromaticity and on its basis, identify the aromatic systems among the following structures :



(i) *(ii)* *(iii)* *(iv)*

(c) What are carbenes? Why are they classified as singlet and triplet? Draw the structures of singlet and triplet carbenes taking CH_2 as the example.

(d) What are carbon free radicals? Describe how such free radicals are formed through photochemical and redox reactions.

(e) What are carbonium ions? Illustrate with suitable examples, four important factors which contribute to the stability of carbonium ions.

(f) Provide an explanation to the observations depicted in the table given below :

Structure where, **R** = alkyl group **X** = halogen			
S_N1 reaction	no	yes	good
S_N2 reaction	good	yes	no

(g) State Saytzeff Rule of elimination reaction. Taking the example of dehydrochlorination of 2-chloro-2-methyl butane, illustrate the rule.

2. Answer the following questions :

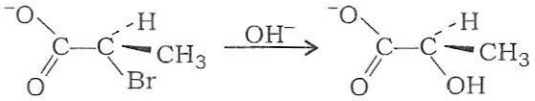
(a) Define thermodynamic and kinetic control of reaction products. Draw the energy profile diagrams for them. Taking the enolization of 2-pentanone in presence of a base, illustrate the concept of thermodynamic and kinetic control of reaction products. 20

(b) [18]-annulene and [14]-annulene are both aromatic in terms of Hückel's rule. Explain why [18]-annulene is more stable than [14]-annulene. 15

(c) Describe two formation methods of carbenes. Taking the insertion reaction of an alkene, explain why the reaction is stereospecific only for singlet carbene and not for triplet carbene. 15

3. Answer the following questions :

(a) Define anchimeric assistance in the context of aliphatic nucleophilic substitution reaction. Treatment of 2-bromo-propanoic acid with dilute alkali results in lactic acid with complete retention of configuration. Suggest a mechanistic explanation for this observation. 20



(b) Reaction of aryl bromide with potassium amide yields aniline. Suggest a mechanism for this reaction providing the proof for the existence of an intermediate, if any. 15

(c) Describe the S_Ni mechanism for aliphatic nucleophilic substitution reaction. Illustrate with a suitable example. 15

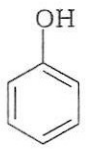
4. Answer the following questions :

(a) Write the product of addition of bromine to cyclopentene. Provide a mechanistic justification for the product formed. Do you expect similar product on addition of chlorine? If not, why? 20

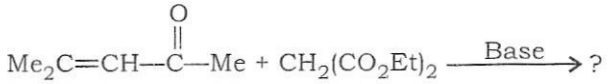
(b) Give the products of the following reactions along with the mechanisms : 15

(i) $PhCHO \xrightarrow[2.\ [H_2O]/H^+]{1.\ Zn/BrCH_2COOEt} ?$

(ii) EtO_2C (CH$_2$)$_4$ $CO_2Et \xrightarrow[2.\ HCl/H_2O]{1.\ NaOEt/EtOH} ?$

(iii)  $\xrightarrow[NaOH]{CHCl_3} ?$

(c) State the circumstances under which nucleophilic addition takes place to a C=C. Suggest a mechanism to explain the product formed in the following reaction : 15



SECTION—B

5. Answer *any* **five** of the following questions : 10×5=50

(a) What are pericyclic reactions? Give examples of pericyclic reactions. State few characteristic features of pericyclic reactions.

(b) What are Nylon-6 and Nylon-6,6 and why are they called so? Name the monomers used for their syntheses. Describe in brief the synthesis of Nylon-6,6.

(c) Describe the process of vulcanization of natural rubber. How does vulcanization improve the quality of natural rubber?

(d) Define a photochemical reaction. Draw a labelled Jablonski diagram to show the various unimolecular photophysical processes associated with an electronically excited molecule.

(e) Taking a linear triatomic molecule, draw all the possible vibrational modes.

(f) Write in brief the basic principle of NMR-spectroscopy.

(g) Define the following terms in the context of photochemistry : singlet excited state, triplet excited state, allowed transition and forbidden. Give reason why the triplet excited state is relatively more stable than the singlet state.

6. Answer the following questions :

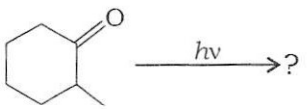
(a) Write in brief on pinacol-pinacolone rearrangement and aldol condensation. 20

(b) Explain from the FMO approach why the dimerization product of buta-1,3 diene is not favoured while the Diels-Alder product is favoured. 15

(c) What are nucleoside, nucleotide and nucleic acid? Name the purine and pyrimidine bases present in nucleic acid and draw their structures. What is base-pairing slight in the context of the structure of DNA? 15

7. Answer the following questions :

(a) Describe the principle of Norrish type-I and type-II photochemical reactions of ketones and hence complete the following reactions : 20

(i) 

(ii) $PhCH_2COCHPh_2 \xrightarrow{h\nu} ?$

(iii) $PhCO(CH_2)_3CH_2 \xrightarrow{h\nu} ?$

(b) Discuss the important synthetic applications of SeO_2 and *N*-bromo-succinimide. 15

(c) What is sigmatropic rearrangement reaction? Illustrate with suitable examples, [1, 3] and [3, 3]-sigmatropic reactions. 15

8. Answer the following questions :

(a) Describe the basic principle of a mass spectrometer. What is mass spectrum? Define the terms molecular ion peak and base peak in the context of mass spectrum. 20

(b) Define the term : chemical shift, spin-spin splitting and coupling constant in the context of proton NMR spectra. Illustrate your answer taking any example of your choice. 15

(c) Define the following terms in the context of electronic spectroscopy :

Chromophore, Auxochrome, Bathochromic shift and Hypochromic shift

Explain why conjugated double bond exhibits a bathochromic shift in comparison to non-conjugated double bond. 15

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