JQL

2011

301041

CHEMISTRY (Optional)
(Paper – II)

Standard : Degree **Total Marks : 200**

Nature : Conventional (Essay) type **Duration : Three hours**

N.B. :

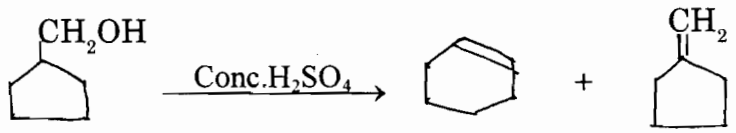
1) *Answers must be written in English.*
2) *Question **No. 1** is **compulsory**. Of the remaining questions, attempt **any four** selecting one question from **each Section**.*
3) *Figures to the **RIGHT** indicate marks of the respective question.*
4) *Use of log table, Non-Programmable calculator is permitted, but any other Table/Code/Reference book are not permitted.*
5) *Make suitable assumptions, wherever be necessary and state the same.*
6) *Number of optional questions upto the prescribed number in the order in which they have been solved will only be assessed. Excess answers will not be assessed.*
7) *Credit will be given for orderly, concise and effective writing.*
8) *Candidate should not write roll number, any name (including their own), signature, address or any indication of their identity anywhere inside the answer book otherwise he/she will be penalised.*

SEAT

Marks

1. Answer **any four** of the following (**10 marks each**) : **40**

(a) $CH_3CHBr\ CH_2Br$ reacts with one equivalent of alcoholic KOH to give mainly $CH_3CH = CHBr$ rather than $CH_2 = CHCH_2\ Br$ or $CH_3C(Br) = CH_2$. Explain. What is Markownikov's rule ? Explain the addition of hydrogen bromide to propene on the basis of this rule. Give the mechanism of the following reaction



(b) Give the preparation of benzene sulphonic acid and how it is converted into benzoic acid and thiophenol ? Give the Skraup synthesis of quinoline.

(c) What are proteins ? Give its classification. Describe the solid phase peptide synthesis of polypeptides with advantages.

(d) Explain the term quantum yield. What are the reasons for high and low quantum yield of a photochemical reaction ?

(e) How alkynes are prepared by dehydrohalogenation of vic dihalides and haloalkenes ? How will you convert 1, 3 – butadiene to tetrahydrophthalic anhydride and propyne to acetone ?

P.T.O.

Marks

SECTION – A

2. Answer the following sub-questions :

(a) What are free radicals ? How are they formed by photolysis ? Explain the chlorination of methane to methyl chloride on the basis of a free radical mechanism. Write down the hybridisation of carbon in the compound methane and ethene. 10

(b) Explain the terms enantiomers and meso compounds. Discuss the geometrical isomerism in oxime. 10

(c) State and explain Lambert-Beer's law. What is absorption spectrum, bathochromic and hypscochromic shift ? Explain the application of U.V. absorption spectroscopy to distinguish between cis and trans isomers. 10

(d) What is rotational spectroscopy ? Discuss its uses and limitations. Calculate the bond length of carbon monoxide molecule if its first rotational spectrum line appears at 38400 m^{-1}

Given : $h = 6.626 \times 10^{-34}$ Js, $C = 3 \times 10^{8}$ ms^{-1}

At.wt. of C = 12, O = 16, 1 a.m.u. = 1.66×10^{-27} kg. 10

3. Answer the following sub-questions :

(a) What is carbene ? Discuss the structure and shape of two types of carbenes. Explain the role of use of isotopes in the determination of reaction mechanism. 10

(b) Draw the preferred conformations of cyclohexane. Explain the stabilities of these conformations. Explain the term plane of symmetry with suitable example. 10

(c) Explain the selection rule in I.R. spectroscopy. Why chloroform absorbs significantly I.R. radiation whereas carbontetrachloride do not ? Discuss the application of I.R. spectroscopy in establishing the identity of a compound. 10

(d) Explain chemical shift in PMR. How is it quantitatively expressed ? Discuss low and high resolution NMR spectrum of ethanol. 10

SECTION – B

4. Answer the following sub-questions :

(a) Explain the mechanism of nitration of benzene : 10

Give the following conversions :

i) Phathalic acid to phthalic anhydride

ii) Phathalic acid to phthaloyl chloride.

Marks

(b) Write the note on Fries Rearrangement of phenolic esters and explain its application in the preparation of n-hexylresorcinol. 10

(c) Complete the following reactions. Name the reaction and give its mechanism.

i) $C_6H_5CHO + C_6H_5CHO \xrightarrow[\Delta]{KCN / C_2H_5OH} .....$

ii) $C_6H_5CHO + CH_3COO\,COCH_3 \xrightarrow[\Delta]{CH_3COONa} ..... + ...$ 10

(d) How will you prepare p-toluic acid from toluene ? Give the following conversions : 10

i) Sulphanilic acid to methyl orange

ii) Nitrobenzene to aniline.

5. Answer the following sub-questions :

(a) Which of the following molecules or ionic species are aromatic and why ? 10

i) Cyclopentadiene

ii) Tropylium cation

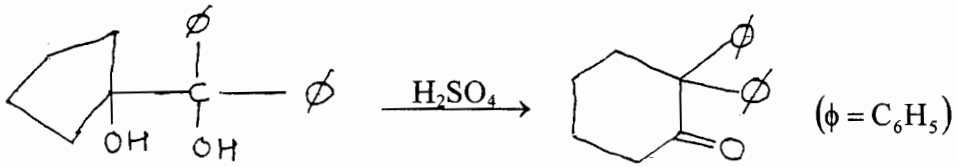
iii) Cyclobutadiene

iv) Cyclopropenyl anion

v) Cyclopentadienyl anion.

How will you prepare benzoic acid from bromobenzene and oil of winter green from salicylic acid ?

(b) Write the note on Claisen Rearrangement of alkoxy arenes. How will you obtain salicylaldehyde from phenol ? Write suitable mechanism of the following reaction : 10



$(\phi = C_6H_5)$

(c) Write the note on Mannich reaction with mechanism and applications. 10

(d) How are amines obtained by Hoffman reaction ? Give its mechanism. What is reductive amination of aldehydes ? How will you convert benzaldehyde to benzylamine ? 10

SECTION – C

6. Answer the following sub-questions :

(a) Discuss the synthesis and mechanism of ethyl acetoacetate by Claisen condensation method. Give the synthesis of adipic acid from diethyl malonate. 10

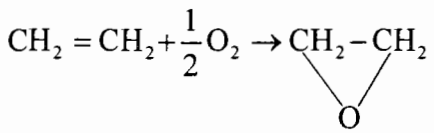
(b) What are disaccharides and polysaccharides ? Discuss the structure of Maltose and Lactose. 10

(c) Distinguish between addition and condensation polymerisation reaction. Give the preparation and use of phenol formaldehyde resin. 10

P.T.O.

Marks

(d) What are essential features of dye ? Explain the term percentage atom economy and E factor. Calculate the percentage atom economy of the following reaction :



(Given atomic weight of C = 12, H = 1, O = 16) 10

7. Answer the following sub-questions :

(a) What is reactive methylene group ? How will you convert acetoacetic ester into ethyl methyl ketone ? What are enamines ? Illustrate their use in the conversion of cyclohexanone to 2-methyl cyclohexanone. 10

(b) What is mutarotation ? Explain its mechanism in $\alpha - D$ glucose. Assuming configuration of D (–) arabinose how is configuration of D (+) glucose determined. 10

(c) What are characteristics of fibres ? Give the preparation of Nylon 66. Explain the mechanism of polymerisation of isobutylene in presence of boron trifluoride catalyst. 10

(d) What are basic dyes ? Give the synthesis of Malachite Green. Discuss any five principles of green chemistry. 10

SEAL

SECTION – D

8. Answer the following sub-questions :

(a) State and explain the Kohlrausch law. How is it useful to determine the dissociation constant for weak electrolytes ? Represent calomel electrode and write the electrode reaction. 10

(b) Describe solar cell with reference to principle, construction, working and advantages. What is corrosion ? Explain electroplating method to prevent corrosion. 10

(c) State and explain the postulates of quantum mechanics. 10

(d) Describe in brief digital computer with block diagram. What is meant by the following interactions in computer aided analysis ?
i) On-line ii) In-line 10

9. Answer the following sub-questions :

(a) Discuss the fundamental principles of conductometric titrations. Explain the nature of curve when a mixture of strong acid and weak acid titrated against strong base. 10

(b) How will you determine pH of a solution using quinhydrone electrode potentiometrically ? Derive the necessary expression for it. What are the advantages of Ni-Cd and fuel cells ? 10

(c) State and explain Schrodinger wave equation. Explain the physical significance of wave function. 10

(d) Give an account of active and passive applications of computers in chemical analysis. 10