Roll No. ..... **Total No. of Pages : 5**

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Chemistry

(05)

Paper—II

Time : Three Hours] [Maximum Marks : 300

Note :— (i) Answers must be written in English.

(ii) The number of marks carried by each question are indicated at the end of the question.

(iii) Part/Parts of the same question must be answered together and should not be interposed between answers to other questions.

(iv) The answer to each question or part thereof should begin on a fresh page.

(v) Your answers should be precise and coherent.

(vi) Attempt any **five** questions.

(vii) If you encounter any typographical error, please read it as it appears in the text-book.

I. (a) Define carbenes. Write two methods of generation of carbene. How will you trap a carbene ? 12

(b) Discuss the planar pyramidal structure of carbanions. 12

(c) Write the mechanism of Reimer-Tiemann reaction. How will you prove that reaction involves dichloro carbene as intermediate ? 12

(d) Deduce the structural formula of the following Compound having molecular formula $C_4H_8O_2$

IR (Neat film) 1740 cm^{-1}

^1H NMR δ 1.2 (t, 3 H), 2 – 3(q, 2 H), 3.8 (S, 3 H). 12

(e) Which spectroscopy is based on the principle of change of spin ? What is the frequency range in which such spectroscopy is carried out ? 12

II. (a) Write the mechanism of Friedal Craft's reaction. What are the limitations of this reaction ? 12

(b) Explain why reduction of cyclohexanone with less hindered hydride donor like $NaBH_4$ or Li AlH_4 give predominantly the equitorial alcohol. 12

(c) Give the preparation, important uses and the mechanisms of the reactions brought about by the following :

(i) N-bromo succinimide

(ii) Lithium aluminium hydroxide. 12

(d) What is Wagner-Meerwein rearrangement ? What is its mechanism ? What is the driving force for it ? 12

(e) What is the principle involved in pinacol-pinacolone rearrangement ? Give its mechanism. Discuss the migratory aptitude of different groups. 12

III. Give the mechanism of any **five** of the following :

(i) Base catalysed aldol condensation

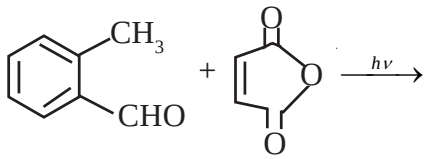
(ii) Perkin Reaction

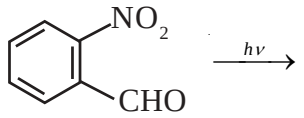
(iii) Cannizaro's reaction

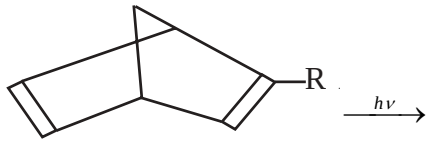
(iv) Addition of bromine to cis-but-2-ene and trans-but-2-ene.

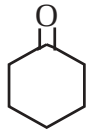
(v) Reaction mechanism of tert-butylchloride with aqueous sodium.

(c) Write the products of the following photo reactions :

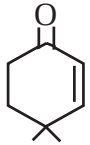
(i) 

(ii) 

(iii) 

(iv) 

give any two products

(v) 

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(d) Discuss the mass spectrum of the following compounds :

(i) 3-methyl-3 hexanol

(ii) 4-methyl -2- pentanone

(iii) 2,2,4,6,6,-pentamethyl heptane

(iv) C_{60}. 20

(vi) Claisen rearrangement mechanism.

(vii) Reformatsky reaction mechanism. (12 each)

IV. (a) Explain any **three** of the following terms :

(i) Coupling constant

(ii) Shielding and deshielding of protons.

(iii) Molecular ion peaks

(iv) Spin-Spin splitting. 20

(b) Give the structure consistent with the following data :

Molecular formula of compound = $C_9H_{11}Br$

multiplet — 2H, τ = 7.85

triplet — 2H, τ = 7.25

triplet — 2H, τ = 6.62

Singlet — 5H, τ = 2.78. 20

(c) What absorption in IR spectrum would be used to distinguish the following ?

(i) CH_3COOH and CH_3COCH_3

(ii) $CH_3CH_2NHCH_3$ and $(CH_3)_3N$

OR

What do you understand by ?

(i) Stretching and bending vibrations

(ii) n – π^*, π — π^* and σ – π^* transitions. 20

V. (a) Give an account of phosphonitrilic compounds with their structural aspects. 12

(b) Give the synthesis and structure of borazine. 12

(c) What are the selection rules for Rotation, Vibration, Raman spectra of diatomic molecules. Applying these rules, explain

what type of rotation vibration Raman spectrum is obtained for a diatomic molecule. 12

(d) Taking the example of carbonyl compounds represent and explain the electronic transitions taking place between them. 12

(e) Define Hooke's Law. Assign IR stretching frequencies (V_C=0) for the following molecules.

$BrCH_2COOH$, $Cl_2CHCOOH$, $ClCH_2COOH$, F3CCOOH, $BrCH_2CH_2CH_2COOH$

1725, 1776, 1751, 1730, 1736 cm^{-1}

OR

Identify the compound by given data :

Mol. wt. = 116

UV – 283 mμ, ξ max : 22

IR – 3000 – 2500 (h), 1715 (s), 1342 (w) cm^{-1}.

^1H NMR – δ 2.12 (s, 3H); 2.6 (t, 2H); 2.25(t, 2H); 11.1 (s, 1H). 12

VI. Attempt any **three** parts.

(a) Discuss briefly the following :

(i) Free-radical polymerization.

(ii) Co polymerization

(iii) Ionic polymerization

(iv) Show that the average molecular weight determined by sedimentation and diffusion is weight average molecular weight. 20

(b) Discuss the photochemistry of $[Ru(hipy)_3]^{2+}$ and also give the example of Taubecrautz and Mayer complex. 20