JL – 8/14
Chemistry
Paper – II

Time : 3 hours

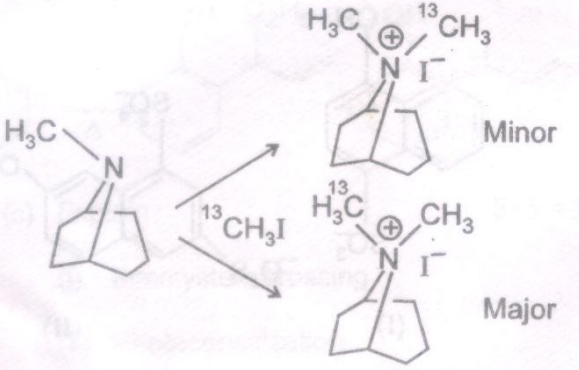
Full Marks : 200

The figures in the right-hand margin indicate marks.

*Answer **five** questions selecting at least **two** each from Section – A and Section – B.*

SECTION – A

1. (a) Discuss the application of Curtin-Hammett principle in the product distribution in the following reaction : 10



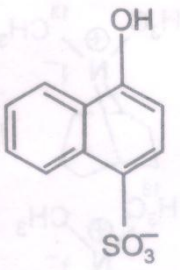
(b) Illustrate with R and S configurations, the optical isomerization in biphenyls. 10

(c) What is Sharpless reagent for enantioselective epoxidation reaction ? Discuss its application on substituted allyl alcohol. 10

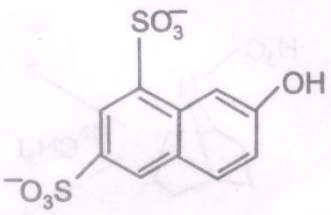
(d) Discuss the stereochemistry of the products in aliphatic nucleophilic substitution reactions involving SN1, SN2, SN^i and ion-pair mechanism. 10

2. (a) Write the mechanism of Von Richter reaction. What are the evidences in support of the mechanism ? 10

(b) Explain, in the diazonium reaction of the following compounds (I and II) there is no. isotope effect (k_H/k_D) for (I) while the isotope effect is 6.55 for (II). 10



(I)



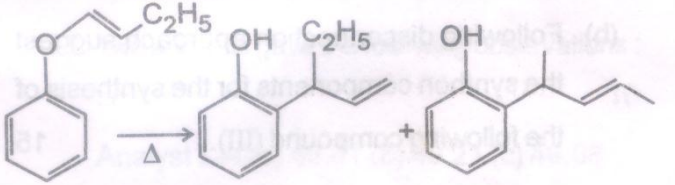
(II)

(c) Write the mechanism of benzoin condensation reaction ? Discuss the catalytic role of cyanide in the reaction. 10

(d) Illustrate, with one example each, for the elimination reaction obeying Hoffmann and Zaitsev rule. 10

3. (a) Through correlation diagram explain contotatory cyclization of 1, 3-butadiene to cyclobutene. 10

(b) Discuss the mechanism of the following reaction : 10

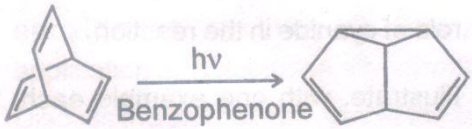


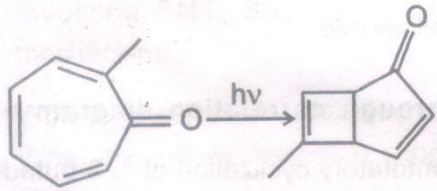
(c) Explain : 5+5 = 10

(i) Intersystem crossing

(ii) Photosensitization

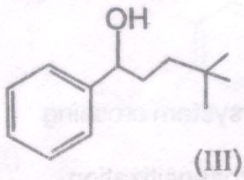
(d) Give mechanism for the following transformations : 5+5 = 10





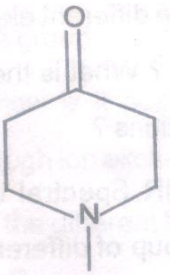
4. (a) With one example for each reaction discuss the protection and deprotection of amino and carboxylic group in peptide synthesis from amino acids. 10

(b) Following disconnection approach suggest the synthon components for the synthesis of the following compound (III). 15



(III)

(c) Through retrosynthetic approach propose the synthesis route of the following compound (IV). 15



(IV)

SECTION – B

5. (a) With example illustrate random sampling and systematic sampling. 10

(b) Two analysts gave the following observations : 10

Analyst I → (a) 49.01 (b) 49.21 (c) 49.08

Analyst II → (a) 49.40 (b) 49.42 (c) 49.44

Calculate precision and accuracy of both analysts. What analyst is more precise and which one is more accurate ?

(c) What is the difference between BOD and COD in water analysis ? Write one method on determination of COD. 20

6. (a) What are the different electronic transitions for acetone ? What is the effect of acid on these transitions ? 10

(b) Match the IR Spectral data (X) with the carbonyl group of different compounds (Y) given below. 10

X	Y
1650	Aliphatic Carboxylic Acid
1690	Aromatic Carboxylic Acid
1710	Aliphatic Ester
1735	Anhydride
1760	Amide

(c) A compound has a molecular formula $C_8H_8O_2$. Its IR spectra exhibits a characteristic peak at 1684 cm^{-1}. The peaks of NMR spectra appear at 9.9 (1H, S), 7.85 (2H, dd), 7.0 (2H, dd)

and 3.9 (3H, S) δ. The C-13 NMR spectra exhibits peaks at 190.7, 164.6, 131.9, 114.3, 130.0 and 55.5 δ. Propose the structure of the compound and assign the spectra to the respective group or atoms. 20

7. (a) Discuss how is it possible to soften hard water through ion exchange method. 10

(b) What are the different techniques of solvent extraction ? 10

(c) How do you estimate Mn(VII) and Cr(VI) simultaneously present in a solution ? 10

(d) How is a cube represented through Miller indices ? 10

8. (a) Compare the hyperfine splitting patterns and intensities of ESR spectra of hydrogen atom, deuterium and methyl radical. 10

(b) Which of the following systems will show esr spectra ? Discuss on the basis of MO : 10

C_6H_6, $C_6H_6^+$, $C_6H_6^-$

(c) With sketch discuss the thermogravimetric analysis of pentahydrated copper sulfate. 10

(d) Describe how cyclic voltammetry is used to obtain the diffusion coefficient. 10