Time: 2.5 Hours Total Marks: 60

NB : (1) Answer all questions.
(2) Figures to the right indicate full marks.

Q. 1 a) Answer any **two** of the following.

i) Give any two methods for the generation of nitrenes and ketenes. 04

ii) What is Neighbouring group participation? Discuss it with respect to norbornyl cation. 04

iii) Explain molecular orbital basis for the α effect. 04

iv) Draw molecular orbitals of 1, 3, 5 – hexatriene and comment upon their symmetry properties. 04

b) Answer any **one** of the following.

i) Give the reaction of generation of benzyne from anthranilic acid and phthaloyl chloride. What is the action of furan and alkyl amine on benzyne? 04

ii) Explain the role of FMO in reactions involving hard and soft nucleophiles and electrophiles. 04

Q. 2 a) Answer any **two** of the following.

i) With the help of FMO method, show that the Diels-Alder reaction is a thermally allowed process. 04

ii) Discuss any two examples of [4+6] cycloadditions. 04

iii) Discuss cycloaddition reaction of ketene with the necessary orbital diagram. 04

iv) What are electrocyclic reactions? Draw correlation diagram for disrotatory opening of cyclobutene. 04

b) Answer any **one** of the following.

i) Explain the mechanism and stereochemistry of Simmons–Smith reaction. 04

ii) Explain in detail, sigmatropic migrations of carbon. 04

Q. 3 a) Answer any **two** of the following.

i) Suggest the symmetry elements and point group present in 1,4- dichlorobenzene. 04

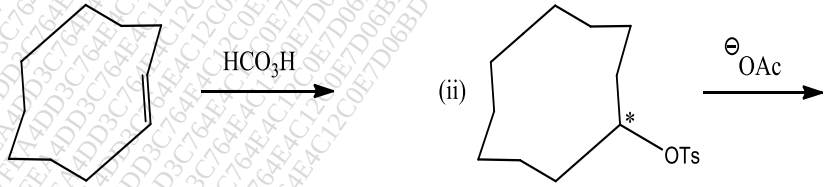
ii) Draw all the possible conformations of cyclooctane. Which conformation is most stable? Comment on the symmetry elements present in it. 04

iii) Discuss the structural features, symmetry and stability of cis and trans hydrindanes. 04

iv) Explain Meerwein-Ponndorf-Verley reduction of cyclohexanone. 04

b) Answer any **one** of the following.

i) Complete the following reactions with their appropriate stereochemical outcome (and mechanism if any) : 04



ii) Explain the reactivity and mechanism of E_2 elimination as shown by pair of epimers of menthyl chloride. 04

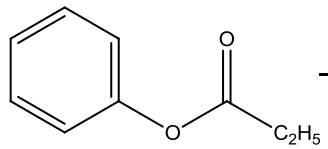
Q. 4 a) Answer any **two** of the following.

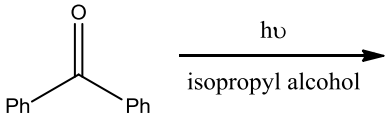
i) Discuss the mechanism and stereochemistry of Paterno-Buchi reaction. 04

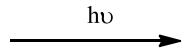
ii) What is meant by photosensitization? Give its mechanism, importance and two examples. 04

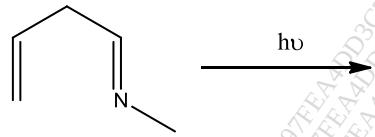
iii) Explain the process of chemiluminiscence with examples. 04

iv) Predict the products in the following reactions : 04

(I) 

(II) 

(III) C_6H_5-CH=CH-NO_2 

(IV) 

b) Answer any **one** of the following.

i) Explain the following reactions with examples: 04
I) Photoisomerization. II) Photodimerisation

ii) Discuss the photochemistry of α,β-unsaturated ketones with examples. 04

Q. 5 Answer any **four** of the following.

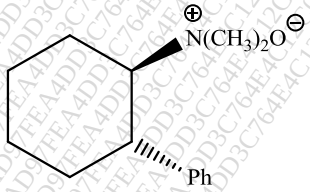
a) Explain the terms - Ambident Nucleophiles and Ambident Electrophiles. 03

b) The rate of acetolysis of trans-2-iodocyclohexylbrosylate is much faster than the acetylosis of its cis isomer- Justify. 03

c) Write a brief note on cheletropic reactions. 03

d) Give synthesis of vitamin-D from 7-dehydrocholesterol. 03

e) Explain the stereochemistry and the formation of major product by Cope elimination of following compound. 03



f) State Bredt's rule. 'Bicyclo[3.3.2]dec-1-ene does not follow Bredt's rule'- explain. 03

g) Write a note on photo-oxygenation reactions. 03

h) Define: I) Quantum yield II) Selection rules III) Quenching 03

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