PG – 556

III Semester M.Sc. Examination, December 2016
(CBCS)
CHEMISTRY
301 – OC : Organic Reaction Mechanisms

Time : 3 Hours Max. Marks : 70

Instruction *: Answer question No.* ***1*** *and* ***any five*** *of the remaining.*

1. Answer **any ten** of the following : **(10×2=20)**

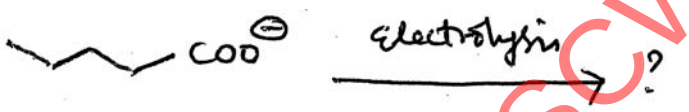
   a) What is allylic rearrangement reaction ? Give the mechanism with an example.

   b) With a suitable example give the mechanism of haloform reaction.

   c) Sketch the mechanism of SE1 reaction with an example.

   d) Give any two methods of generation of carbon-free radicals.

   e) Predict the product of the following reaction and propose a mechanism.



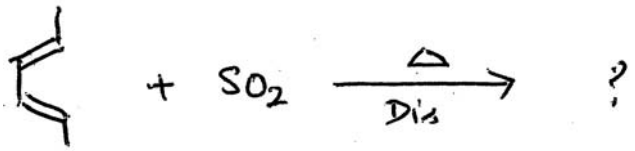
   f) What is Meerwein arylation ? Give the mechanism with an example.

   g) Draw the structures of all the photoproducts of benzene and give the mechanism for the formation of Dewar's Benzene.

   h) What is Norrish Types I reaction ? Explain with a suitable example.

   i) Sketch the Frontier Orbitals of 1, 3-butadiene and indicate the HOMO and LUMO under thermal and photochemical conditions.

   j) Predict the product and propose a mechanism.



   k) Draw the structure of Coenzyme-A and give the mechanism of conversion of oxaloacetate into citrate in biological systems.

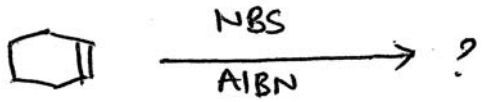
   l) What is aza-Cope rearrangement ? Give the mechanism with an example.

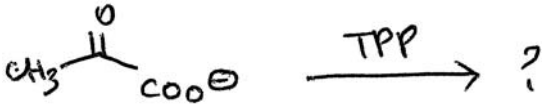
2. a) Discuss the mechanism of base catalyzed hydrolysis of esters and acid catalysed hydrolysis of amides with suitable examples.

   b) Give a comparative account of SE2 and SEi reaction mechanisms. **(6+4=10)**

P.T.O.

3. a) Predict the products and propose mechanisms.

i) 

ii) 

b) Write briefly on the mechanistic aspects of :

i) Gomberg-Bechmann reaction.

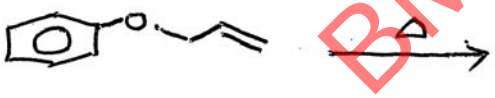
ii) Hunsdiecker reaction. **(4+6=10)**

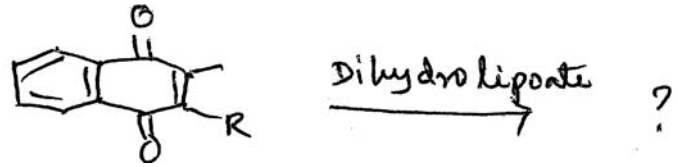
4. a) Give a brief account of reactivity of carbon-free radicals at the bridge heads.

b) Draw the Jabalonski diagram and discuss about the fate of the organic molecules under photo irradiation.

c) What is Paterno-Buchii reaction ? Discuss the stereochemistry of the products formed in this reaction. **(3+4+3=10)**

5. a) Predict the products and propose the mechanisms :

i) 

ii) 

b) Give the application of cyclohexadienone rearrangement in the synthesis of any two natural products. **(4+6=10)**

6. a) Write a note on cycloaddition of singlet molecular oxygen across 1, 3-butadiene system.

b) Describe the mechanism of $[{}_{\pi}m_{s} + {}_{\pi}n_{a}]$-cycloaddition reaction with a suitable example.

c) What is Walk rearrangement ? Explain with a suitable mechanism. **(3+4+3=10)**

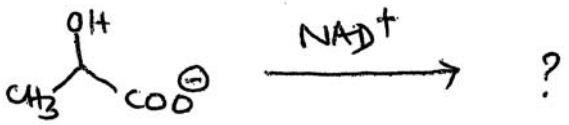
7. a) With suitable examples, discuss the regio-and endo-selectivities in the Diels-Alder reaction.

   b) Derive the Woodward-Hofmann correlation diagram for any one [1, 5]-sigmatropic rearrangement reaction.

   c) Give the mechanistic role of PLP in the dealdolization of (–)-serine. **(4+3+3=10)**

8. a) With a suitable mechanism discuss the conversion of deoxyuridylate into thymidylate by N^5, N^{10}-methylenetetrahydrofolate coenzyme.

   b) Predict the product and propose of suitable mechanism.



   c) Give the role of Flavin coenzyme in the following biological reaction.

(4+3+3=10)