



III Semester M.Sc. Degree Examination, December 2016  
(2010-11 Scheme) (NS) (Repeaters)

CHEMISTRY

C-301 – OC : Organic Reaction Mechanisms

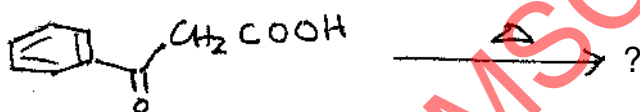
Time : 3 Hours

Max. Marks : 80

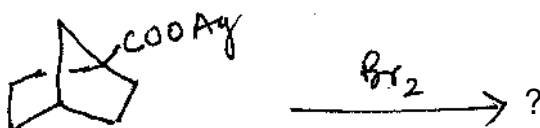
**Instruction** : Answer Question No. 1 and **any five** of the remaining.

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

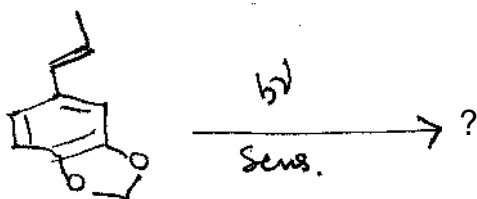
- a) With a suitable example give the mechanism of nucleophilic substitution at a vinylic carbon.
- b) Predict the product and propose a mechanism.



- c) What is the product of the following reaction ? Give a mechanism for its formation.

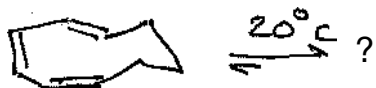


- d) Give any two methods of generation of carbon free-radicals.
- e) What do you mean by quantum efficiency of a photochemical reaction ? Explain with an example.
- f) Give the product and propose a mechanism for its formation.

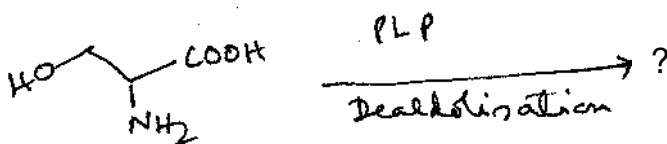




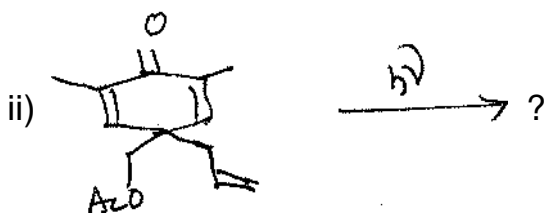
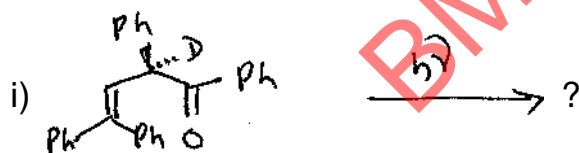
- g) What is Norrish type I reaction ? Explain with an example.  
 h) Use FMO approach to predict the product of the following reaction.



- i) Draw the Frontier Orbital diagram of the ground and excited 1, 3-butadiene molecule and indicate HOMO and LUMO among them.  
 j) What is “Walk rearrangement” ? Give the mechanism with an example.  
 k) Predict the product and propose a mechanism.



- l) What is the function of NADP<sup>+</sup> in nature ? Explain with a suitable example.  
 2. a) Give an account of free-radical substitution mechanisms.  
 b) Predict the products and propose mechanisms.

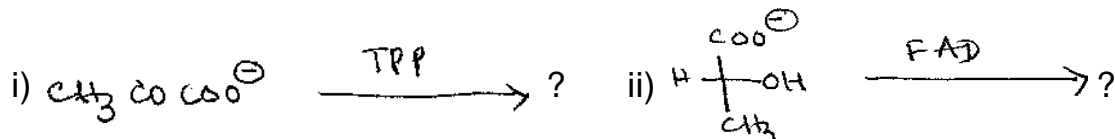


- c) Write briefly on the following in an electrophilic substitution at an aliphatic carbon.  
 i) Hydrogen exchange  
 ii) Migration of double bonds. (3×4=12)

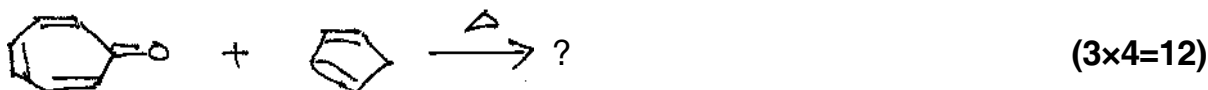
3. a) With suitable examples give the mechanisms of the following reactions :  
 i) Sandmeyer arylation  
 ii) Hydroxylation at an aromatic carbon.



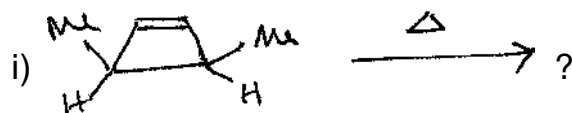
b) Give the products and propose mechanisms.



c) Use FMO approach for predicting the major product in the following  $[\pi 6_s + \pi 4_s]$  - cycloaddition reaction.

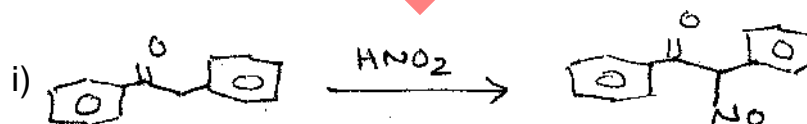


4. a) Explain the results of the following electrocyclic reactions by FMO approach.

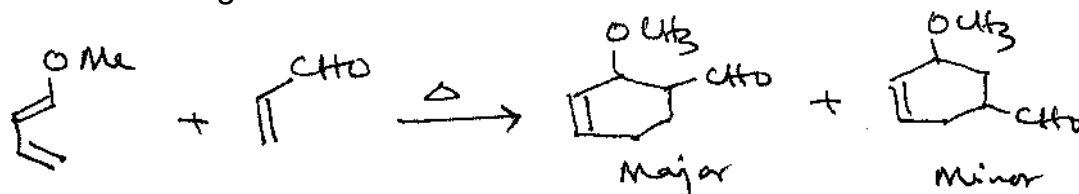


b) What are the probable transitions that may occur on absorption of visible and UV light in a photochemical reaction ?

c) Propose suitable mechanisms for the following reactions.

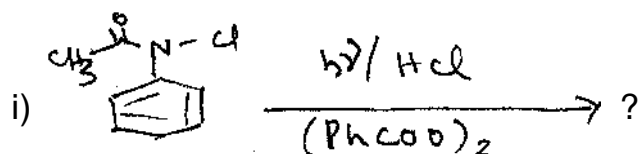


5. a) HOMO-LUMO energy separation and coefficients of HOMO and LUMO orbitals determine the regioselectivity of Diels-Alder reaction. Discuss this with respect to the following reaction.





- b) Discuss the mechanism of formation of thymidilic acid from deoxy-uridylate in the presence of tetrahydrofolate co-enzyme.
- c) Predict the product/s and propose mechanisms.



(3×4=12)

6. a) Thermal [1, 3]-sigmatropic shift of carbon occurs with inversion of configuration, whereas thermal [1, 5]-shift of carbon occurs with retention of configuration in the migrating group. Explain this observation by FMO approach.
- b) Discuss the mechanism of [2 + 2] – and [4 + 2] – addition of singlet molecular oxygen.
- c) What is the biological function of vitamin K<sub>2</sub> ? Explain with a suitable example. (3×4=12)
7. a) Give an account of carbene and nitrene insertion reactions in organic synthesis.
- b) Write briefly on the following:
- Norrish Type-II reaction.
  - Paterno-Buchi reaction.
- c) Predict the products and propose mechanisms.

