



III Semester M.Sc. Degree Examination, December 2013/January 2014
(2010-11 (NS) Scheme)

CHEMISTRY

C-301 – OC : Organic Reaction Mechanisms

Time : 3 Hours

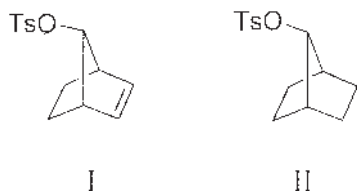
Max. Marks : 80

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

Answer any ten of the following :

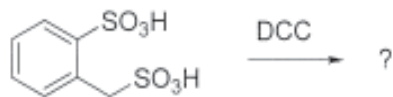
(10×2=20)

1. a) The acetolysis of 7-norbornenyl tosylate (I) is faster than 7-norbornyl tosylate (II). Explain.



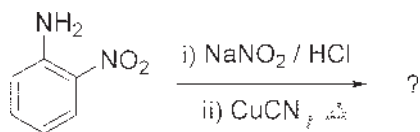
- b) What is Haller-Bauer reaction? Give its mechanism.

- c) Complete the following reaction and propose a suitable mechanism :



- d) Write the products of bromination of 1-butene with NBS and indicate the major product.

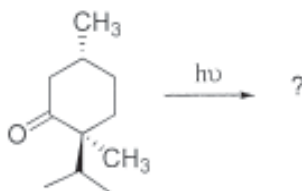
- e) Give the product and propose a mechanism :



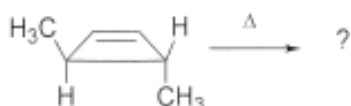
- f) Illustrate oxa-di-pi-methane rearrangement with an example.



- g) Give the product with correct stereochemistry and propose a mechanism for its formation.

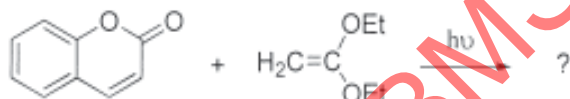


- h) Predict the product with correct stereochemistry :

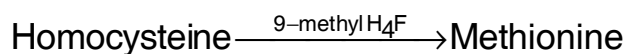


- i) Distinguish between antarafacial and suprafacial hydrogen shifts in sigmatropic rearrangements.

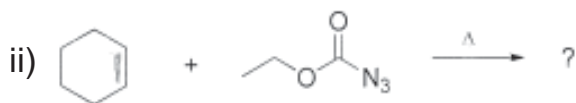
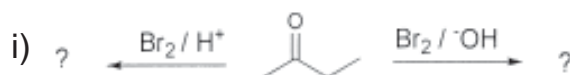
- j) Complete the following :



- k) Outline the mechanism for the oxidation of ethanol to acetaldehyde by NAD^+ .
- l) Write the steps involved in the following conversion.



2. a) Predict the products and suggest suitable mechanism for the following :

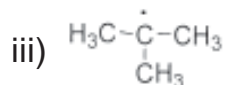
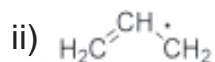


- b) Give an example each for S_{E}^1 and S_{E}^2 reaction with mechanism.

(6+6=12)



3. a) Arrange the following free radicals in the order of decreasing stability with justification



b) How will you bring about the following conversions ? Propose a suitable mechanism.

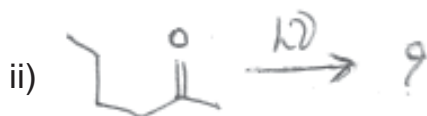
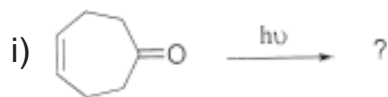


c) Give a brief account of Meerwein arylation.

(4+4+4=12)

4. a) What are the various processes involved in photochemical excitation reactions ? Explain neatly using Jablonski's diagram.

b) Predict the products with adequate explanation.



(6+6=12)

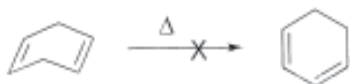
5. a) Predict the product for the following :



b) Using molecular orbital correlation diagram show that [4+2] cycloaddition reaction is thermally allowed.

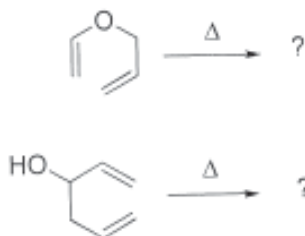


c) Explain why the following conversion is not possible.



(4+4+4=12)

6. a) Using FMO approach, show that whether thermal cyclization of $(4n+2)$ π electron system is conrotatory or disrotatory.
- b) Using π -molecular orbital, predict whether the (1,5) sigmatropic rearrangement is suprafacial or antarafacial under thermal condition.
- c) Predict the product with mechanism :



(4+4+4=12)

7. Explain the mechanistic role of the following in biochemical reactions :

- a) Biotin in the carboxylation reactions
- b) Thiamine pyrophosphate in decarboxylation of α -keto acids.
- c) Pyridoxal phosphate in elimination reaction of amino acids.

(4+4+4=12)
