

III Semester M.Sc Degree Examination, December 2014 (2010 –11 Scheme) (NS) CHEMISTRY C–301-OC : Organic Reaction Mechanisms

Time : 3 Hours

Max. Marks : 80

Instruction : Answer question 1 and any five of the remaining.

Answer any ten of the following :

- (10×2=20)
- 1. a) Give one example each for SE1 and SE2 mechanism.
 - b) Vinyl halides are unreactive towards both S_N^1 and S_N^2 reactions. Why ?
 - c) Predict the major product for the following reactions. Justify your answer.

d) Give different methods for the generation of free radicals.

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- e) Explain why benzophenone is used as photosensitizer to get triplet 1,3butadiene state instead of direct photolysis.
- f) Name and write the different isomers of benzene molecule under photochemical condition.
- g) During electrocyclic reaction, which orbital symmetry is involved in conrotatory motion? Explain with illustration.
- h) Predict the product for the following :



- i) With suitable example, explain the terms supra and antarafacial interactions.
- j) Mention different sources for the generation of acetyl coenzymes in our body.
- k) Write the structures of Coenzyme A and thiamine pyridoxyl pyrophosphate.
- I) Name the important reactions that are catalyzed by pyridoxal phosphate.

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2. a) Complete the following with suitable mechanism :

RCOCH₃ $\xrightarrow{\text{NH}_3}$

b) Compound A on heating in 1-methyl pyrrolidine with tetrabutyl ammonium benzoate yields compound B. Explain the observations.



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- c) With suitable mechanism, explain the role of DCC in the formation of anhydrides from carboxylic acids. (4+4+4=12)
- 3. a) Complete the following with suitable mechanism :

$$\operatorname{ArN}_2\operatorname{Cl}^- + \overset{R}{\underset{H}{\longrightarrow}} \overset{EWG}{\underset{R}{\longrightarrow}} ?$$

b) Predict the products for the following reactions. Justify your answer.

$$\begin{array}{c} \mathsf{RCOOH} \xrightarrow[heat]{\mathsf{NH}_4\mathsf{OH}/} \\ & Ag\mathsf{NO}_3/\mathsf{Br}_2 \end{array} ?$$

- c) With suitable example, explain allylic bromination reaction. (4+4+4=12)
- 4. a) Under photochemical condition trans alkene is less stable than cis alkene. Justify.
 - b) Write a reasonable mechanism for the following :



c) Write a reasonable step for the following conversions.



- 5. a) Show that HOMO-LUMO interaction occur during [4+2] cycloaddition of diene possessing electron donating group and dienophile possessing electron withdrawing groups.
 - b) Using FMO approach prove that [1, 3] sigmatropic rearrangement is antara facial under thermally condition.
 - c) Show what is happening in each step for the following concerted electrocyclic transformations? (5+3+4=12)

$$R \xrightarrow{heat} ? \xrightarrow{heat} ? \xrightarrow{heat} R$$

- 6. a) How pyridoxal phosphate is useful in dealdolization of serine?
 - b) With suitable examples, discuss the mechanism of [3, 3] [5, 5] sigma tropic rearrangement.
 - c) Discuss the role of tetrahydrofolic acid in converting homocycteine to methionine. (4+4+4=12)
- 7. a) What happens when RCOCH_2R ' react with nitrous acid? Give mechanism.
 - b) Write a reasonable mechanism for the following :



c) Draw the Jablonski diagram and define the terms phosphorescence and fluorescence. (4+4+4=12)