

PG - 233

III Semester M.Sc. Examination, January 2018 (CBCS Scheme) **CHEMISTRY**

C-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:

- a) Allylchloride undergoes nucleophilic substitution by S_N^1 mechanism whereas vinylchloride neither undergoes S_N^1 nor S_N^2 reaction. Give reason why?
- b) N, N-Dimethylaniline couples with benzene diazonium chloride to give azo-derivative where as 2, 6-dimethyl – N, N-dimethylaniline does not couple with benzene diazonium chloride. Why?
- c) Predict the product and explain the mechanism.

Indene
$$\xrightarrow{\mathsf{CHBr}_3}$$
 ?

d) How do you achieve the following conversion. Highlight the mechanism involved.

e) Predict the product and propose a mechanism for the following:

Benzene
$$\xrightarrow{\text{Cl}_2, \text{hv}}$$
 ?

- f) How do you explain the stability of tertiary radical over primary radical?
- g) What is quantum efficiency? Mention under what conditions quantum efficiency will be greater than 1?
- h) Predict the product(s) in the following and give reason.

Butene Benzophenone,
$$h_{\nu}$$
?

i) What is optical pumping? Explain by taking suitable examples.



- j) With an example give the mechanism of oxy-cope rearrangement.
- k) Write the structure of biotin. Give its biological importance.
- I) Highlight the role of nicotinamide in any one biological transformation.
- 2. a) How will you differentiate between SE2 and SE1 mechanisms? Explain taking suitable examples.
 - b) What are nitrenes? How are they generated? Explain any two reactions involving nitrenes. (5+5=10)
- 3. a) What are bridge head radicals? Give examples. Explain the role of neighbouring group assistance in free radical reactions at bridgehead carbons.
 - b) How do you achieve the following conversion ? Propose suitable mechanism.

Aniline $\stackrel{?}{\longrightarrow}$ chlorobenzene. Give the evidences to support the formation of the ensuing reactive intermediate. (5+5=10)

4. a) Predict the product(s) and propose mechanism

$$(CH_3)_2 C = CH - CH_3 + (C_6H_5)_2 C = O \xrightarrow{hv} ?$$

- b) With the help of correlation diagram predict the con-rotatory interconversion of 1, 3-butadiene to cyclobutene. Is the reaction thermally or photochemically allowed? (5+5=10)
- 5. a) How do you analyze an sigmatropic rearrangement? Explain taking the example of 1, 3-pentadiene.
 - b) Explain the role and its mechanism in the decarboxylation of α -ketoacids by thiamine pyrophosphate. (5+5=10)
- 6. Write briefly on the following:
 - i) Substitution at allylic carbon
 - ii) Formation of methionine from homoserine by vitamin B₁₂ coenzyme and SAM⁺.
 - iii) Meerwein arylation. (3+4+3=10)

7. a) Predict the products in the following:

i)
$$H_3C$$
 + O \longrightarrow ?

2E, 4Z-Hexadiene

b) Discuss the mechanism of transamination of amino acids by PLP. (6+4=10)

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8. a) Compute the following reactions

i)
$$H_3C$$
 CH_3 CH_3 CH_3

ii)
$$C_6H_5 \xrightarrow{\Delta} ?$$

b) Explain the role of Flavin coenzymes in oxidation reactions. (3+3+4=10)