Reg. No.					
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**CH 503** 

## Third Semester M.Sc. Degree Examination, December 2018 (CBCS Scheme) (Old Syllabus) CHEMISTRY (Repeater) (2015 Batch) Reaction Mechanisms and Heterocyclic Chemistry

Time: 3 Hours Max. Marks: 70

**Note**: i) Answer Part – **A** and **any five** questions from Part – **B**.

ii) Figures to the **right** indicate marks.

PART - A

1. Answer any ten subdivisions :

 $(10 \times 2 = 20)$ 

a) Predict the product in the following reaction and outline its mechanism:

$$\frac{\text{NaNH}_2/\text{Toluene}}{\Delta}$$

b) Write the products A and B in the following reaction:

c) How do you achieve the following transformation?

Benzaldehyde — ? Phenylacetaldehyde.

- d) Predict the stereochemical structure of an oxime of acetophenone which undergoes rearrangement to give acetanilide.
- e) Give evidence to show that Favorskii rearrangement involves a cyclopropanone intermediate.
- f) What is Demaynov rearrangement? Illustrate with an example.



g) Write the systematic name for the following:

- h) Outline a method for the synthesis of an azepine derivative.
- i) Illustrate how Skraup's reaction can be applied for the synthesis of 7-methoxy quinoline.
- j) What is oxy-cope rearrangement? Give an example.
- k) What are pericyclic reactions? How are they classified?
- I) During electrocyclic reactions, which orbital symmetry is preserved in conrotatory motion? Give an example.

Answer any five of the following:

 $(5 \times 10 = 50)$ 

2. a) Predict the product/s and propose the mechanism for the following :

i)

Meo

CHO

$$t_{BuO}$$
 $t_{BuOH}$ 
 $t_{BuOH}$ 

ii) 
$$+ H-C=O \xrightarrow{NaOH} ?$$

b) Explain Woodward – Prevost hydroxylation.

(6+4=10)

- 3. a) Explain the following reactions with reaction mechanism.
  - i) Suzuki coupling
  - ii) Benzoin condensation.
  - b) Give an account of wittig reaction.

(6+4=10)

- 4. a) With suitable examples, explain the optitude of migrating groups in Pinacol-Pinacolone rearrangement.
  - b) Explain briefly the mechanism of Wagner-Meerwein rearrangement.
  - c) Discuss the mechanism and synthetic applications of Benzidine (3+3+4=10)rearrangement.
- 5. a) Predict the products in the following reactions and propose mechanism:

ii) 
$$CO - CH_3$$
  $CF_3 - CO_3H$  ?

- (6+4=10)b) Give a comparative account of Curtius and Lossen reaction.
- 6. a) How do you bring about the following conversions?
  - i)  $\beta$  Phenylethylamine  $\stackrel{?}{\longrightarrow}$  Isoquinoline.
  - ii) Uric acid  $\stackrel{?}{\longrightarrow}$  purine.
  - b) Propose a reasonable mechanism for the following conversions : (6+4=10)

O H Me 
$$\frac{\text{MeMgBr}}{\text{Et}_2\text{O}}$$
  $\frac{\text{Aq. NH}_3}{\text{Warm}}$  ?



- 7. a) Outline a method for the synthesis of Naphthyridine.
  - b) Give the mechanism of the rearrangement involved when 3-fluropyrazine is treated with sodium azide.
  - c) Discuss the reactions of quinolines.

(3+3+4=10)

- 8. a) Deduce Woodward-Hoffmann rules for electrocyclic reaction of  $4n\pi$  electron system under thermal and photochemical conditions.
  - b) Using correlation diagram show that addition of butadiene and ethyline is thermally allowed and photochemically forbidden process. (5+5=10)
- 9. a) With the help of FMO method predict whether the thermal  $4\pi + 2\pi$  cycloaddition is suprafacial or antarafacial.
  - b) Analyze a [1, 5] sigmatropic rearrangement.
  - c) Give a brief account of 1, 3 dipolar cyclo addition reactions. (4+3+3=10)

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