Reg. No.					
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**CHH 502** 

## III Semester M.Sc. Examination, December 2018 CHEMISTRY (CBCS – 2016-17 Syllabus) Organic Reaction Mechanism and Heterocyclic Chemistry

Time: 3 Hours Max. Marks: 70

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

ii) Figures to the right indicate marks.

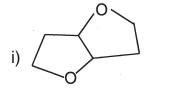
PART - A

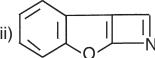
1. Answer all the sub-divisions.

 $(9 \times 2 = 18)$ 

- a) Employing FMO mehtod predict the thermal interconversion of butadiene to cyclobutene is con-rotation or dis-rotation.
- b) Explain Norrish Type-I reaction.
- c) Triplet excited state is more stable than singlet excited state? Give reason.
- d) Give evidence to show that Favorskii rearrangement involves cyclopropanone intermediate.
- e) Predict the product in the following reaction

- f) 'Benzoin condensation is specifically catalyzed by cyanide ion". Justify this statement.
- g) Name the following heterocycles:







h) Predict the product in the following reaction

i) Suggest a suitable mechanism for the following reaction:

$$CH_3$$
  $CH_2$   $CO_2Et$   $+ CH_2O$   $+ NH_3$   $ii)$   $HNO_3$   $CH_3$   $CH_3$ 

## Answer any four questions:

 $(4 \times 13 = 52)$ 

- 2. a) With the help of correlation diagram show that  $\pi^4$ s +  $\pi^2$ s cycloaddition is thermally allowed process.
  - b) What is Barton reaction? Explain its synthetic utility taking suitable examples. (7+6=13)
- 3. a) How do you analyze sigmatropic rearrangement. Explain whether the 1, 5-hydrogen shift by suprafacial mode is thermal or photochemical.
  - b) Predict the product in the following reaction

c) Explain whether the following reaction proceeds by con-rotation or dis-rotation? (7+3+3=13)



4. a) Predict the product in the following and suggest mechanism.

$$i) \qquad \qquad H^{\oplus}$$

ii) 
$$CF_3-CO_3H \rightarrow ?$$

$$\overset{\text{(iii)}}{\overbrace{\hspace{1.2cm}}}\overset{\text{O}}{\underbrace{\hspace{1.2cm}}}\overset{\text{H}^{\oplus}}{\xrightarrow{\hspace{1.2cm}}}?$$

iv) 
$$Ph-CH_2-C-CH_2-CI \xrightarrow{NaOEt} ?$$
 (3+3+3+4=13)

5. a) How do you achieve the following transformation. Suggest mechanism.

$$\begin{array}{c}
O \\
| | \\
C - CH_3
\end{array}
\begin{array}{c}
? \\
C - CH_3
\end{array}$$

- b) Explain the mechanism and synthetic utility of the following reactions by taking suitable example.
  - i) Prevost hydroxylation
  - ii) Sharpless asymmetric epoxidation? (5+4+4=13)



- 6. a) Discuss the mechanism of Fischer indole synthesis.
  - b) Predict the product in the following reaction and suggest mechanism in each case.
    - i) P-Cresol + Ethylautoacetate C.H<sub>2</sub>SO<sub>4</sub> 7
    - ii) Salicylaldehyde + Acetic anhydride NaoAc ?

iii) 
$$H_3C$$
  $CH_3 \xrightarrow{P_2S_5}$ ? (4+3+3+3=13)

- 7. a) Explain the mechanism of Hantzsch pyridine syntehsis.
  - b) Explain any one synthesis of azitidine and give any two of its important reactions.
  - c) Outline the synthesis of pyrimidine. Explain any two reactions of it with mechanism. (4+4+5=13)

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