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M.Sc. (Chemistry) (2018 Batch) (Sem.-2) REACTIVE INTERMEDIATES-II

> Subject Code : CHL-412-18 M.Code : 75982

Time: 3 Hrs. Max. Marks: 70

### INSTRUCTIONS TO CANDIDATES:

- SECTION-A is COMPULSORY consisting of TEN questions carrying TWO marks each.
- SECTION-B contains EIGHT questions carrying FIVE marks each and students have to attempt any SIX questions.
- SECTION-C will comprise of two compulsory questions with internal choice in both these questions. Each question carries TEN marks.

### SECTION-A

# Answer Briefly :

- Addition of an electrophile to 2,4-hexadiene generates two intermediates. Write their structures and tell which one is more stable.
- Discuss the use of organozine reagent for nucleophilic addition reaction.
- Write the mechanism of Wittig-Horner reaction.
- d. Selenium dioxide is quite often used in bringing about allylic oxidation. Presuming selenious acid or equivalent as the oxidant. Write steps involved in this process.
- e. What reagents are used for the oxidation of glycols and amines to aldehyde and ketones? Write their reactions only.
- f. What is the use of 9BBN reagent in organic chemistry?
- g. Write the reagents for hydrogenation of alkynes to cis and trans alkenes.
- Write a short note on Neber rearrangement.
- Discuss the use of Arndt-Eistert synthesis.
- j. Predict the products and name the following rearrangements:

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### SECTION-B

- Discuss the mechanistic and stereochemical outcome for the addition of bromine in electrophilic addition reactions.
- Explain briefly free radical addition reaction of hydrogen halides and thioles to carboncarbon double bonds. Illustrate with examples for the possibility of these reactions.
- With suitable examples, illustrate the role of Pb(OAc)<sub>4</sub> and O<sub>3</sub> for the oxidation of olefinic double bond.
- How will you oxidize alcohols through Swern Oxidation and Pyridinium Chlorochromate (PCC)? Support your answer with suitable mechanism.
- Discuss with mechanism for the use of sodium triacetoxyborohydride and diisopinocamphenyl borane.
- What are the product(s) formed when (i) an aromatic hydrocarbon and (ii) an α,β-unsaturated ketone is treated with sodium and liquid ammonia? Discuss the mechanism of formation of these products.
- Write a short note on oxymercuration and Sharpless asymmetric epoxidation reactions.
- With suitable example, illustrate the role of various reagents used for the oxidation of glycols, halides and amines.

# SECTION-C

- Write a short note on the following rearrangements :
  - a. Pinacol-pinacolone rearrangement

(5)

b. Criegee rearrangement

(5)

#### OR

- 10. a. Discuss the mechanistic and stereochemical aspects of the reduction by lithium aluminium hydride. What is meant by steric approach control and product development control in such reactions?
  (6)
  - b. With suitable examples, illustrate the oxidation of methylene and aryl methanes. (4)
- Discuss with mechanism for following rearrangements :

 $(2.5 \times 4)$ 

- Isonitrile-Nitrile rearrangement
- b. Hofmann rearrangement
- c. Demanov rearrangement
- d. Wagner-Meerwein rearrangement

## OR

 What is Fries rearrangement and Baeyer-Villiger rearrangement? Illustrate their mechanism by a suitable example. (10)

NOTE: Disclosure of Identity by writing Mobile No. or Making of passing request on any page of Answer Sheet will lead to UMC against the Student.

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