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## MANIPAL UNIVERSITY, MANIPAL

SECOND SEMESTER M.Sc. (CHEMISTRY) END SEMESTER EXAMINATION, MAY, 2016 SUB: ORGANIC CHEMISTRY-II (CHM-604)

Time: 3 Hrs. Date: 06/05/2016 Max. Marks: 50

Note: a) Answer any five full questions b) Write chemical structures and reactions where necessary.

- **1**. **A**. i) Describe the mechanism of Wolf-Kishner reduction. Give merits and demerits of this reaction.
  - ii) What is benzidine rearrangement? Explain the mechanism.
  - **B**. i) Predict the product in the following reaction. Explain your reasoning.

$$+$$
  $-$  Br  $-$  Anhy. AlCl<sub>3</sub>

- ii) Describe the mechanism of Baeyer-Villiger reaction. Discuss the migratory aptitude of migrating groups and stereochemistry of the product.
- C. Give reason for the following;
  - i) Hoffmann rearrangement proceeds with the retention of configuration.
- ii) Meerwein-Ponndorf-Verley reduction is highly chemoselective.

[4+4+2]

2. A. Suggest a retrosynthetic scheme for the following molecules;

$$NH_2$$
  $NH_2$   $NH_2$ 

**B.** i. What is 1,2-diX relationship? Give the retrosynthetic strategy for the following compound.

- ii. Give reason: Two group C-X disconnections are better than one group C-X disconnection
  - C. Describe the general methods for the protection and deprotection of amines.

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- 3. A. i) Write the conversion of malonic ester into glycine using Curtius rearrangement.
  - ii) What is Perkin reaction? Describe the mechanism and comment on the stereochemistry of product.

- **B**. i) Describe the mechanism of Reformatsky reaction. What are the merits of this reaction over Grignard reaction?
  - ii) What is ene reaction? Give an evidence to show that it is concerted.
  - C. Give suitable retrosynthetic analysis for the following compound

- **4. A.** Describe the mechanism of Peterno-Buchi reaction. Explain evidences to show that it not stereospecific.
  - **B**. i) How is benzodiazepine derivative prepared from  $\alpha$ -amino acids? Write its importance.
    - ii) Predict the product and write the mechansim for the following reaction;

C. Explain the factors affecting photocyclization vs  $\beta$ -cleavage during Norrish type-II reaction.

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- **5**. **A**. Account for the following observatins.
  - i) Norbornene reacts with benzophenone to from oxetane where with acetophenone gives dimer of norbornene.
  - ii) Stability of free radical intermediate can predict the course of photochemical reaction.
- **B**. Write the steps involved in the preparation of tomolol from d-mannitol.
  - C. Distinguish between the following;
    - i) Asymmetric synthesis vs conventional synthesis.
    - ii) Chiral catalysts vs metal halide catalyst.

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- **6**. **A**. Describe the course of primary and secondary photochemical reaction of 2-butanone. Write the mechanism and account for the various products formed.
  - **B**. i) Write the structure of swainsonine. Write two of its properties.
    - ii) Explain how chiral reducing agents is useful in asymmetric reduction reactions.
  - **C**. Write the mechanism of di-pi-methane rearrangement reaction.

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