Seat No. : \_\_\_\_\_

## **DN-107**

## December-2013

## M. Sc. (Sem-I)

## CHE-402 : Chemistry

## (Organic Chemistry)

Time : 3 Hours]

[Max. Marks: 70

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<b>Instructions :</b>	(1)	All questions are compulsory.
	(2)	Figure to the right indicate full marks.

- 1. (A) Answer the following :
  - (I) Giving orientation draw structures for all possible E<sub>2</sub> products when
    2-bromo butane reacts with concentrated potassium ethoxide.
  - (II) Explain Hoffmann and Saytzeff's rule of elimination with evidence.

#### OR

- (I) Discuss  $E_1$  reaction with supporting evidences.
- (II) Compare Chugaev and Cope reactions with suitable example.
- (B) Answer the following :
  - (I) When enantiomerically pure (S)-2-bromo propanoic acid reacts with conc.
    KOH it gives (R)-lactic acid. When the same reaction is carried out in the presence of Ag<sub>2</sub>O and low concentration of hydroxide ion it gives (S)-lactic acid. Explain.
  - (II) What is allylic rearrangement ? Explain allylic rearrangement giving suitable example.

#### OR

- (I) Acetolysis of erythro 3-phenyl-2-tosyl butane gives erythro 3-phenyl-2acetyl butane with retention of configuration while its threo isomer gives racemic mixture. Explain.
- (II) Compare  $SN^1$  and  $SN^2$  reaction with suitable examples.
- 2. (A) Answer the following :
  - (I) Using frost circle method show why cyclooctatetraene is not aromatic while cycloheptatrienyl cation is aromatic ?
  - (II) Discuss aromaticity in different annulenes.

## OR

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- (I) State Huckel's rule of aromaticity. Explain the terms of non-aromaticity and anti-aromaticity given illustrations.
- (II) Discuss aromatic character of azulene.
- (B) Answer the following :
  - (I) Discuss the effect of hydrogen bonding on the strength of an acid.
  - (II) Discuss the applications and limitations of Hammett equation. Explain deviation from Hammett equation.

#### OR

- (I) Comment on the acidity of C-H bond in a haloform.
- (II) Give Hammett equation. Explain all the terms and show that the Hammett equation is a linear free energy relationship.
- 3. (A) Answer the following :
  - (I) Discuss three different reactions in which carbanion is a reactive intermediate. 4
  - (II) Discuss non-classical carbocations.

#### OR

- (I) What are free radicals ? How they are generated ? Discuss their stability.
- (II) Discuss methods to distinguish singlet & triplet carbenes.
- (B) Answer the following :

(I) 
$$Ph - \begin{array}{ccc} OH & NH_2 & HNO_2 \\ | & | & 2 & HNO_2 \\ C & - & C & -H & \longrightarrow A \\ | & | & H & H \\ CH & CH & H & H \\ \end{array}$$

Identify product A. Name the rearrangement and offer suitable mechanism for this conversion.

(II) Discuss the mechanism and application of Favorskii rearrangement.

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# $\frac{OR}{HN_3/H_2SO_4}$

- (I) Cyclohexanone → A
  Identify product A. Name the rearrangement and offer suitable mechanism for this conversion.
- (II) Discuss migratory aptitude in Baeyer-Villiger's rearrangement.

#### 4. (A) Answer the following :

- (I) What is resolution ? Give any three methods of resolution of racemates. 4
- (II) Discuss stereochemistry of allenes.

#### OR

- (I) Discuss prochiral relationship with suitable examples.
- (II) Discuss stereochemistry of spiranes.

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(B) Discuss the stereochemistry of quaternary ammonium salts.

## OR

Explain stereo-selective and stereo-specific reactions. Give a brief account on asymmetric synthesis.

- 5. Answer the following :
  - (I) Arrange Se, O, Te and S in increasing order of nucleophilicity.
  - (II) Name the factors which affect the overall reactivity of elimination reaction.
  - (III) Giving the reaction show the end product when alcohol is dehydrated ?
  - (IV) Give the limitations of Huckel's rule.
  - (V) Which is more basic ? Aniline or methyl amine ? Why ?
  - (VI) What are nitrenes ?
  - (VII) Which of the following carbanions are more stable ?

$$CH_3 - CH = \stackrel{\Theta}{CH}, CH_3 - C \equiv \stackrel{\Theta}{C}$$

- (VIII) Which type of doubl bonded compounds will produce carbene on photolysis ?
- (IX) Giving example discuss geometrical isomerism.
- (X) Giving one example each define chiral and achiral molecule.
- (XI) How acid chloride is converted to urethane ?
- (XII) Give mechanism for carbyl amine reaction.
- (XIII) Explain helicity.
- (XIV) Explain homotopic & enatiotopic hydrogen atoms.

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