2016

ADVANCED ORGANIC CHEMISTRY

Time: Three Hours] [Maximum Marks: 80

Answer from both the Section as directed. The figures in the right hand margin indicate marks.

SECTION-A

- 1. Answer any four of the following (a-f) of Q1: 4×4
 - (a) Discuss Huckel-Mobius method in [1,3]sigmatropic rearrangement.
 - (b) Explain Paterno-Buchi reaction citing one example.
 - (c) What is Lossen rearrangement? How will you bring about following conversion?

$$\begin{array}{c|c}
O \\
N \\
I \\
H
\end{array}$$

$$OH \xrightarrow{H^{\oplus} \text{ or } OH^{\ominus}} R-N=C=0$$

(d) How many types are given by organocopper reagents? Give atleast one example of each. (e) Complete the following reaction:

(f) Define the Internal Conversion and Inter System Crossing in photochemical reactions.

. OR

2. Answer all the questions:

2×8

- (a) Draw only The HOMO and LUMO of 1,3butadiene.
- (b) What is conrotatory motion in pericyclic reaction?
- (c) What is Barton reaction? Give an example.
- (d) Comment on photochemistry of vision.
- (e) Define Neber rearrangement with a suitable example.
- (f) What is molecular rearrangement? Explain.
- (g) Write the name of two organomercury reagents.

(h) Complete the following reaction:

$$R-X + 2Li \xrightarrow{(C_2H_5)_2O} R-Li + Lix$$

$$\downarrow R_1-CH = CH-BR$$

SECTION-B

Answer all questions:

16×4

 (a) Discuss the Woodward-Hoffmann method and Huckel-Mobius approach for pericyclic reactions producing suitable examples in each case.

OR

(b) Give the product with its stereochemistry in the following reactions:

(ii) Me
$$\frac{h\nu}{\text{Me}}$$
?

- 4. (a) Write short note on the following with examples:
 - Paterno-Buchi Reaction or Barton Reaction.
 - (ii) Di-Pi methane rearrangement.
 - (iii) Photo-oxidation of alkene.
 - (iv) Photo-Fries rearrangement.

OR

(b) How will you bring about following conversions?

(5)

(iii) ButHO

- (iv) Barrelene \xrightarrow{hv} Sens
- (a) Explain Beckmann and Wagner-Meerwein rearrangement by giving example and discuss their mechanism also. Complete the following reactions and suggest a suitable pathway.

(i)
$$R \xrightarrow{N-OTs} R^1 \xrightarrow{C_2H_5O}$$
?

(ii) Ph
$$\stackrel{\oplus}{\sim}$$
 $\stackrel{\cap}{\sim}$ $\stackrel{\cap}{\sim}$ $\stackrel{\cap}{\sim}$ $\stackrel{\circ}{\sim}$ $\stackrel{\circ}{\sim$

(b) Discuss the stobbe condensation and shapiro reaction in detail. How will you bring about following conversions:

$$(i) \bigcirc O \longrightarrow O \longrightarrow O \longrightarrow O$$

$$(ii) \quad Ph \xrightarrow{O} Ph \xrightarrow{OH} OH$$

- 6. (a) Write short note on the following:
 - (i) Carbocationic behaviour and carbanionic behaviour of reagents in organometallic reactions.
 - (ii) How is the M-C ionic character is related to the reactivity among different organometallic reagents. Explain with facts.

OR

(b) Discuss the synthetic application of following:

(Continued)

(i) Organocopper reagents

- (ii) Organolithium reagent
- (iii) Organocadmium reagent
- (iv) Organomercury reagent