# M.Sc. 1st Semester Examination, 2013 CHEMISTRY

(Organic)

PAPER-CEM-102

Full Marks: 40

Time: 2 hours

Answer any five questions taking at least two from each Group

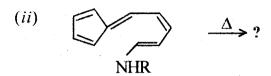
The figures in the right-hand margin indicate marks

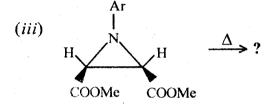
### GROUP - A

1. Write Woodward-Hoffmann rule for electrocyclic reactions and hence predict the product of the following reactions indicating frontier-orbital -interactions (F.O.I.) (answer any three): 2 + 2 × 3

$$(i) \quad \bigcirc O \quad \xrightarrow{hv} ?$$

( Turn Over )





$$(iv) \qquad \begin{array}{c} \text{Cl} \\ \\ \hline \\ \hline \\ 3h \end{array} ?$$

- 2. (a) What is supra and antarafacial cycloaddition? Write Woodward-Hoffmann selection rules for cycloaddition reactions.
  - (b) Predict the product of the following reactions indicating F.O.I. (attempt any three):  $2 + 2 \times 3$

(i) 
$$H_3C \stackrel{CH_2}{\longleftarrow} I + \bigcirc \frac{\text{NaOEt}}{\Delta}$$
?

(ii) 
$$CH_2N_2 + CO_3Me CO_2Me \xrightarrow{\Delta} ?$$

(iii) 
$$+ \sum_{CN}^{NC} CN \stackrel{CN}{\longrightarrow}$$

$$(iv) \quad OH \quad O$$

$$\triangle \qquad ?$$

- 3. (a) Define site 'selectivity' and 'periselectivity' with specific example and explain indicating Frontier Orbital interaction.
  - (b) Predict the product of the following reaction indicating F.O.I. in each case: 2+2+4

$$\begin{array}{c|c}
\hline
 & hv \\
 & hv \\
\hline
 & hv$$

4. Write Woodward-Hoffmann Rule for carbon migration indicating frontier orbital interaction in each case and hence predict the product of the following reaction (attempt any two):  $4 + 2 \times 2$ 

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5. Predict the products with plausible mechanism (any four):  $2 \times 4$ 

(a) 
$$R-C-H + R-NH_2 + R-N=\ddot{C} +$$

$$0$$

$$R-C-OH \longrightarrow ?$$

(b) 
$$CH_3$$
  $H$   $CO_2CH_3$   $P\phi_3$ , DEAD  $P\phi_3$   $P\phi_$ 

HO P
$$\phi_3$$
, CCl<sub>4</sub> ?

(Turn Over)

(e)
$$0 \longrightarrow [A] \xrightarrow{hv} [B]$$

$$0 \longrightarrow [Cl_2]$$

#### GROUP - B

- 6. Predict the possible (i) monocyclic, (ii) bicyclic and (iii) tricyclic products by acid catalyzed transformation of squalene epoxide (with Plausible mechanism):  $2\frac{1}{2}+2\frac{1}{2}+3$
- 7. Synthesize (20R) dammarene-diol, 1, euphol 2, bacchara-12, 21-dien-3-ol 3, 18-lupen-3-ol 4, δ-amyrin 5, α-amyrin 6 and bauerenol 7 from squalene epoxide (any four, with plausible mechanism):

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(Turn Over)

8. (a) Predict the products in the following transformations (any two):  $2 \times 2$ 

(i) OTs 
$$\frac{(i) B_2 H_6}{(ii) OH}$$

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## (b) Synthesize the following:

$$2 + 2$$

## 9. Answer any four:

 $2 \times 4$ 

- (a) What is multi-component-reaction? Give an example.
- (b) What is metathesis reaction? Illustrate with example.
- (c) What is a phase transfer catalyst? Illustrate with mechanism.
- (d) What is Grob fragmentation reaction?

- (e) What is the necessary condition for nuclear magnetic resonance? How is it maintained?
- (f) Explain the term "chemical shift" with reference to proton magnetic resonance spectroscopy.
- (g) What would be the multiplicity of the signals for the proton in  $CH_3-CH_2-OH$ ?
- 10. A monoterpenoid having molecular weight,  $C_{10}H_{18}O(A)$  on reduction with Ni/H<sub>2</sub> yields  $C_{10}H_{22}O(B)$  and on acetylation yields monoacetyl derivative. Compound (A) on permanganate (KMnO<sub>4</sub>/H<sup>+</sup>) oxidation gives Laevulic acid, Oxalic acid and acetone and on treating with dilute HCl yields isomeric product geraniol (C). Compound (B) on heating with cone. H<sub>2</sub>SO<sub>4</sub> produces a known compound 3, 7 dimethyl -oct-2-ene. Deduce the structure for these observations.

- (a)  $10 \pi$  electron system cyclodecapentaene is very unstable why? What modification in the structure is required to make the system more stable?
- (b) What do you mean by the term "antiaromaticity". Explain with a suitable example.
- (c) How many non-equivalent protons are there in the following compounds:

(i) 
$$CH_2CH_3$$

$$C \equiv C - CH - C - CH_2CH_3$$
O

3