## M.Sc. (Part-II) Semester-III (C.B.C.S.) Examination CHEMISTRY (OLD)

## Paper—XI

## (Organic Chemistry—I)

Time: Three Hours] [Maximum Marks: 80

Note: — ALL questions are compulsory and carry equal marks.

- (a) Discuss the mechanism of the photoreduction of benzophenone leading to the formation of benzpinacol.
  - (b) What is meant by quantum yield? Explain with suitable example.
  - (c) Comment upon the following:
    - (a) Norrish type I reaction
    - (b) Paterno-Buchi reaction.

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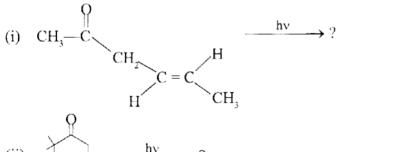
OR

- (p) Draw the Jablonski diagram and explain:
  - (i) Fluorescence
  - (ii) Inter system crossing
  - (iii) Phosphorescence.

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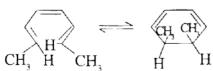
(q) Complete the following and explain:



(r) What is the role of photosensitizer in photochemical reaction? Illustrate your answer with suitable example.

2. (a) What is sigmatropic rearrangement? Explain Cope and Claisen Rearrangement. 6

(b) On the basis of FMO method explain the following process:



- (c) Comment on:
  - (i) 1, 3 dipolar cycloaddition
  - (ii) Symmetry properties of Butadiene.

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OR

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- (p) When benzene is irradiated at 254 nm which isomers are formed? Describe.
- (q) Complete the following:

(i) 
$$\xrightarrow{\text{NO}_2}$$
  $\xrightarrow{\text{hv CN}}$  ?

(iii) CH.—C—CH, — 
$$^{hv}$$
 — ?

(iv) 
$$2CH_3COCH_3 + CH_3 - CHOHCH_3 \xrightarrow{hv}$$
?

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- (r) Comment on:
  - (i) Photochemistry of enones and
- (ii) Photofries rearrangement.
- 3. (a) Discuss the reduction of nitro and nitroso compounds.
  - (b) How can you distinguish between the following alkenes by using ozone?

(i) 
$$R - CH = C \setminus \frac{R'}{R'}$$

(ii) 
$$R - CH_2 - CH = CHR'$$
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(c) Explain the reduction/oxidation of following compounds:

(i) 
$$\begin{array}{c} CHO \\ \hline NO_2 \\ \hline CH_1 \\ \hline CH_2 \\ \hline CH_3 \\ \hline CH_4 \\ \hline CH_4 \\ \hline CH_5 \\ \hline KOH/A \\ \end{array}$$
(ii) 
$$\begin{array}{c} Al(OiPr)_3 \\ \hline FrOH \\ \hline KOH/A \\ \hline \end{array}$$

(iii) 
$$\frac{M\text{-CPBA}}{\text{CH}_{z}\text{Cl}_{z}} \rightarrow$$

OR

(p) Explain the oxidation of alkyl side chain in aromatic compounds, alcohols using CO(III) with example.

(g) Indicate the stereochemistry of major alcohol that would be formed by sodium borohydride reduction of each of the cyclohexanone derivatives :

(ii) 
$$CH_3$$
 $C(CH_3)_3$ 

Predict the product with mechanism:

(i) 
$$\xrightarrow{i) \text{ NH}_2\text{NH}_2} ?$$

(ii) 
$$C_6H_5 - C_6H_5 - Na, liq NH_3 \rightarrow ?$$
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(a) Design the synthesis of the given molecule with synthons: 4.

(b) Comment on:

(i) Claisen condensation

(ii) Perkin reaction. 6

(c) Discuss the synthetic applications of aceto acetic esters (any four). 4

OR

Write the steps involved in the retrosynthesis of following:

(i) 
$$C_6H_5$$
—C  $CH = CHC_6H_5$   
(ii)  $C_6H_5$ —CH = CH  $COOH$  6

Name the reaction and give its mechanism :

(q) Name the reaction and give its mechanism:

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- (r) Discuss in brief:
  - (i) Stobbe's condensation
  - (ii) Friedal Craft acylation.

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- 5. (a) Explain how sulphur ylides are generated? Give its synthetic applications.
  - (b) Explain the dipole inversion and suggest the mechanism for the given reaction: 5

$$\frac{\text{HS}}{\text{dry HCl}} \xrightarrow{\text{SH}} \rightarrow \text{S}$$

(c) What are imines and enamines? Give the synthetic applications of enamines.

## OR

(p) How would you employ enamines in the following transformations? Explain. 4

$$H_3C$$
  $CH_3-CH_2CN$ 

- (q) What are Wittig reagents? Discuss its reaction with aldehyde and ketones with mechanism.
- (r) Comment on the following:
  - (i) Umpolung concept
  - (ii) Sulphur ylides.

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