## Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur

## Post Graduate Teaching Department of Chemistry,

## Master of Science (M.Sc.) CHEMISTRY Examination (CBCS): Third Semester

Paper IX (Code: 3T1) (Special I- Organic Chemistry)

N. B.: (1) All questions are compulsory.

**Time: Three Hours** 

## (2) All questions carry equal marks.

Q. 1 Indicate the type of the reaction and mechanism involved in each step of the following transformations.

(b) 
$$0000.$$

$$i) hv$$

$$ii) H3O+$$

$$(OH)$$

$$(c) \qquad \qquad \underbrace{\begin{array}{c} hv^{3}(sens) \\ Ph \end{array}} \qquad Ph \qquad \qquad 4$$

OR

Q. 1 Explain the difference in the photoreaction of the two stereoisomers in isopropanol.

$$(d) \qquad \stackrel{\mathsf{Ph}}{\longrightarrow} \qquad \qquad \\ \begin{matrix} \mathsf{Ph} \\ \mathsf{hv} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \\ \mathsf{(CH_3)_2CHOH} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \\ \mathsf{hv} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \\ \mathsf{hv} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \\ \mathsf{hv} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \\ \mathsf{(CH_3)_2CHOH} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \\ \mathsf{hv} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \end{matrix} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \\ \mathsf{hv} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \end{matrix} \end{matrix} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \end{matrix} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \end{matrix} \end{matrix} \end{matrix} \qquad \begin{matrix} \mathsf{Ph} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \end{matrix} \qquad$$

(e) Identify the products  $\mathbf{P}$  and  $\mathbf{Q}$  in the following reactions with suitable mechanism.

(f) What is cis-trans photoisomerization? Give mechanism involved in the isomerization of 4 alkenes. Predict the equilibrium product in the following reaction:

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Max. marks: 60

Q. 2 Propose a mechanism for the following reactions.

(c) 
$$\xrightarrow{O}$$
  $\xrightarrow{RLi}$   $\xrightarrow{CrO_3}$   $\xrightarrow{\Phi}$   $\xrightarrow{R}$   $\xrightarrow{R}$ 

OR

(d) Which of the reactions shown below will occur under the influence of heat? Light?

$$(i)$$

$$(ii)$$

$$(iii)$$

$$(iiii)$$

$$H$$

(e) Propose a mechanism to account for the following deuterium scrambling experiment. 4

(f) Write a substrate for the formation of following target molecules using intra-molecular 4 Diels-Alder reaction.

Q. 3 Write a suitable mechanism for the following transformations.

(c) Identify major products [X] and [Y] formed in the following reactions.

$$\begin{array}{c}
OCH_3 & 1. \text{ Na, NH}_3, \\
CO_2^t Bu & \frac{t\text{-BuOH (1 equiv)}}{2. i\text{-Prl}} & \xrightarrow{\text{Prl}} & \text{IX}
\end{array}$$

$$\begin{array}{c}
O \\
\text{NaBH}_4 \\
\text{CeCl}_3.6H_2O
\end{array}$$

OR

(d) How will you bring about the following transformations?

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(f) Predict the product(s) of the following reaction with suitable stereochemistry.

Maleic acid 
$$\xrightarrow{\text{RhCl(PPh}_3)_3, D_2}$$
? Fumaric acid  $\xrightarrow{\text{RhCl(PPh}_3)_3, D_2}$ ? benzene ?

Q 4. Propose a suitable mechanism for the following transformation.

(b) Complete the following reaction sequence with the structures of intermediates.

CHO CHO

$$\begin{array}{c}
\text{CHO} & \text{CHO} \\
\text{SH} & \text{SH} & \text{SH} \\
\text{(2 equiv)}
\end{array}$$

$$\begin{array}{c}
\text{BF}_{3}.\text{OEt}_{2} \\
\text{EtOH}
\end{array}$$

$$\begin{array}{c}
\text{A} \left[C_{21}H_{24}S_{4}\right] \\
\text{ii) Br(CH}_{2})_{3}CI
\end{array}$$

$$\begin{array}{c}
\text{B} \left[C_{24}H_{28}S_{4}\right] \\
\text{iii) Br(CH}_{2})_{3}CI$$

(c) How will prepare the following organoboranes compounds using hydroboration reaction.

OR

(d) Propose a suitable mechanism for the following transformation.

(e) Explain the outcome of the following reactions by identifying the structures of [X] and [Y].

$$O \xrightarrow{\text{(CH}_3)_2\text{S=CH}_2} [X]$$

$$THF, 0 \text{ °C} \qquad [Y]$$

(f) Propose a suitable mechanism for the following transformation.

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- Q. 5 Give mechanism involved in Norrish type II reaction and predict the products in the 4
- (a) following reaction:

(b) Propose structures for the products **A-E** in the following scheme:

$$\textbf{C} \hspace{0.1cm} [\hspace{0.1cm} \text{C}_8 \text{H}_{10} \text{I}_2] \xrightarrow{\hspace{0.1cm} \text{ether}} \hspace{0.1cm} \textbf{D} \hspace{0.1cm} [\hspace{0.1cm} \text{C}_8 \text{H}_{10}] \hspace{0.1cm} \xrightarrow{\hspace{0.1cm} \text{H}_3 \text{CO}_2 \text{C} - \hspace{0.1cm} \text{---} \text{CO}_2 \text{CH}_3} \hspace{0.1cm} \textbf{E} \hspace{0.1cm} [\hspace{0.1cm} \text{C}_{14} \text{H}_{16} \text{O}_4]$$

(c) Identify the compounds **A-F** formed in the following reaction sequence.

$$\textbf{C} \ [C_9H_{14}O_2] \xrightarrow{\text{MCPBA}} \textbf{D} \ [C_9H_{14}O_3] \xrightarrow{\text{i) LiAIH}_4} \textbf{E} \ [C_7H_{12}O_2] \xrightarrow{\text{DMSO}} \textbf{F} \ [C_7H_{10}O_2]$$

(d) Consider the scheme below and use all the information provided to identify the structures 4 of **A**, **B**, **C** and **D**.

$$\underbrace{ \begin{array}{c} \text{i) BH}_3 \\ \text{ii) NaOH, H}_2\text{O}_2 \end{array} }_{\text{OSiMe}_2\text{t-Bu}} \underbrace{ \begin{array}{c} \text{i) DMSO, (COCI)}_2 \\ \textbf{A} \\ \text{C}_{14}\text{H}_{24}\text{O}_2\text{Si} \end{array} }_{\text{C}_{14}\text{H}_{22}\text{O}_2\text{Si}} \underbrace{ \begin{array}{c} \text{i) DMSO, (COCI)}_2 \\ \text{ii) Et}_3\text{N} \end{array} }_{\text{C}_{14}\text{H}_{22}\text{O}_2\text{Si}}$$

$$\begin{array}{c|c} \hline \text{Ph}_3 \text{P} & \text{CO}_2 \text{Et} \\ \hline \\ \hline \\ \text{C}_{18} \text{H}_{28} \text{O}_3 \text{Si} \\ \hline \end{array} \begin{array}{c|c} \hline \text{Bu}_4 \text{NF} \\ \hline \\ \text{C}_{12} \text{H}_{14} \text{O}_3 \\ \hline \end{array} \begin{array}{c|c} \hline \\ \hline \\ \text{C}_{02} \text{Et} \\ \hline \end{array}$$

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