M.Sc. 2nd Semester Examination, 2013

CHEMISTRY

(Organic)

PAPER-CEM-202

Full Marks: 40

Time: 2 hours

Answer any five questions taking at least two from each Group where Q. No. 6 or Q. No. 7 is compulsory

The figures in the right-hand margin indicate marks

GROUP - A

1. (a) Define Diels-Alder reaction of 'Reverse electron demand' with a proper example, showing the energy diagram.

(b) Predict the products of the following reaction under different conditions indicating Frontier-Orbital interactions;

$$+$$
 \downarrow COOMe $\xrightarrow{\Delta}$ $A + B$

Without catalyst: 88% 12% With catalyst: 96% 4%

2. Differentiate between 'Site Selectivity' and 'periselectivity' and hence predict the products of the following reactions specifying mode of reaction in each case, showing Frontier Orbital Interactions (F.O.I.); (attempt any two) 2+2+2×2

$$(i) \qquad \longrightarrow ?$$

$$(ii) \qquad + \qquad \bigoplus \qquad \triangle \rightarrow$$

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(Continued)

$$(iii) \qquad \stackrel{\text{Me}}{\longleftarrow} \qquad \stackrel{\Delta}{\longrightarrow} ?$$

3. Predict the product/s of the following reactions indicatings F.O.I. in each case: 4×2

(i)
$$H$$
 + SO₂ \longrightarrow ?

(ii)
$$\longleftrightarrow$$
 + $C \equiv C \longrightarrow CO_2Me$ $\xrightarrow{\Delta}$?

(iii)
$$CH_2 + \bigcup_{CO_2 \to 1}^{CO_2 \to 1} \longrightarrow ?$$

$$(v) \qquad \stackrel{CH_3}{\searrow} + CH_2 \stackrel{ZnI}{\searrow} \longrightarrow ?$$

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4. (a) Predict the product/s (any three) with plausible mechanism: 2 x 3

(i)
$$\frac{\text{SeO}_2}{\text{^tBuOOH}}$$

$$OH$$
 $Ti(O^{ipr})_4$, tBuOOH

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(Continued)

- (b) What is 'Asymmetric-Dihydroxylation' mixture? Give an example of asymmetric transformation using 'Asymmetric Dihydroxylation' mixture.
- 5. (a) Predict the product/s with plausible mechanism: 2×2

(i)
$$OH \xrightarrow{D(-)DET} BuOOH$$
?

$$(ii) \qquad OH \qquad H_3O^{\dagger} \qquad ?$$

$$SiMe_3 \qquad BuO \qquad ?$$

(iii)
$$CO_2H$$
 OMe $Na/liq NH_3$?

(b) What are cheletropic reactions? Delineate HOMO & LUMO of a cheletropic species. Show linear and non-linear approach of a carbene towards ethylene for cyclo addition reaction.

(Turn Over)

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GROUP - B

- 6. (a) Comment on the following statements (answer any two):
- 3
- (i) The two -CHOHCO₂H groups in mesotartaric acid are enantiotopic to each other.
- (ii) Compounds with point symmetry C_s and C_i cannot have a set of enantiotopic ligands exceeding two.
- (iii) When a molecule possesses homotopic ligands it must have $C_n (n > 2)$.
- (b) From the following observations determine whether pro-R or pro-S H is eliminated when undeuterated ethanol undergoes dehydrogenation in the presence of alcohol dehydrogenase to yield acetaldehyde:

 $(S)-1-d-\text{Ethanol} \xrightarrow{\text{Alc. dehydrogenese}} \text{CH}_3\text{CDO}$

(Continued)

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(c) Comment on the chirality of the molecule (A) and the topic relationship between H_a and H_b . Now comment on the expected multiplicity of the ¹H-NMR signal of H_a and H_b .

$$\begin{array}{c}
H_{b} \\
\downarrow \\
O \\
\hline
O \\
CH_{2}OH
\end{array}$$

$$\begin{array}{c}
H_{b} \\
\downarrow \\
O \\
CH_{2}OH
\end{array}$$

$$\begin{array}{c}
(A) \\
CH_{2}OH
\end{array}$$

- 7. Attempt any two of the following:
 - (a) Explain the stereoselective formation of
 - (E)-/(Z)-enolates in the following reactions:

$$\begin{array}{c}
\begin{array}{c}
LiN Pr_{2}^{i} \\
(R=Et)
\end{array}
\begin{array}{c}
LiO \\
Et
\end{array}
\begin{array}{c}
H \\
Me
\end{array}$$

$$\begin{array}{c}
H \\
Me
\end{array}$$

$$\begin{array}{c}
Me \\
(98\%)
\end{array}$$

$$\begin{array}{c}
H \\
(98\%)
\end{array}$$

$$\begin{array}{c}
LiN(SiMe_{2}Ph)_{2} \\
(R=Et)
\end{array}
\begin{array}{c}
LiO \\
Et
\end{array}
\begin{array}{c}
Me \\
H
\end{array}$$

$$\begin{array}{c}
H \\
(-100\%)
\end{array}$$

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(b) What is a haptophilic group? How do you obtain stereoselectively (Q) and (R) from (P)? Explain your answer.

$$(P) \xrightarrow{\text{MeO}} O \xrightarrow{\text{CO}_2\text{Et}} O \xrightarrow{\text{MeO}} O \xrightarrow{\text{CH}_2\text{OH}} O$$

(c) How do you achieve the following stereoselective synthesis is one or more step(s)?

$$A \leftarrow A \rightarrow A^{O}$$

$$A \leftarrow A \rightarrow A^{Me}$$

$$A \leftarrow A \rightarrow A^{Me}$$

$$OH$$

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(Continued)

8. (a) Carry out the following transformations (any three) with plausible mechanism: 2×3

$$0 \xrightarrow{H} 0 \xrightarrow{H} 0$$

$$CH_{3}O \xrightarrow{CCH_{3}} OCH_{3} \xrightarrow{CCH_{3}O} COOH$$

$$CH_{3}O \xrightarrow{CCH_{3}O} OCH_{3}$$

$$(iii) \qquad OH \qquad OH \qquad OOO$$

$$O = \bigcup_{H} \bigcup_{H}$$

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(b) Synthesize any one of the following from easily available starting material:

$$(ii)$$

$$(\beta$$
-carotene)

- 9. (a) State the isoprene rule and explain with an example.
 - (b) The following monotere penoid (A) undergoes the following transformations:

geraniol
$$C_{10}H_{18}O$$
 $C_{10}H_{18}O$ $C_{10}H_{18}O$ $C_{10}H_{22}O$ $C_{10}H_{18}O$ $C_{10}H_{22}O$ $C_{10}H_{22}O$ $C_{10}H_{22}O$ $C_{10}H_{20}O$ $C_{10}H_{20}O$

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(Continued)

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Identify (B), (C), (D) and (E) and from the results elucidate the structure of (A) and confirm the structure of (A) from its synthesis. 2+6

Or

10. The following compound 'A' undergoes the oxidative degradation reaction as follows:

Compound (F) was identified as terebic acid with the structure,

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Draw backwards and write the structures of the intermediate products **B**, **C**, **D**, **E** and identify the structure of **A** and confirm the structure through its synthesis.

MV-200