P.G. 1st Semester - 2017

CHEMISTRY

(ORGANIC)

Paper: MCHECCT103

Full Marks: 40

Time: 2 Hours

The figures in the right-hand margin indicate marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer any **five** questions taking at least **two** from each group:

GROUP-A

1. a) To which point group the following molecules belong?

H
$$Cl$$
 $C = C = C$
 Cl
 CH_3

b) Assign R/S designation of the following compounds:

$$H_3C$$
 H_3C
 $COOOH$
 $COOOH$
 H_3C
 CH_3
 NO_2
 NO_2

c) In each of the following compounds the hydrogens (marked) H_a & H_b are homotopic, enantiotopic or diastereotopic. Give replacement test in each case.

d) Give the Re-Re, Re-Si or Si-Si descriptors to π -faces of the following compound.

$$\begin{array}{c|c} Ph & H \\ \hline C & \\ H & Ph \end{array}$$

$$2+2+3+1=8$$

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[2]

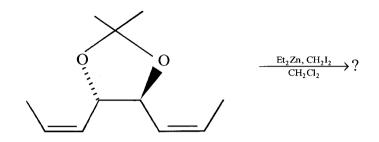
2. a) Write the major product of the following reaction using Felkin-Auh model.

$$(R)$$
 - PhCHMeCOMe $\xrightarrow{(i) L_i AlH_4} \xrightarrow{(ii) H_3 O}$

b) Which of the following structures represents the configuration of the (-)-menthol if its ester with benzoyl formic acid gives (R)-atrolactic acid as the major product when reacted with CH₃MgX followed by hydrolysis. Give the mechanism of reactions.

- c) Write the structure of (E)-2-Methyl cyclohexylidene acetic acid and explain which structure is more stable & why?
- d) A prostereogenic centre may or may not be prochiral centre— Explain with proper example. 2+2+2=8
- 3. a) Tosyl hydrazones are good starting materials for generation of carbenes. Outline the mechanism of generation of carbene using this reaction.

b) Give the product indicating the stereochemistry with mechanism



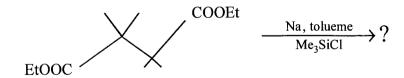
c) Interpret the formation of racemic mixture of two exo-acetates from optically active exo-2-bornyl brosylate in Acetic acid medium.

$$2\frac{1}{2} + 2\frac{1}{2} + 3 = 8$$

4. a)
$$\bigwedge_{1} + \bigwedge_{CN} \xrightarrow{Bu_3SnH(1.2equiv)} \bigwedge_{CN} \stackrel{CN}{\longrightarrow}$$

Write down the detail mechanism of the reaction indicating the chemo-selectivity of different radicals generated in the reaction.

b) Give product(s) with proper mechanism:



c) Discuss the effect of electron with drawing groups and electron releasing groups on radical stability considering the frontier molecular orbital approach. 3+2+3=8

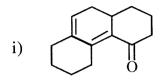
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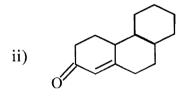
GROUP-B

- 5. a) What do you mean by risonance point in NMR spectroscopy?
 - b) Why TMS is used as a reference standard in NMR-spectroscopy?
 - c) An organic compound with molecular formula $C_8H_{14}O_4$ shows absorption in UV region at 213 nm t_{max} 60. In infra-red, absorption bands are formed at 2941- 2857 cm⁻¹ (m), 1745 cm⁻¹(s) and 1458 cm⁻¹(m). In NMR, the signals observed are (i) δ 4.14 quartet (J=7.2cps, 10.4 squares) (ii) δ 2.6 singlet (10.8 squares) (iii) δ 1.27 triplet (J=7.2cps, 16 squares). Suggest the most suitable structure for the compound from the given spectral data. 2+2+4=8
- 6. a) What is the effect of hybridisation of carbon on the stretching frequency of C–H bonds?
 - b) How will you distinguish between the following pairs on the basis of infra red spectroscopy?

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c) Calculate λ_{max} for the following compound according to Woodward-Fieser Rules for clienes:





d) Illustrate the AMX coupling in proton NMR spectrum of Furan-2-aldehyde.

$$1\frac{1}{2}+1\frac{1}{2}+2+3=8$$

7. a) Give product with probable mechanism for the following multicomponent reaction:

i)
$$R + R' - NH_2 + R'' - C + R - NC \xrightarrow{\text{MeOH} \atop \text{heat}} ?$$

ii) EtO₂C
$$\xrightarrow{Ph}$$
 \xrightarrow{O} $\xrightarrow{H^*, EtOH}$?

b) Write a short note on:

Baylis-Hillman Reaction. $2\frac{1}{2} + 2\frac{1}{2} + 3 = 8$

- 8. a) In the mass spectrum of toluene, strong peaks are formed at m/e 91 & m/e 65. Also a broad peak appears at 46.4. Justify the origin of these signals.
 - b) How do you explain that m/e 94 ion is formed in the spectrum of phenetol?
 - c) Define McLatterty rearrangement with suitable example.
 - d) What do you understand by N₂ rule?

$$2\frac{1}{2} + 2\frac{1}{2} + 2 + 1 = 8$$