U.G. 4th Semester Examination - 2021

CHEMISTRY

[HONOURS]

Course Code: CHEM-H-CC-T-10

(Organic Chemistry)

Full Marks: 20 Time: 1 Hour

The figures in the right-hand margin indicate marks.

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

1. Answer any **five** questions:

 $1\times5=5$

- a) In Nef reaction nitronate salt is poured into strong acid (pH<1), why?
- b) How would you distinguish the axial and equatorial –OH group of cyclohexanol from IR spectral data?
- c) Carbonyl stretching frequency in 1-acetyl-cyclohexene slightly differs from that 1-acetyl-2-methylcyclohexene— Explain.
- d) Explain why ethanol is a good solvent for UV-measurement but not for IR.

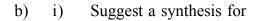
- e) Which compound is used as internal standard for running ¹H-NMR spectra of water soluble compound in D₂O?
- f) Why the unit of chemical shift (δ) is dimensionless?
- g) Write the peak intensity ratio of a proton having quintet multiplicity.
- h) Why does the more substituted group migrate (compare to less substituted) in the Baeyer-Villiger reaction?
- 2. Answer any **one** question:

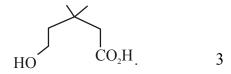
 $5 \times 1 = 5$

a) i) Write down the product of the following reaction with proper mechanism:

$$CH_2CH_3 \xrightarrow{\Delta} ? \qquad 3$$

ii) What type of electronic transitions are possible for the following compounds?





ii) Predict the product of the following reaction with suitable mechanism.

$$Ph_{2}CH \xrightarrow{CH_{3}} \xrightarrow{PCl_{5}} ? \qquad 2$$

$$OH$$

c) i) Compare the λ_{max} of I and II.

and
$$=$$
CH-CH= (II) 2

ii) Write the most plausible structure of C_4H_8O isomer with the following 1H -NMR data.

<u>S-value</u>	No. of 'H'
1.84	4H(m)
3.73	4H(m)

[Turn Over]

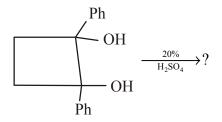
iii) Why are TMS protons usually in the upfield in NMR?

[3]

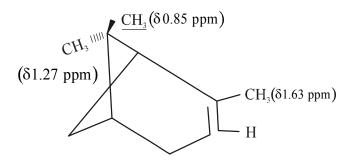
3. Answer any **one** question:

 $10 \times 1 = 10$

a) i) Write down the product of the following reaction with proper mechanism:



ii) Explain the lower δ (chemical shift) value of the marked methyl proton.



iii) Design a retrosynthesis of the following compound and suggest a forward synthesis of TM1:

iv) Give an evidence in favour of antimigration with respect to leaving group in Beckmann rearrangement.

$$3+2+3+2=10$$

b) i) Arrange these molecules according to their increasing order of IR streehing frequency with proper logic:

$$\bigcirc$$
0, \bigcirc 0 and \bigcirc 0

ii) Predict the product with suitable mechanism:

$$\begin{array}{c}
CH_3 \\
O \\
\hline
(ii) HCN \\
(iii) H_2/Pt \\
(iii) HNO_2, 0°C
\end{array}$$

iii) A compound 'A' exhibit only one singlet in 1 H-NMR at $\delta_{2.17}$. When A is treated with PhCHO in presence of ethanolic NaOH form B. The IR spectrum of B displays band at 3025, 1665, 1630, 1600, 763 and 753 cm $^{-1}$ and 1 H-NMR spectrum shows signals at

δ 7.82(d, 2H, J=18 Hz), 7.60(10H, m) and 7.05(2H, d, J=18 Hz).

What are the structures of A and B?

iv) Design a retrosynthesis of the following molecules and suggest a forward synthesis of TM2:

c) i) Predict the product with proper mechanism:

$$C_6H_5N_2^+Cl^-+$$
 $CN \xrightarrow{Cu^{2+}} ?$

- ii) A conjugated diene in hexane solution shows λ_{max} at 219 nm. What will happen if the solvent is changed to ethanol?
- iii) In 1,2-migration reaction, the migrating group retain its stereochemistry— Explain the facts with orbital interactions.

- iv) Tert-butyl fluoride in 1 H-NMR shows a doublet at δ 1.5 with J=20 Hz, while on adding SbF₅ it shows only a singlet at δ 4.6– explain.
- v) Design a retrosynthesis of the following molecule:
