MASTER OF SCIENCE (CHEMISTRY) (CBCS - 2018 COURSE)
M.Sc. (Chemistry) Sem-II :SUMMER- 2022
SUBJECT : ORGANIC CHEMISTRY - II

Day : Saturday
Date : 16-07-2022

S-20146-2022

Time : 03:00 PM-06:00 PM
Max. Marks : 60

N.B.:

1) All questions are **COMPULSORY**.
2) Figure to the right indicate **FULL** marks.
3) Answer to the both sections should be written in the **SEPARATE** answer books.

SECTION-I

Q.1 Attempt **ANY THREE** of the following: **[15]**

a) What is Mannich reaction? Discuss its mechanism and applications.

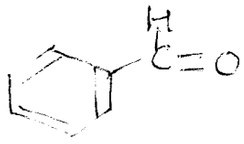
b) What are phosphorous ylides? Explain preparation and applications of phosphorous ylides.

c) Explain the preparation and applications of organo-lithium compounds.

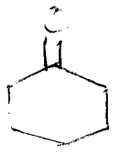
d) Explain mechanism and applications of Dieckmann condensation.

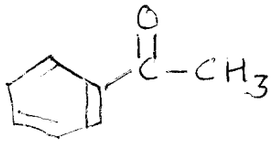
e) Write a note on: Oppenauer oxidation.

Q.2 Predict the product/s in **ANY THREE** of the following reactions by giving mechanism. Justify your answer. **[15]**

a)  $\xrightarrow[\Delta]{H_2N-NH_2/NaOH}$?

b)  $\xrightarrow[ii)\ H_2O/H^{\oplus}]{i)\ Alkaline\ KMnO_4}$?

c)  $\xrightarrow{CH_3-\overset{O}{\overset{\|}{C}}-O-O-H}$?

d)  $\xrightarrow[ii)\ H_2O/H^{\oplus}]{i)\ LiAlH_4/Ether}$?

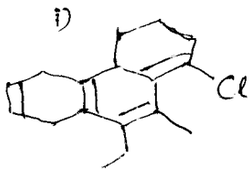
e) $H-\overset{COOH}{\underset{COOH}{C}}=O + CH_2\begin{matrix}COOH\\COOH\end{matrix} \xrightarrow[ii)\ H_2O/H^{\oplus}]{i)\ Pyridine}$?

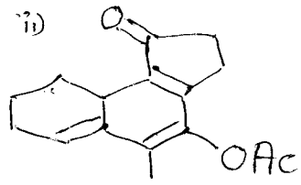
P.T.O.

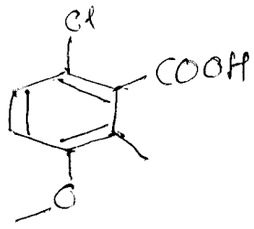
SECTION-II

Q.3 Answer **ANY THREE** of the following: **[15]**

a) Calculate λ_{max} for the following compounds:

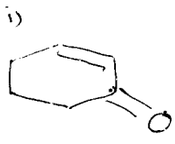
i) 

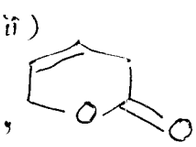
ii) 

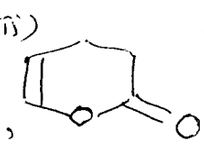
iii) 

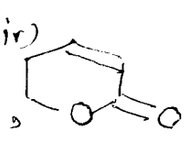
b) Absorption band of phenol at 270 nm shows red shift at 290 nm when treated with NaOH. Explain.

c) Arrange the following compounds in increasing order of carbonyl frequencies.

i) 

ii) 

iii) 

iv) 

d) A compound having M.F. $C_9H_{14}O$, shows positive iodoform test and λ_{max} is 249 nm. Determine the structure.

e) Write short note on Metastable ion.

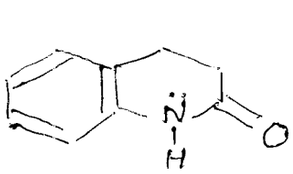
Q.4 Attempt **ANY THREE** of the following: **[15]**

a) Assign the structure with the given data. Justify your answer.
M.F. : C_9H_{10}
U.V. : 255 nm,
I. R. : 3030, 1550, 1500, 740 cm^{-1}
NMR : 2.04 δ (quintet, 2H)
2.90 δ (t, 4 H)
7.20 δ (s, 4 H)

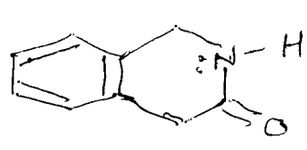
b) Assign the structure with the given data. Justify your answer.
M.F. : $C_4H_8O_2$
U.V. : Transparent above 210 nm
I. R. : 2500 – 3300 (br), 1721, 1250 cm^{-1} .
NMR : 0.98 δ (t, 3 H)
1.2 δ (sextet, 2 H)
2.15 δ (t, 2 H)
9.90 δ (br.s, exchangeable with D_2O, 1 H)

c) Assign the structure with the given data. Justify your answer.
M.F. : $C_{10}H_{14}$
U.V. : 260 nm.
I. R. : 1600, 1500, 750, 700 cm^{-1} .
NMR : 0.90 δ (t, J= 6 H_z , 3 mm)
1.22 δ (d, J = 6 H_z ,3 mm)
1.61 δ (quintet, J= 6 H_z , 2 mm)
2.58 δ (sextet, J = 6 H_z ,1 mm)
7.20 δ (m, 5 mm)

d) Distinguish the following pair by NMR



and



e) Give the Genesis of n-Propyl ethyl ketone.

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Table 1 :

Some characteristic IR data in cm^{-1}. Only approximate values are listed.

≡ C–H 3300,	= C–H 3050
O = C – H 2800,	N–H 3300
O – H 3600 (free),	C ≡ N 2250
C ≡ C 2200,	C = C 1620 – 1680
Aromatic (C = C) 1600 to 1500,	– C = N 1660
Saturated ketone 1720,	Saturated ester 1750
Saturated acids 1720,	Saturated aldehydes 1730,
Saturated amides 1650	$CH = CH_2$ 900 and 910
CH = CH (trans) 960,	CH = CH – (cis) 690
$C = CH_2$ 890	C = CH 790 – 840
NO_2 1530 and 1050	

Bands for aromatic compounds depends on the number of adjacent free aromatic hydrogens :

5 free – 690 – 710 and 730 – 770

1 free 850 – 900,	4 free 735 – 770
3 free 750 – 810	2 free 770, 800 – 860

Table 2 :

Approximate chemical shifts on methyl, methylene and methine protons, in δ values TMS as internal reference.

$C – CH_3$ 0.9,	$O – C – CH_3$ 1.4
$C = C – CH_3$ 1.6,	$Ar – CH_3$ 2.3,
$O = C – CH_3$ 2.2,	$N – CH_3$ 2.3,
$S – CH_3$ 2.1,	$O - CH_3$ 3.3
C–H in cyclopropane 0.7,	$C = CH_2$ exocyclic 4.6,
$C = CH_2$ open chain 5.3	C – CH 5.1
C ≡ CH cyclic 5.3,	Ar – H 7 to 9