

T.Y.B.SC. SEM – VI (2014 COURSE) : WINTER - 2017

SUBJECT: CHEMISTRY: ORGANIC CHEMISTRY – VI

Day : Friday
Date : 27/10/2017

W-2017-0683

Time : 12.00 NOON TO 02.00 PM
Max. Marks : 40

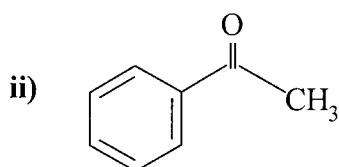
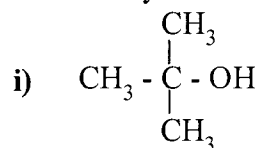
N.B.

- 1) All questions are **COMPULSORY**.
- 2) Figures to the right indicate **FULL** marks.
- 3) Answers to both the sections should be written in the **SAME** answer book.

SECTION – I

Q.1 Attempt any **TWO** of the following: (10)

a) Give retrosynthetic approach for the following compounds:



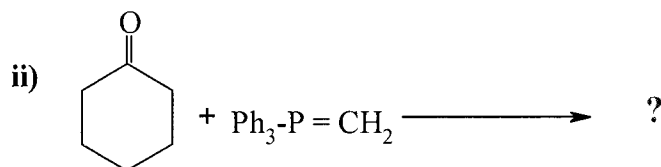
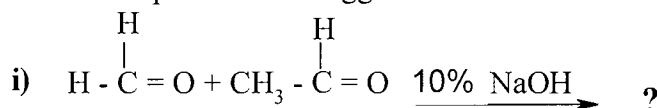
- b) What are carbonions? Discuss the preparation and stability of carbonion.
- c) Write a note on : Perkin's reaction.

Q.2 Attempt any **TWO** of the following: (10)

a) Define the following terms with one example of each.

- i) Synthetic equivalent
- ii) Retrosynthesis
- iii) Functional group interconversion

b) Predict the product and suggest the mechanism.



c) Write a note on : Dieckmann condensation.

P.T.O.

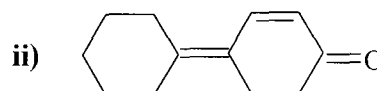
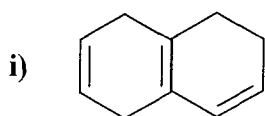
SECTION – II

Q.3 Attempt any **TWO** of the following: **(10)**

- a) Explain the following:
- i) Trans Cinnamic acid absorbs at longer wavelength than its cis-isomer.
 - ii) Ethylene shows λ max at 171 nm while 1,3 –Butadiene shows λ max at 217 nm.
- b) How will you distinguish the following pairs by IR spectroscopy?
- i) Ph - CH₂ - C \equiv N and Ph - C \equiv C - H
 - ii) CH₃ - CH₂ - OH and CH₃ - O - CH₃
- c) Write a note on : shielding and deshielding of protons.

Q.4 Attempt any **TWO** of the following: **(10)**

a) Calculate λ max for the following:



b) Assign structure of the compound using following spectral data:

MF : C₉ H₁₁Br

PMR : i) 7.2 δ (s, 15mm)

ii) 2.4 δ (d, 6 mm)

iii) 3.5 δ (m, 3 mm)

iv) 1.1 δ (d, 9 mm)

c) Assign structure of the compound using following spectral data:

MF : C₇ H₈O

IR 3350, 1600 & 1500 cm⁻¹

PMR : i) 3.8 δ (s, 1H)

ii) 4.3 δ (s, 2 H)

iii) 7.2 δ (s, 5H)

* * *

TABLE : 1

Characteristic Infrared Absorptions of Functional Groups

Group	Frequency Range cm^{-1}	Intensity
A. Alkyl		
C-H (stretching)	2853 – 2962	(m-s)
Isopropyl – CH (CH_3) ₂	1380 – 1385	(s)
	and 1365 – 1370	(s)
tert-Butyl – C (CH_3) ₃	1385 – 1395	(m)
	and – 1365	(s)
B. Alkenyl		
C-H (stretching)	3010 – 3095	(m)
C=C (stretching)	1620 – 1680	(v)
R-CH=CH ₂	985 – 1000	(s)
	and 905 – 920	(s)
R ₂ C=CH ₂ (out-of-plane C-H bendings)	880 – 900	(s)
cis-RCH=CHR	675 – 730	(s)
trans-RCH=CHR	960 – 965	(s)
C. Alkynyl		
\equiv C-H (stretching)	3300	(s)
C = C (stretching)	2100 – 2260	(v)
C \equiv N (stretching)	2210 – 2260	(v)
D. Aromatic		
Ar-H (stretching)	3030	(v)
Aromatic substitution type (C-H out-of-plane bendings)		
Monoasubstituted	690 – 710	(very s)
	and 730 – 770	(very s)
o-Disubstituted	735 – 770	(s)
m-Disubstituted	680 – 725	(s)
	and 750 – 810	(very s)
p-Disubstituted	800 – 840	(very s)
E. Alcohols, Phenols, Carboxylic Acids		
OH (alcohols, phenols, dilute solns)	3590 – 3650	(sharp v)
OH (alcohols, phenols, hydrogen bonded)	3200 – 3550	(broad, s)
OH (carboxylic acids, hydrogen bonded)	2500 – 3000	(broad, v)
F. Aldehydes, Ketones, Esters and Carboxylic Acids		
C = O stretch	1630 – 1780	(s)
Aldehydes	1690 – 1740	(s)
Ketones	1680 – 1750	(s)
Esters	1735 – 1750	(s)
Carboxylic acids	1710 – 1780	(s)
Amides	1630 – 1690	(s)
G. Amies	3300 – 3500	(m)
N – H		
H. Nitriles	2220 – 2260	(m)
C \equiv N		

TABLE : 2

Approximate Proton Chemical Shifts in N M R

Type of Proton	Chemical Shift, Delta, PPM (δ)
1° Alkyl, RCH ₃	0.8 – 1.0
2° Alkyl, RCH ₂ R	1.2 – 1.4
3° Alkyl R ₂ CH	1.4 – 1.7
Alkyl ester, R- $\overset{\text{O}}{\parallel}$ -O-CH ₂ -R	4 to 4.5
Alkylic, R ₂ C = $\underset{\text{R}}{\underset{ }{\text{C}}}$ - CH ₃	1.6 – 1.9
Benzylic, ArCH ₂	2.2 – 2.5
Alkyl chloride, RCH ₂ Cl	3.6 – 3.8
Alkyl bromide, RCH ₂ Br	3.4 – 3.6
Alkyl iodide, RCH ₂ I	3.1 – 3.3
Ether, ROCH ₂ R	3.3 – 3.9
Alcohol, HOCH ₂ R	3.3 – 4.0
Ketone, RC(=O)CH ₃	2.1 – 2.6
Aldehyde, RCH(=O)	9.5 – 9.6
Vinylic, R ₂ C = CH ₂	4.6 – 5.0
Vinylic, R ₂ C = $\underset{\text{R}}{\underset{ }{\text{CH}}}$	5.2 – 5.7
Aromatic, ArH	6.0 – 9.5
Acetylenic, RC \equiv CH	2.5 – 3.1
Alcohol hydroxyl, ROH	0.5 – 6.0 ^a
Carboxylic, RCOH	10 – 13 ^a
Phenolic, ArOH	4.5 – 7.7 ^a
Amino R - NH ₂	1.0 – 5.0

^a The chemical shifts of these groups vary in different solvents and with temperature and concentration.

TABLE : 3

U. V. Absorption rules for diene chromophores		U.V. Absorption rules for Enone System	
1) Parent	215 nm	1) Parent	215 nm
2) Each extra conjugation	30 nm	2) Each extra conjugation	30 nm
3) Homoannular	39 nm	3) Homoannular	39 nm
4) Exocyclic double bond	05 nm	4) Substituents	
5) Each alkyl (R)	05 nm	a) Alkyl group at α	10 nm
substituent directly		b) Alkyl group at β	12 nm
attached to double		c) Alkyl group at γ, δ	18 nm
bounded carbon			