

**T.Y.B.SC. SEM – VI (2014 Course) : WINTER - 2018**  
**SUBJECT : CHEMISTRY : ORGANIC CHEMISTRY – VI**

Day : Friday  
Date : 12/10/2018

Time : 03.00 PM To 05.00 PM  
Max. Marks : 40

**W-2018-0868**

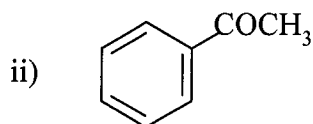
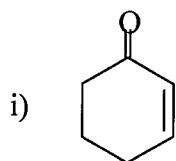
**N.B.:**

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

**SECTION – I**

**Q.1** Attempt **ANY TWO** of the following: **[10]**

- a) Give retrosynthetic approach for the following compounds:



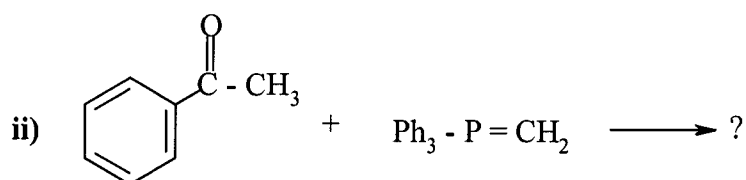
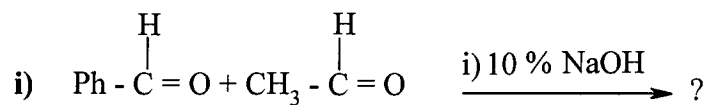
- b) What is Claisen – ester condensation? Discuss its mechanism.  
c) Write a note on : Perkin's reaction.

**Q.2** Attempt **ANY TWO** of the following: **[10]**

- a) Define the following terms with one example of each:

- i) Synthons
- ii) Disconnection
- iii) Synthetic equivalent

- b) Predict the product and suggest the mechanism:



- c) Write a note on : Dieckmann condensation.

**P.T.O.**

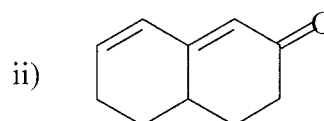
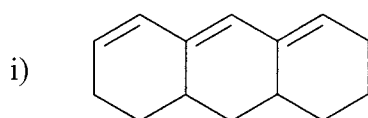
**SECTION – II**

**Q.3** Attempt **ANY TWO** of the following: **[10]**

- a)** Explain the following:
- i)** In ethanol the proton of OH group shows only a singlet although – CH<sub>2</sub> group is adjacent to it.
  - ii)** TMS is used as an internal reference standard in NMR spectroscopy.
- b)** A compound C<sub>6</sub>H<sub>10</sub>O shows positive iodoform test. It shows IR peak at 1690 cm<sup>-1</sup> and UV absorption at 240 nm. Suggest its structural formula.
- c)** Write a note on : Application of UV spectroscopy.

**Q.4** Attempt **ANY TWO** of the following: **[10]**

- a)** Calculate  $\lambda_{\max}$  for the following:



- b)** Assign the structure to the following compound using following spectral data:

MF : C<sub>4</sub>H<sub>8</sub>O  
 IR : 1715 cm<sup>-1</sup>  
 PMR : **i)** 1.07  $\delta$  (t, 3H)  
           **ii)** 2.12  $\delta$  (s, 3H)  
           **iii)** 2.48  $\delta$  (q, 2H)

- c)** Assign the structure to the following compound using following spectral data:

MF : C<sub>3</sub>H<sub>6</sub>O  
 IR : 1725, 2725 cm<sup>-1</sup>  
 PMR : **i)** 9.77  $\delta$  (s, J = 6Hz, 2 mm)  
           **ii)** 2.5  $\delta$  (q, J = 6Hz, 4 mm)  
           **iii)** 1.2  $\delta$  (t, J = 6 Hz, 6 mm)

\* \* \* \*

TABLE : 1

## Characteristic Infrared Absorptions of Functional Groups

Group	Frequency Range $\text{cm}^{-1}$	Intensity
A. Alkyl		
C-H (stretching)	2853 - 2962	(m-s)
Isopropyl - CH (CH <sub>3</sub> ) <sub>2</sub>	1380 - 1385	(s)
	and 1365 - 1370	(s)
	1385 - 1395	(m)
tert-Butyl - C (CH <sub>3</sub> ) <sub>3</sub>	and - 1365	(s)
B. Alkenyl		
C-H (stretching)	3010 - 3095	(m)
C=C (stretching)	1620 - 1680	(v)
R-CH=CH <sub>2</sub>	985 - 1000	(s)
	and 905 - 920	(s)
R <sub>2</sub> C=CH <sub>2</sub> (out-of-plane	880 - 900	(s)
cis-RCH=CHR C-H bendings)	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)

TABLE : 2

Approximate Proton Chemical Shifts in NMR

Type of Proton	Chemical Shift, Delta, PPM ( $\delta$ )
1° Alkyl, RCH <sub>3</sub>	0.8 – 1.0
2° Alkyl, RCH <sub>2</sub> R	1.2 – 1.4
3° Alkyl R <sub>2</sub> CH	1.4 – 1.7 Ester R-C(=O)-O-CH <sub>2</sub> -R 4 to 4.5
Alkylic, R <sub>2</sub> C = C - CH <sub>3</sub>   R	1.6 – 1.9
Benzylic, ArCH <sub>3</sub>	2.2 – 2.5
Alkyl chloride, RCH <sub>2</sub> Cl	3.6 – 3.8
Alkyl bromide, RCH <sub>2</sub> Br	3.4 – 3.6
Alkyl iodide, RCH <sub>2</sub> I	3.1 – 3.3
Ether, ROCH <sub>2</sub> R	3.3 – 3.9
Alcohol, HOCH <sub>2</sub> R	3.3 – 4.0
Ketone, RCCH <sub>3</sub>    O	2.1 – 2.6
Aldehyde, RCH    O	9.5 – 9.6
Vinylic, R <sub>2</sub> C = CH <sub>2</sub>	4.6 – 5.0
Vinylic, R <sub>2</sub> C = CH   R	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 <sup>a</sup>
Carboxylic, RCOH    O	10 – 13 <sup>a</sup>
Phenolic, ArOH	4.5 – 7.7 <sup>a</sup>
Amino R - NH <sub>2</sub>	1.0 – 5.0

<sup>a</sup> 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) substituent directly attached to double bounded carbon	05 nm	a) Alkyl group at $\alpha$	10 nm
		b) Alkyl group at $\beta$	12 nm
		c) Alkyl group at $\gamma, \delta$	18 nm