# BACHELOR OF SCIENCE (CBCS-2018 COURSE) T. Y. B. Sc. Sem-VI :SUMMER- 2022 SUBJECT : CHEMISTRY : ORGANIC CHEMISTRY-II

Day: Thursday Date: 7/7/2022

S-18472-2022

Time: 11:00 AM-02:00 PM

Max. Marks: 60

N.B.

- 1) All questions are **COMPULSORY**.
- 2) Figures to the **RIGHT** indicate **FULL** marks.
- 3) Draw neat and labeled diagram wherever necessary.

### Q.1 Attempt ANY TWO of the following:

(12)

- a) What is Aldol condensation? Discuss its mechanism and applications.
- **b)** Explain the following:
  - i) Bands in UV spectrum are very broad.
  - ii) Phenol shows bathochromic shift in presence of alkali
- c) How will you distinguish the following pairs by IR spectroscopy?

i) 
$$CH_3 - CH_2 - C \equiv N$$
 and  $CH_3 - CH_2 - C \equiv C - H$ 

## **Q.2** Attempt **ANY TWO** of the following:

(12)

- a) What is Wittig reaction? Discuss its mechanism and applications.
- **b)** Explain the following:
  - i) Only one signal appears in the NMR spectrum of acetone, however propanal shows three peaks in its NMR spectrum.
  - ii) TMS is used as an internal reference standard in NMR Spectroscopy.
- c) Write a note on : Applications of UV spectroscopy.

#### **Q.3** Attempt **ANY TWO** of the following:

(12)

- a) What are carbanions? Discuss their generation and stability.
- **b)** How will you distinguish the following pairs by NMR spectroscopy?

i) 
$$CH_3 - O - CH_3$$
 and  $CH_3 - CH_2 - OH$ 

How will you monitor the following reactions by IR spectroscopy?

i)  $HNO_3 + H_2SO_4$  Sn/HClii)  $H-CHO \xrightarrow{i) CH_3MgBr} CH_3 - CH_2 - OH \xrightarrow{i) PCl_5} CH_3 - CH_2 - C \equiv N$ 

- Q.4 Assign the structure of ANY THREE of the following using spectral data: (12)
  - a) MF :  $C_8H_9Br$  PMR :  $2.0\delta(d,3H)$  $5.15\delta(q,IH)$

 $7.55 \delta(s, 5H)$ 

**b)** MF :  $C_9H_{10}O$  IR : 1715  $cm^{-1}$ ,1590,1550 and 1460 cm<sup>-1</sup> PMR : 2.09 $\delta$ (s,3H)

 $3.65\,\delta\,(\mathrm{s},2\,\mathrm{H})$ 

 $7.25 \delta(s, 5H)$ 

**c)**  $MF : C_3H_8O$ 

*IR* :  $3300 \text{ cm}^{-1}$ *PMR* :  $0.9 \delta (t, 3 \text{ H})$ 

 $1.5\delta$  (sextet, 2 H)

 $3.4 \delta (t, 5 H)$ 

 $4.1\delta$  (s,1H)

**d)** MF :  $C_4H_8O$ 

*UV* : 290*nm* 

IR : 1720 cm<sup>-1</sup>

*PMR* : 1.05  $\delta$  (t, J = 6 Hz, 15 mm) 2.05  $\delta$  (s, 15 mm)

 $2.4 \, \delta \, (q, J = 6 \, Hz, 10 \, mm)$ 

## Q.5 Attempt ANY FOUR of the following:

a) What is spectroscopy? What are advantages of spectroscopic methods?

(12)

- **b)** Indicate different sets of protons in the following compounds:
  - i)  $CH_3-CH_2-CH_3$
  - ii)  $CH_3-O-CH_2-O-CH_2-CH_3$
  - iii) CH<sub>3</sub>-O-CH<sub>2</sub>-CH<sub>3</sub>
- c) Calculate fundamental modes of vibrations for:
  - i) H<sub>2</sub>O
  - ii) CO<sub>2</sub>
  - iii) CS<sub>2</sub>
- **d)** Explain the terms:
  - i) Chromophores
  - ii) Auxochromes
- e) Calculate  $\lambda$  max for the following compound.



f) A compound  $C_6H_{10}O$  shows negative iodoform test. It shows IR peaks at 2720 & 1700 cm<sup>-1</sup>. It shows UV absorption at 240 nm. Suggest the structure.

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TABLE: 1 Characteristic Infrared Absorptions of Functional Groups

	Group	Frequency Range cm <sup>-1</sup>	Intensity
Α.	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)
	$R_2C=CH_2$ (out-of-plane	880 - 900	(s)
	cis-RCH=CHR C-H bendings)	675 - 730	(s)
	trans-RCH=CHR	960 – 965	(s)
C.	Alkynyl		
	≡ C-H (stretching)	3300	(s)
	C = C (stretching)	2100 - 2260	(v)
	C = 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, Pinenols, 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.	Amics	3300 - 3500	(m)

Appro	Allinute 1700
Type of Proton	Chemical Shift, Delta, PPM $(\delta)$
1° Alkyl, RCH <sub>3</sub>	0.1 - 8.0
2° Alkyl, RCH2R	1.2 – 1.4 O
3° Alkyl R₂CH	1.4 - 1.7 Ester R-C-O-CH <sub>2</sub> -R 4 to 4.5
Alkylic, $R_2C = C - CH_3$	1.6 – 1.9
l R	
Benzylic, ArCH <sub>3</sub>	2.2 - 2.5
Alkyl chloride, RCH2Cl	3.6 - 3.8
Alkyl bromide, RCH2Br	3.4 - 3.6
Alkyl iodide, RCH2I	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, RCCH3	2.1 – 2.6
0 0	
Aldehyde, RCH	9.5 - 9.6
Vinylic, $R_2 C = CH_2$	4.6 - 5.0
Vinylic, R <sub>2</sub> C = CH	5.2 – 5.7
l R	
Aromatic, ArH	6.0 - 9.5
Acetylenic, RC = CH	2.5 – 3.1
Alcohol hydroxyl, RÖH	$0.5 - 6.0^{a}$
Carboxylic, RCOH	$10 - 13^{a}$
O	
Phenotic, ArOH	$4.5 - 7.7^n$
Amino R – NH <sub>2</sub>	1.0 – 5.0

<sup>&</sup>lt;sup>a</sup> The chemical shifts of these groups vary in different solvents and with temperature and concentration.

#### TABLE: 3

<ul><li>U. V. Absorption rul for diene chromosph</li></ul>		U.V. Absorption rules for Enone System		
Parent     Each extra conjugation     Homoannular     Exocylic double bond	215 nm 30 nm 39 nm 05 nm	<ol> <li>Parent</li> <li>Each extra conjugation</li> <li>Homoannular</li> <li>Substituents</li> </ol>	215 nm 30 nm 39 nm	
5) Each alkyl (R) substituent directly attached to double bounded carbon	05 nm	<ul> <li>a) Alkyl group at α</li> <li>b) Alkyl group at β</li> <li>c) Alkyl group at γ, δ</li> </ul>	10 nm 12 nm 18 nm	