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

Day : Friday
Time : 10:00 AM-01:00 PM

Date : 9/12/2022
W-18472-2022
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 Dieckmann condensation? Discuss its mechanism and applications.

b) Explain the following :
i) Bands in UV spectrum are very broad.
ii) Ethanol can be used as a solvent in UV but acetone can't be used.

c) How will you distinguish the following pairs by IR spectroscopy?

i) CH_3-CH_2-OH and $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

ii) $Ph-CH_2-C\equiv N$ *and* $Ph-C\equiv C-H$

Q.2 Attempt **ANY TWO** of the following : **(12)**

a) What is Aldol condensation? Discuss the mechanism of crossed Aldol condensation.

b) Explain the following :
i) Chemical shift ii) Spin-Spin splitting.

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.

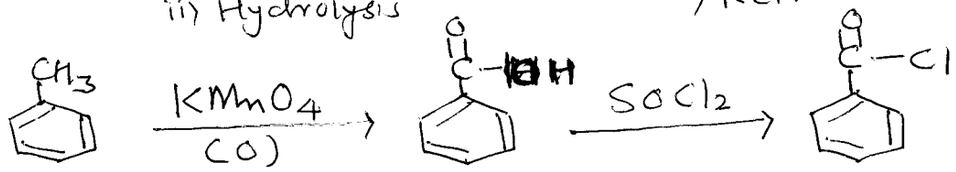
b) How will you distinguish the following pairs by NMR spectroscopy?

i) CH_3-O-CH_3 *and* $CH3-\overset{H}{\overset{|}{C}}=O$

ii) CH_3-CH_2-OH *and* CH_3-CH_2-Cl

c) How will you monitor the following reactions by IR spectroscopy?

i) $H-\overset{H}{\overset{|}{C}}=O \xrightarrow[\text{ii) Hydrolysis}]{\text{i) Ph-Mg-Br}} Ph-CH_2-OH \xrightarrow[\text{ii) KCN}]{\text{i) } PCl_5} Ph-CH_2-C\equiv N$

ii) 

Q.4 Assign the structure **ANY THREE** of the following using spectral data : **(12)**

a) MF : $C_9H_{10}O$
IR : 1715 cm^{-1} & 1600 cm^{-1}
PMR : 2.09 δ (s, 3H)
3.65 δ (s, 2H)
7.2 δ (s, 5H)

PTO

b) MF : $C_8H_8O_2$
IR : 2700 – 3300 cm^{-1} (broads), 1700, 1600, 1500 & 920 cm^{-1}
PMR : 3.5 δ (s, 12 mm)
7.2 δ (s, 30 mm)
12.3 δ (s, 6 mm)

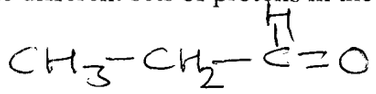
c) MF : C_3H_5ON
IR : 2250 cm^{-1}
PMR : 3.49 δ (s, 3H)
4.22 δ (s, 2H)

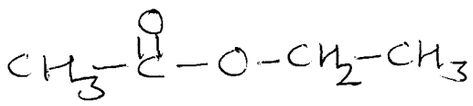
d) MF : C_8H_7N
IR : 2220, 1620 & 1510 cm^{-1}
PMR : 2.4 δ (s, 3H)
7.2 δ (d, 2H)
7.5 δ (d, 2H)

Q.5 Attempt **ANY FOUR** of the following : **(12)**

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

b) Indicate different sets of protons in the following compounds:

i) 

ii) 

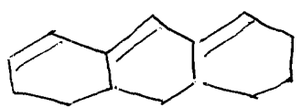
iii) CH_3–CH_3

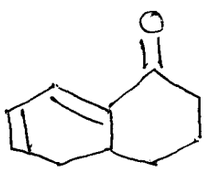
c) Calculate fundamental modes of vibrations for :
i) H_2S ii) –N=O iii) NH_3 .

d) Explain the terms :
i) Bathochromic shift
ii) Hypsochromic shift.

e) A compound C4H6 shows λ max at 217 nm and IR bands at 1620, 990 and 910 cm^{-1}. Assign the structure.

f) Calculate λ max for the following :

i) 

ii) 

*****

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_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, 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 ≡ 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_2R	1.2 – 1.4
3° Alkyl R_3CH	1.4 – 1.7 Ester $R-C(=O)-O-CH_2-R$ 4 to 4.5
Alkylic, $R_2C=C(R)-CH_3$	1.6 – 1.9
Benzylic, $ArCH_3$	2.2 – 2.5
Alkyl chloride, RCH_2Cl	3.6 – 3.8
Alkyl bromide, RCH_2Br	3.4 – 3.6
Alkyl iodide, RCH_2I	3.1 – 3.3
Ether, $ROCH_2R$	3.3 – 3.9
Alcohol, $HOCH_2R$	3.3 – 4.0
Ketone, $RC(=O)CH_3$	2.1 – 2.6
Aldehyde, $RC(=O)H$	9.5 – 9.6
Vinylic, $R_2C=CH_2$	4.6 – 5.0
Vinylic, $R_2C=CH(R)$	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[a]
Carboxylic, $RC(=O)OH$	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 temperatu[re and] concentration.

TABLE : 3

U. V. Absorption rules for diene chromosphores		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) Exocylic double bond	05 nm	4) Substituents	
5) Each alkyl (R) substituent directly attached to double bounded carbon	05 nm	a) Alkyl group at α	10 nm
		b) Alkyl group at β	12 nm
		c) Alkyl group at γ, δ	18 nm