T.Y.B.SC. SEM – VI (CBCS - 2016 Course) : SUMMER - 2019
SUBJECT : CHEMISTRY : ORGANIC CHEMISTRY – II

Day : Friday
Date : 12/04/2019

S-2019-0908

Time: 03.00 P.M. To 06.00 P.M
Max. Marks : 60

N.B.:

1) All questions are **COMPULSORY**.
2) Figures to the right indicate **FULL** marks.

Q.1 Attempt **ANY TWO** of the following: **[12]**

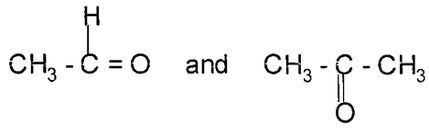
a) What is Claisen condensation? Discuss its mechanism and application.

b) Explain the following:
i) Bands in UV spectrum are very broad.

ii) Nitrophenol 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 $CH_3 - CH_2 - C \equiv C - H$

ii)  and

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.

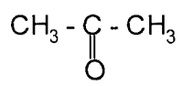
c) Write a note on : Applications of UV spectroscopy.

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?

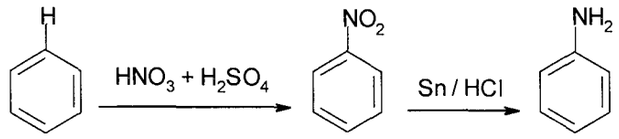
i) $CH_3 - O - CH_3$ and $CH_3 - CH_2 - OH$

ii)  and $CH_3 - CH_2 - Cl$

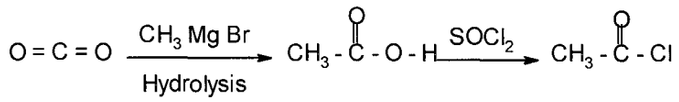
P.T.O.

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

i)



ii)



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

a) MF : C_8H_9Br
PMR : 2.0 δ (d, 3H)
: 5.15 δ (q, 1H)
: 7.55 δ (s, 5H)

b) MF : $C_8H_8O_2$
IR : 2700 – 3300 cm^{-1} (broad), 1700, 1600, 1500 and 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_8O
IR : 3300 cm^{-1}
PMR : 0.9 δ (t, 3H)
: 1.5 δ (sextet, 2H)
: 3.4 δ (t, 2H)
: 4.1 δ (s, 1H)

d) MF : $C_{10}H_{14}$
PMR : 1.3 δ (s, qH)
: 7.28 δ (s, 5H)

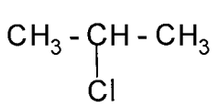
Q.5 Attempt **ANY FOUR** of the following: **[12]**

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

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

i) $CH_3 - CH_2 - CH_3$ **iii)** $CH_3 - O - CH_2 - CH_3$

ii)

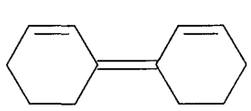


c) Calculate fundamental modes of vibrations for:
i) C_6H_6 **ii)** CO_2 **iii)** CS_2

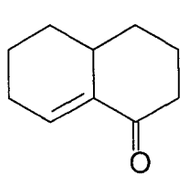
d) Explain the terms:
i) Chromophores **ii)** Auxochromes

e) Calculate λ_{max} for the following compound:

i)



ii)



f) A compound $C_6H_{10}O$ shows negative iodoform test. It shows IR peaks 2720 and 1700 cm^{-1}. It show UV absorption at 240 nm. Suggest the structure.

* * * *

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)
			1385 – 1395	(m)
	tert-Butyl – C $(CH_3)_3$		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_2CH	1.4 – 1.7
Alkylic, $R_2C = C - CH_3$ (R)	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, $RCCH_3$ (O)	2.1 – 2.6
Aldehyde, RCH (O)	9.5 – 9.6
Ester $R-\overset{O}{\overset{\|}{C}}-O-CH_2-R$	4 to 4.5
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, RCOH (O)	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 concentration.

TABLE : 3

U. V. Absorption rules for diene chromosphores

1) Parent	215 nm
2) Each extra conjugation	30 nm
3) Homoannular	39 nm
4) Exocylic double bond	05 nm
5) Each alkyl (R) substituent directly attached to double bounded carbon	05 nm

U.V. Absorption rules for Enone System

1) Parent	215 nm
2) Each extra conjugation	30 nm
3) Homoannular	39 nm
4) Substituents	
a) Alkyl group at α	10 nm
b) Alkyl group at β	12 nm
c) Alkyl group at γ, δ	18 nm