CHC 107

Total No. of Printed Pages:08

B.Sc. (CBCS) (Semester -V)
EXAMINATION NOVEMBER 2022
Chemistry
Organic Chemistry

[Duration : 2 Hours] **[Total Marks :80]**

Instructions:
1. All questions are compulsory.
2. Figures to the right indicate full marks
3. Answers to the two sections should be written on separate answer books.
4. Spectroscopic table is attached at the end

Section- A

Q.1 Answer **any four** of the following. (4 x 4=16 marks)

a) Give analytical evidence for the following:
   i. Nature of nitrogen atom in Nicotine
   ii. Presence of pyridine nucleus with a side chain at C-3 position in Nicotine.

b) Write the structures and indicate the number of signals in the ^{13}C NMR spectrum of the following compounds.
   i. Pyridine
   ii. Ethylbenzene

c) Give mechanism for the sulphonation of benzene and identify the electrophile.

d) Define the following terms:
   i. Base peak
   ii. Coupling constant

e) Explain, with resonance contributing structures why Electrophilic Aromatic Substitution in Nitrobenzene gives meta product?

f) Comment on isotope effect in methyl bromide using mass spectrometry.

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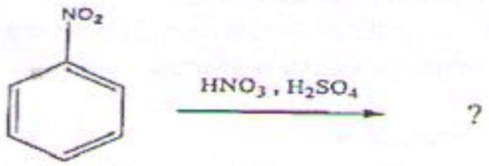
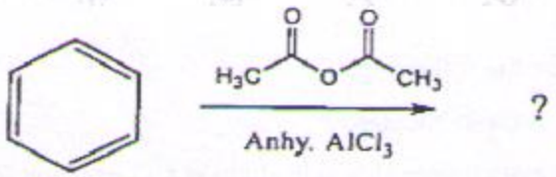
Q.2 A) i) A compound with MF: $C_5H_{10}O_2$ shows following data in its ^1H NMR spectrum. 4

Suggest a probable structure and assign the peaks.

^1H NMR : δ 1.12 (doublet, 6H), δ 4.31 (septet, 1H), δ 2.12 (singlet, 3H)

ii) Complete the following reactions with correct products. 2

a) 

b) 

OR

A) iii) Indicate the number of ^1H NMR signals in the following compounds. 4

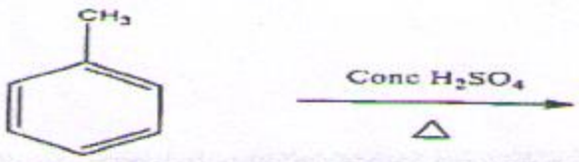
a) n-Propyl chloride

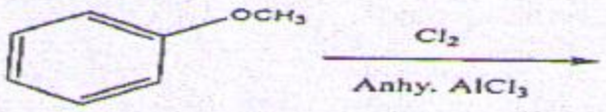
b) Acetic acid

c) Benzaldehyde

d) Vinyl bromide

iv) Write the correct products for the following reaction. 2

a) 

b) 

B) i) Write the structures for the following degradation reaction. 4

ii) Account for the following mass peaks for 3-Pentanone. 2

MS m/e: 15, 29, 57, 86

Q.3 A) i) A compound with MF: $C_9H_{12}0$ shows following NMR data. 4

Suggest a probable structure and assign the peaks.

^{1}H NMR : δ 7.5 (singlet, 5H), δ 2.3 (triplet, 2H), δ 3.9 (triplet, 2H),
δ 3.8 (singlet, 3H)

ii) Suggest the use of Zeisel's method in the structure elucidation of Papaverine. 2

OR

A) iii) A compound with MF: $C_5H_{10}O_2$ shows following ^{1}H NMR data. 4

Deduce the structure and assign the peaks.

^{1}H NMR : δ 1.2 (doublet, 6H), δ 2.7 (multiplet, 1H) δ 3.8 (singlet, 3H)

iv) Outline the synthesis of Veratric acid using p-Hydroxybenzoic acid. 2

B) i) Show Mc-Lafferty mass fragmentation pattern in 2-hexanone. 4

ii) A compound with MF: C_4H_7N shows following ^{1}H NMR data. Predict the structure. 2

^{1}H NMR : δ 1.3 (doublet, 6H), δ 2.7 (multiplet, 1H)

IR: 2210 cm^{-1}

Section – B

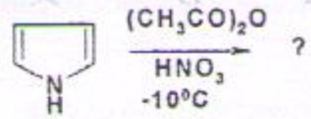
Q.4 Answer **Any four** of the following. (4 x 4=16 marks)

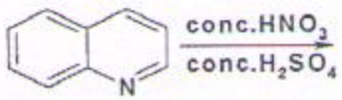
a. Give the steps involved in the conversion of catechol to Adrenaline.

b. i) Match the column A with B

A	B
Indole	Paal Knorr
Isoquinoline	Skraup
Thiphene	Fischer synthesis
Quinoline	Bischler Napieralski reaction

ii) Predict the major product for the following.

I) 

II) 

c. Give synthesis and one use of Crystal Violet.

d. i) Write the reaction for Hantzch synthesis of substituted pyridine.

ii) Pyridine is least reactive towards electrophilic aromatic substitution. Justify this statement.

e. Explain giving reasons the following:

i) β-Carotene is orange coloured.

ii) Graphite is black in Colour.

f. The electrophilic aromatic substitution in quinoline takes place at $5^{th}/8^{th}$ position and not 6^{th} positions. Explain giving resonance structures.

Q.5 A. i) With respect to "**Pyrrole**" answer the following. 4

a. Give the structure and numbering for pyrrole.

b. Name and give the synthesis for 2,5-dimethylpyrrole.

c. Give industrial synthesis of pyrrole.

ii) Give synthesis of Methyl orange. 2

OR

A. iii) With respect to "**Indole**" answer the following. 4

a. Give structure, numbering and resonance structures for indole.
b. Give the synthesis of indole from phenyl hydrazine. Name the synthesis.

iv) Define a vat dye, giving an example. 2

B. i) Give analytical evidence for the following. 4

a. Presence of β-ionone nucleus in Vitamin A
b. Presence of catechol unit in Adrenaline.

ii) Give any two electrophilic aromatic substitution reactions of pyridine. 2

Q.6 A) i) Complete the following, and answer the questions given below. 4

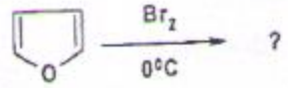
a. Name the final product and the synthesis involved.

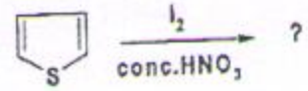
b. What is the role of $POCl_3$ and Pd/C in the first and second step respectively.

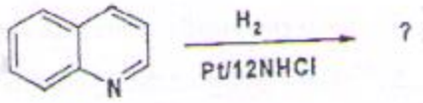
ii) Give the structure of Vitamin C and prove presence of enediol grouping in it. 2

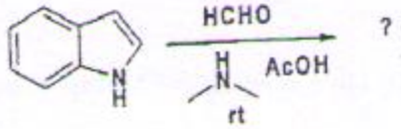
OR

A) iii) Predict the major product for the following. 4

a) 

b) 

c) 

d) 

iv) Prove the presence of aminoacid grouping in thyroxine. 2

B) i) Explain with resonance structures, why electrophilic aromatic substitution in pyrrole takes place at 2nd / 5th position and not 3rd position. 4

ii) Giving reasons, identify the most basic and least basic of the following? 2

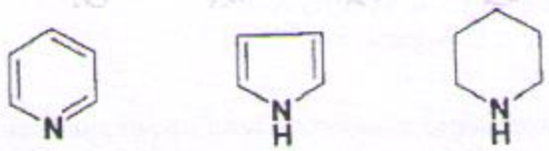


TABLE-1

Characteristic Infrared Absorptions of Functional Groups

GROUP		FREQUINCY MANGE car	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 C–H bending)	880 – 900	(s)
cis – RCH = CHR		675 – 730	(s)
trans – RCH = CHR		960 – 975	(s)
C. Alkynyl			
≡ C–H (stretching)		3300	(s)
C ≡ C (stretching)		2100 – 2260	(v)
D. Aromatic			
Ar – H (stretching)		3030	(v)
Aromatic substitution type (C–H out-of-plane bendings)			
Monosubstituted		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 solutions)		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. Amines			
N – H		3300 – 3500	(m)
H. Nitriles			
C ≡ N		2220 – 2260	(m)

TABLE – 3

Approximate Proton Chemical Shifts in NMR

TYPE OF PROTON	CHEMICAL SHIFT, DELTA, PPM (δ)
Cyclopropane	0.2 – 0.8
1° Alkyl, RCH_3	0.8 – 1.0
2° Alkyl, RCH_2R	1.2 – 1.4
3° Alkyl R_3CH	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
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 – 5.0a

Ester $R-C(=O)-O-CH_2-R$ 4 to 4.5

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

TABLE – 4

Typical[13] CMR Chemical Shifts and Units

Alkanes	1 – 60
C – O and C – N	30 – 80
C ≡ C	70 – 95
C = C	100 – 150
Aromatic C	110 – 135
C = O in acids, easter, amides	150 – 180
C = O in aldehydes and ketones	195 – 250