CARMEL COLLEGE OF ARTS, SCIENCE & COMMERCE FOR WOMEN, NUVEM-GOA

Semester End Examination, January 2022

Semester: V of B.Sc.

Course name & Code: Organic Chemistry CHC107

Total marks:80 **Date:** **Duration:2 hours** **Total No of pages:5**

Instructions: 1) Answers to the two sections should be written on separate books.
2) All questions are compulsory
3) Figures to the right indicate full marks
4) For questions 2,3,5 & 6 there is choice for question A

Section A

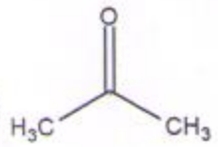
Q1) Answer **Any four** of the following. **(4 x 4 = 16 marks)**

i) Give analytical evidence for the presence of pyrrolidine nucleus in Nicotine.

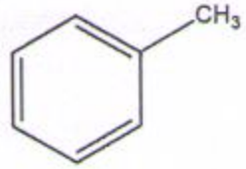
ii) Giving examples discuss how inductive and mesomeric effects influence the carbonyl absorption frequency.

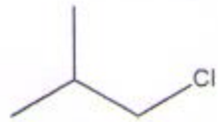
iii) Explain mechanism involved in nitration of benzene.

iv) Indicate the number of ^{1}HNMR signals for the following compounds:

a) 

b) 

c) 

d) 

v) Explain the mechanism involved in sulphonation of benzene.

vi) Explain anisotropic effect in aromatic compounds with an example.

Q2) A) i) How will you distinguish the following pairs of compounds on the basis of IR spectroscopy? **(4 marks)**

a) CH_3NH_2 and $(CH_3)_3N$

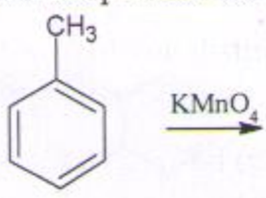
b) $CH_3CH_2CH_3$ and CH_3CH_2COOH

ii) Cyclopropenyl cation is aromatic. Explain. **(2 marks)**

OR

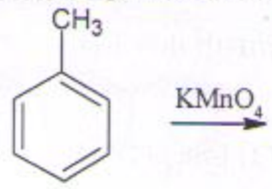
Q2) A)iii) How will you study the progress of an organic reaction using IR spectroscopy? **(4 marks)**

iv) Predict the product for the following: **(2 marks)**

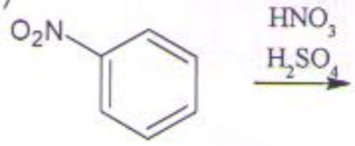
a) 

iv) Predict the product for the following: **(2 marks)**

a)



b)



Q2)B) i) Outline the synthesis of Hygrine from Pyrrole. **(4 marks)**

ii) Why TMS is used as a reference standard in NMR spectroscopy? **(2 marks)**

Q3) A) i) A compound C_4H_9Br shows following data in its ^{1}HNMR spectrum: δ 1.04 (doublet, 6H); δ 1.95 (multiplet, 1H) and δ 3.33 (doublet, 2H). Suggest probable structure of a compound and assign the peaks. **(4 marks)**

ii) How does Zeisel's method help in the structure elucidation of Papaverine? **(2 marks)**

OR

Q3)A)iii) An organic compound C_7H_8O shows a broad band at 3500 cm^{-1} in infra-red spectrum and following data in its ^{1}HNMR spectrum: δ 2.43 (singlet, 1H); δ 4.58 (singlet, 2H) and δ 7.28 (singlet, 5H). Suggest probable structure of a compound and assign the peaks. **(4 marks)**

iv) State the importance of Herzig-Meyer's method in structure elucidation of alkaloids. **(2 marks)**

Q3)B) i) Explain McLafferty rearrangement in 2-hexanone. **(4 marks)**

ii) Define the following terms:

a) Base peak b) Molecular ion peak **(2 marks)**

Section B

Q4) Answer **Any four** of the following. **(4 x 4 = 16 marks)**

a) Give analytical evidence for the presence and size of lactone ring in ascorbic acid.

b) Outline the synthesis of vitamin C.

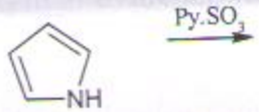
c) Nitrobenzene is pale yellow in colour whereas p-nitroaniline is dark yellow. Justify the statement with reason.

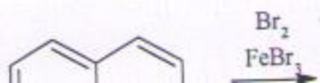
d) Explain Skraup synthesis mechanism with an appropriate example.

e) Outline the synthesis of congo red dye

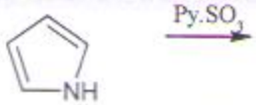
f) Explain the mechanism involved in the nitration of pyridine.

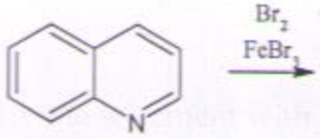
Q5) A) i) Predict the product for the following: **(4 marks)**

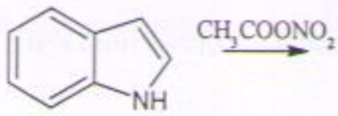
a) 

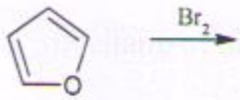
b) 

Q5) A) i) Predict the product for the following: **(4 marks)**

a) 

b) 

c) 

d) 

ii) Illustrate Azo dyes with an example. **(2 marks)**

OR

Q5 A) iii) Outline the synthesis of thyroxine **(4 marks)**

iv) Define acidic dyes. Give an example with structure. **(2 marks)**

Q5.B) i) Give analytical evidence for the following: **(4 marks)**

a) presence of catechol unit in adrenaline.
b) presence of ene diol in vitamin C

ii) Explain the Paal-Knorr synthesis of pyrrrole. **(2 marks)**

Q6) A) i) Explain the mechanism involved in Fisher-indole synthesis with an appropriate example **(4 marks)**

ii) Outline the synthesis of Adrenaline. **(2 marks)**

OR

Q6) A) iii) Electrophilic aromatic substitution on pyrrole takes place at C2 position. Explain. **(4 marks)**

iv) Write a note on classification of vitamins. **(2 marks)**

Q6.B) i) Provide a detailed mechanism for the sulphonation of indole. **(4 marks)**

ii) what are the starting materials used in Hantzsch synthesis? **(2 marks)**

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 bending)	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			

G.	Amines		
	N – H	3300 – 3500	(m)
H.	Nitriles		
	C = N	2220 – 2260	(m)

TABLE – 4
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 = 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]
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 – 5
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

TABLE – 5

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