GV – 26

B.Sc. (Semester – V) Examination, October/November 2016
CHEMISTRY (Paper – III) (6 Units)
Organic Chemistry

Duration : 2 Hours | Total Marks : 80

Instructions : *1) **All** questions are **compulsory**.*
*2) Answer to the **two** Sections should be written on **separate** answer books.*
3) Tables of UV, IR and NMR values are attached at the end.

SECTION – I **Marks : 40**

1. Answer **any four** of the following : **16**

i) Explain the splitting of signals in sec-butylchloride and Isobutylchloride w.r.t. ^{1}H NMR.

ii) Comment on isotope effect of Chlorine and Bromine in MS.

iii) What is meant by proton coupled and proton decoupled CMR spectrum ?

iv) Give the Machenzi-Wood synthesis of tropic acid.

v) Addition of Br_2 to 2-butene is both stereoselective and stereospecific. Explain.

vi) How many signals Ortho, Meta and Para dichloro-benzene will show in its ^{13}C NMR spectrum ? Justify your answer.

2. A) i) A compound C_8H_7N shows following data in its ^{1}H NMR spectrum. Deduce the probable structure for a compound and give the number of signals it gives in its CMR spectrum.

δ 3·70, s, 2H IR – 2250 cm^{-1}
δ 7. 3, s, 5H **4**

ii) How the presence of carboxyl group is detected in alkaloids ? **2**

OR

iii) Give a structure consistent with the following NMR data and assign peaks. **4**
Molecular formula $C_8H_{10}O$ IR : 3600 cm^{-1}
δ1.3, d, 3H; δ 3.4, s, 1H; δ 4.7, q, 1H; δ7.2, s, 5H

iv) What is meant by stereoselective and stereospecific reaction ? **2**

P.T.O.

B) i) A compound $C_{10}H_{12}O_2$ shows following NMR data. Suggest the structure for a compound and assign the signals to the protons. 4

IR : 1742 cm^{-1}.

δ1.52, d, 3H; δ2.05, s, 3H; δ5.87, q, 1H; δ7.3, s, 5H

ii) Give the use of Herzig – Meyer's method in structure elucidation of alkaloids. 2

3. A) i) Give a structure consistent with the following ^{13}C NMR data and assign the peaks. 4

Mol. For. C_3H_5Br

δ 32.6, triplet; δ 118.2, triplet; δ 134.2, doublet

ii) Write the reaction and name the product when 2-methyl-2-butene reacts with HI. 2

OR

iii) A compound $C_3H_5Cl_3$ shows two signals in its ^1H NMR and ^{13}C NMR spectrum. Assign the structure for the compound and justify your answer. 4

iv) Explain the terms : Non equivalent protons and metastable ion. 2

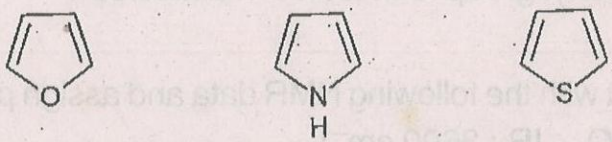
B) i) Discuss EICB mechanism. 3

ii) Explain with suitable example α-cleavage of Ketones in MS. 3

SECTION – II 40 Marks

4. Answer **any four** of the following :

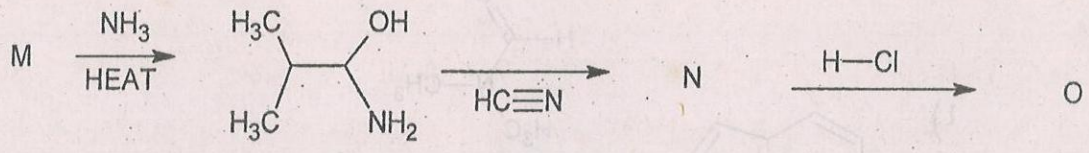
i) List the following five membered heterocyclic compounds in order of decreasing relative aromaticity, giving reasons. 4



ii) Write the structures and name of all the dipeptides that can be made from Glycine and Alanine. 4

iii) Explain with equation Skraup synthesis. 4

iv) Identify M, N, O in the following sequence of reactions and give the name of product O 4

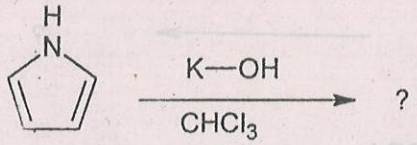


v) Explain with equation Bischler-Napieralski synthesis of Isoquiniline. 4

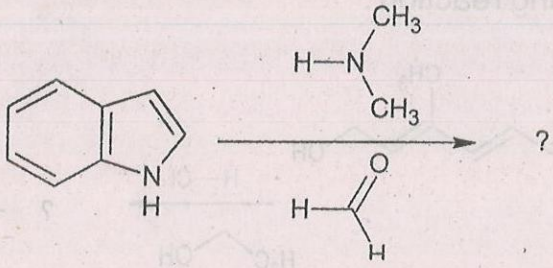
vi) Give the synthesis of Vitamin-A. 4

5. A) i) Complete the following reactions : 3

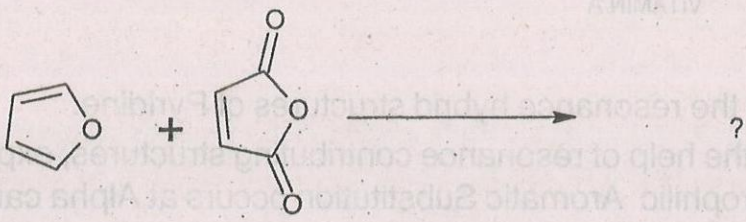
1)



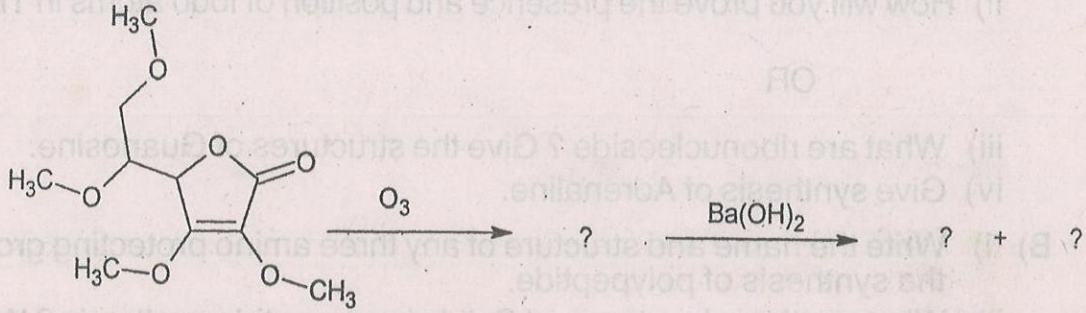
2)



3)

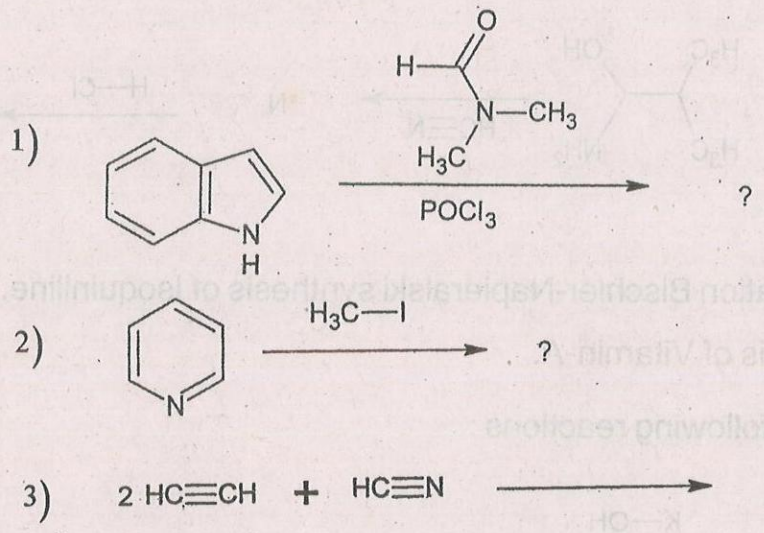


ii) Complete the following reaction : 3

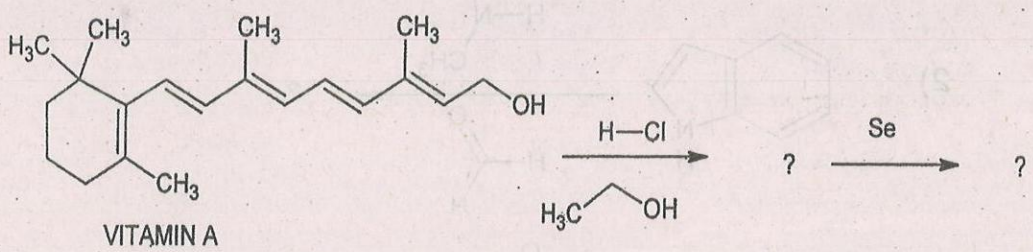


OR

iii) Complete the following reactions : 3



iv) Complete the following reaction : 3



B) i) Write the resonance hybrid structures of Pyridine. 3

ii) With the help of resonance contributing structures, explain why Electrophilic Aromatic Substitution occurs at Alpha carbon in Furan ? 3

6. A) i) Give three important structural differences between RNA and DNA. 3

ii) How will you prove the presence and position of Iodo atoms in Thyroxine ? 3

OR

iii) What are ribonucleoside ? Give the structures of Guanosine. 3

iv) Give synthesis of Adrenaline. 3

B) i) Write the name and structure of any three amino protecting group used in the synthesis of polypeptide. 3

ii) What are the advantages of Solid phase peptide synthesis ? What is the composition of polymer support used in the Merrifield synthesis ? 3

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 – 1389	(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	(out of plane C–H bending)	985 – 1000	(s)
			and 905 – 920	(s)
	$R_2C = CH_2$		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 – 2

U.V. Absorption Rules for Diene Chromophores

1) Base value for heteroannular dicues and open chain dicues	214 nm
2) Base value for homoannular dicues	253 nm
3) Increments for :	
i) Double bond extending conjugation	+ 30 nm
ii) Alkyl substituent or ring residue	+ 5 nm
iii) Exocyclic double bond	+ 5 nm

TABLE – 3

U.V. Absorption Rules for α,β-resaturated Carbonyl Chromophore

α,β – unsaturated ketones	215 nm	Base values
α,β – unsaturated aldehydes	210 nm	
Double bond extending conjugation	+ 30 nm	
Exocylic double bond	+ 5 nm	
Homoannular diene component	+ 39 nm	
Alkyl substituent/ring residue		
α – position	+ 10 nm	
β – position	+ 12 nm	
γ – and higher	+ 18 nm	

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, $R_2C=C(R)-CH_3$	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, $RCCH_3$ (‖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 $R-O-\overset{\overset{O}{\|}}{C}-CH_2-R$ 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
Aromatic C	110 – 135
C = O in acids, easter, amides	150 – 180
C = O in aldehydes and ketones	195 – 250