DA-003-001607 Seat No. _____

B. Sc. (Sem. VI) (CBCS) Examination

April / May – 2015

C-602 : Organic Chemistry & Spectroscopy

Faculty Code : 003
Subject Code : 001607

Time : $2\frac{1}{2}$ Hours [Total Marks : **70**

Instructions : (1) Q.1 carry 20 marks. Multiple choice questions (MCQ answers give in supplementary)

(2) Q. 2 carry 25 marks

(3) Q.3 carry 25 marks

(4) Write university no. on question paper, do not write any rough work and tick mark in question paper.

1 Multiple Choice Questions : **20**

(1) Which molecular formula is correct of limonene ?

(A) $C_{10}H_{14}O$

(B) $C_9H_{17}O$

(C) $C_{10}H_{16}$

(D) $C_{10}H_{18}O$

(2) Ozonolysis of citral gives the products are

(A) Propanol, Laevulic acid, P-cymene

(B) Propane - 2-ol, P-cymene, Nerol

(C) Propane, 3 - Ketobutanal, Ethanal

(D) Prop - 2 - one, 4 - oxopentanal, Ethane-1, 2-dial

(3) Which melting point is correct of L(–) serine ?

(A) 260°C (B) 228°C

(C) 284°C (D) 315°C

(4) Alanine on heating with hydroiodic acid at 200°C temp. gives corresponding compound is

(A) 2-Iodo propanoic acid

(B) 2-Amino butanoic acid

(C) Propionic acid

(D) 2-Iodo butyric acid

(5) Methyl - 2 - benzimidazole Carbamate is a

(A) Acaricide (B) Fungicide

(C) Rodantacide (D) Herbicide

(6) S-Tri methylene trinitramine obtained after the nitration of

(A) Penta Erythritol (B) E.D.T.A.

(C) D.M.G. (D) H.M.T.A.

(7) 4-phenyl butyric acid is heated with conc. sulphuric acid, followed by reduction with Zn-Hg/HCl to formed

(A) Naphthalene (B) Fluorene

(C) α-Tetralone (D) Tetralin

(8) Naphthalene is ozonolysis with O_3 followed by hydrolysis to yield

(A) Declain

(B) Phthalic acid

(C) Phthaldehyde

(D) 1,4-Naphthaquinone

(9) The distance between carbon-carbon atom in ethane molecule is

(A) 1.54 A^o (B) 1.74 A^o

(C) 1.24 A^o (D) 1.94 A^o

(10) Total potential energy in Boat conformation of cyclohexane molecule is

(A) 14.8 k.Cal/mole (B) 7.2 k.Cal/mole

(C) 11.7 k.Cal/mole (D) 10.4 k.Cal/mole

(11) How many NMR signal possible in methyl cyclo propane ?

(A) 1 (B) 2

(C) 3 (D) 4

(12) Which order is correct for the Tau value of methyne, methyl, methylene ?

(A) Methylene > Methyne > Methyl

(B) Methylene > Methyl > Methyne

(C) Methylene < Methyl < Methyne

(D) Methyne < Methylene < Methyl

(13) Tau values for the aldehydic protons are generally

(A) higher (B) equal

(C) lower (D) increase

(14) The loss of an alkene fragment by a cyclic rearrangement of a carbonyl compounds with ν-hydrogen is termed as

(A) Base Peak

(B) Nitrogen rule

(C) Mass spectroscopy

(D) McLaffarty rearrangement

(15) Which solvents are utilised in NMR sample preparation ?

(A) $CDCl_3$, DMSO-d_6 (B) $F_3C.COOH$, D_2O

(C) MeOH-d_4, C_6D_6 (D) above all

(16) What is the strength of the earth's magnetic field ?

(A) 0.27 gauss (B) 0.17 gauss

(C) 0.57 gauss (D) 0.97 gauss

(17) Chemical shift (δ) =

(A) $\frac{V_{TMS} - V_S(Hz)}{Operating\ frequency\ (MHz)}$

(B) $\frac{V_{TM} - V_S(Hz)}{Operating\ frequency(MHz)}$

(C) $\frac{V_S - V_{TMS}\ (Hz)}{Observed\ difference\ in\ Hz}$

(D) $\frac{V_S - V_{TMS}\ (Hz)}{Operating\ frequency(MHz)}$

(18) Which unit is correct of coupling constant–'J' ?

(A) QMz (B) Hertz

(C) Hz (D) (B) and (C)

(19) Which m/e peak is possible in mass spectrum of Neopentane ?

(A) 72, 59, 43, 31, 27

(B) 72, 57, 41, 29, 27

(C) 72, 53, 40, 30, 28

(D) 72, 56, 40, 28, 26

(20) Which characteristics correct of metastable ions or peaks ?

(A) They do not necessarily occur at the integral m/e values.

(B) These are much broader than the normal peaks

(C) These are of relatively low abundance

(D) Above all

2 (a) Give answers of following questions : (any three) **6**

(1) Give synthesis method of 1H - Benzimidazole - 2 - yl-Carbamic acid methyl ester.

(2) Give conversion of :

Terpenyllic acid from E.A.A.

(3) Give only reactions :

2 - amino - 3 - [4' - (4" - Hydroxy phenoxy) phenyl]-propanoic acid react with Potassium hydroxide/H2 and Potassium hydroxide/250°C temp.

(4) Phthaldehyde from Tetralin

(5) Define conformation and configuration

(6) Write Millon's test and Molish test.

(b) Give answers of following questions : (any three) **9**

(1) Give synthesis and uses of 2-isopropoxy phenyl-N-methyl carbamate

(2) Give conversion of terebic acid from α-terpeniol

(3) Give conversion of :

Alanyl glycine from Naphthalene

(4) Give conversion of :

Tetralin from butane-1, 4-dioic acid

(5) Explain conformational analysis of Ethane

(6) Synthesis of L(–) Tyrosine from Hippuric acid by Erlenmayer method.

(c) Give answers briefly : (any two) **10**

(1) Explain constitution of 3,7-Dimethyl-2,6-diene octanal.

(2) Give synthesis of : 2-Amino-3',5'-diiodo-4'-(4''-Hydroxy phenoxy phenyl) propanoic acid from benzene.

(3) Complete it :

(a) Diphenyl $\xrightarrow[(-20^{o}C)]{O_3}$

(b) Diphenyl methane $\xrightarrow[(2)\,KOH]{(1)\,Br_2/hv}$

(c) 4-phenyl-1-butene $\xrightarrow[\Delta \text{ Red hot tube}]{CaO}$

(d) Naphthalene $\xrightarrow{alk.KMnO_4}$

(e) Glycine $\xrightarrow{LiAlH_4}$

(4) Give synthesis of :

(a) Cyclonite

(b) Musk ketone

(c) Parathion

(5) Explain conformational analysis of cyclohexane

3 (a) Give answers of following : (any three) **6**

(1) Mention some important characteristics of solvents used in NMR.

(2) Why TMS is used as reference standard in NMR spectroscopy ?

(3) Acetylene protons are more shielded than ethylenic protons ? Explain.

(4) Give the typical fragmentation pattern in benzyl methyl ether.

(5) How a molecular ion is a powerful tool for structure determination ?

(6) At what pressure the vapours of the given sample are introduced in the mass spectrometer ? Explain.

(b) Give answers of following questions : (any three) **9**

(1) What do you say about the induced magnetic fields in the multiple bonded systems?

(2) What is meant by (n + 1) rule in spin-spin coupling ?

(3) How will you distinguish Cis and Trans stilbene by means of NMR spectroscopy ?

(4) Determination of the structure of the compound, whose m/e values in the mass spectrum are 100, 85, 71, 57, 43 (B.P) 41, 29, 27.

(5) How would you distinguish between Ethylamine, diethylamine and triethylamine on the basis of mass spectroscopy ?

(6) How will you distinguish three isomeric butanols on the basis of mass spectroscopy?

(c) Give answers briefly : (any two) **10**

(1) How many different types of protons are present in allyl bromide ? Explain it.

(2) A compound with molecular formula $C_6H_{12}O_2$ shows four signals

(i) Singlet 1.1 δ (6H)

(ii) Singlet 2.1 δ (3H)

(iii) Singlet 2.6 δ (2H)

(iv) Singlet 3.9 δ (1H)

Prove the propose a structure consistent with given data.

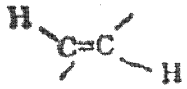
(3) Explain important features of the mass spectra of hydrocarbons.

(4) An organic compound $C_5H_{10}O_2$ displays the significant ion peaks at m/z 102, 87, 74, 71, 59, 43 (B.P). Deduce its structure and fragmentation.

(5) Predict the structure and fragmentation of the compound $C_{10}H_{12}O$, which shows ion peaks at m/z 15, 43, 57, 91, 105 and 148.

Spectral Data -

Infra - Red Data

Alkene (strcteching)	–C–H	2850-2960(v)
Alkene	=C–H	3100-3200(m)
Alkyene	=C–H	3200-3300(s)
Aromatic	ArC–H	3010-3100(m)
Aromatic ring	C=C	1500-1600(v) (two to three)
Alkene	>C=C<	1610-1680(v)
Alkyene	–C=C².	2100-2260(s)
Alkene (Bending)	–C-H	1340(w)
	$-C(C_2H_3)_3$	1430-1470(m) & 1380-1385(s)
	$-C(CH_2)_3$	1365 (8)
Aldehyde	–C–H	2820-2000(w)&2650 2760(s)
Adehyde	C=O	1740-1720(s)
Ketone	C=O	1725-1710(s)
Carboxylic acid	C=O	1725-1705(s)
Ester	C=O	1750-1730(s)
Amide	C=O	1670-1640(s)
Anhydride	C=O	1810-1860(s)&1740-1790
Alecohols, Ethers, esters Carboxylic acids, Anhydride	C-O	1300-1000(s)
Alcohols, phenols		
Free	O-H	3650-3600(sh)
bonded	O-H	3500-3200(b)
Carboxylic acids free		
Free	O-H	3500-3650(m)
H-bonded	O-H	2500-3200(b)
amines (stretch)	N-H	3330-3500(m)
Bnding	-N-H	1640-1550(m)
Nitrile	-C=N	2210-2280(s)
Ether	-O-	1070-1150(s)
Alkene bending disulstituted Cis.		-690(s)
disulstituted Trans.		960-970(s)

Aromatic substitution :

Type C-H out of plane bending No. of adjacent H atom.	range cm
5	750(s) & 700(s)
4	750
3	780
2	830
1	850

NMR Data : Chemical Shift

Types of proton		Chemical shift in δ_{ppm}
Primary	$R\text{-}CH_3$	0.9
Secondary	$R_2\text{-}CH_3$	1.3
Tertiary	$R_3\text{-}CH$	1.5
Vinylic	C=C-H	4.6-5.9
Acetylinic	Cr-C-H	2.3
Aromatic	Ar-H	6-8.5
Benzylic	Ar-C-H	2.2-3
Allylic	$C\text{=}C\text{-}CH_3$	1.7
Florides	H-C-F	4-4.5
Chlorides	HC-Cl	3.4
Bromides	HC-Br	2.5-4
Iodides	HC-I	2.4
Alcohols	HC-OH	3.4-4
Ethers	HC-OR	3.3-4
Esters	R-COO-CH	3.7-4.1
Acids	HC-COOH	2-2.6
Carbonyl comp.	HC-C=O	2-2.7
Adehyde	R-CHO	9-10
Hydroxylic	R-OH	1-5.5
Phenolic	Ar-OH	4-12
Carboxylic	R-COOH	10.5-12
Amino	$R\text{-}NH_2$	1.5