PA-003-1016007 Seat No. _____

B. Sc. (Sem. VI) (CBCS) (W.E.F. 2016) Examination

March / April – 2020

Chemistry : Paper - C - 602

(Organic Chemistry & Spectroscopy) (New Course)

Faculty Code : 003
Subject Code : 1016007

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

Instructions :

(1) Total five questions, all are compulsory.

(2) The figure to the right side indicate the mark of the sub question.

(3) Write university seat no. on your question paper.

(4) Do not write any rough work on question paper.

1 (a) Give answer of following questions : **4**

(1) Citral is an _____ monoterpene.
(cyclic, acyclic, heterocyclic)

(2) Write the structure of 2-methyl-1,3-Butadiene.

(3) Give full name of RDX.

(4) Write the structure of Musk xylene.

(b) Give answer of following questions : (any **one**) **2**

(1) Complete it : Citral $\xrightarrow[(2)\,CrO_3]{(1)\,KMnO_4}$.

(2) (a) Write the structure of Baygon.

(b) Give uses of Trinitro Toluene

(c) Give answer of following questions : (any **one**) **3**

(1) (a) Write the structure of P-cymene.

(b) Complete it : Citral + 2NOCl $\rightarrow$

(c) Write the structure of terabic acid.

(2) Synthesis of : Musk ketone.

(d) Give answer of following questions : (any **one**) **5**

(1) Explain constitution of α-Terpineol.

(2) Give synthesis of :

(a) Penta-Erythritol tetra nitrate

(b) Carbendazin.

2 (a) Give answer of following questions : **4**

(1) Define : Amino acids.

(2) Write the structure of Ninhydrin.

(3) Complete it : $R - \underset{\underset{NH_2}{|}}{CH} - COOH$ + Nitrous acid $\rightarrow$

(4) Glycine is chiral compound. (True/False)

(b) Give answer of following questions : (any **one**) **2**

(1) Define Dipeptides, give one example of it.

(2) Give method of preparation of α-amino acid by Hydantoin method.

(c) Give answer of following questions : (any **one**) **3**

(1) Synthesis of Thyroxine.

(2) Give synthesis of Glycylalanine by Bergmann method.

(d) Give answer of following questions : (any **one**) **5**

(1) Explain constitution of Thyroxine.

(2) Explain : Erlenmeyer Azlactone method.

3 (a) Give answer of following questions : **4**

(1) Complete it : Diphenylmethane + Br_2 $\rightarrow$

(2) Write the structure of Tetralin.

(3) Define : Conformation.

(4) Define : Base Peak

(b) Give answer of following questions : (any **one**) **2**

(1) Give any two method, preparation of Diphenyl methane.

(2) Give uses of mass spectra (any two).

(c) Give answer of following questions : (any **one**) **3**

(1) Draw Boat, chair and twisted boat form of cyclohexane with represent a, e, Fp, bs form.

(2) Explain reduction with H_2/Ni and acetylation reaction of Anthracene.

(d) Give answer of following questions : (any **one**) **5**

(1) Write a note on : Mass Instrumentation.

(2) Explain conformational analysis of 1, 2 - Disubstituted cyclohexane.

4 (a) Give answer of following questions : **4**

(1) Define : Induced magnetic field.

(2) Define : "Coupling constant J", shortly.

(3) Give full name of NMR.

(4) Which solvents are used in NMR spectroscopy ?

(b) Give answer of following questions : (any **one**) **2**

(1) Define equivalent protons and Non-equivalent protons, shortly.

(2) State the basic principle of NMR spectroscopy.

(c) Give answer of following questions : (any **one**) **3**

(1) Discuss the importance of TMS in NMR spectroscopy.

(2) Discuss magnetic anisotropy in Benzene.

(d) Give answer of following questions : (any **one**) **5**

(1) Derive the difference between chemical shift and coupling costant.

(2) Explain the factors affecting on chemical shift in NMR spectra.

5 (a) Give answer of following questions : **4**

(1) Calculate the DBE of $C_9H_{11}NO$.

(2) Give full name of DBE.

(3) Which groups give greater than 3200 cm^{-1} intensity in IR spectra ?

(4) Give full name of : UV.

(b) Give answer of following questions : (any **one**) **2**

(1) Which information, we get from IR spectra ?

(2) Write shortly : UV spectral information.

(c) Give answer of following questions : (any **one**) **3**

(1) Give the structure of the compound $C_8H_{18}O$ giving one one NMR signal.

(2) Explain it :

(a) Germinal protons (b) Vicinal protons.

(d) Give answer of following questions : (any **one**) **5**

(1) Assign the structure from the following data :

M. F. : $C_8H_{10}O_2$

IR : 3300 - 3200 cm^{-1} (Broad), 2950, 2845, 1605, 1510, 1460, 1310, 1250, 1175, 1032, 820 cm^{-1}.

NMR : (a) Singlet : δ 3.2 (1 H)

(b) Singlet : δ 4.5 (3 H)

(c) Singlet : δ 2.69 (2 H)

(d) Complex : δ 7.17 (4 H)

(2) Assign the structure from the following data :

M. F. : $C_8H_8Br_2$

UV : Above 220 nm gives UV bonds.

NMR : (a) doublet : $\delta = 4.0$ (1 H)

(b) doublet : $\delta = 4.1$ (1 H)

(c) two doublet : $\delta = 5.1$ (1 H)

(d) singlet : $\delta = 7.4$ (5 H)

IR : 3080, 1640, 1580, 1510, 1405, 1215, 930, 760 and 710 cm^{-1}

NMR-Data : Chemical Shift

Type	Type of Proton	Chemical Shifts in δ p.p.m.
Primary	R- $\underline{CH_3}$	0.9 (1.0)
Secondary	R_2 - $\underline{CH_2}$	1.3 (1.5)
Tertiary	R_2 - $\underline{CH}$	1.5 (1.8)
Vinylic	C = C - $\underline{H}$	4.6 - 5.9
Acetytinic	C≡C - $\underline{H}$	2-3
Aromatic	Ar - $\underline{H}$	7-8
Benzylic	 - C - $\underline{H}$	Ar - C - H 2.2-3
Allylic	C = C - $\underline{CH_3}$	1.7
Flourides	$\underline{HC}$ - F	4-4.5
Chlorides	$\underline{HC}$ - Cl	3-4
Bromides	$\underline{HC}$ - Br	H - C - X 2.5-4 (2-4.5)
Iodides	$\underline{HC}$ - I	2-4 (2-4.5)
Alcohols	$\underline{HC}$ - OH	3.4-4
Ethers	$\underline{HC}$ - OR	H - C - OR(H) 3.3-4
Esters	R - C(H)(O) - OCH_3	RCOO · $\underline{CH_3}$ 3.7-4.1
Acids	$\underline{HC}$ - COOH	2.6-3
Carbonyl compounds	$\underline{HC}$ - C = O	2-2.7
Carboxylic	R - COO$\underline{H}$	10-12
Aldehyde	R - C$\underline{H}$O	9-10
Hydroxylic	R - O$\underline{H}$	1-5.5 (depend on H-bond)
Phenolic	Ar - O$\underline{H}$	4-12
Enolic	C = C - O$\underline{H}$	15-17
Amino	R - $\underline{NH_2}$	1-5
CYN.	$\underline{CH}$ - CN	2.7

Spectral Data

U.V. :

Empirical rules for Dienes :

	(A) Homoannular λ = 253 nm.	(b) Heteroanuular λ = 215 nm.
Increments for double bond extending conjugation	30 nm.	30 nm.
Exocyclic double bond	5	5
Alkyl substitution or ring residue	5	5
Homocyclic Diene components	39	39
Polar groups :		
– $OCOCH_3$	0	0
– OR	6	6
– Cl, -Br	5	5
– NR_2	60	60

(C) Simple Diene :

Parent λ = 217 nm.

Polar groups :

Alkyl subst for ring residue	5 nm
–Cl, -Br	17
–OH	5
–OR	5
$-NR_2$	60
–SR	30

(D) Empirical Rules for Enones and Dienones :

		λ
(a)	Z = C	
	(1) 6 membered ring or acyclic	215
	(2) 5 membered ring	202
(b)	Z = H	207
(c)	Z = OH or OR	193
(d)	Acyclic dienone	245
	Increment for :	
	Doyble bond extending conjugation	30
	Alkyl group of ring residue	α 10
		β 12
	γ or higher	18
	Exocyclic double bond position	5
	Homocyclic diene component	39

Polar groups	α	β	γ	δ' other
-Cl	15	12	.	
-OH	35	30	50	50
-OR	35	30	17	31
$-NR_2$	.	93	.	.
-O	.	75	.	.
-NHCOR	.	95	.	.
$-OCOCH_2$	6	6	.	6
-SR	.	85	.	.
-Br	25	30	.	.
$-NO_2$	.	95	.	.

(e) Empirical Rules for Benzoyl Derivative :

Parent Chromophor : mm

Z = alkyl or ring residule 246

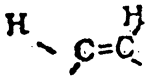
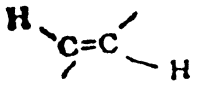
Z = H 250

Z = -OH or -OR 230

Increment for each substituent :	O	m	P
Alkyl or ring residue	3	3	10
-OH; $-OCH_3$ -OR	7	7	25
-O	11	20	78
-Cl	0	0	10
-Br	2	2	15
$-NH_2$	13	13	58
$-NHCOCH_2$	20	20	45
$-NHCH_3$	.	.	73
$-N(CH_2)_3$	20	20	85

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	$-C\equiv C^{2}.$	2100-2260(s)
Alkene (Bending)	-C-H	1340(w)
	$-C(C_2H_3)_3$	1430-1470(m) & 1880-1385(s)
	$-C(CH_2)_8$	1365 (s)
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	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	— mono subst —	750(s) & 700(s)
4	— ortho " —	750 ± 20
3	meta (two bands)	780 710 & 750
2	— para sub —	830
1		850 820 ± 20