SARDAR PATEL UNIVERSITY
M. Sc. SEMESTER – III (Organic Chemistry) Examination
Friday, 01st January 2021
Time: 10.00 a.m. to 12.00 noon
PS03CORC21: Organic Spectroscopy

Total Marks: 70

Q . 1 [A] Select the correct answer from the alternatives given below to the each question   **[08]**

[1]   Which of the following band is a symmetry forbidden electronic transition?
   [A] $\pi \rightarrow \pi^*$ [B] $n \rightarrow \pi^*$
   [C] $\sigma \rightarrow \sigma^*$ [D] E-band

[2]   Which of the following gives correct information about the IR bands observed for CO_2 molecule?
   [A] 4 IR active & 2 IR inactive bands   [B] 2 IR active & 3 IR inactive bands
   [C] 2 IR active & 1 IR inactive bands   [D] 4 IR active bands

[3]   _____ coupling constant vary with change in dihedral angle.
   [A] Geminal   [B] W
   [C] Allylic   [D] Vicinal

[4]   Which is correct for the two protons of 1,1-difluoro ethene?
   [A] They are chemically & magnetically equivalent   [B] They are chemically & magnetically non-equivalent
   [C] They are chemically equivalent but magnetically non-equivalent   [D] They are chemically non-equivalent but magnetically equivalent

[5]   The normal chemical shift range for the ^{13}C NMR is _____
   [A] 0-200 ppm   [B] 0-20 ppm
   [C] 0-100 ppm   [D] 0-10 ppm

[6]   Among the following _____ will give relatively more complex spectrum.
   [A] HETCOR   [B] HMQC
   [C] HMBC   [D] Both A & B

[7]   In the mass spectrum of the molecule CH_2Cl_2 the relative intensities of the peaks in the molecular ion will be which of the following?
   [A] 9:3:1   [B] 9:6:1
   [C] 9:6:3   [D] 3:1

[8]   Which species among the following is used to bombard with the sample for which mass spectroscopy has been performed?
   [A] Alpha particles   [B] Neutrons
   [C] Electrons   [D] Protons

Q.1 [B] Answer the following questions   **[16]**

[1]   Write equation for Lambert-Beer's law.

[2]   What is the effect of electronic complementary group on the K-band of di-substituted benzene ring?

[3]   Define Fermi resonance in IR spectroscopy.

[4]   Write the characteristic group frequency of nitrile functional group.

[5]   Enlist the various aspects of ^{1}H NMR.

[6]   What are the limitations of shift reagents used in ^{1}H NMR?

[7] $_6C^{12}$ is NMR active while $_6C^{13}$ is NMR inactive. (True/False)

[8]   Match the following

Column I	Column II
(I) p-dibromo benzene	(A) AA'BB'
(II) o-dichloro benzene	(B) A_3X
(III) Isopropyl bromide	(C) A_4
(IV) 1,1-Dibromo ethane	(D) A_6X

[9]   ____ MHz ^{1}H NMR instrument will act as 150 MHz ^{13}C NMR instrument.

[10]   Give full form of the following: (i) FID (ii) HMQC

[11]   Off-Resonance ^{13}C NMR spectra will show coupling only due to protons directly attached to carbon. (True/False)

[12]   What are the limitations of the INADEQUATE technique?

[13]   Give the examples of mass analyzer.

[14]   Write the structure of fragment ion for the m/z = 91 in the mass spectrum of toluene.

[15]   What are metastable ions in mass spectrometry?

[16]   Molecular ion peak of aromatic amine is very intense. (True/False)

Q.2 Answer the following questions (ANY SEVEN)   **[14]**

[1]   How steric hindrance at ortho position affects the UV-Visible spectrum of *N,N*-dimethylaniline?

[2]   Define bathochromic and hypsochromic shift.

[3]   Discuss spin-lattice relaxation process involved in ^{1}H NMR.

[4]   What is coupling constant? Discuss geminal coupling constants.

[5]   In ^{1}H NMR spectrum, *N,N*-dimethyl formamide gives three signals at room temperature while two signal above 123°C.Explain.

[6]   How to interpret a HETCOR spectrum?

[7]   Predict number of signals as well as multiplicity and relative height of the each signal for the following deuterated solvents in the ^{13}C NMR?

          (i) Acetonitrile-d_3

          (ii) Tetrahydrofuran-d_8

[8]   An organic compound gives the molecular ion group peaks M at 142 and M+1 at 143 with relative abundance of 100:1.14 in the mass spectrum. What is the molecular formula for the compound?

[9]   Give brief about McLafferty rearrangement.

Q . 3   Answer the following questions.

[1]   Calculate λ_{max} for the following compound: **[03]**
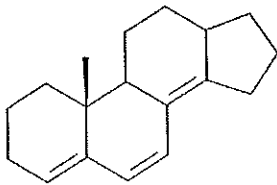
[2]   Explain the factors affecting carbonyl stretching frequency in ketone.   **[05]**
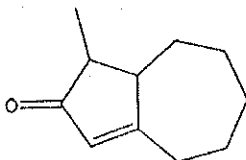
OR

Q . 3   Answer the following questions.

[1]   Calculate the λmax value for the following compound: **[03]**

[2]   Write a note on molecular vibrations in IR spectroscopy.   **[05]**

Q . 4   Answer the following questions.

[1]   Draw the structures of all the possible isomers for the compound with   **[04]**
molecular formula $C_4H_{10}O$. How many ^1H NMR signal(s) will be produced by
each isomer?

[2]   Define first order and second order ^1H NMR spectra. List the various methods   **[04]**
for simplification of complex ^1H NMR spectrum. Discuss "Proton exchange &
Deuterium exchange" in detail.

OR

Q . 4   Answer the following questions.

[1]   What is pople notation? Give pople notation to the aromatic protons of   **[04]**
furfuraldehyde. Draw detailed PMR spectrum for the same.

[2]   Define chemical shift. What are the factors which affects the chemical shift?   **[04]**
Discuss effect of **Inductive effect** and **van der Waals forces** on chemical shift
in detail.

Q . 5   Answer the following questions.

[1]   Draw ^{13}C NMR, DEPT 45° DEPT 90° and DEPT 135° spectra for 1-Phenyl-1 -   **[04]**
pentanone (**I**).
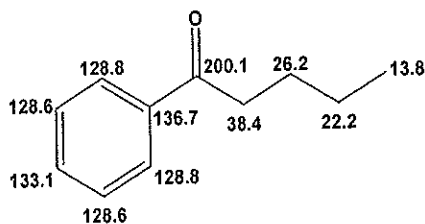
(I)

[2]   How will you distinguish following pairs of the isomers by their ^{13}C NMR   **[04]**
spectra?

    (i)   Anthracene & Phenanthene
    (ii)   Cyclohexane & 1-Hexene
    (iii) o-Nitro aniline & p-Nitro aniline
    (iv)   2-Butanone & Butanal

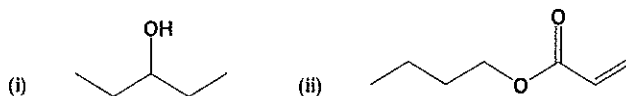**Q . 5 Answer the following questions.**

[1]   Calculate ^{13}C NMR chemical shift for the following compounds.   [04]

(i)   (ii)

[2]   Draw DQF-COSY and HMBC spectra for **1-butyne** by taking approximate   [04]
       chemical shift value for each signal.

Q . 6 Answer the following questions.

[1]   How 2-pentanone and 3-pentanone can be differentiated by mass   [03]
       spectrometry?

[2]   Give the molecular ion peak and structures of possible fragments for benzene   [05]
       and 1-pentanol in the mass spectrometry.

OR

Q . 6 Answer the following question.

[1]   Spectral data for the unknown organic compound with molecular formula   [08]
       $C_{12}H_{14}O_2$ is given below. Interpret the data and assign the structure for the
       compound.
       IR: 3035, 2942, 1715, 1632, 1585, 1450, 1375, 1200, 1050, 765, 715 cm^{-1}
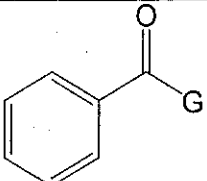
^{1}H NMR			^{13}C NMR	
Signal (δ)	Multiplicity	Protons	^{13}C (δ)	DEPT 135°
1.08	Triplet	3H	10.3	+Ve
1.45	Sextet	2H	22.0	-Ve
4.13	Triplet	2H	64.5	-Ve
6.35	Doublet (J = 16 Hz)	1H	116.2	+Ve
7.62	Doublet (J = 16 Hz)	1H	127.9	+Ve
7.22-7.55	Multiplet	5H	128.6	+Ve
			130.8	+Ve
			135.2	-
			145.1	+Ve
			167.2	-

Mass (m/z): 190, 131 (base peak), 103, 77, 51.

—X—

Table 1. Characteristics absorptions for dienes	
Base value for homo-annular diene	253 nm
Base value for hetero-annular diene	214 nm
Increment for:	
Double bond extending conjugation	+30 nm
Alkyl substituent or ring residue	+5 nm
Exocyclic double bond	+5 nm
Polar groups (auxochrome):	
-OAc	+0 nm
-OR	+6 nm
-SR	+30 nm
-Cl , -Br	+5 nm
-NR$_2$	+60 nm

Table 2. Characteristics absorptions for substituted benzene derivatives

	G	Base value
	Alkyl or ring residue (Ketone)	246 nm
	H (Aldehyde)	250 nm
	-OR / -OH (Ester/ Acid)	230 nm

Increment for each substituent on aromatic ring:		
Alkyl / ring residue	o, m	+ 3 nm
	p	+ 10 nm
- OCH$_3$ / - OH / -OR	o, m	+ 7 nm
	p	+ 25 nm
-O$^-$ (Oxy anion)	o	+11 nm
	m	+20 nm
	p	+78 nm
- Cl	o , m	+ 0 nm
	p	+ 10 nm
- Br	o , m	+ 2 nm
	p	+ 15 nm
- NH$_2$	o , m	+13 nm
	p	+58 nm
- NHCOCH$_3$	o , m	+ 20 nm
	p	+ 45 nm
- NHCH$_3$	o , m	+ 73 nm
-N (CH$_3$)$_2$	o , m	+ 20 nm
	p	+ 85 nm

⑤

(P.T-O)

Table 3. Characteristic absorption for α,β –unsaturated carbonyl compounds (enones)			
Base values:			
Acyclic α,β- unsaturated ketones	215 nm		
Six membered cyclic α,β- unsaturated ketones	215 nm		
Five membered cyclic α,β- unsaturated ketones	202 nm		
α,β- unsaturated aldehyde	210 nm		
α,β- unsaturated carboxylic acid/ester	195 nm		
Increment for:			
Double bond extending conjugation	+30 nm		
Homocyclic diene component	+39 nm		
Exocyclic double bond	+5 nm		
Alkyl substituent or ring residue			
		α	+10 nm
		β	+12 nm
		γ & higher	+18 nm
Polar groups:			
	-OH	α	+35 nm
		β	+30 nm
		δ	+50 nm
	-OCOCH$_3$	α, β, δ	+6 nm
	-OCH$_3$	α	+35 nm
		β	+30 nm
		γ	+17 nm
		δ	+31 nm
	-SR	β	+85 nm
	-Cl	α	+15 nm
		β	+12 nm
	-Br	α	+25 nm
		β	+30 nm
	-NR$_2$	β	+95 nm
Solvent correction:			
		Ethanol	+0 nm
		Methanol	+0 nm
		Chloroform	+1 nm
		Ether	+7 nm
		Water	-8 nm
		Hexane	+11 nm
		Cyclohexane	+11 nm

Characteristic Infrared Absorption Frequencies

Bond	Compound type	Frequency range, cm^{-1}
C-H	Alkanes	2850-2960 / 1350-1470
C-H	Alkenes	3020-3080 (m) / 675-1000
C-H	Aromatic rings	3000-3100 (m) / 675-870
C-H	Alkynes	3300
C=C	Alkenes	1640-1680 (v)
C≡C	Alkynes	2100-2260 (v)
C=C	Aromatic rings	1500, 1600 (v)
C-O	Alcohols, ethers, carboxylic acids, esters	1080-1300
C=O	Aldehydes, ketones, carboxylic acids, esters	1690-1760
O-H	Monomeric alcohols ,phenols / Hydrogen bonded alcohols, phenols / Carboxylic acids	3610-3640 (v) / 3200-3600 (broad) / 2500-3000 (broad)
N-H	Amines	3300-3500 (m)
C-N	Amines	1180-1360
C≡N	Nitriles	2210-2260 (v)
-NO$_2$	Nitro compounds	1515-1560 / 1345-1385

CHARACTERISTIC PROTON CHEMICAL SHIFTS

Type of proton		Chemical shift, ppm δ
Cyclopropane		0.2
Primary	RCH$_3$	0.9
Secondary	R$_2$CH$_2$	1.3
Tertiary	R$_3$CH	1.5
Vinylic	C=C—H	4.6-5.9
Acetylenic	C≡C—H	2-3
Aromatic	Ar—H	6-8.5
Benzylic	Ar—C—H	2.2-3
Allylic	C=C—CH$_3$	1.7
Fluorides	HC—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	RCOO—CH	3.7-4.1
Esters	HC—COOR	2-2.2
Acids	HC—COOH	2-2.6
Carbonyl compounds	HC—C=O	2-2.7
Aldehydic		9-10
Hydroxylic		1-5.5
Phenolic		4-12
Enolic	C=C—OH	15-17
Carboxylic	RCOOH	10.5-12
Amino	RNH$_2$	1-5

Table 5.1 The ¹³C Shift Parameters in Some Linear and Branched Hydrocarbons

¹³C Atoms	Shift (ppm) (A)
α	+9.1
β	+9.4
γ	-2.5
δ	+0.3
1° (3°)ᵃ	-1.1
1° (4°)ᵇ	-3.4
2° (3°)ᵇ	-2.5
2° (4°)	-7.2
3° (2°)	-3.7
3° (3°)	-9.5
4° (1°)	-1.5

Table 5.2 The ¹³C Shifts for Some Linear and Branched-Chain Alkanes (ppm from TMS)

Compound	C-1	C-2	C-3	C-4	C-5
Methane	-2.3				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2		
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Nonane	14.2	23.3	32.6	30.0	30.3
Decane	14.2	23.2	32.6	31.1	30.5
Isobutane	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neopentane	31.7	28.1			
2,2-Dimethylbutane	29.1	30.6	36.9	8.9	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH₃)	
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
2,3-Dimethylpentane	7.0	25.3	36.3	(14.6, 3-CH₃)	

Table 5.3 Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal (+ left, - right)

Terminal   Internal

Y	α Terminal	α Internal	β Terminal	β Internal	γ
CH₃	+9	+6	+10	+8	-2
CH=CH₂	+20		+6		-0.5
C≡CH	+4.5		+5.5		-3.5
COOH	+21	+16	+3	+2	-2
COO⁻	+25	+20	+5	+3	-2
COOR	+20	+17	+3	+2	-2
COCl	+33	+28		+2	
CONH₂	+22			+2.5	-0.5
COR	+30	+24	+1	+1	-2
CHO	+31		0		-2
Phenyl	+23	+17	+9	+7	-2
OH	+48	+41	+10	+8	-5
OR	+58	+51	+8	+5	-4
OCOR	+51	+45	+6	+5	-3
NH₂	+29	+24	+11	+10	-5
NH₃⁺	+26	+24	+8	+6	-5
NHR	+37	+31	+8	+6	-4
NR₂	+42		+6		-3
NR₃⁺	+31		+5		-7
NO₂	+63	+57	+4	+4	
CN	+4	+1	+3	+3	-3
SH	+11	+11	+12	+11	-4
SR	+20		+7		-3
F	+68	+63	+9	+6	-4
Cl	+31	+32	+11	+10	-4
Br	+20	+25	+11	+10	-3
I	-6	+4	+11	+12	-1

EMPIRICAL PREDICTIONS FOR OTHER ALKYNE CARBONS

Chemical shift (δ) = 72 + Σ(increments for carbon atoms)

C—C—C—C—C≡C—C—C—C—C

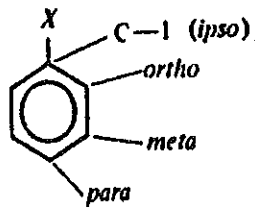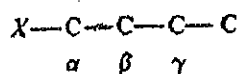|	δ	γ	β	α		α′	β′	γ′	δ′
increments	+0.5	0	+5	+7		-6	+2	-1	+0.5
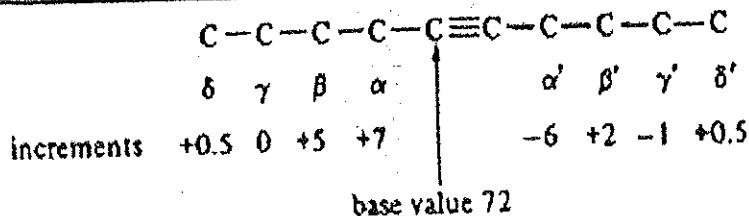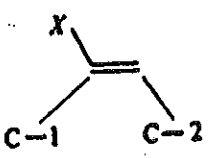
base value 72

Table 3.16 Influence of functional group X on the chemical shift positions (δ) of nearby carbons in alkene groups and benzene rings

Base values: ethylene (δ 123) and benzene (δ 128)

	Alkenes		Benzenes			
	C—1	C—2	C—1 (ipso)	ortho	meta	para
—CH₃	10	−8	9	0	0	−2
R,	16	−8	15	0	0	−2
R,	23	−8	21	0	0	−2
—CH=CH₂	15	−6	9	0	0	−2
—CH≡CH	−	−	−6	4	0	0
—C₆H₅, —Ar	13	−11	13	−1	1	−1
—F	25	−34	35	−14	1	−5
—Cl	3	−6	6	0	1	−2
—Br	−8	−1	−5	3	2	−2
—I	−38	7	−32	10	3	−1
—NH₂	−	−	18	−13	1	−10
—NHR	−	−	20	−14	1	−10
—NR₂	−	−	22	−16	1	−10
—NO₂	22	−1	20	−5	1	6
—NHCOR, —NRCOR	−	−	10	−7	1	−4
—CN	−15	15	−16	4	1	6
—SH	−	−	4	1	1	−3
—OH	−	−	27	−13	1	−7
—OR	29	−39	30	−15	1	−8
—OCOR	18	−27	23	−6	1	−2
—COOH, —COOR, —CON<	4	9	2	2	0	5
—COR, —CHO	14	13	9	1	1	6
—SO₃H, —SO₂N<	−	−	16	0	0	4
—PMe₂	−	−	14	1.6	0	−1
—PAr₂	−	−	9	5	0	0

Influence of functional group X on the chemical shift position (δ) of nearby carbons in alkane chain

$$X-C-C-C-C$$
$$\quad\;\; \alpha \;\; \beta \;\; \gamma$$

X	α-shift			β-shift	γ-shift
	$X-CH_2-$	$X-\underset{R}{CH}-$	$X-\underset{R}{\overset{R}{C}}-$		
	1°	or 2°	or 3°		
—CH$_3$	9	6	3	9	-3
— R: see table 3.11					
axial —CH$_3$	1	—	—	5	-6
equatorial—CH$_3$	6	—	—	9	0
(in cyclohexanes)					
—CH=CH$_2$	22	16	12	7	-2
—C≡CH	4	—	—	3	-3
—C$_6$H$_5$, —Ar	23	17	11	10	-3
—F	70	—	—	8	-7
—Cl	31	35	42	10	-5
—Br	19	28	37	11	-4
—I	-7 to 20	—	—	11	-2
—NH$_2$, —NHR, —NR$_2$	29	24	18	11	-4
—NO$_2$	62	—	—	3	-5
—NHCOR, —NRCOR	10	—	—	0	0
—NH$_3^+$	25	—	—	7	-3
—CN	3	4	—	2	-3
—SH	2	—	—	2	-2
—OH	50	45	40	9	-3
—OR	50	24	17	10	-6
—OCOR	52	50	45	7	-6
—COOH, —COOR, —CON<	20	16	13	2	-3
—COR, —CHO	30	24	17	2	-3
—SO$_3$H, —SO$_2$N<	50	—	—	3	0

TABLE 4.12 Incremental Shifts for the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from benzene at 128.5 ppm). ^{13}C Chemical Shifts of Substituents in ppm from TMS[a]

Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH_3	9.3	0.7	−0.1	−2.9	21.3
CH_2CH_3	15.6	−0.5	0.0	−2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	20.1	−2.0	0.0	−2.5	34.4 (CH), 24.1 (CH_3)
$C(CH_3)_3$	22.2	−3.4	−0.4	−3.1	34.5 (C), 31.4 (CH_3)
$CH{=}CH_2$	9.1	−2.4	0.2	−0.5	137.1 (CH), 113.3 (CH_2)
$C{\equiv}CH$	−5.8	6.9	0.1	0.4	84.0 (C), 77.8 (CH)
C_6H_5	12.1	−1.8	−0.1	−1.6	
CH_2OH	13.3	−0.8	−0.6	−0.4	64.5
$CH_2O(C{=}O)CH_3$	7.7	~0.0	~0.0	~0.0	20.7 (CH_3), 66.1 (CH_2), 170.5 (C=O)
OH	26.6	−12.7	1.6	−7.3	
OCH_3	31.4	−14.4	1.0	−7.7	54.1
OC_6H_5	29.0	−9.4	1.6	−5.3	
$O(C{=}O)CH_3$	22.4	−7.1	−0.4	−3.2	23.9 (CH_3), 169.7 (C=O)
$(C{=}O)H$	8.2	1.2	0.6	5.8	192
$(C{=}O)CH_3$	7.8	−0.4	−0.4	2.8	24.6 (CH_3), 195.7 (C=O)
$(C{=}O)C_6H_5$	9.1	1.5	−0.2	3.8	196.4 (C=O)
$(C{=}O)F_3$	−5.6	1.8	0.7	6.7	
$(C{=}O)OH$	2.9	1.3	0.4	4.3	168
$(C{=}O)OCH_3$	2.0	1.2	−0.1	4.8	51.0 (CH_3), 166.8 (C=O)
$(C{=}O)Cl$	4.6	2.9	0.6	7.0	168.5
$(C{=}O)NH_2$	5.0	−1.2	0.0	3.4	
$C{\equiv}N$	−16	3.6	0.6	4.3	119.5
NH_2	19.2	−12.4	1.3	−9.5	
$N(CH_3)_2$	22.4	−15.7	0.8	−11.8	40.3
$NH(C{=}O)CH_3$	11.1	−9.9	0.2	−5.6	
NO_2	19.6	−5.3	0.9	6.0	
$N{=}C{=}O$	5.7	−3.6	1.2	−2.8	129.5
F	35.1	−14.3	0.9	−4.5	
Cl	6.4	0.2	1.0	−2.0	
Br	−5.4	3.4	2.2	−1.0	
I	−32.2	9.9	2.6	−7.3	
CF_3	2.6	−3.1	0.4	3.4	
SH	2.3	0.6	0.2	−3.3	
SCH_3	10.2	−1.8	0.4	−3.6	15.9
SO_2NH_2	15.3	−2.9	0.4	3.3	
$Si(CH_3)_3$	13.4	4.4	−1.1	−1.1	

[a] See Ewing, D.E. (1979). *Org. Magn. Reson.*, 12, 499, for 709 chemical shifts of monosubstituted benzenes.