

(64 & A-27) Seat No.: _____

No of printed pages: 4+6

SARDAR PATEL UNIVERSITY

M.Sc. SEMESTER -IV (Organic Chemistry) Examination (NO)

Saturday, 22nd October-2016

PS04CORC01: Spectroscopy -II

Time: 02:00 p.m. to 05:00 p.m.

Total Marks: 70

Note: Right hand figures indicate marks.

Q. 1: Answer the following multiple choice questions.

[08]

- In UV, electronic transition shown by ethanol is _____.
a) $n \rightarrow \pi^*$ b) $n \rightarrow \sigma^*$ c) $\pi \rightarrow \pi^*$ d) $\sigma \rightarrow \pi^*$
- Which of the following molecules will not show the Infrared spectrum.
a) HCl b) H₂O c) H₂ d) CH₄
- The pople notation for the protons in ethyl chloride is _____.
a) A₂M₃ b) A₃M₂ c) A₃B₂ d) A₃X₂
- In PMR spectrum of 2-bromopropene ____ signals are obtained.
a) 4 b) 3 c) 2 d) 1
- The DEPT-90 spectrum will show only ____ signals.
a) -CH b) -CH₂ c) -CH₃ d) None
- In ¹³C-NMR spectrum ethyl benzene will give ____ signals.
a) 4 b) 6 c) 2 d) 3
- The carrier gas used in CI method for recording Mass spectra is _____.
a) Nitrogen b) Butane c) Methane d) Argon
- As the degree of branching decreases, the relative height of molecular ion peak ____
a) remains constant b) becomes zero c) decreases d) increases

Q. 2: Answer the following questions (Any seven)

[14]

- Explain the effect of conjugation on absorption of λ_{max} in UV spectroscopy.
- Draw the various stretching and bending vibrations observed in H₂O.
- Discuss the various electronic transitions observed in UV spectroscopy.

1

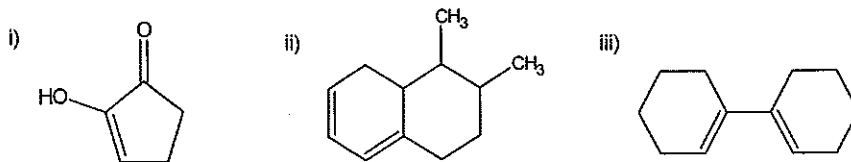
(P.T.O.)

4. Explain the long range coupling in PMR with suitable example.
5. Sketch the PMR spectrum of ethyl acetate by taking approximate δ -value for each signal and showing appropriate multiplicity.
6. Sketch ^1H - ^1H COSY spectrum for ethyl chloride by taking approximate δ value for each signal.
7. How will you differentiate o, m and p-dinitrobenzene with the help of ^{13}C NMR spectra?
8. Write a note on Mc-Lafferty rearrangement.
9. Discuss the chemical ionization techniques used in Mass spectroscopy.

Q.3: A) Answer the following

- i) Write a short note on Chromophores and auxochromes. [03]
- ii) Discuss the important IR absorptions shown by benzene and toluene. [03]

B) Calculate the λ_{max} for the following compounds. [06]

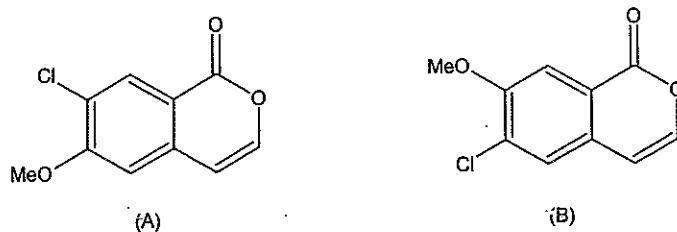


OR

B) Discuss the important characteristics vibrations observed the IR spectra of ketones and esters. [06]

Q.4: A) i) Write a short note on vicinal and germinal couplings in PMR. [03]

ii) Explain nuclear Overhauser effect in PMR. How will you differentiate following isomers using NOE PMR spectra? [03]



B) i) List the methods used for simplification of PMR spectra. Discuss the use of shift reagent in detail. [03]

ii) Write short note on spin relaxation process in PMR. [03]

OR

B) i) A compound has a molecular formula $C_9H_{10}O_2$. It gives the following signals in PMR spectrum.

Assign the structure of the compound by interpreting PMR data.

[03]

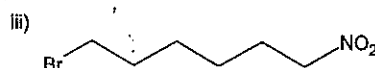
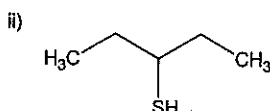
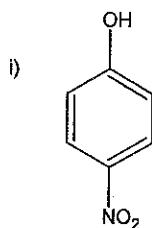
Signal position δ	Multiplicity	Protons
3.55	Singlet	2H
3.60	Singlet	3H
7.35	Singlet	5H

ii) Write a short note on D_2O exchange in PMR.

[03]

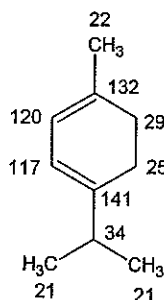
Q.5: A) Do the ^{13}C NMR chemical shift calculations for the following molecules.

[06]



B) i) Sketch proton decoupled ^{13}C NMR DEPT 45° and DEPT 90° spectra for following compound [03]

(δ values for each carbon is assigned in the structure)



ii) Calculate the chemical shift values for each carbon signals and sketch the proton coupled and decoupled ^{13}C NMR spectra for methyl benzoate. [03]

OR

B) i) A compound with molecular formula $C_5H_{10}O$ shows following signals in its proton [03]

coupled ^{13}C NMR. Interpret the data and assign the structure of the compound.

18 δ (Quartet)

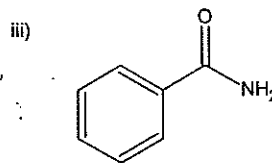
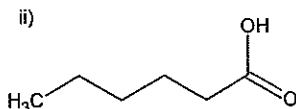
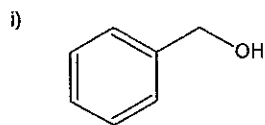
28 δ (Quartet)

42 δ (doublet)

212 δ (Singlet)

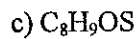
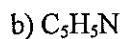
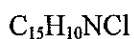
ii) Sketch the HMBC spectrum for 3-heptanone by taking approximate δ -value for each signal. [03]

Q.6: A) Do the mass fragmentation for the following molecules. [06]



B) i) Discuss the Fast Atomic Bombardment [FAB] and electron spray ionization techniques used in Mass spectroscopy. [03]

ii) Discuss the nitrogen rule and guidelines for correct molecular formula determination used in Mass spectroscopy. Using this guidelines indicate whether the following formulae are correct or incorrect. [03]



OR

B) A compound has molecular formula C₅H₁₀O₂. It gives the following spectral data. Interpret the spectral data determine the structure of the compound. [06]

IR(cm^{-1}): 2900, 1200, and 1100

UV: λ_{max} 205nm

¹HNMR

Signal δ	Multiplicity	Protons
1.2	Triplet	3H
1.3	Triplet	3H
2.3	Quartet	2H
4.1	Quartet	2H

¹³CNMR

¹³ C (δ)	DEPT (135)
11	+ve
15	+ve
28	-ve
61	-ve
75	-ve

Mass (m/z) (% r. a.): 102 (10%), 57(60%), 29(100%)

← X →
(4)

CHARACTERISTIC PROTON CHEMICAL SHIFTS

Type of proton	Chemical shift, ppm
Cyclopropane	0.2
Primary	RCH_3 0.9
Secondary	R_2CH_2 1.3
Tertiary	R_3CH 1.5
Vinyllic	$C=C-H$ 4.6-5.9
Acetylenic	$C\equiv C-H$ 2-3
Aromatic	$Ar-H$ 6-8.5
Benzylic	$Ar-CH_3$ 2.2-3
Allylic	$C=C-CH_2$ 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	$R-CHO$ 9-10
Hydroxylic	$R-OH$ 1-5.5
Phenolic	$Ar-OH$ 4-12
Enolic	$C=C-OH$ 15-17
Carboxylic	$RCOOH$ 10.5-12
Amino	RNH_2 1-5

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	3610-3640 (v)
	Hydrogen bonded alcohols, phenols	3200-3600 (broad)
	Carboxylic acids	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

(P.T.O.)

Characteristic absorption for dienes

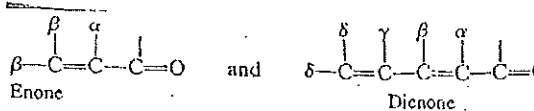
Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
N(Alk) ₂	+60
Solvent correction ^a	+0

$$\lambda_{calc} = \text{Total}$$

Characteristic absorption for substituted benzene derivatives

ArCOR/ArCHO/ArCO ₂ H/ArCO ₂ R	λ_{max}^{EtOH} (nm)
Parent chromophore: Ar = C ₆ H ₅	
G = Alkyl or ring residue, (e.g., ArCOR)	246
G = H, (ArCHO)	250
G = OH, OAlk, (ArCO ₂ H and ArCO ₂ R)	230
Increment for each substituent on Ar:	
—Alkyl or ring residue	o-, m- +3 p- +10
—OH, —OCH ₃ , —OAlk	o-, m- +7 p- +25
—O ⁻ (oxyanion)	o- +11 m- +20 p- +78 ^a
—Cl	o-, m- +0 p- +10
—Br	o-, m- +2 p- +15
—NH ₂	o-, m- +13 p- +58
—NHCOCH ₃	o-, m- +20 p- +45
—NHCH ₃	p- +73
—N(CH ₃) ₂	o-, m- +20 p- +85

Characteristic absorption for α, β -unsaturated carbonyl compounds



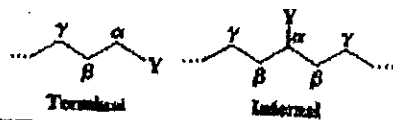
Base values	(nm)
Acyclic α, β -unsaturated ketones	215
Six-membered cyclic α, β -unsaturated ketones	215
Five-membered cyclic α, β -unsaturated ketones	202
α, β -Unsaturated aldehydes	210
α, β -Unsaturated carboxylic acids and esters	195

Increments for

Double bond extending conjugation	+30
Alkyl group, ring residue	α +10 β +12 γ and higher +18
Polar groupings: —OH	α +35 β +30 δ +50
—OAc	α, β, δ +6
—OMe	α +35 β +30 γ +17 δ +31
—SAlk	β +85
—Cl	α +15 β +12
—Br	α +25 β +30
—NR ₂	β +95

Exocyclic double bond	+5
Homodiene component ^a	+39

¹³C shifts for terminal and internal systems



Y	alpha		beta		gamma
	Terminal	Internal	Terminal	Internal	
CH ₃	+ 9	+ 6	+10	+ 8	-2
CH=CH ₂	+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	
CONH ₂	+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
NH ₂	+29	+24	+11	+10	-5
NH ₃ ⁺	+26	+24	+ 8	+ 6	-5
NHR	+37	+31	+ 8	+ 6	-4
NR ₂	+42		+ 6		-3
NR ₃ ⁺	+31		+ 5		-7
NO ₂	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	-3
SH	+14	+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

¹³C Shifts for some linear and branched chain alkanes

Compound	C-1	C-2	C-3	C-4	C-5
Methane	-23				
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	
Isobutane	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-CH ₃)	
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-CH ₃)	

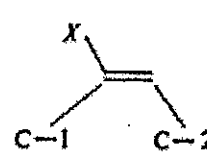
(P.T.O)

¹³C shifts for substituted benzenes
Base value for benzene is 128.5 ppm

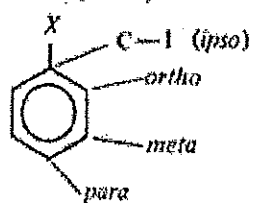
Substituent	C-1 (Attachment)	C-2	C-3	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH ₃	+9.3	+0.7	-0.1	-2.9	21.3
CH ₂ CH ₃	+15.6	-0.5	0.0	-2.6	29.2 (CH ₂), 15.8 (CH ₃)
CH(CH ₃) ₂	+20.1	-2.0	0.0	-2.5	34.4 (CH), 24.1 (CH ₃)
C(CH ₃) ₃	+22.2	-3.4	-0.4	-3.1	34.5 (C), 31.4 (CH ₃)
CH=CH ₂	+9.1	-2.4	+0.2	-0.5	137.1 (CH), 113.3 (CH ₂)
C=CH	-5.8	+6.9	+0.1	+0.4	84.0 (C), 77.8 (CH)
C ₆ H ₅	+12.1	-1.8	-0.1	-1.6	
CH ₂ OH	+13.3	-0.8	-0.6	-0.4	64.5
CH ₂ OOCCH ₃	+7.7	-0.0	-0.0	-0.0	20.7 (CH ₂), 66.1 (CH ₃), 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 ₂ H ₅	+29.0	-9.4	+1.6	-5.3	
$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	+22.4	-7.1	-0.4	-3.2	23.9 (CH ₂), 169.7 (C=O)
$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	+8.2	+1.2	+0.6	+5.8	192.0
$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	+7.8	-0.4	-0.4	+2.8	24.6 (CH ₂), 195.7 (C=O)
$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	+9.1	+1.5	-0.2	+3.8	196.4 (C=O)
$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	-5.6	+1.8	+0.7	+6.7	
$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	+2.9	+1.3	+0.4	+4.3	168.0
$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	+2.0	+1.2	-0.1	+4.8	51.0 (CH ₂), 166.8 (C=O) 168.5
$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	+4.6	+2.9	+0.6	+7.0	
$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	+5.0	-1.2	0.0	+3.4	
C≡N	-16.0	+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
$\begin{array}{c} \text{O} \\ \\ \text{O}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	+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 ₂ NH ₂	+15.3	-2.9	+0.4	+3.3	
S(CH ₃) ₂	+13.4	+4.4	-1.1	-1.1	

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


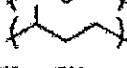
Base values: ethylene (δ 123) and benzene (δ 126)



Alkene structure: $\text{C}-1$ is bonded to X and $\text{C}-2$.



Benzene structure: $\text{C}-1$ (ipso), ortho, meta, para.

	Alkenes		Benzenes			
	C-1	C-2	C-1 (ipso)	ortho	meta	para
$-\text{CH}_3$	10	-8	9	0	0	-2
R, 	16	-8	15	0	0	-2
R, 	23	-8	21	0	0	-2
$-\text{CH}=\text{CH}_2$	15	-6	9	0	0	-2
$-\text{CH}\equiv\text{CH}$	-	-	-6	4	0	0
$-\text{C}_6\text{H}_5, -\text{Ar}$	13	-11	13	-1	1	-1
$-\text{F}$	25	-34	35	-14	1	-5
$-\text{Cl}$	3	-6	6	0	1	-2
$-\text{Br}$	-8	-1	-5	3	2	-2
$-\text{I}$	-38	7	-32	10	3	-1
$-\text{NH}_2$	-	-	18	-13	1	-10
$-\text{NHR}$	-	-	20	-14	1	-10
$-\text{NR}_2$	-	-	22	-16	1	-10
$-\text{NO}_2$	22	-1	20	-5	1	6
$-\text{NHCOR}, -\text{NRCOR}$	-	-	10	-7	1	-4
$-\text{CN}$	-15	15	-16	4	1	6
$-\text{SH}$	-	-	4	1	1	-3
$-\text{OH}$	-	-	27	-13	1	-7
$-\text{OR}$	29	-39	30	-15	1	-8
$-\text{OCOR}$	18	-27	23	-6	1	-2
$-\text{COOH}, -\text{COOR}, -\text{CON} <$	4	9	2	2	0	5
$-\text{COR}, -\text{CHO}$	14	13	9	1	1	6
$-\text{SO}_2\text{H}, -\text{SO}_2\text{N} <$	-	-	16	0	0	4
$-\text{PMe}_2$	-	-	14	1.6	0	-1
$-\text{PAr}_2$	-	-	9	5	0	0