

SARDAR PATEL UNIVERSITY

M. Sc. SEMESTER – III (Organic Chemistry) Examination

Tuesday, 23rd October 2018

Time: 02.00 p.m. to 05.00 p.m.

PS03CORC21: Organic Spectroscopy

Total Marks: 70

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

- [1] Electronic transition(s) expected from 1,3-butadiene is(are) _____
transitions
[a] $n \rightarrow \sigma^*$ [b] $\pi \rightarrow \pi^*$
[c] $\sigma \rightarrow \sigma^*$ [d] Both b & c
- [2] Among the following, _____ have highest " $>C=O$ " stretching frequency.
[a] Cyclobutanone [b] Cyclopropanone
[c] Cyclopentanone [d] Cyclohexanone
- [3] DEPT-90° NMR experiment show(s) signals for _____
[a] only tertiary carbons [b] primary, secondary and tertiary carbons
[c] only quaternary carbons [d] primary and tertiary carbons
- [4] 2-Chloropropene will give _____ PMR signals in its 1H NMR spectrum.
[a] 5 [b] 2
[c] 4 [d] 3
- [5] Pople notation for the protons present in 1,4-dichloro benzene is _____
[a] A_2B_2 [b] A_4
[c] A_2X_2 [d] $AA'BB'$
- [6] _____ is a carbon analogue of DQF-COSY.
[a] HETCOR [b] INADEQUATE
[c] HMBC [d] HMQC
- [7] If an organic compound contains two Br and one Cl atom in its molecular formula then relative abundance of $M:M+2:M+4:M+6$ will be
[a] 9 : 15 : 7 : 1 [b] 2 : 2 : 3 : 1
[c] 1 : 3 : 3 : 1 [d] 3 : 7 : 5 : 1
- [8] Which of the following is INCORRECT for meta-stable ion peaks?
[a] They are broader than normal peaks [b] They have relatively high abundance
[c] They mostly have non-integral m/z values [d] Position of metastable ion peaks are determined by $m^* = \frac{m_2^2}{m_1}$

(1)

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Q. 2 Answer the following questions (ANY SEVEN)

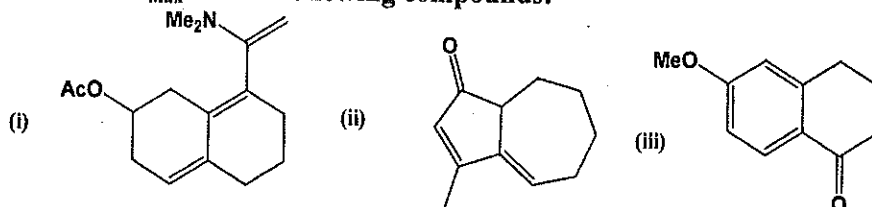
[14]

- [1] Define : (i) Hypsochromic shift (ii) Hyperchromic effect
- [2] Discuss effect of conjugation on λ_{\max} with suitable examples.
- [3] Discuss various bending vibrations.
- [4] How to differentiate two geometrical isomers of cinnamic acid by ^1H NMR?
- [5] Sketch the ^1H NMR spectrum of **propanal** by taking approximate δ value for each signal and showing appropriate multiplicity.
- [6] Give full form of: (i) INADEQUATE (ii) DEPT
- [7] How will you differentiate following pairs of isomers by ^{13}C NMR?
 - (i) Cyclohexane and 1-Hexene
 - (ii) Propanal and Acetone
- [8] What is nitrogen rule? Which of the following compounds will follow it?
 - (i) $\text{C}_4\text{H}_5\text{N}$ (ii) $\text{C}_6\text{H}_{14}\text{N}$ (iii) $\text{C}_4\text{H}_{10}\text{N}_2$
- [9] Explain the terms: (i) Base peak (ii) Molecular ion peak

Q. 3

[a] Calculate λ_{\max} for the following compounds:

[06]



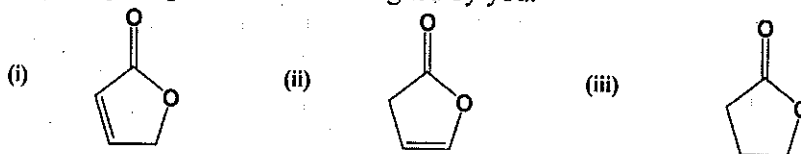
[b] Answer the following questions.

- [1] How will you distinguish following pairs of compounds by IR? [03]
 - (i) Butanoic acid and Ethylbutanoate
 - (ii) 1-Butene and 1-Butyne
 - (iii) Ethanol and Ethanal
- [2] List the factors affecting $>\text{C}=\text{O}$ stretching frequency. Discuss any two in detail. [03]

OR

[b] Answer the following questions.

- [1] Discuss "Fermi resonance". [03]
- [2] Arrange following compounds in increasing order of $>\text{C}=\text{O}$ stretching frequency. Explain the order assigned by you. [03]



Q. 4

[a] Answer the following questions.

- [1] Draw the structures of all the possible isomers for the compound with molecular formula $\text{C}_3\text{H}_6\text{Cl}_2$. How many ^1H NMR signal(s) will be produced by each isomer? [03]
- [2] List the various methods for simplification of complex ^1H NMR spectrum. Discuss "double resonance" with example. [03]

2

[b] Answer the following questions.

[1] Define coupling constant. Discuss geminal and vicinal coupling constants in detail. [03]

[2] In ^1H NMR, generally aldehyde protons are deshielded compared to ethylenic protons while acetylenic protons are shielded compared to ethylenic protons. Explain it. [03]

OR

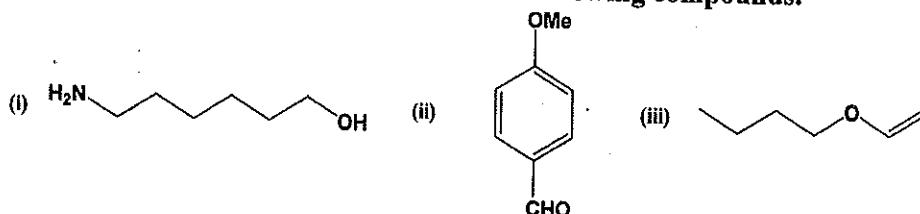
[b] Answer the following questions.

[1] Discuss "effect of H-bonding on chemical shift in ^1H NMR" with examples. [03]

[2] What is Nuclear Overhauser Effect (NOE)? Discuss use of NOE experiments to distinguish isovanillin and vanillin. [03]

Q.5

[a] Calculate ^{13}C NMR chemical shift for the following compounds. [06]



[b] Answer the following questions.

[1] Draw HMQC and HMBC spectra for 1-nitro propane by taking approximate chemical shift value for each signal. [03]

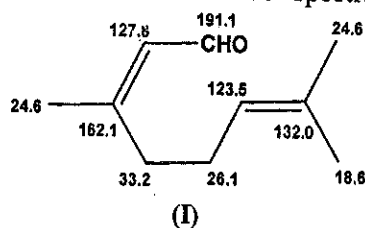
[2] Predict number of signals for following deuterated solvents in ^{13}C NMR at 25°C. Give multiplicity for each signal. [03]

- (i) Pyridine- d_5
- (ii) Dimethylformamide- d_7
- (iii) Dichloromethane- d_2

OR

[b] Answer the following questions.

[1] Draw ^{13}C NMR, DEPT 90° and DEPT 135° spectra for Citral (I). [03]



[2] Explain following: [03]

- (i) ^{13}C NMR spectra are recorded always as proton decoupled spectra.
- (ii) FT-NMR instrument is preferred over CW-NMR instrument in recording ^{13}C NMR spectra.

3

(P.T.O)

Q.6

[a] Answer the following questions.

- [1] How will you distinguish following isomers using mass spectrometry? [03]
(i) 1-Pentanol (ii) 2-Pentanol (iii) 2-Methyl-2-butanol
- [2] Discuss following ionization techniques in mass spectrometry. [03]
(i) FAB (ii) MALDI

[b] Answer the following questions.

- [1] Write fragmentation pattern for following compounds. [03]
(i) n-Propylbenzene (ii) 3-Pentanone (iii) Benzamide
- [2] Write note on "McLafferty Rearrangement". [03]

OR

[b] Spectral data for the compound with molecular formula $C_7H_{12}O_3$ is given below. Interpret the data and assign the structure for the compound. [06]

IR: 2960, 1725, 1715, 1160, 1030 cm^{-1}

1H NMR			^{13}C NMR	
Signal (δ)	Multiplicity	Protons	^{13}C (δ)	DEPT
1.25	Triplet	3H	14	+Ve
2.20	Singlet	3H	28	-Ve
2.55	Triplet	2H	29	+Ve
2.75	Triplet	2H	37	-Ve
4.10	Quartet	2H	60	-Ve
			172	-
			208	-

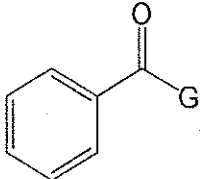
Mass (m/z): 144, 129, 116, 101, 99, 74, 55, 43.

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(4)

(165)

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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

①

(P-7,00)

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	

(2)

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

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-CH ₂ -H 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 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

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

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

Y	α		β		γ
	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	+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

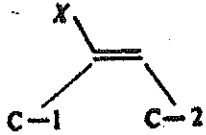
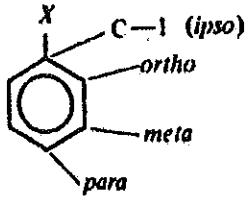


EMPIRICAL PREDICTIONS FOR OTHER ALKYNE CARBONS

$$\text{Chemical shift } (\delta) = 72 + \Sigma(\text{increments for carbon atoms})$$

	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)			
	C-1	C-2	C-1 (ipso)	ortho	meta	para
						
						
	Alkenes		Benzenes			
	C-1	C-2	C-1 (ipso)	ortho	meta	para
-CH ₃	10	-8	9	0	0	-2
R, 	16	-8	15	0	0	-2
R, 	23	-8	21	0	0	-2
-CH=CH ₂	15	-6	9	0	0	-2
-CH≡CH	-	-	-6	4	0	0
-C ₆ H ₅ , -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
-NH ₂	-	-	18	-13	1	-10
-NHR	-	-	20	-14	1	-10
-NR ₂	-	-	22	-16	1	-10
-NO ₂	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
-SO ₃ H, -SO ₂ N<	-	-	16	0	0	4
-PMe ₂	-	-	14	1.6	0	-1
-PAr ₂	-	-	9	5	0	0

(5)

(P.T.O.)

TABLE 4.12 Incremental Shifts for the Aromatic Carbon Atoms of Monosubstituted Benzenes (ppm from benzene at 128.5 ppm). ¹³C 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 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	0.9	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 O(C=O)CH ₃	7.7	-0.0	-0.0	-0.0	20.7 (CH ₂), 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 ₂ H 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 ₆ H 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≡N	-16	3.6	0.6	4.3	119.5
NH ₂	19.2	-12.4	1.2	-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	0.7	-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	2.1	-1.0	
I	-32.2	9.9	2.7	-7.3	
CF ₃	2.6	-3.1	0.4	3.4	
SH	2.3	0.6	0.7	-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	
Si(CH ₃) ₃	13.4	4.4	-1.1	-1.1	

^aSee Ewing, D.B. (1979). *Org. Magn. Reson.*, 11, 499, for 709 chemical shifts of monosubstituted benzenes.

— X —
 (7)

