

KRISHNAVENI DEGREE & PG COLLEGE, NARSARAOPET

Under affiliated by

ACHARYA NAGARJUNA UNIVERSITY (ANU)

2nd YEAR M.Sc

IV Semester

Paper-I: Organic Spectroscopy-II (R22OC41)



Department of Chemistry

Krishnaveni Degree & PG College

Narasaraopet - 522601

ACHARYA NAGARJUNA UNIVERSITY
DEPARTMENT OF CHEMISTRY

M.Sc. ORGANIC CHEMISTRY:: SEMESTER-IV

PAPER-I: ORGANIC SPECTROSCOPY-II (R22OC41)

(For the students admitted from the A.Y. 2022-2023 onwards)

Max. Marks: 100

(Internal-30M & External-70M)

SYLLABUS

Learning Objectives:

- ✓ To learn about the basics of ^{13}C NMR, Mass, and 2D NMR spectroscopic techniques.
- ✓ To understand the instrumentation of Mass, types of ionizations, types of analyzers in Mass spectroscopic techniques.
- ✓ To apply the spectroscopy knowledge for the structural elucidation of natural products and stereochemistry of organic compounds.
- ✓ To learn about the structural elucidation of natural products.
- ✓ To know the spectral problems – UV; ^1H , ^{13}C , Mass spectrometry.

UNIT-I

12H

^{13}C NMR Spectroscopy:

(Types of ^{13}C NMR spectra, Undecoupled, proton- decoupled, single frequency off-resonance decoupled (SFORD) and selectively decoupled spectral) Signal enhancement by Nuclear OVER HAUSER effect. ^{13}C chemical shifts, factors affecting the chemical shifts. Noise decoupled and off-resonance spectra of simple Compounds. Calculation of chemical shifts of alkanes, alkenes, alkynes, and aromatic compounds.(Typical examples of CMR spectroscopy –problems.)

UNIT-II

12H

Mass Spectroscopy:

Introduction, Principles of Ionization Methods: EI, CI, FDI, PDI, LDI, FAB, TSI and ESI, Types of mass analyzers; Types of fragments-odd electron and even electron containing neutral and charged species (even electron rule), nitrogen rule, molecular-ion peak, base peak, metastable ion, isotopic abundance. High Resolution-MS (HRMS), index of hydrogen deficiency (IHD). Fragmentation of typical organic compounds-hydrocarbons, aromatics, alcohols, alkyl halides, ethers, Carbonyls, carboxylic acids, esters, amines, amides, nitro compounds. General methods of mass spectral fragmentation- β -cleavage, McLafferty rearrangement, retro Diels-Alder fragmentation and ortho effect. Factors affecting fragmentation-Mass spectra related problems.

UNIT-III

12H

2D NMR Techniques:

Principles of 2D NMR, classification of 2D-experiments, 2D-J-resolved spectroscopy. Correlation spectroscopy (COSY), HOMO COSY (^1H - ^1H COSY), COSY of *m*-dinitrobenzene, isopentyl acetate, Hetero COSY (^1H , ^{13}C COSY) Hetero COSY of isopentyl acetate and 4-methyl-2-pentanol, HMQC, HMQC of codeine, long range ^1H , ^{13}C COSY (HMBC), HMBC of codeine and NOESY, NOESY of 9-benzylanthracene, 2-D INADEQUATE experiments.

UNIT-IV

12H

Spectral Characteristics of Natural Products involving all Spectral Data: Use of spectroscopic methods UV, IR, ^1H and ^{13}C NMR and Mass spectra in the structure elucidation of natural products. Illustration with suitable compounds like Apigenin (Flavone), Kaempferol (flavonol), Umbelliferone (coumarin), Camphor (Terpenoid), Lawsone (Naphthoquinone), Papaverine (Alkaloid), and Equilenine (steroid).

UNIT-V *

12H

Spectral Problems:

Applications of ^{13}C NMR spectroscopy: Stereochemistry, and reaction mechanisms.

Applications of ^1H NMR spectroscopy: Stereochemistry-Geometrical and optical isomerism.

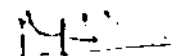
Spectral Problems involving all spectral data UV-Vis. ^1H NMR, ^{13}C NMR, Mass spectrometry & 2D NMR techniques.

Reference Books:

- 1) Spectrometric identification of organic compounds by R.N.Silverstein & G.C.Bassier (John Willey)
- 2) Spectroscopic methods in Organic Chemistry by Williams and Fleming (McGraw Hill).
- 3) Organic photochemistry by R.O.Kan (Mc Graw Hill)
- 4) Advanced organic Chemistry Reaction Mechanisms and Structure by J March (Mc Graw Hill & Kogshusha).
- 5) Carbon-13 NMR Spectroscopy by J.B. Stothers.

Learning Outcomes:

- ✓ Students can understand the fundamentals of ^{13}C NMR and Mass spectroscopic techniques and apply to investigate the structural information of molecules.
- ✓ It can provide ability to apply the spectroscopy knowledge for the structural elucidation of natural products and stereochemistry of organic compounds.
- ✓ It also provides platform for awareness towards ^{13}C NMR and Mass Spectrometry which aims to apply these knowledge towards research.
- ✓ Students can understand the spectral characteristics of natural products involving all spectral data.
- ✓ Students can understand the spectral problems involving all spectral data UV-Vis. ^1H NMR, ^{13}C NMR, Mass spectrometry & 2D NMR techniques.



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Paper-I: Organic Spectroscopy-II (R22OC41)

UNIT - I

UNIT-I, Carbon-13 NMR Spectroscopy [CMR]

@K.B.P.R@

In organic chemistry the most significant magnetic nucleus other than the proton is ^{13}C , which has a net nuclear spin equal to half. The magnetic moment of ^{13}C is about one-quarter that of ^1H , so signals are inherently weaker.

Because it has a low natural abundance (1.1%) and is inherently less sensitive than the proton because of its lower gyromagnetic ratio.

The principles of ^{13}C NMR are similar to that of ^1H spectroscopy, although the scale of observed shifts and couplings are greater than proton spectroscopy. On this scale ^{13}C shifts range from 0 to 250 ppm from the TMS. As in proton spectra, the chemical shift of the nucleus depends on the atom or atoms attached to it.

Because of the greater range of chemical shifts ^{13}C spectra contains a separate and distinct resonance for each nucleus in the molecule i.e. overlapping is rarely occurs.

Carbon-13 NMR spectra are much more difficult to record than ^1H spectra. This due to two reasons. Firstly, the most abundant isotope of carbon ^{12}C (~99%) is not detectable by nuclear magnetic resonance. Because, this isotope has an even number of protons and even number of neutrons (no magnetic spin). The less abundant isotope ^{13}C has an odd number of neutrons and it has a magnetic spin of $\frac{1}{2}$ similar to that of proton.

(2)

Secondly, the magnetic resonance of ^{13}C is much weaker because of its lower abundance and is inherently less sensitivity due to its lower gyromagnetic ratio, which is one-fourth that of a proton. These factors show that ^{13}C NMR is much less sensitive than PMR.

This sensitivity is so low that unaided standard NMR spectrometers are not adequate for its study. The availability of Fourier transform instrumentation, which permits simultaneous irradiation of all ^{13}C nuclei has now resulted in an explosion of ^{13}C spectroscopy.

An advantage of the low abundance is the absence of carbon-carbon coupling. In ^{13}C spectra, the coupling between neighbouring ^{13}C nuclei is ignored i.e. such coupling does not exist because of lesser abundance in nature.

On the other hand, the coupling between ^{13}C and neighbouring protons takes place which helped to assign resonances to particular nuclei in a molecule.

Since, most carbon atoms in organic compounds are attached to hydrogens, $^{13}\text{C}-^1\text{H}$ spin-spin interactions are pronounced and hence spin decoupling is most essential. This can be done with a wide band oscillator, to decouple all protons simultaneously, allowing all ^{13}C multiplets to collapse to singlets. Other double resonance methods allow retention of coupling information concerning directly attached protons, but elimination of that due to protons on adjacent or further removed carbons. This technique is known as off-resonance decoupling in which a non protonated ^{13}C gives a singlet, ^{13}CH a doublet, $^{13}\text{CH}_2$ a triplet & $^{13}\text{CH}_3$ a quartet.

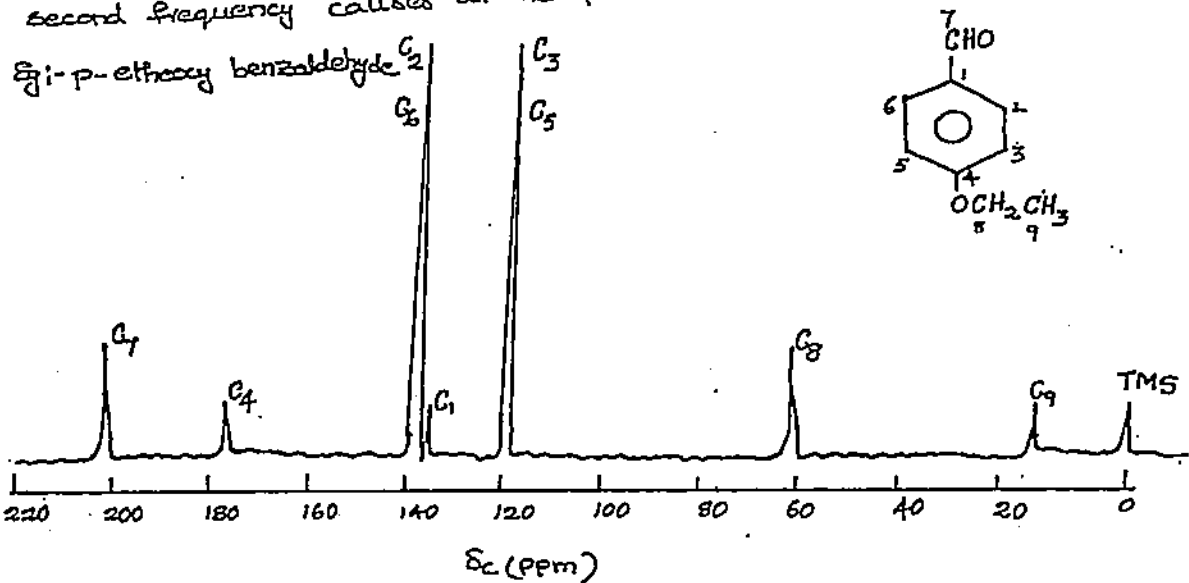
Because of large J values for $^{13}\text{C-H}$ (~110-320 Hz) and appreciable values for $(^{13}\text{C-C-H})$ and $(^{13}\text{C-C-C-H})$, non decoupled ^{13}C spectra usually show complex overlapping multiplets that are very difficult to interpret.

Proton (^1H) decoupling (or) Noise decoupling (or) Broad band decoupling:

To eliminate the complicating effects of the proton coupling in the ^{13}C spectra, it is necessary to decouple the ^1H nuclei, by double irradiation at their resonance frequencies. This is an example of heteronuclear decoupling.

In this technique a decoupling signal is used that has all the ^1H frequencies spread around 100 MHz and thus is a form of radio frequency noise. The spectra thus obtained are decoupled or noise decoupled.

Thus proton decoupled CMR spectrum is recorded by irradiating the sample at two frequencies. The first radio frequency is used to effect carbon magnetic resonance, while the simultaneous second frequency causes all the protons to be in resonance at the



(4)

same time, and they flip from their α spins to β spins very fast and the attached carbon nuclei no longer see the distinct α and β spin states of the neighbouring hydrogens but they see an average spin. The net result is the absence of coupling and each carbon appears as a singlet at the position corresponding to its chemical shift.

Off-Resonance decoupling :-

The proton-decoupled spectra support a particular structure by displaying the right number of signals at proper δ -values for the carbon atoms present. The proton-undecoupled spectra give useful information particularly in the case of simple molecules by showing splitting of the carbon signal by the protons directly attached to that carbon. But in case of large molecules the multiplets may become more complicated and very difficult to identify the no. of protons attached to the carbon because of overlapping of the signals.

In such cases off-resonance decoupling is used.

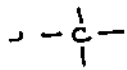
In this technique while recording the CMR spectrum the sample is irradiated at a frequency close to, but not coinciding with the resonance frequency of protons.

As a result, the multiplets become narrow and not removed as in fully decoupled spectra. This also results in residual coupling from protons directly bonded to ^{13}C atoms, while long range coupling is usually lost. Thus in a CMR spectrum recorded using off resonance decoupling, the ^{13}C nuclei are split by the protons directly attached to them.

(5)

Now we compare the off-resonance decoupled CMR spectrum and undecoupled CMR spectrum, we can detect the no. of hydrogens, that are directly attached to the carbon nuclei.

Thus the multiplicities of the ^{13}C bands can be readily observed, usually without overlap with other ^{13}C bands. Thus methyl carbon atoms appear as quartets, methylene as triplets (or as pair of doublets if the protons are not equivalent and coupling constants are quite different), methines as doublets and quaternary carbon atoms as singlets.



No protons
singlet



one proton
doublet

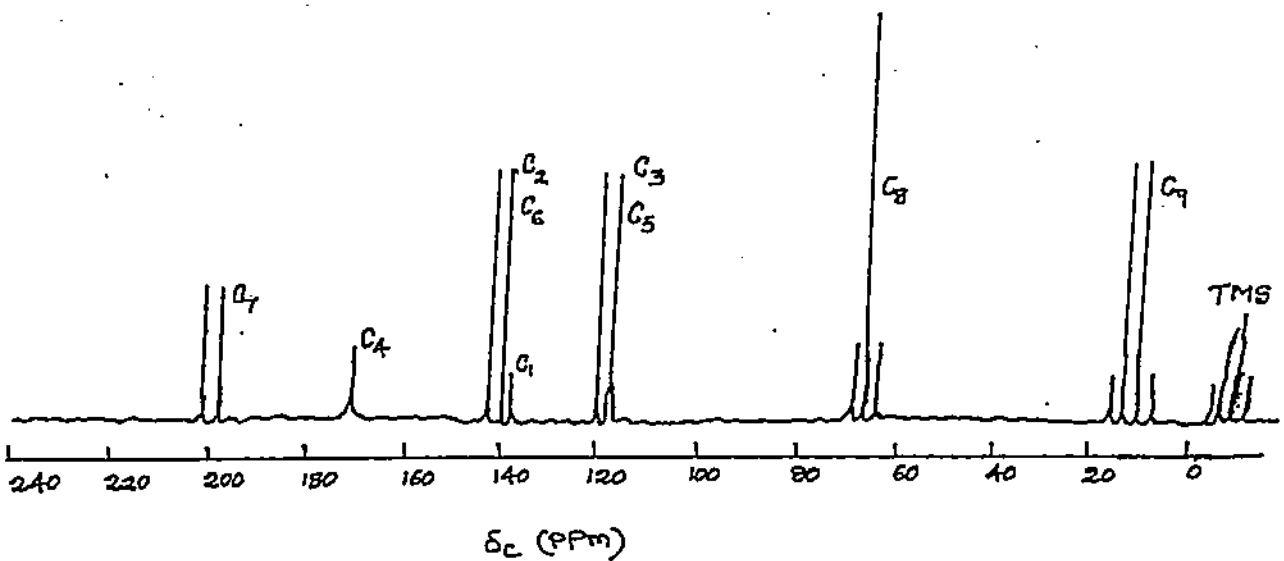
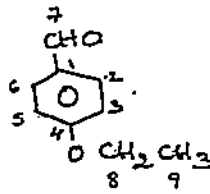


Two protons
Triplet



Three protons
quartet

Eg:- p-ethoxy benzaldehyde



⑥

Chemical shift Equivalence :

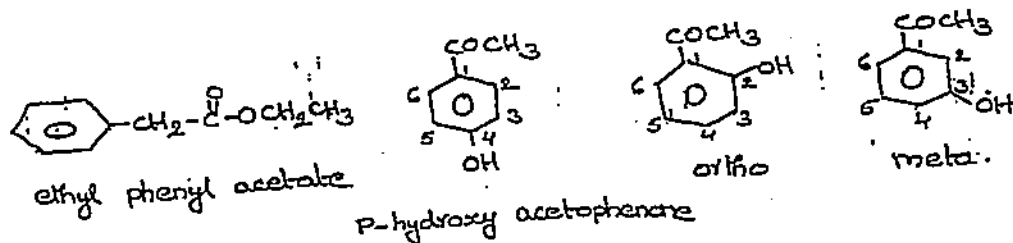
The presence of equivalent carbon atoms in a molecule results in simplification of the spectrum. For example ^{13}C carbon atoms of methyl groups in tertiary butyl alcohol are equivalent by rapid rotation in the same sense in which the protons of a methyl group are equivalent.

Similarly, in the case of tertiary butyl chloride, ^{13}C atoms of methyl group are also equivalent. The ^{13}C spectrum of tertiary butyl alcohol shows two peaks, one much larger than the other. The carbonyl carbon peak (quaternary) is much less than the intensity of the peak representing the carbons of the methyl group.

In the spectrum of ethyl phenyl acetate, there are eight signals inspite of the fact that there are ten carbon atoms in the molecule. Phenyl C-2 and C-6 are equivalent, while C-3 & C-5 are also equivalent. Thus the no. of CMR signals gives an idea about the o-, m- and p-hydroxy acetophenone.

In case of p-isomer only six signals are expected, because of the presence of six non-equivalent carbons.

In the case of o- and m- isomers eight signals are expected because each isomer now has eight non-equivalent carbons.

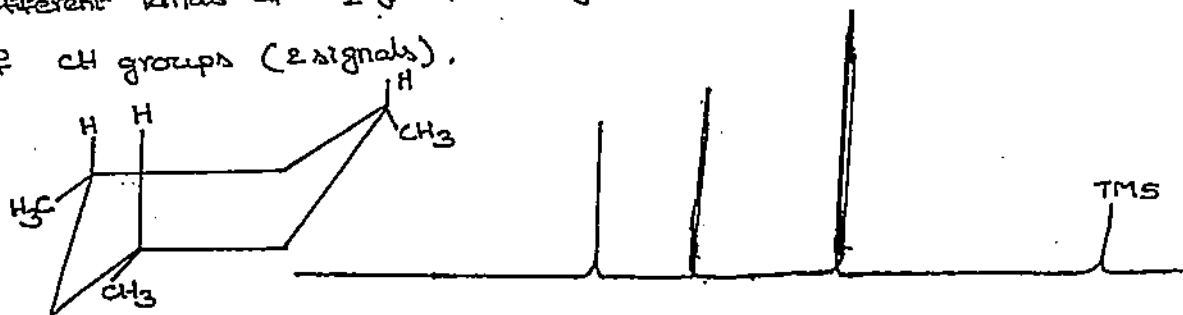


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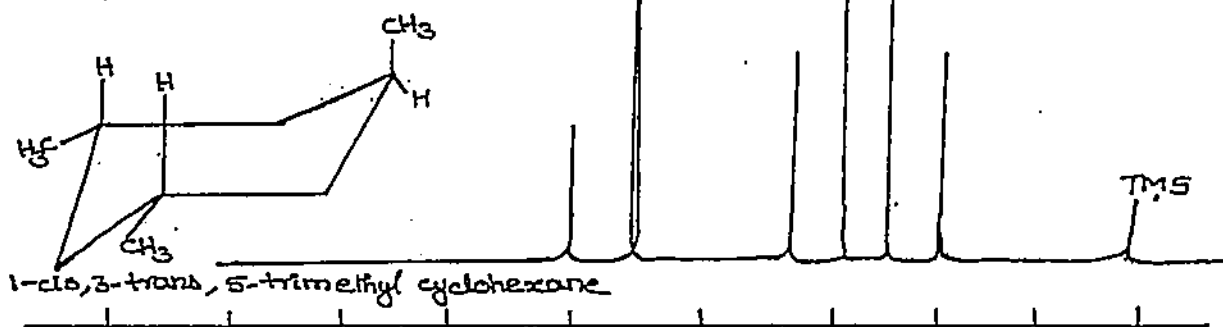
Another related example is of differentiation between the two diastereomers of 1,3,5-trimethyl cyclohexane. When one examines the proton-decoupled spectra of the two isomers, it is seen that one isomer shows only three signals. In this isomer all the methyl groups must be cis.

As all the methyl groups are equatorial only one CMR signal is expected. In a similar fashion one signal each is expected from the remaining equivalent CH_2 and CH groups.

In the other isomer, however, the two equatorial methyl are equivalent to give the signal and the axial methyl being different, it gives a separate signal. One is again dealing with two different kinds of CH_2 groups (2 signals) as well as two different kinds of CH groups (2 signals).



1-cis,3-cis,5-trimethyl cyclohexane



1-cis,3-trans,5-trimethyl cyclohexane

60 δ_c (ppm) 20 0

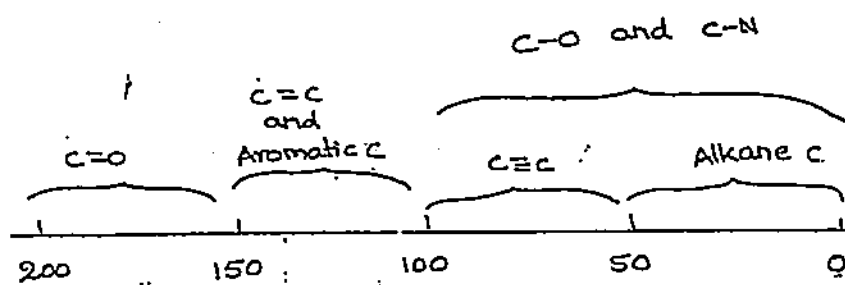
The equivalence or non-equivalence of carbons is therefore in the same manner as in the case of proton NMR. To be chemically equivalent carbons must also be equivalent stereochemically. In a chiral molecule, diastereotopic carbons display different signals, while enantiotopic carbons do not.

(8)

Chemical shift :

Like the PMR, chemical shifts of ^{13}C nuclei are expressed in units of parts per million (ppm) down field from TMS. However the range of ^{13}C -chemical shifts is much greater (0-200 ppm) than the proton chemical shifts. Because of this wide spread of signals, it is unlikely that the two ^{13}C -nuclei will have identical chemical shifts unless they are equivalent or enantiotopic.

The trends in chemical shifts of ^{13}C are somewhat parallel to those of ^1H and thus there are overall similarity to proton chemical shifts.



shifts are related mainly to hybridisation

and substituent electronegativity. Solvent effects are also very important as in proton spectra. Chemical shifts for ^{13}C are affected by substitutions as far removed as the δ -position. Pronounced shifts for ^{13}C are caused by substituents at the ortho, meta and para positions in the benzene ring.

The alkanes absorb about 60 ppm downfield from TMS, while methane absorbs at 2.6 ppm upfield from TMS (-2.6).

9

There is a general trend in the increase in chemical shift in going from primary to secondary to tertiary to quaternary carbon atoms.

δ_C TMS	CH ₄	CH ₃ CH ₃	CH ₃ -CH ₂ -CH ₃	CH ₃ - ↑ CH-CH ₃ ↑ CH ₃
	↑	↑	↑	↑
	-2.6	5.7	16	25

The presence and number of carbon atoms two and three bonds away from the carbon atom whose chemical shift is to be determined also affects its chemical shift. The chemical shift of a carbon in an acyclic alkane is generally calculated by the formula.

$$\delta = -2.5 + \sum nA$$

where δ is the predicted shift for a carbon atom, A is the additive shift parameter, n is the number of carbon atoms for each shift parameter.

13C shift parameters in linear and branched hydrocarbons	
13C Atoms	Shift (ppm) A
α	+9.1
β	+9.4
γ	-2.5
δ	+0.3
ϵ	+0.1
1° (3°)	-1.1
1° (4°)	-3.4
2° (3°)	-2.5
2° (4°)	-7.2
3° (2°)	-3.7
3° (3°)	-9.5
4° (1°)	-1.5
4° (2°)	-8.4

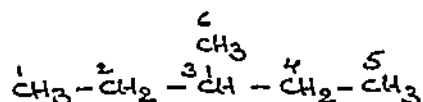
(10)

In the simple form, the above formula may be written as

$$\delta_i = -2.5 + 9.1 n_\alpha + 9.4 n_\beta - 2.5 n_\gamma + 0.3 n_\delta$$

where n_α is the number of carbon atoms bonded directly to the i th carbon atom and n_β, n_γ and n_δ are the number of carbon atoms two, three and four bonds removed.

Now, consider the shifts for the carbon atoms of 3-methyl pentane.



$$\delta_1 = -2.5 + (9.1 \times 1) + (9.4 \times 1) + (-2.5 \times 2) + (0.3 \times 1) = +11.3$$

$$\delta_2 = -2.5 + (9.1 \times 2) + (9.4 \times 2) + (-2.5 \times 1) + (-2.5 \times 1) = 29.5$$

$$\delta_3 = -2.5 + (9.1 \times 3) + (9.4 \times 2) + (-3.7 \times 2) = +36.2$$

$$\delta_4 = -2.5 + (9.1 \times 1) + (9.4 \times 2) + (-2.5 \times 2) + (-1.1 \times 1) = +19.3$$

The calculated values are in good agreement with the observed values.

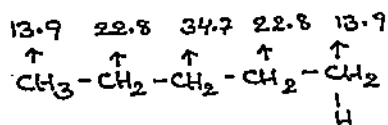
* In the above table $1^\circ(3^\circ)$ and $1^\circ(4^\circ)$ represent CH_3 group bound to R_2CH group and to R_3C group, respectively. The $2^\circ(3^\circ)$ denotes a RCH_2 group bound to a R_2CH group and so on.

The resonance frequencies in CMR spectra are basically influenced the same way as in PMR spectra by the nature and number of substituents attached on the carbon under observation.

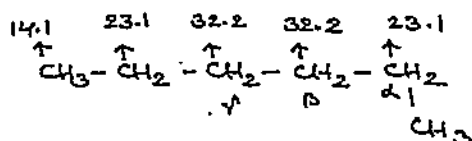
Significantly however, simple alkyl substitution has a much larger effect on ^{13}C chemical shifts than it does on PMR shifts.

Consider, the chemical shifts of alkanes, n-pentane and n-hexane, assuming n-hexane to be n-pentane with a methyl substituent on C-1.

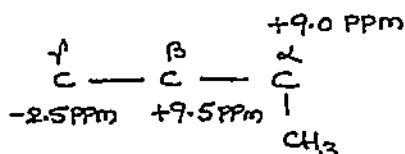
(11)



Pentane



Hexane

 γ -effect upfield. α - and β -effects downfield

A methyl group on α -carbon causes a downfield shift of 9.0 ppm at the α -carbon (δ 23.1) in n-hexane as compared to this relative carbon in n-pentane (δ 13.9). This shift for the carbon bearing the substituent is known as α -effect.

The methyl on β -carbon in n-hexane also exerts a down field from δ 22.8 to δ 32.2 PPM (9.5 PPM). Such a shift for the carbon once removed from the carbon bearing the substituent is called the β -effect.

At γ -carbon atom, there is a reversal of the substituent effect. This shift results in an upfield of 2.5 PPM. Such a shift for the carbon twice removed from the carbon bearing the substituent is called the γ -effect.

In keeping with these data it is generally found that a substituent in the α or β position generally deshields the carbon nucleus but one in the γ -position is shielding.

For example, the appropriate chemical shifts for 3-pentanol,

	calculated	observed	
δ_{α}	$34.7 + 4.1 = 75.8$	73.8	γ β α β γ
δ_{β}	$22.8 + 8 = 30.8$	30.0	$\text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3$
δ_{γ}	$13.9 - 5 = 8.9$	10.1	$\quad \quad \quad $
			$\quad \quad \quad \text{OH}$

(2)

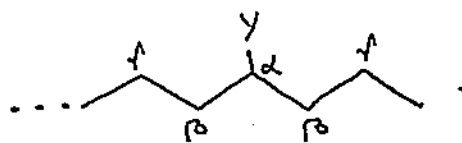
^{13}C shift for linear and branched chain alkanes (ppm from TMS).

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	14.2	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
Iso butane	24.5	25.4			
Iso pentane	22.2	31.1	32.0	11.7	
Isohexane	22.7	28.0	42.0	20.9	14.3
Neo pentane	31.7	28.1			
3-Methyl pentane	11.5	29.5	36.9		

Increment substituent effects (ppm) on replacement of H by Y in Alkanes. Y is terminal or internal.



Terminal



Internal

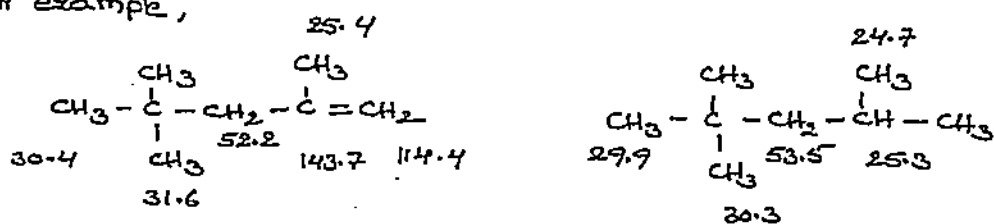
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Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH ₃	+9	+6	+10	+8	-2
CH=CH ₂	+20		+6		-0.5
-C≡CH	+4.5		+5.5		-3.5
COOH	+21	+16	+3	+2	-2
COO ⁻	+25	+20	+5	+3	-2
COOR	+20	+17	+3	+2	-2
COCl	+33	+28		+2	
CONH ₂	+22		+2.5		-0.5
COR	+30	+24	+1	+1	-2
CHO	+31		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	-3
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

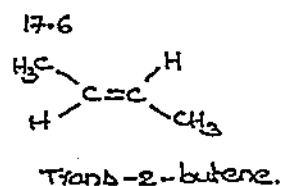
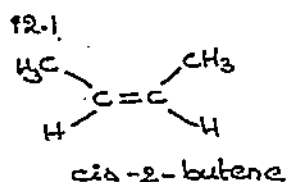
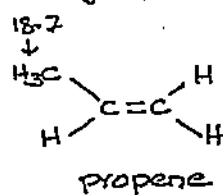
There is also a significant effect of hybridisation of the carbon atom on the chemical shift. The sp^3 hybridised carbon atom absorbs at high field (0-60 ppm down field from TMS), sp^2 hybridized carbon atom absorbs at low field ($\sim 110-150$ ppm down field from TMS) and a sp -hybridized carbon atom absorbs at intermediate values (65-90 ppm).

The sp^2 carbon atoms of alkenes substituted only by alkyl groups absorb in the range of $\sim 110-150$ ppm downfield from TMS. The double bond has a small effect on the shifts of sp^3 carbon in the molecule.

For example,

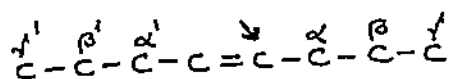


In general, the terminal $=\text{CH}_2$ group absorbs upfield than an internal $=\text{CH}$ group and cis $-\text{CH}=\text{CH}-$ are upfield than those of trans groups.



Calculations of approximate shifts can be made from the following parameters where α, β and γ' represent substituents on the same end of the double bond and α', β' and γ' represent substituents on the far side.

(15)



$$\alpha \quad - +10.6$$

$$\beta \quad - +7.2$$

$$\gamma \quad - -1.5$$

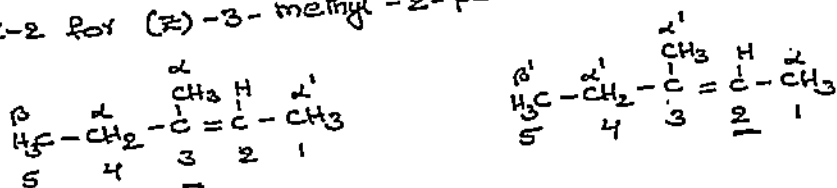
$$\alpha' \quad - -7.9$$

$$\beta' \quad - -1.8$$

$$\gamma' \quad - -1.5$$

$$\Sigma \text{ (cis correction)} \quad - -1.1$$

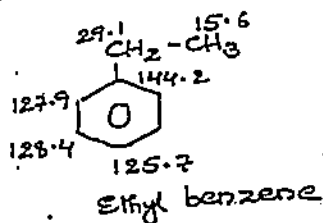
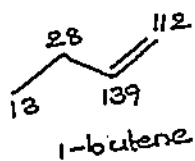
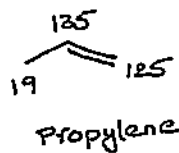
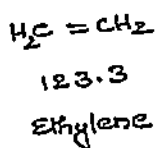
These parameters are added to 123.3 PPM, the shift for ethylene. For example, we can calculate the values of C-3 and C-2 for (Z)-3-methyl-2-pentene as follows.



$$\delta_{\text{C-3}} = 123.3 + (2 \times 10.6) + (1 \times 7.2) + (1 \times -7.9) - 1.1 = 142.7 \text{ PPM}$$

$$\delta_{\text{C-2}} = 123.3 + (1 \times 10.6) + (2 \times -7.9) + (1 \times 1.8) - 1.1 = 115.2 \text{ PPM}$$

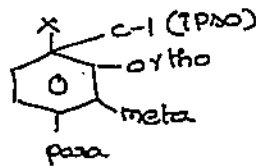
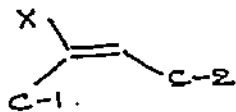
The sp^2 hybridized carbon atoms in alkenes and benzene hydrocarbons appear in the same general region of the CMR spectrum. Thus PMR is more useful in distinguish between two types of unsaturation than CMS. Benzene carbon atoms absorb at 128.5 PPM either as neat or as solutions in CDCl_3 or C_6D_6 .



(16)

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

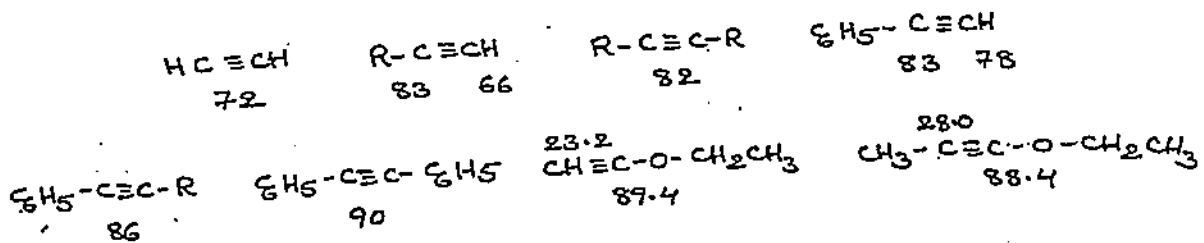
Base value Ethylene ($\delta 123$) and benzene ($\delta 128$)



	Alkenes		Benzenes			
	C-1	C-2	C-1 (IPso)	ortho	meta	para
-CH ₃	10	-8	9	0	0	-2
-CH ₂ CH ₃	16	-8	15	0	0	-2
-CH(CH ₃) ₂	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	8
-NHCO _R , -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
-OOCOR	18	-27	23	-6	1	-2

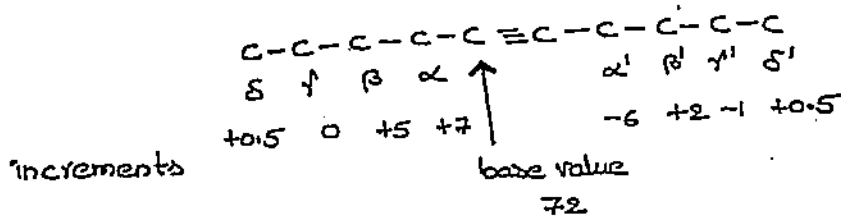
-COOH, -COOR, -CON<	4	9	2	2	0	5
-COR, -CHO	14	13	9	1	1	6
-SO ₃ H, -SO ₂ N<	-	-	16	0	0	4
-PMe ₂	-	-	14	1.6	0	-1
-PAx ₂	-	-	9	5	0	0

The sp carbon atoms of alkynes substituted only by alkyl groups absorb in the range of ~65-90 ppm. The triple bond (C≡C) causes a shift of about 5-15 ppm upfield to the sp³ carbons (directly attached) relative to the corresponding alkane. The terminal ≡CH absorbs upfield from the internal ≡CR.



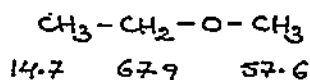
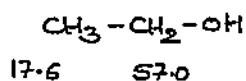
For other alkyne carbons :-

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



(18)

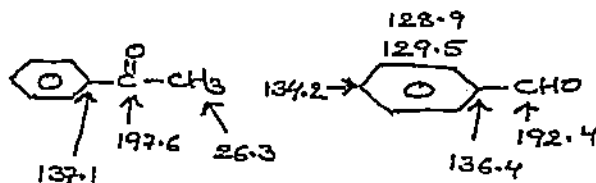
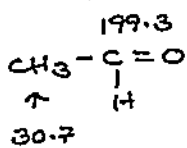
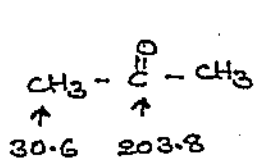
shift at C-1 than that of a hydroxy substituent.



An NH_2 group attached to an alkyl chain causes a downfield shift of ~ 30 ppm at C-1, a downfield shift of ~ 11 ppm at C-2 and an upfield shift of ~ 4.0 ppm at C-3.

In aldehydes and ketones, the $\text{R}_2\text{C}=\text{O}$ and $\text{RCH}=\text{O}$ carbons absorb in a characteristic downfield region. Acetone absorbs at 203.8 ppm and acetaldehyde at 199.3 ppm. Alkyl substitution on α -C causes a downfield shift of C=O absorption of 2-3 ppm. Replacement of CH_3 of acetone or acetaldehyde by a phenyl group causes an upfield shift of C=O absorption.

Thus, acetophenone absorbs at 195.7 ppm and benzaldehyde at 190.7 ppm. α, β -unsaturation causes upfield shifts of the C=O absorption.



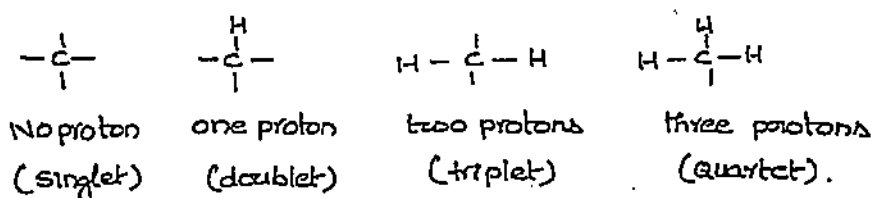
Important points regarding the chemical shifts of carbon nuclei :-

- (i) Alkanes generally absorb from -2 to 55 ppm.
- (ii) Increasing alkylation generally moves the carbon resonance downfield.
- (iii) The values of the chemical shifts indicate the type of hybridization at each carbon.
- (iv) carbons of both benzene ring and alkenes absorb in the same region. This makes $^1\text{H-NMR}$ useful to distinguish between two types of compounds.

(V) In proton-decoupled ^{13}C -NMR spectra, the number of signals exhibits how many different carbons or different sets of equivalent carbons are present in the molecule.

(VI) carbon of carbonyl group absorbs far downfield ($\sim 200\text{ppm}$).

(VII) In ^{13}C -proton off-resonance decoupled NMR spectrum, the splitting of a signal indicates the number of hydrogen atoms attached to the carbon giving rise the signal.



(VIII) In ^{13}C -NMR spectrum, the peak areas are not necessarily proportional to the number of identical ^{13}C -nuclei, under conditions normally used to run the spectrum.

Approximate ^{13}C -NMR chemical shifts:

Type of carbon atom	Chemical shift (δ , ppm)
1. Alkyl group	-2 to 55
a) 1° alkyl, RCH_3	0-40
b) 2° alkyl, R_2CH_2	10-50
c) 3° alkyl, R_3CH	15-55
2. Alkyl halide or amine	
$-\text{C}-\text{x}$ ($\text{x}=\text{Cl, Br}$ or $\text{N}-$)	10-65
3. Alcohols or ether	
$-\text{C}-\text{O}$	50-90
4. Alkynes ($-\text{C}\equiv$)	65-90
5. Alkene ($-\text{C}=\text{}$) & aryl	110-170

(20)

6. Nitriles ($-C\equiv N$)

130-150

7. Amides ($-C(=O)-N<$), carboxylic

150-185

-acids and esters ($-C(=O)-O$)

8. Aldehydes and ketones ($-C(=O)-$)

180-220.

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Paper-I: Organic Spectroscopy-II (R22OC41)

UNIT - II

V.R.S. & Y.R.N. COLLEGE, CHIRALA

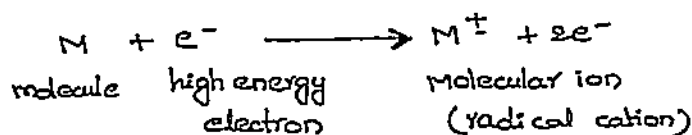
UNIT-II, Mass Spectrometry

Mass spectrometry is the most accurate method for determining the molecular mass of the compound and its elemental composition. A mass spectrum is not a spectrum with respect to electromagnetic radiation as in the case of IR and NMR. It is a plot of m/z values of various positively charged fragments (including the molecular ion) versus their relative abundance.

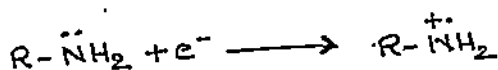
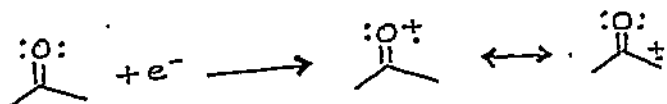
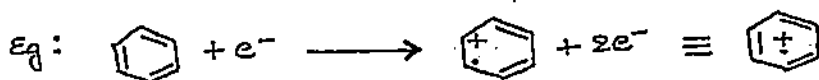
In this technique, molecules are bombarded with a beam of energetic electrons. The molecules are ionised and broken up into many fragments, some of which are positive ions. Each kind of ion has a particular m/z value. For most ions, the charge is one and thus m/z value is simply the molecular mass of the ion.

The molecular ion or parent ion is a positively charged ion with an odd electron, produced by the loss of one electron from the molecule during bombardment. which is designated as M^+ . The fragment (or) daughter ions are analysed in such a way that a signal is obtained for each value of m/z that is represented.

The intensity of each signal represents the relative abundance of the ion. The largest peak in the structure is called base peak and its intensity is taken as 100. The intensities of other peaks are represented relative to the base peak.

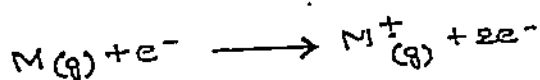


(2)



Molecular ion and its intensity :

✓ The electron bombardment with energy 10-15 eV usually removes one electron from the molecule of the organic compound in vapour phase. It results in the formation of molecular ion (M⁺) parent ion.



The highest occupied orbital of aromatic system and non-bonding electron orbitals on oxygen and nitrogen atoms readily lose one electron. An electron from double bond or triple bond is usually lost.

The molecular ion gives the mass of the sample. The molecular ion peak is usually the peak at high mass number except for the isotopes (M+1, M+2 etc). The m/z values of the molecular ion is the molecular weight of the compound. ✓

Often, the molecular ion peak is the base peak and this can be easily recognised. But it is not always so. The lower energy needed for ionisation of a molecule, more stable and intense molecular ion will be formed.

(3)

Strong

Aromatic hydro carbons,
Aromatic fluorides,
chlorides, nitriles and
amines,
saturated cyclic
compounds.

medium

Aromatic iodides and
bromides,
conjugated alkenes,
Benzyl and benzof. com-
pounds, straight chain
aldehydes, ketones, acids,
esters, amides, ethers,
alkyl halides.

Weak (or) non-existent

Aliphatic alcohols, amines,
and nitriles,
Branched chain compou-
nds, acids, esters,
amides, ethers,
alkyl halides.

(The intensity (abundance) of the molecular ion peak can be increased with respect to the abundance of fragment ions by running the spectrum at low ionisation potential i.e. by bombarding with low energy electrons.)

Some important features of molecular ion :

- (i) The molecular ion peak in aromatic compounds is much intense due to the presence of π -electron system.
- (ii) The molecular ion peak is more intense in conjugated olefins than non-conjugated olefins with same no. of unsaturation.
- (iii) Unsaturated compounds give more intense peak than saturated or cyclic compounds.
- (iv) The relative abundance of the straight chain hydrocarbon is more than branched chain compound with the same number of carbon atoms.
- (v) [✗] The substituents like $-OH$, $-OR$, $-NH_2$ etc. which lower the ionisation potential and increases the relative abundance, whereas the groups like $-NO_2$, $-CN$ increases the ionisation and decreases the relative abundance in case of aromatic compounds.
- (vi) Absence of molecular ion peak in the mass spectrum means that the compound is highly branched or tertiary alcohol.

(4)

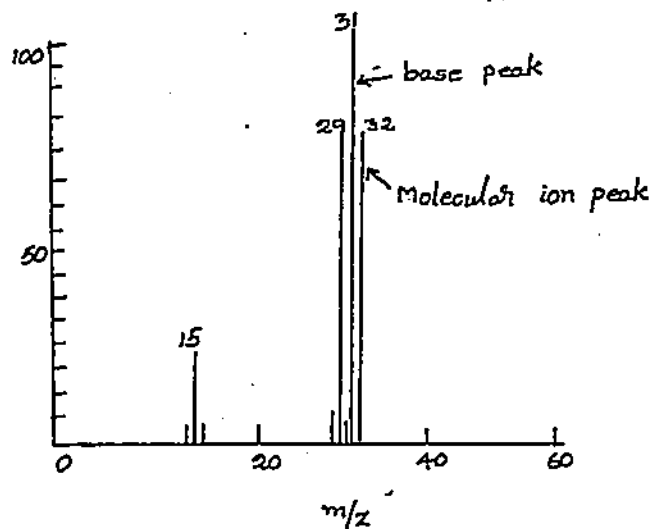
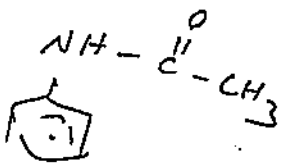
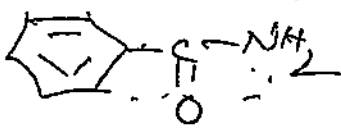
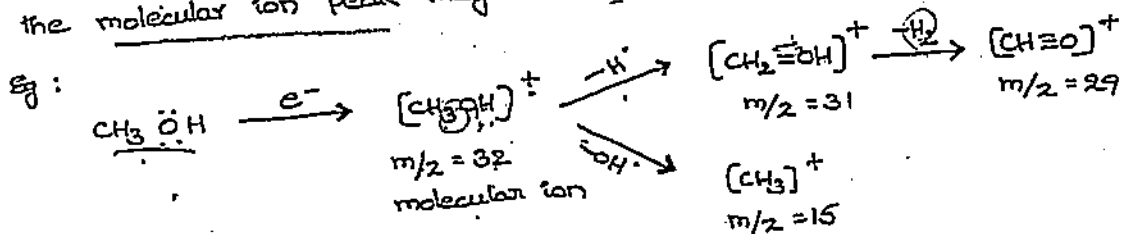
(vii) In case of chloro or bromo compounds, isotope peaks are also formed along with molecular ion peak. In case of bromo compounds M^+ and (M^++2) peaks are formed in the intensity ratio 1:1. In case of chloro compounds (M^++2) peaks are formed in the intensity ratio 1:3.

The mass spectrum - The base peak :-

The graphic representation of the mass spectrum of a compound is constructed by plotting mass/charge ratio versus relative abundance.

The largest peak in the mass spectrum corresponds to the most abundant ion or the intense peak in the spectrum is called the base peak.

Depending on the nature of the compound, the base peak may be either a fragment peak or molecular ion peak. Of course the molecular ion peak may sometimes be the base peak.



(5)

Instrumentation :-

The instrument needed to produce the mass spectrum of a compound consists of the following parts.

(i) Sample Insertion - Inlet systems :-

Organic compounds that have moderate vapour pressures at temperatures up to around 300°C can be placed in an ampoule connected via reservoir to the ionization chamber.

Depending on volatility, it is possible to cool or heat the ampoule etc. to control the rate at which the sample volatilizes into the reservoir from which it will diffuse slowly through the sinter into the ionization chamber.

Samples with lower vapour pressures are inserted directly into the ionization chamber on the end of a probe and their volatilization is controlled by heating the probe tip.

(ii) Ion production in the Ionization Chamber :-

The common technique used for the production of ions in mass spectrometer is by the bombardment of electrons. The bombarding electrons are produced from an electrically heated tungsten filament.

Organic molecules react on electron bombardment in two ways; either an electron is captured by the molecule, giving a radical anion, (or) an electron is removed from the molecule giving a radical cation.

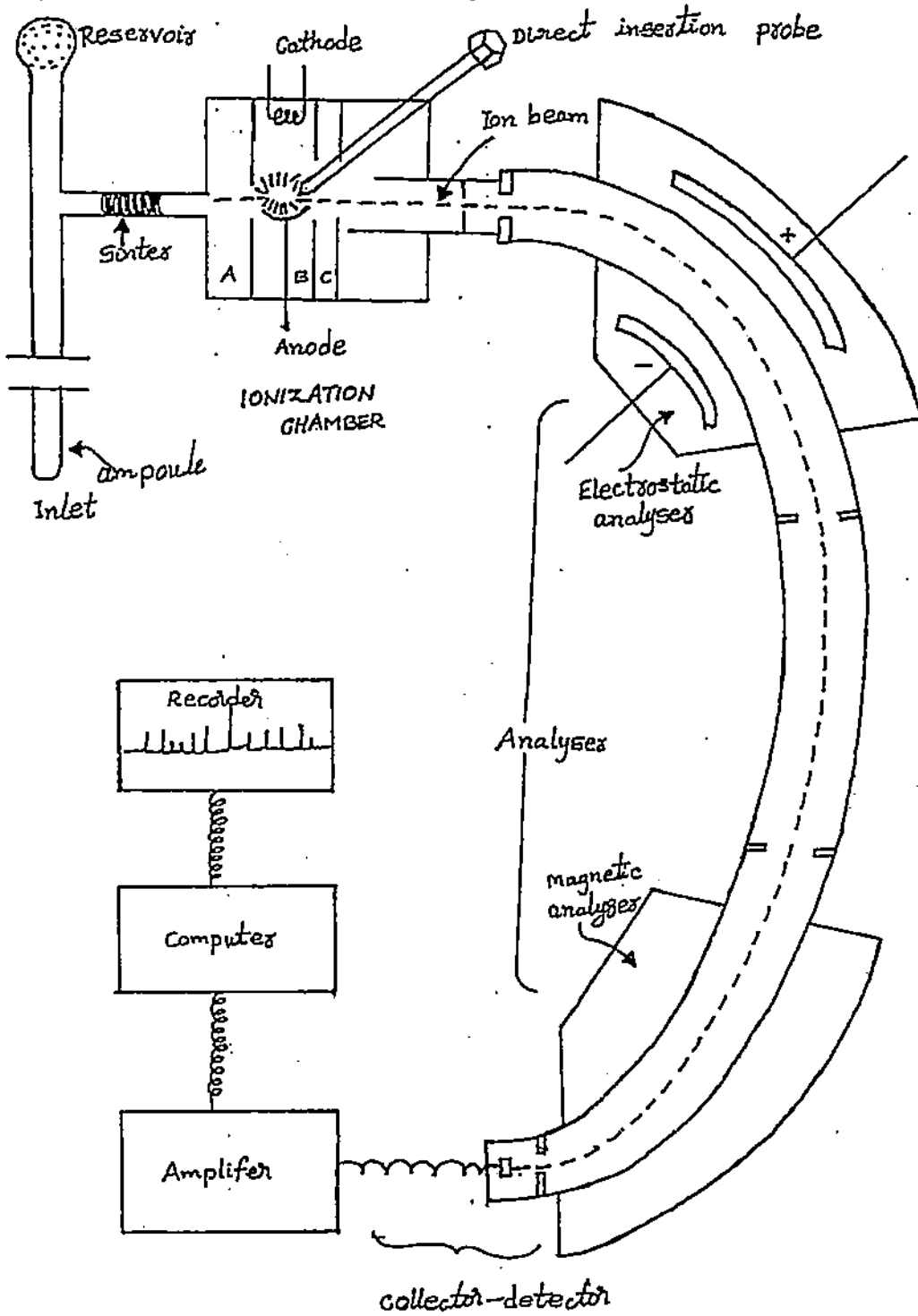


the latter is more probable.

When the molecular ions have been generated in the ionization chamber, they are expelled electrostatically by means of

⑥

a low positive potential on a repeller plate (A) in the chamber. Once out, they more accelerated down the ion tube by the much higher potential between the accelerating plates B and C.



(7)

Separation of the ions in the Analyser :-

Ions repelled by the accelerator plates do not have identical kinetic energies. Hence, preliminary focusing can be carried out by passing the ion beam between two curved plates, which are electrostatically charged i.e. electrostatic analyser.

The electrostatic analyser focuses ions of identical kinetic energy into monitor slit, whatever their m/z values and coupled with a magnetic analyser to resolve m/z values.

In the magnetic analyser ions are separated on the basis of m/z values. The kinetic energy E , of an ion of mass m travelling with velocity v is given by,

$$E = \frac{1}{2} mv^2 \text{ ————— ①}$$

The potential energy of an ion of charge z being repelled by an electrostatic field of voltage V is zV . When the ion is repelled, the potential energy zV , is converted into the K.E $\frac{1}{2}mv^2$, so that

$$zV = \frac{1}{2} mv^2$$
$$\therefore v^2 = \frac{2zV}{m} \text{ ————— ②}$$

When ions are shot into the magnetic field of the analyser, they are drawn into circular motion by the field and at equilibrium the centrifugal force of the ion ($\frac{mv^2}{r}$) is equal to the centripetal force exerted on it by the magnet (zBv), where r is the radius of the circular motion and B is the field strength.

Thus,

$$\frac{mv^2}{r} = zBv$$
$$\therefore r = \frac{zBv}{m} \text{ ————— ③}$$

From eq's ② and ③

$$\frac{2zV}{m} = \left[\frac{zBv}{m} \right]^2$$

⑧

$$\therefore \frac{m}{z} = \frac{B^2 r^2}{2V}$$

From this equation, it is clear that at a given magnetic field strength and accelerating voltage, the ions of m/z value will follow a circular path of radius r . The ions of various m/z values reach the collector, amplified and recorded. The mass spectrum is obtained either by

- (i) changing B at constant V (or)
- (ii) changing V at constant B .

When the magnetic field is varied, the method is called magnetic scanning. It is called electric voltage scanning when potential is varied at constant field strength.

The detector - Recorder :

The focused ion beam passes through the collector slit to the detector which must convert the impact of a stream of positively charged ions into an electrical current. This must be amplified and recorded either graphically or digitally.

Determination of Molecular Formula :-

The mass spectrum is a plot representing the m/z values of the various ions against their corresponding relative abundances. The value of m/z of molecular ion gives the molecular weight of the compound.

The peak on the extreme right is the molecular ion. Thus, an odd molecular weight indicates an odd number of nitrogen atoms in the compound. The presence of chlorine or bromine will be suggestive by an abundant $(M+2)$ ion, while a less abundant $(M+2)$ ion will show the presence of sulphur. The no. of carbon atoms can be calculated from the relative abundances of the M^+ and $M+1$ peaks.

(9)

Most of the common elements found in organic compounds have naturally occurring heavier isotopes. For three elements - carbon, hydrogen and nitrogen, the principal heavier isotope is one mass unit greater than the most common isotope.

The presence of these elements in a compound give rise to a small isotopic peak with mass one unit greater than the molecular ion i.e. at $M^{\pm}+1$. For four of the elements - oxygen, sulphur, chlorine and bromine the principal heavier isotope is two mass units greater than the most common isotope. The presence of these elements in a compound give rise to an isotopic peak at $M^{\pm}+2$.

$M^{\pm}+1$ elements : C, H, N

$M^{\pm}+2$ elements : O, S, Br, Cl.

Isotopic peaks gives us one method for determining molecular formulas. For molecules with modest number of atoms we can determine molecular formulas in the following way.

In the unknown compound, if the M^{\pm} peak is not the base peak, first we recalculate the intensities of the $M^{\pm}+1$ and $M^{\pm}+2$ peaks to express them as percentage of the intensity of the M^{\pm} peak.

Consider, for example, the mass spectrum of the following unknown compound.

(10)

Mass Spectrum

m/z	Intensity (as percent of base peak)	m/z	Intensity (as percent of M^+)
27	59.0	72 M^+	100.0
28	16.0	73 M^++1	4.5
29	54.0	74 M^++2	0.3
39	23.0		
41	60.0		
42	12.0		
43	79.0		
44	100.0 (base)		
72	73.0 M^+		
73	3.3		
74	0.2		

Recalculated to base
on M^+

In the spectrum, the M^+ peak at $m/z = 72$ is not the base peak. Therefore we need to recalculate the intensities of the peaks in our spectrum at m/z 72, 73, and 74 as percentage of the peak at m/z 72.

It is done by dividing each intensity by the intensity of the M^+ peak, which is 73%, and multiplying by 100.

m/z	Intensity (% of M^+)
72	$73.0 / 73 \times 100 = 100$
73	$3.3 / 73 \times 100 = 4.5$
74	$0.2 / 73 \times 100 = 0.3$

Then we can determine the molecular formula as follows.

- (i) According to the nitrogen rule, for our unknown M^+ is even, hence, the compound must have an even number of nitrogen atoms.
- (ii) The relative abundance of the M^++1 peak indicates the number of carbon atoms.

(ii)

Number of carbon atoms = relative abundance of $(M^+ + 1)/1.1$

For our unknown, number of carbons = $\frac{4.5}{1.1} = 4$

(iii) The relative abundance of $M^+ + 2$ peak the presence or absence of S (4.4%), Cl (33%) or Br (98%).

For our unknown, $M^+ + 2 = 0.3\%$, thus, we can assume that, S, Cl, Br are absent.

(iv) The molecular formula can be established by determining the number of hydrogen atoms and adding the approximate number of oxygen atoms, if necessary.

For our unknown the M^+ peak at m/z 72 gives us the molecular weight. It also tells us that nitrogen is absent because a compound with four carbons and two nitrogens would have a molecular weight (76) greater than that of our compound.

For a molecule composed of C and H only

$$H = 72 - (4 \times 12) = 24$$

but C_4H_{24} is impossible.

For a molecule composed of C, H and one O

$$H = 72 - (4 \times 12) - 16 = 8$$

and thus our unknown has the molecular formula C_4H_8O .

In some cases, a McLafferty rearrangement ion peak gives an important clue in the determination of molecular formula of the compound. For example, all straight chain aldehydes containing a γ -hydrogen atom form a base peak at m/z 44 (McLafferty rearrangement ion peak).

(12)

Also in aldehydes a fairly abundant M^+ peak follows a less abundant (M^+-1) peak. Let us consider a simple mass spectrum having m/z values at 72, 71, 44 (100%), 43, 29 etc.

Here a signal at m/z 44 (100%) is due to McLafferty rearrangement ion. Clearly, it is a straight chain aldehyde as M^+ peak at 72 also accompanies M^+-1 peak at 71. Hence the formula of the compound is $CH_3CH_2CH_2CHO$.

Recognition of the molecular ion peak - The nitrogen rule :-

Quite often, under electron impact (EI), recognition of the molecular ion peak (M) poses a problem. The peak may be very weak or it may not appear at all. In such cases, the nitrogen rule is often helpful.

It states that a molecule of even numbered molecular weight must contain either no nitrogen or an even number of nitrogen atoms; an odd numbered molecular weight requires an odd number of nitrogen atoms.

This rule holds for all compounds containing carbon, hydrogen, oxygen, nitrogen, sulphur and halogens.

Eg: CH_4 ($m/z=16$), CH_3OH ($m/z=32$), N_2H_4 ($m/z=32$), NH_3 ($m/z=17$), $C_2H_5NH_2$ ($m/z=45$).

This rule states that fragmentation at a single bond gives an odd-numbered fragment ion from an even-numbered molecular ion and an even-numbered fragment ion from an odd-numbered molecular ion.

Eg: Nitro benzene ($C_6H_5NO_2$).

(13)

The signal for molecular ion appears at m/z 123 i.e. at odd numbered molecular weight since this compound contains only one nitrogen atom.

The fragment ions NO_2^+ at m/z 46 and NO^+ at m/z 30. i.e. both of these ions appear at even mass number.

Use of the molecular formula - Index of Hydrogen deficiency :-

The molecular formula is usually the most important piece of information, which one derives from the mass spectrum of an organic compound. Thus it becomes very necessary to identify the molecular ion. It gives the index of hydrogen deficiency.

The index of hydrogen deficiency is the number of pairs of hydrogen atoms that must be removed from the corresponding saturated formula ($\text{C}_n\text{H}_{2n+2}$) to produce the molecular formula of the compound of interest. It is also called the no. of sites of unsaturation.

The index is thus the sum of the number of rings, the number of double bonds and twice the number of triple bonds. It can be calculated by using the following formula.

$$\text{Index} = \text{carbons} - \frac{\text{hydrogens}}{2} - \frac{\text{halogens}}{2} + \frac{\text{nitrogens}}{2} + 1$$

Eg:- $\text{C}_7\text{H}_7\text{NO}$

$$\text{Index} = 7 - \frac{7}{2} + \frac{1}{2} + 1 = 7 - 3.5 + 0.5 + 1 = 5$$

Note: The divalent atoms (oxygen and sulphur) are not counted in the formula.

For the generalized molecular formula: $\text{a}_I \text{P}_I \text{b}_II \text{Y}_III \text{S}_IV$

i.e.

(14)

$$\text{The index} = \text{IV} - \frac{1}{2}\text{I} + \frac{1}{2}\text{III} + 1$$

Where, α is H, D or halogen i.e. any monovalent atom

β is O, S or any other bivalent atoms

γ is N, P or any other trivalent atom.

δ is C, Si or any other tetravalent atom.

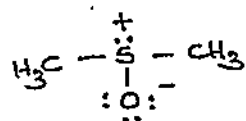
The numerals I-IV designate the numbers of the mono, di, tri and tetravalent atoms respectively.

Eg: $\text{C}_4\text{H}_4\text{S}$ (thiophene)

$$\text{Index} = 4 - \frac{1}{2} \cdot 4 + 1 = 3$$

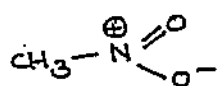
Polar structures must be used for compounds containing an atom in a higher valence state such as sulphur or phosphorus.

Eg: (i) DMSO (dimethyl sulphoxide)



$$\text{Index} = 2 - \frac{6}{2} + 1 = 0$$

(ii) Nitromethane



$$\text{Index} = 1 - \frac{3}{2} + \frac{1}{2} + 1 = 1$$

The index of hydrogen deficiency must be a whole number for an odd electron ion. For an even electron ion the value of I.H.D is non-integral. Thus it gives the chemist very ready information about the structure.

Metastable ions (or) Metastable peaks :-Characteristics of metastable ions :-

- (i) They do not necessarily occur at the integral m/z values.
- (ii) These are much broader than the normal peaks and
- (iii) These are of relatively low abundance.

Formation of metastable ions :-

consider that a large no. of molecules of M are converted into molecular ions M^+ by means of bombarding, but all the M^+ do not possess the same excitation energy and therefore some will have longer lifetimes than others.

The M^+ ions with shorter lifetimes may undergo decomposition in the ionization chamber to form stable daughter ions m_1^+ and radicals m_2 . The daughter ions m_1^+ may travel the whole analyser and detected at the collector normally (as m_1^+ ion).

The molecular ions that leave the ion source intact will be accelerated by the accelerator voltage and thereby possess a translational energy eV . Some of these M^+ ions may survive and reach the collector and get recorded normally. But some are decomposed to m_1^+ and m_2 immediately after acceleration in the second field free region lies between the electrostatic analyser and magnetic analyser.

The translational energy of the parent M^+ (eV) will be shared between m_1^+ and m_2 in proportion to their masses. Thus the translational energy of daughter ion m_1^+ must be lower than that of the parent ion and this ion m_1^+ will arrive at the collector differently from the normal m_1^+ ion produced in the ion source.

(16)

The ion m_1^+ with abnormal translational energy is called metastable ion. Metastable ion m_1^+ will have the same mass as normal m_1^+ ion but simply have lesser translational energy.

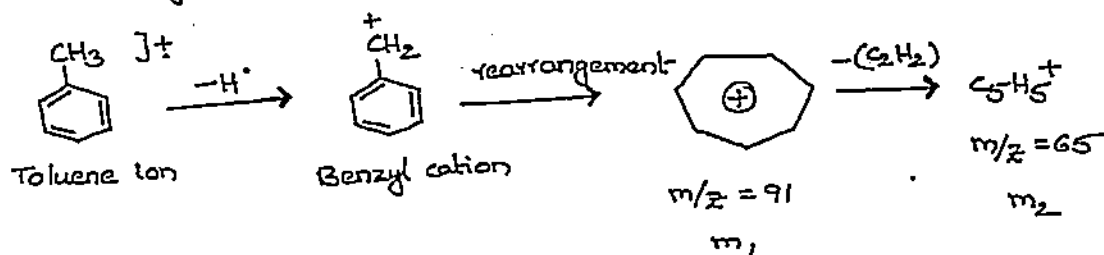
The reason for the broadening of the metastable peak is that some of the excitation energy leading to bond rupture may be converted into additional kinetic energy.

Calculation of metastable ion m/z values:

metastable ion m/z value (m^*) can be calculated from the masses of the parent ion M^+ (m_1) and the normal daughter ion m_2^+ (m_2) by using the following equation.

$$m^* = \frac{(m_2)^2}{m_1}$$

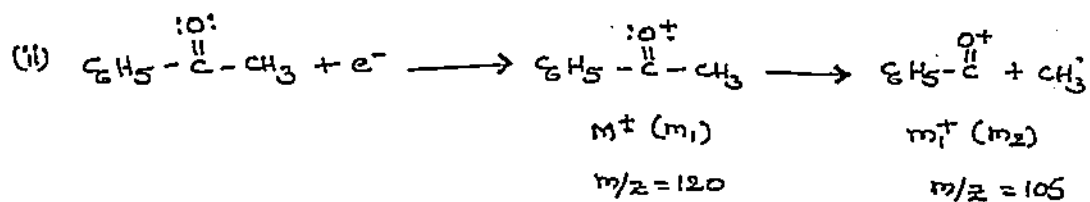
eg:- (i) consider the mass spectrum of toluene. Two strong peaks at m/z 91 and at m/z 65 are formed. The peak at m/z 91 is due to the formation of tropylium cation (stable) which loses a molecule of acetylene (26 mass units) to give $C_5H_5^+$ (m/z - 65).



Suppose the transition $C_7H_7^+$ (91) to $C_5H_5^+$ (65) occurs in the second field free region, then a metastable peak is formed. The position of the broad metastable peak is determined, as

$$m^* = \frac{(m_2)^2}{m_1} = \frac{65 \times 65}{91} = 46.4.$$

(17)



$$\therefore m^* = \frac{(m_2)^2}{m_1} = \frac{105 \times 105}{120} = 93.4$$

Significance of metastable ions:-

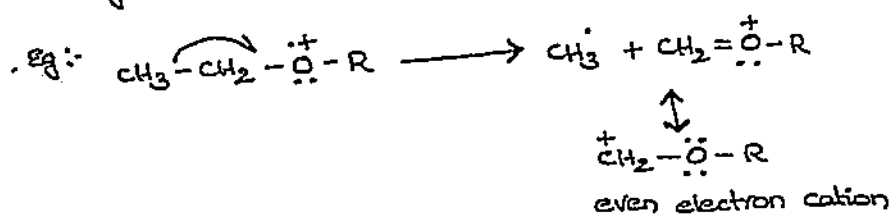
The metastable peaks in the mass spectrum greatly contribute in structure elucidation. From the positions of the parent ion and the daughter ion, the position of metastable ion is calculated. The formation of less intense metastable peak leads weight to the structure of the compound.

Fragmentation :-

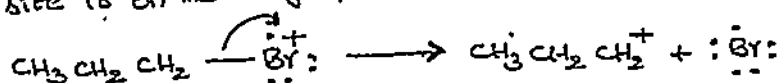
Fragmentation gives the useful information for the identification of the compound. The fragmentation of molecular ion depends on (i) Bond strength (ii) The stability of both the fragmented fractions.

The fragmentation of the odd-electron molecular ion mainly occurs by two processes.

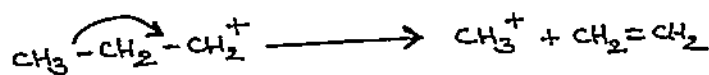
(i) Homolytic cleavage: In this each electron moves independently as shown by a fish hook. The fragments are even electron cation and a radical.



(ii) Heterocyclic cleavage:- In this a pair of electron moves together towards the charged site as shown by the conventional curved arrows. Here also the fragments are even electron cation and radical, but here the final charge site is on the alkyl product.

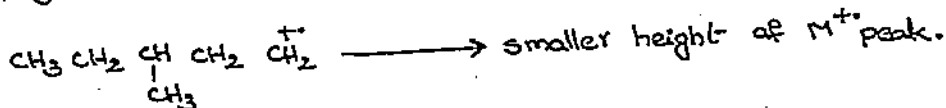
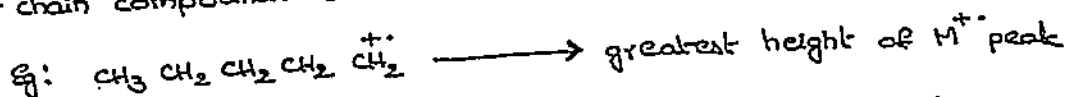


In the absence of rings most of the prominent fragments results in even-electron cation by single cleavage, which is fragmented into another even-electron cation and a neutral molecule.



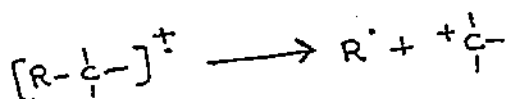
Fragmentation rules :-

(i) The relative height of the molecular ion peak is greatest for the straight-chain compounds and decreases as the branching increases.

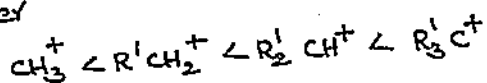


(ii) The relative height of the molecular ion peak usually decreases with increasing molecular weight in a homologous series. i.e. the series in which for each step the mass is increased by 14 units ($-\text{CH}_2-$).

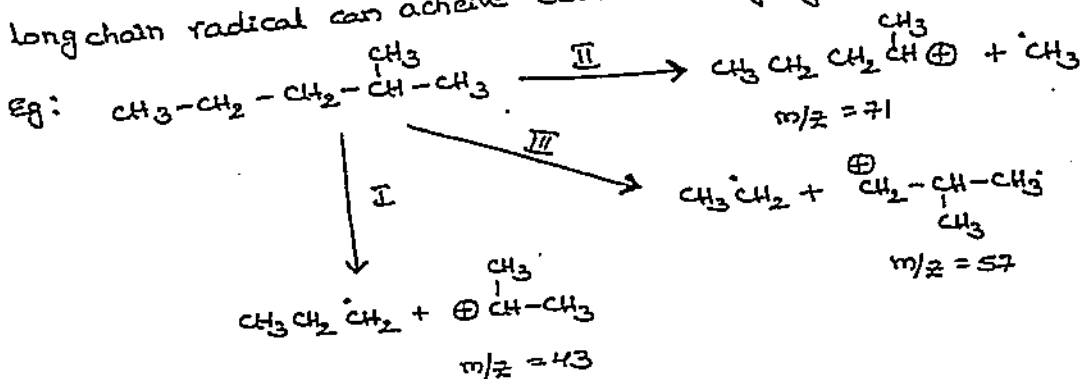
(iii) cleavage is favored at alkyl substituted carbon atoms, the substitution is more, the cleavage is more. This is because of increased stability of cations.



cation stability order



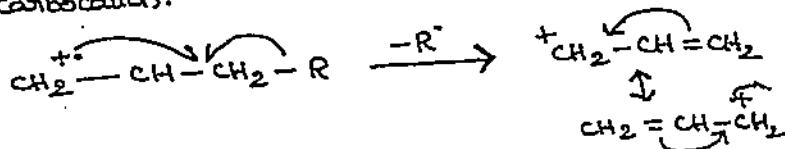
Generally, a large substituent is cleaved first as a radical, because the long chain radical can achieve some stability by delocalization of lone electron.



In the above example, the cleavage I is mostly occurs because the ion and radical are stabilized and the peak at 43 is considered as base peak.

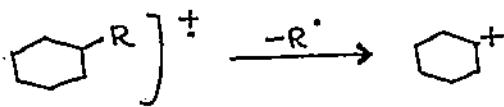
(iv) Double bonds, cyclic structures and aromatic rings stabilizes the molecular ion subsequently which is more intense.

(v) Double bonds favour allylic cleavage and give the resonance stabilized allylic carbocation.

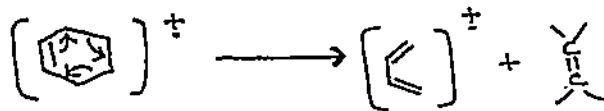


This rule is good for cyclo alkenes than simple alkenes.

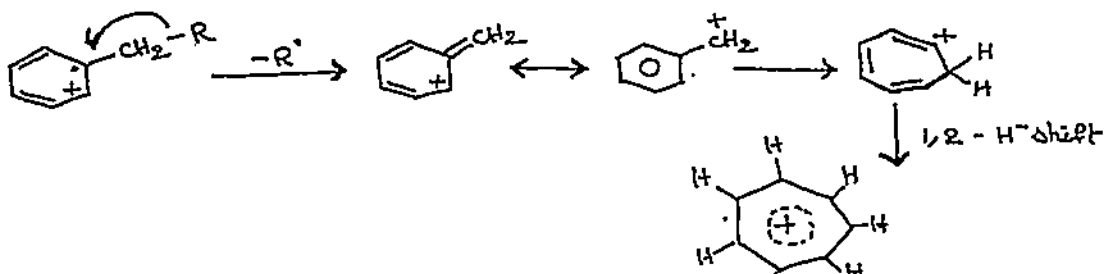
(vi) Saturated rings tend to loose alkyl side chains at the α -bond. The positive charge tends to stay with the ring fragment.



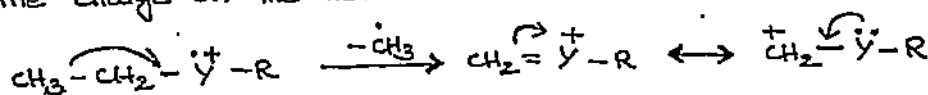
Unsaturated rings can undergo a retro-Diels-Alder reaction.



(vii) In alkyl substituted aromatic compounds, cleavage is probable at the β -bond to the ring, giving the resonance stabilized benzyl cation i.e. tropylium ion.



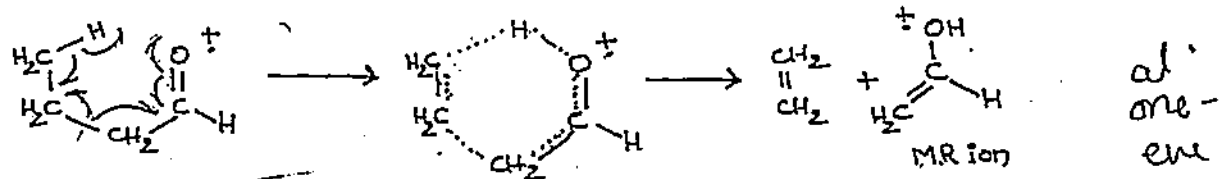
(viii) The C-C bonds next to a hetero atom are frequently cleaved, leaving the charge on the hetero atom.



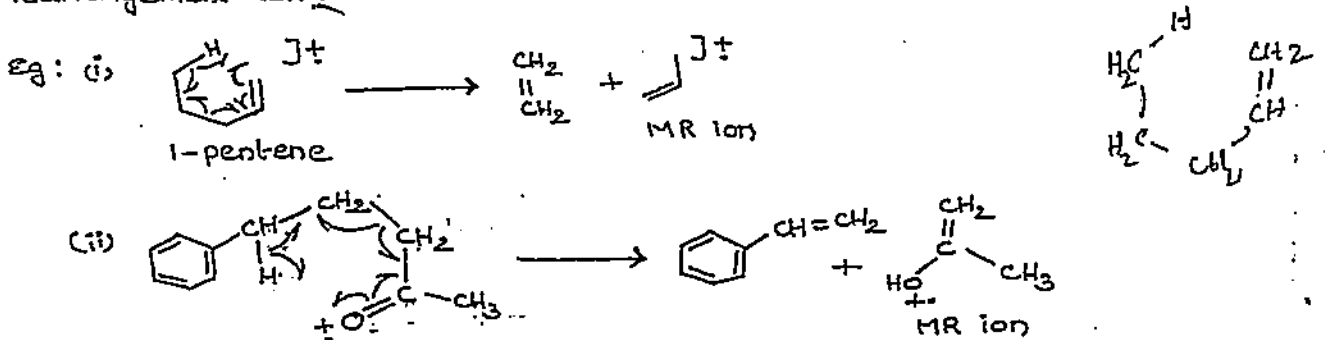
(ix) Cleavage is often associated with elimination of small, stable, neutral molecules such as carbon monoxide, olefins, water, ammonia, hydrogen sulphide, hydrogen cyanide, mercaptans, ketone or alcohols often with rearrangement.

Mc Lafferty rearrangement :-

It involves the migration of γ -hydrogen atom followed by the cleavage of a β -bond. The rearrangement leads to the elimination of neutral molecules from aldehydes, ketones, amines, unsaturated compounds, substituted aromatic compounds etc. The rearrangement proceeds through a sterically hindered six membered transition state.

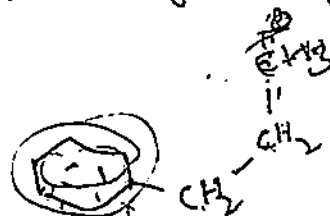


Similarly, a large number of organic compounds viz ketones, amines, alcohols, esters, acids which contain a γ -hydrogen atom forms a Mc Lafferty rearrangement ion.

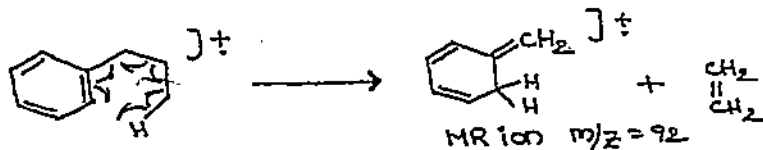


The structural requirement for this rearrangement is a side chain containing at least three carbon atoms, the last bearing a hydrogen atom and a double bond which may be a carbonyl group, an olefinic double bond or an aromatic system.

n-propyl benzene shows a Mc Lafferty rearrangement ion peak in large abundance at m/z 92.



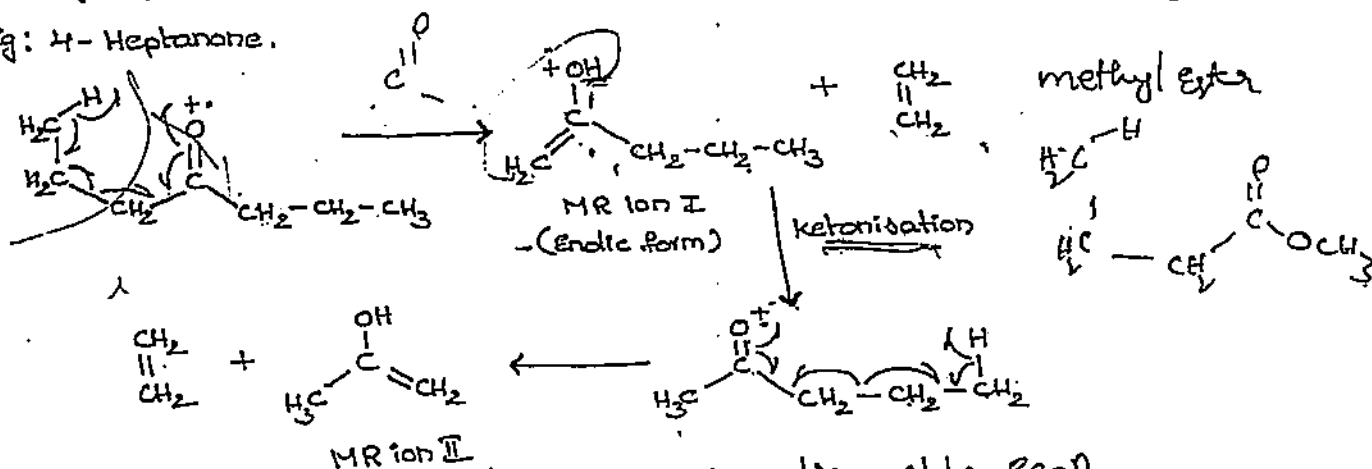
(21)



A double McLafferty rearrangement is also reported in certain ketones. The second hydrogen atom originates exclusively from the γ -position.

The mechanism involves, γ -hydrogen at the two sides of β - γ containing
 (i) ketonisation of the intermediate enol ion by the hydrogen transfer the comp
 (ii) Hydrogen transfer to endic oxygen. (i) McLafferty rearrangement

Eg: 4-Heptanone.

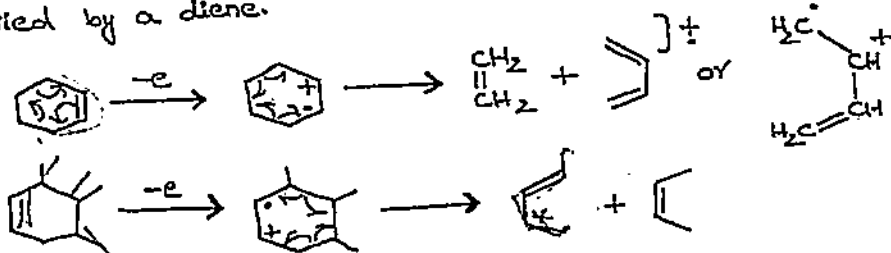


Retro-Diels-Alder Reaction :- opp to Diels-Alder Rean

This reaction is an example of multicentered fragment-ation, which is characteristic of cyclic olefins. It involves the cleavage of two bonds of a cyclic system resulting in the formation of two stable unsaturated fragments in which two new bonds are formed.

This process is not accompanied by any hydrogen transfer rearrangement. The charge can be carried by any of the fragments.

The more highly substituted or more conjugated fragment which has a lower ionisation potential carries a charge. In simple system, the charge is carried by a diene.



Mass spectra of some chemical classes :-

Alkanes :-

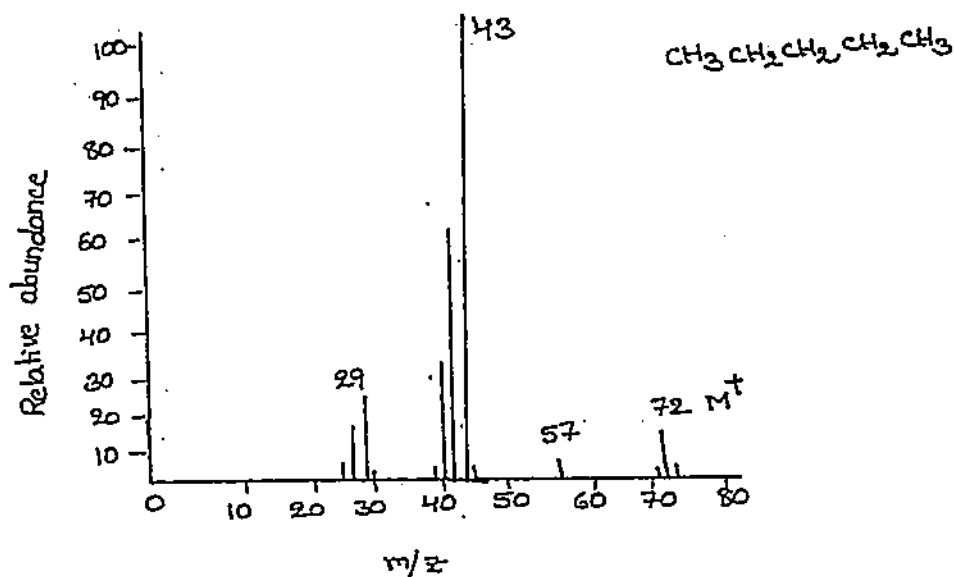
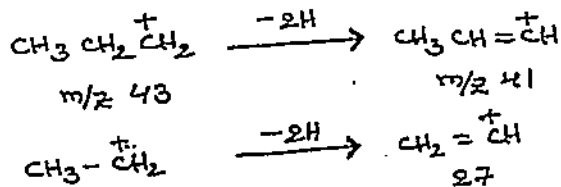
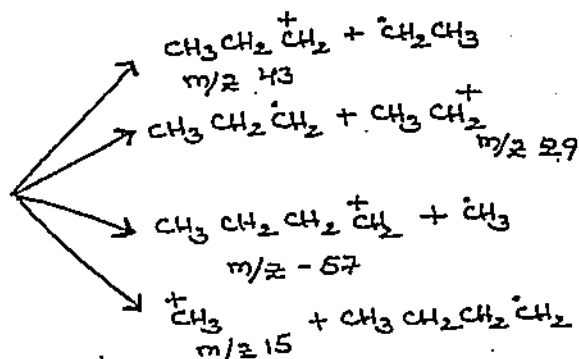
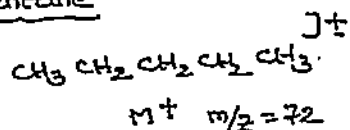
(i) The molecular ion is normally present. The intensity of molecular ion peak decreases with an increase in molecular mass in a homologous series.

(ii) The spectra generally consists of cluster of peaks separated by 14 mass units corresponding to a difference of CH₂ group.

(iii) The largest peak in each cluster represents a C_nH_{2n+1}⁺ fragment. This is accompanied by C_nH_{2n}⁺ and C_nH_{2n-1}⁺ fragments corresponding to the loss of one and two H-atoms respectively with less intensity.

(iv) The most intense peaks are due to C₃⁺ and C₄⁺ ions at m/z 15 and m/z 27 respectively.

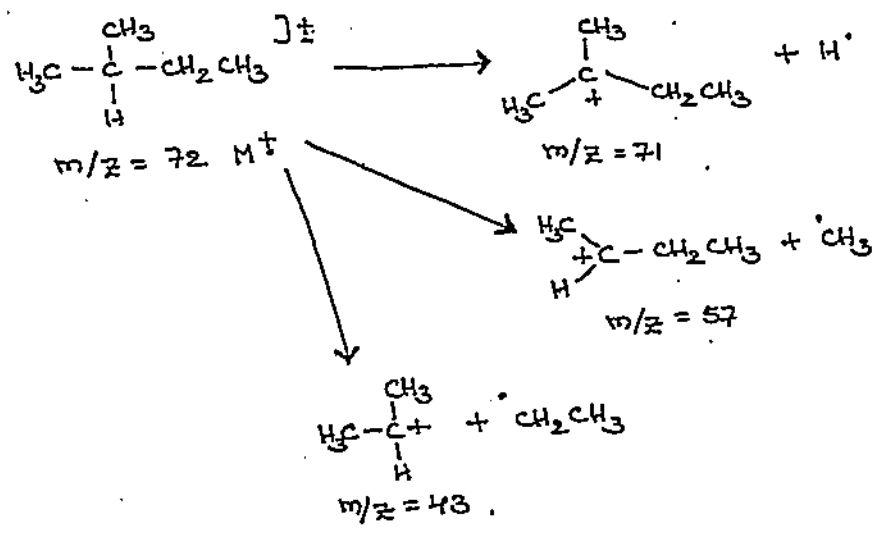
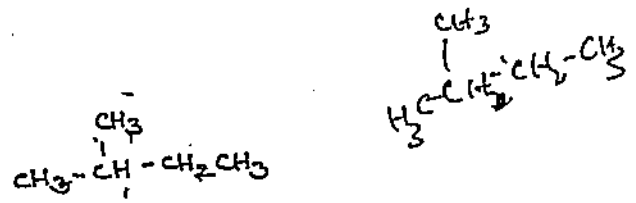
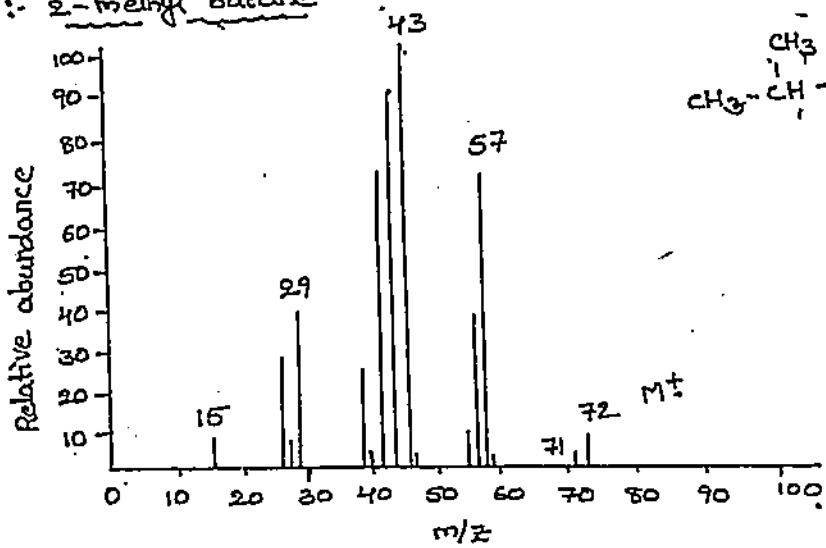
Eg :- n-pentane



Branched chain alkanes :-

- (i) Bond cleavage takes place preferably at the site of branching.
- Because a more stable secondary or tertiary carbonium ion is formed.
- (ii) Generally, largest substituent at a branch is eliminated readily as a radical.
- (iii) The relative abundance of the parent ion is least and is mostly not observed.
- (iv) Great number of fragments are resulted than straight chain compound due to greater pathways available for cleavage.
- (v) The signals corresponding to C_nH_{2n+1} ions follows weak signals, which appear two units below them.

Eg:- 2-methyl butane



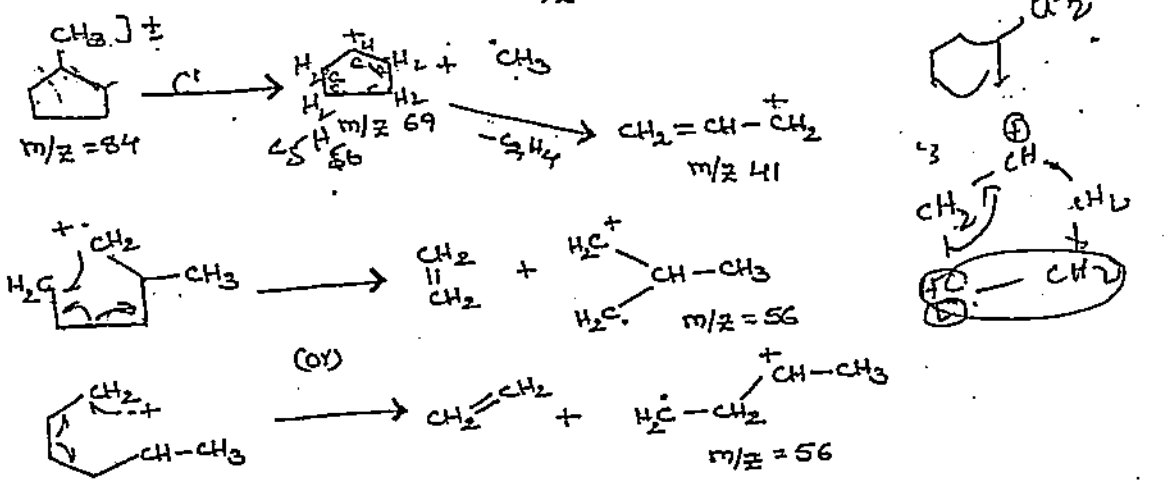
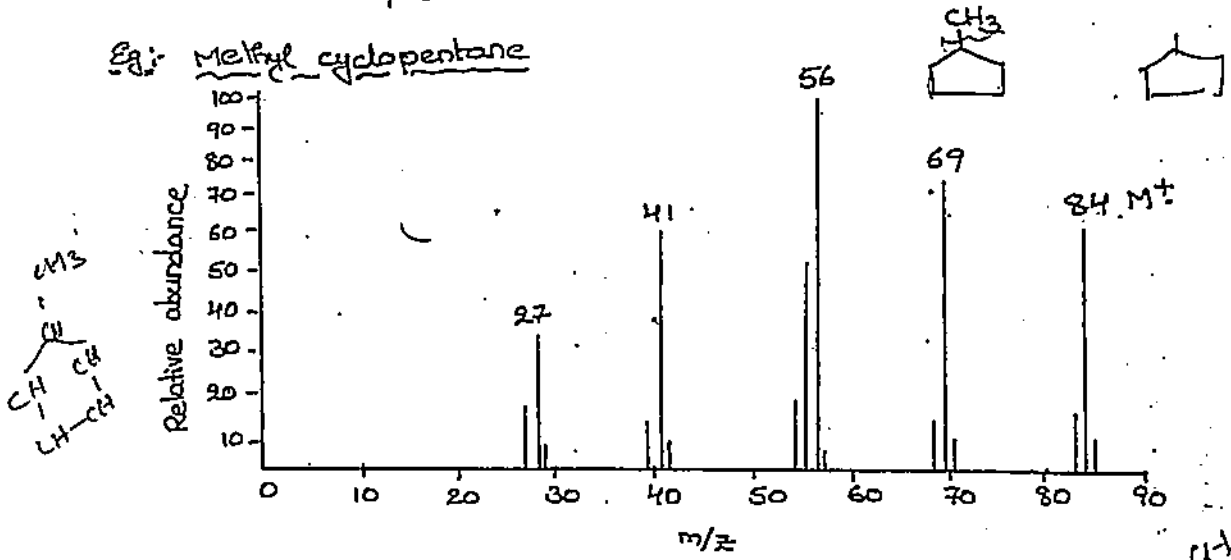
α-cleavage

(24)

Cycloalkanes :-

- (i) The relative abundance of the molecular ion is more as compared to corresponding alkane.
- (ii) It favours cleavage at the bond connecting the ring to the rest of the molecule.
- (iii) Fragmentation of ring is characterized by the loss of two carbon atoms as C_2H_4 (28 mass units) and $C_2H_5^+$ (29 mass units).

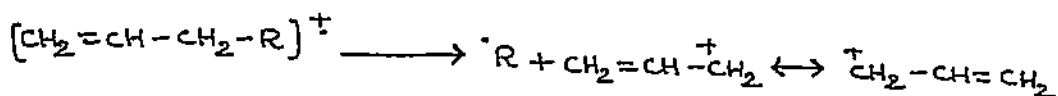
Eg: Methyl cyclopentane



Alkenes :-

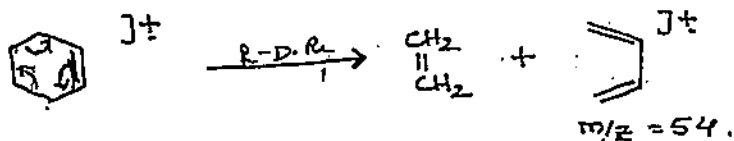
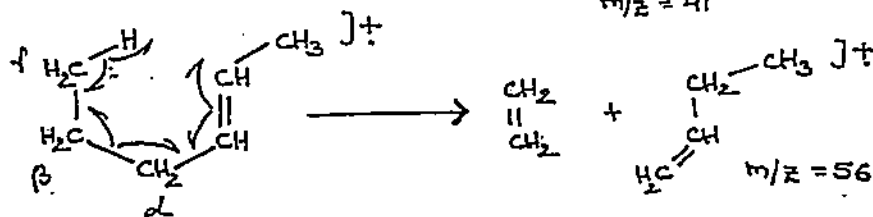
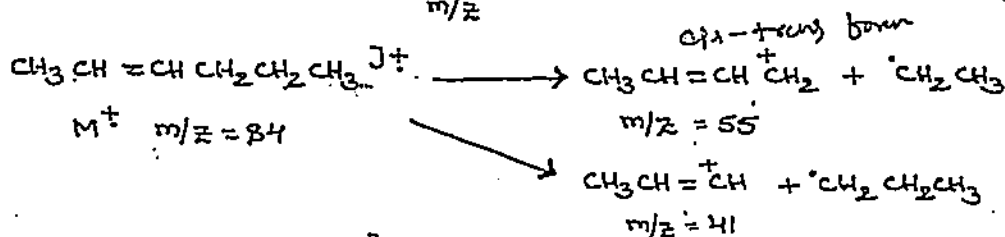
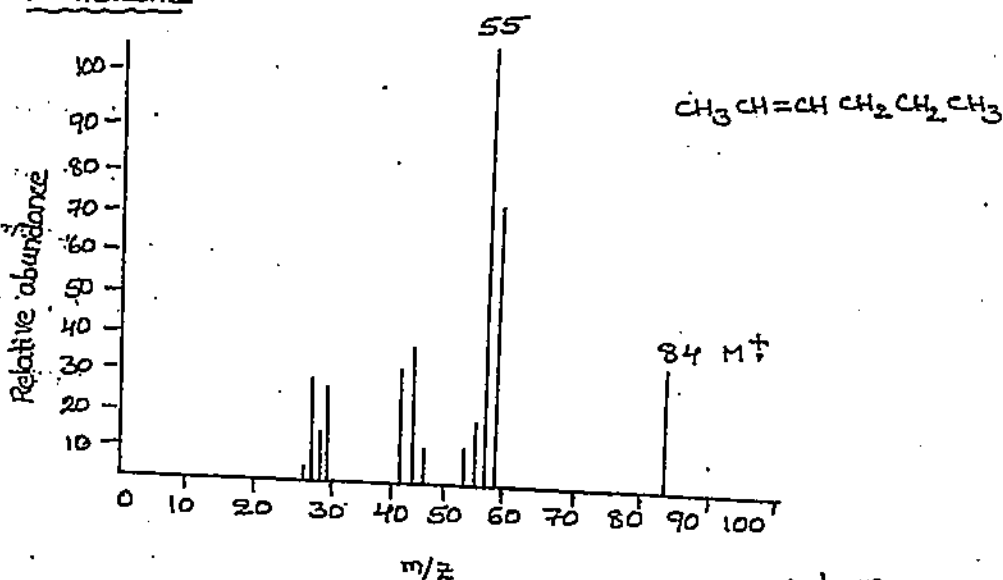
- (i) The molecular ion peak is more intense than the saturated hydrocarbons.
- (ii) The molecular ion of alkene containing one double bond tends to undergo allylic cleavage and gives resonance stabilized allylic cation.

(25)



- (ii) The acyclic olefins are also characterised by clusters of peaks at intervals of 14 mass units as in case of alkanes.
- (iii) When β -hydrogen is available Mc Lafferty rearrangement peak is observed.
- (iv) The mass spectra of alkenes containing one double bond are characterised by the presence of peaks at $\text{C}_n\text{H}_{2n-1}$ and at C_nH_{2n} . These peaks are more intense than $\text{C}_n\text{H}_{2n+1}$ peaks.
- (v) Cyclic olefins exhibit a Retro-Diels-Alder reaction.

Eg: 2-hexene



Alkynes :- The fragmentation pattern for alkynes, is very complex.

For 1-butyne and 2-butyne, the molecular ion peak is the base peak.

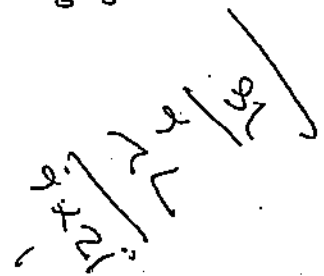
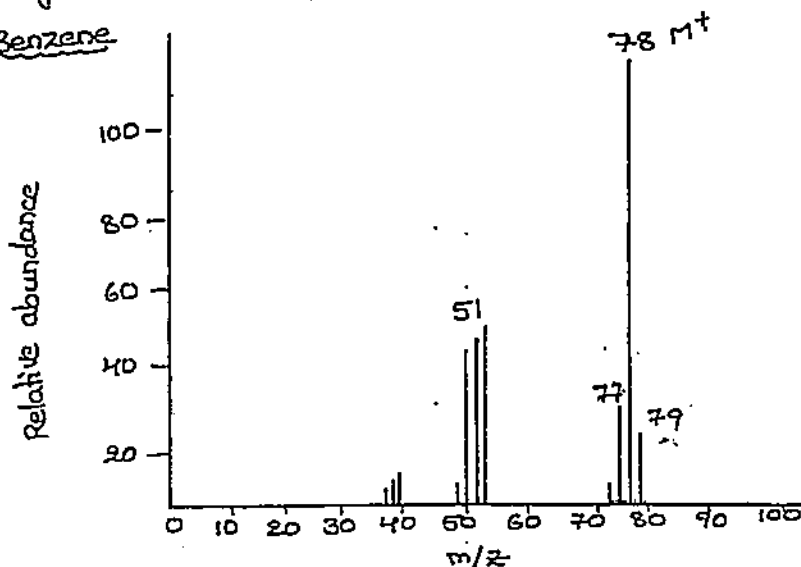
The relative abundance of the molecular ion peak decreases as the molecular mass of the alkyne increases.

In alkynes, the fragment ions are generally formed by the loss of alkyl radicals. Thus $M-15$, $M-29$ etc.

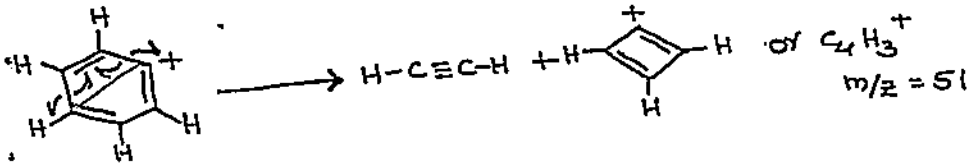
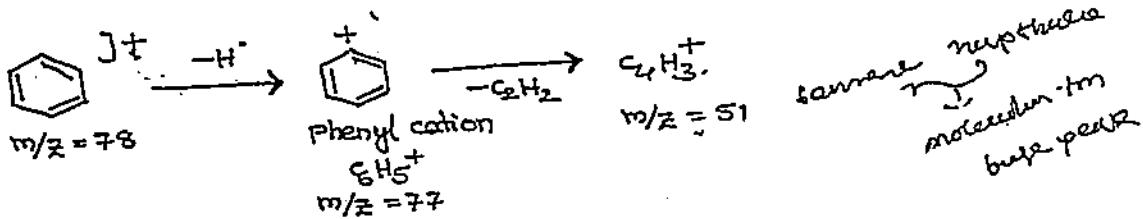
Aromatic compounds :-

- (i) An aromatic hydrocarbon generally show a prominent molecular ion peak as compared to the alkenes and alkanes containing the same number of carbon atoms due to the stabilizing effect of the ring.
- (ii) In benzene and naphthalene molecular ion peak is the base peak.
- (iii) The molecular ion peak is accompanied by small isotopic ($M+1$) and ($M+2$) peaks.
- (iv) Alkyl substituted aromatic compound undergo β -cleavage in the side chain and give resonance stabilized benzyl cation or tropylium ion. A prominent peak at $m/z = 91$ indicates the presence of an alkyl substituted benzene ring.
- (v) The frequently observed peaks at m/z 65 and at m/z 51 are results from the elimination of acetylene molecule from tropylium ion and phenyl cation respectively.
- (vi) Aromatic compounds with alkyl groups having a chain with γ -hydrogen undergoes Mc Lafferty rearrangement.

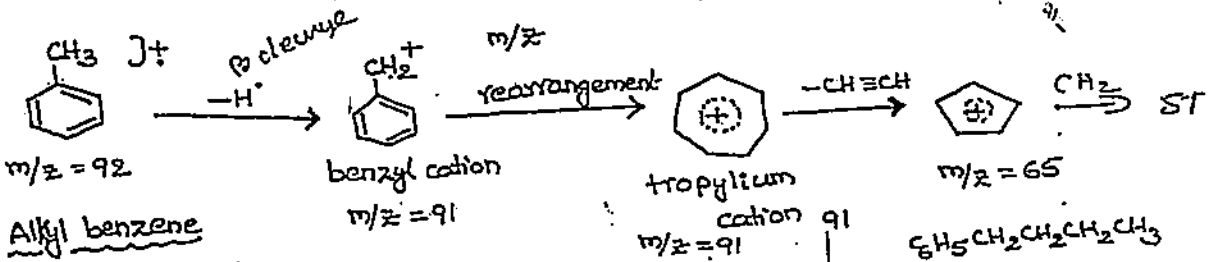
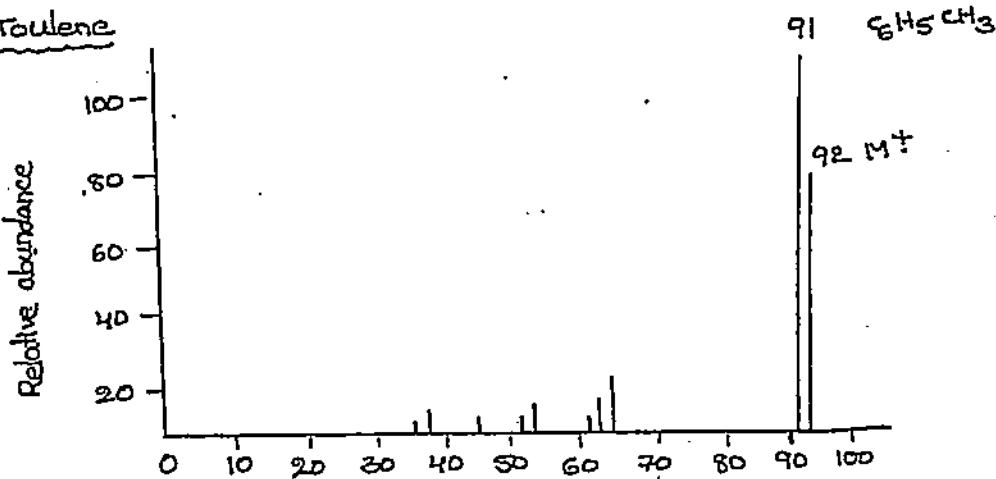
Eg: Benzene



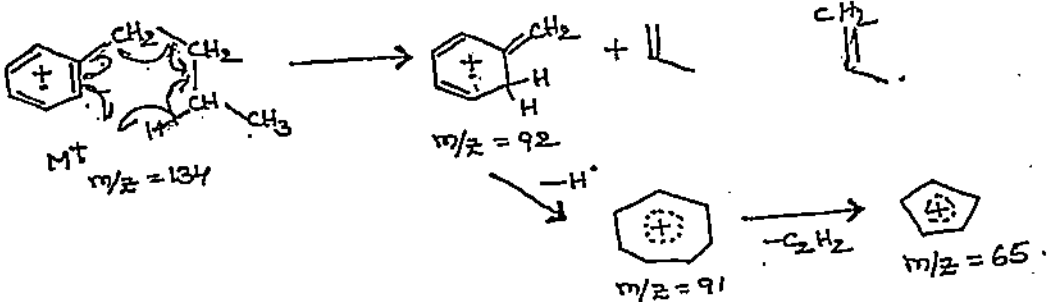
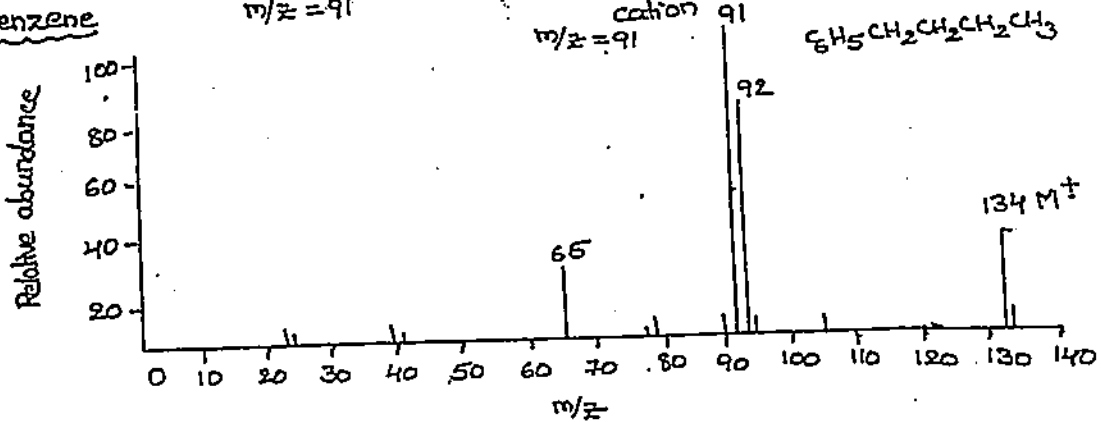
(27)



Ex: Toluene



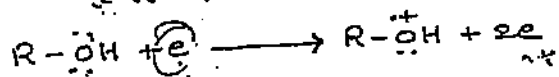
Ex: Alkyl benzene



Alcohols:-

(i) The molecular ion peak for primary or secondary alcohol is quite small and for a tertiary alcohol, it is not detectable.

(ii) The molecular ion is formed as a result of removal of one electron from the lone pair on oxygen atom of the alcohol.



(iii) Fragmentation made in alcohols is depends on the nature of the alcohol.

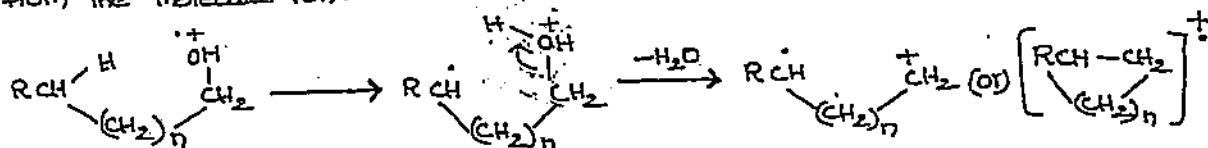
The cleavage of C-C bond next to oxygen atom, is of general occurrence.

primary alcohols show a prominent peak at $m/z = 31$ due to $CH_2 = \overset{+}{O}H$.

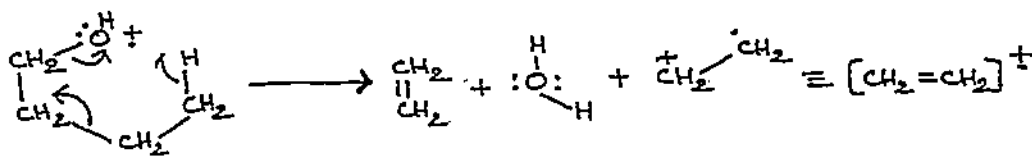
secondary and tertiary alcohols also undergo cleavage similarly to give prominent peaks due to $R-\overset{+}{C}H-OH$ ($m/z = 45, 59, 73$ etc) and $R-\overset{+}{C}H-OH$

($m/z = 59, 73, 87$ etc) respectively. Large substituent is more readily expelled.

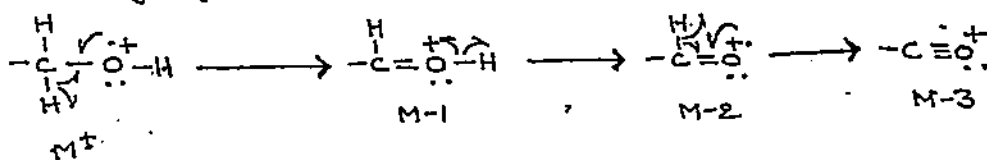
(iv) Primary alcohols give a distinct peak at ~~M-18~~ because of loss of H₂O from the molecular ion.



(v) The elimination of water, in addition with elimination of olefin from the primary alcohols having a four or more carbon atom chain indicates the presence of a peak at $M - (\text{olefin} + \text{water})$ at $m/z = 46; 74; \dots$ etc.



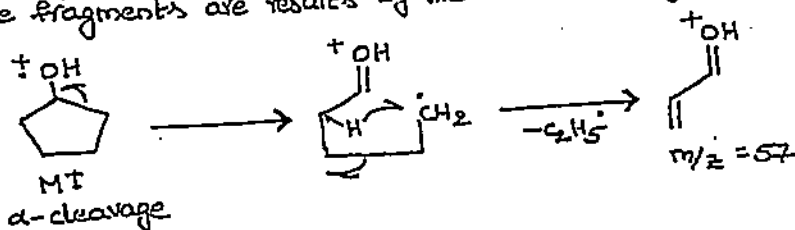
(vi) Alcohols also show peaks at $M-1$, $M-2$ and $M-3$ because of successive removal of hydrogen radicals.



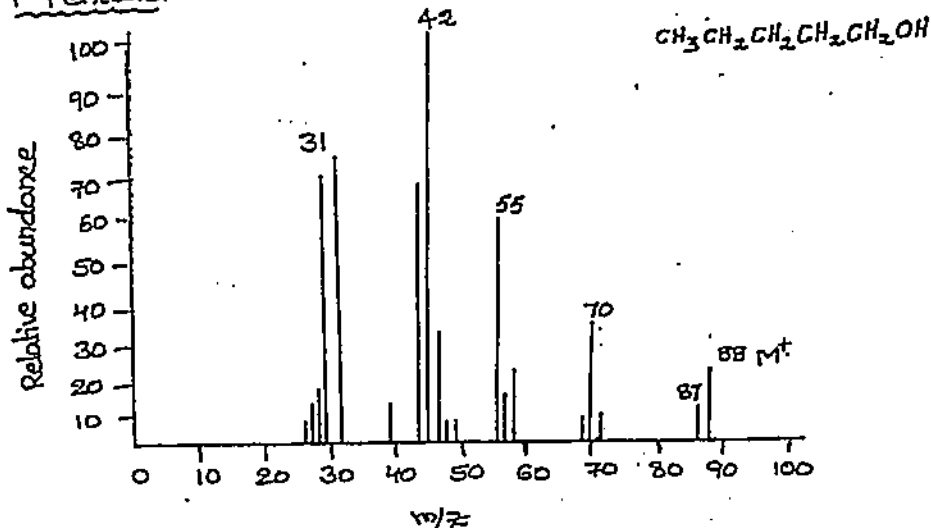
(VII) Alcohols containing branched methyl groups shows a strong peak at $M-33$ resulting from the loss of H_2O and CH_3 .

(VIII) In case of tertiary alcohol besides α -cleavage loss of OH takes place. i.e. tertiary butyl cation peak is observed.

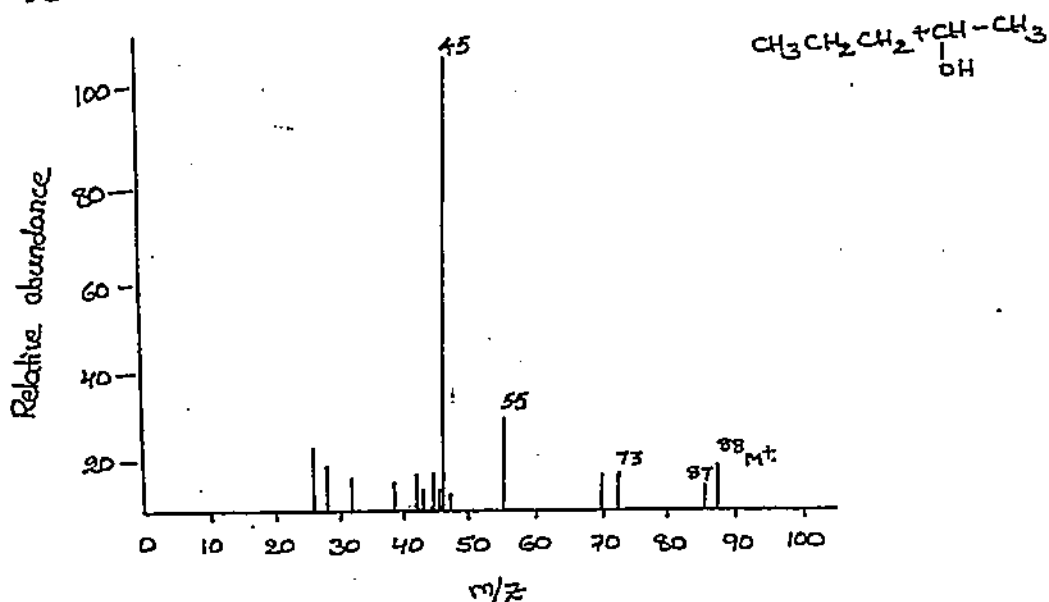
(ix) In the spectra of cyclic alcohol α -cleavage results in ring opening and the fragments are results by the loss of alkyl radicals.



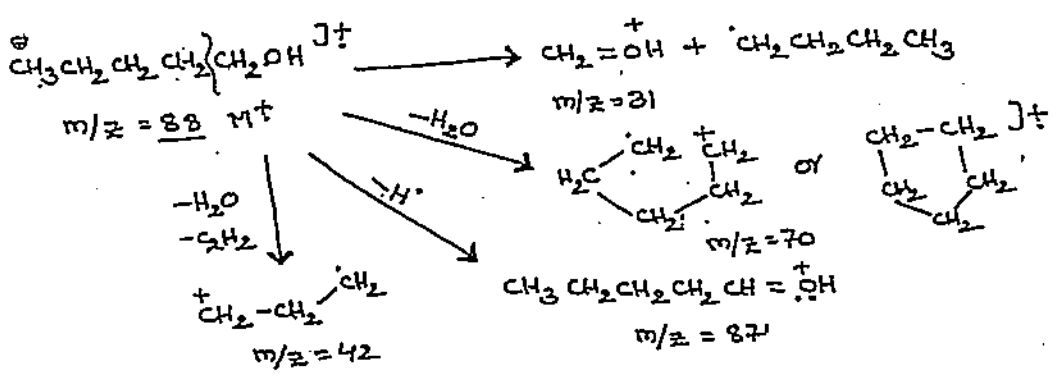
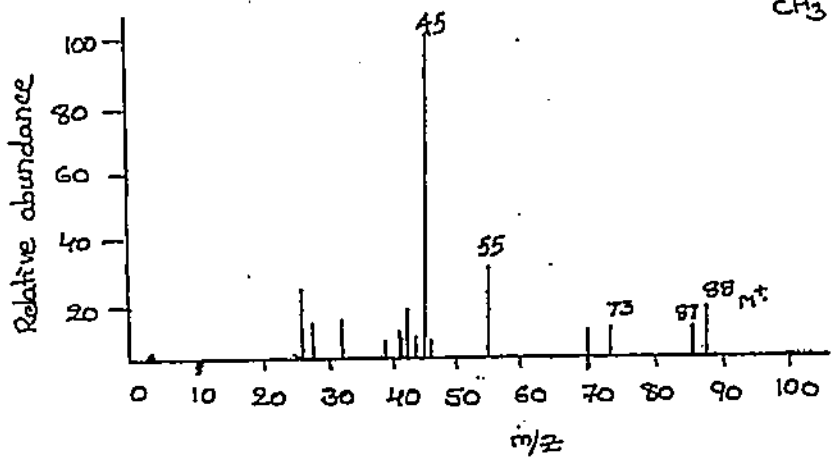
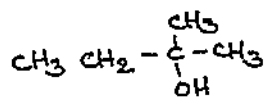
Eg:- 1-Pentanol



Eg:- 2-pentanol

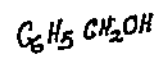


Eg: 2-Methyl-2-butanol

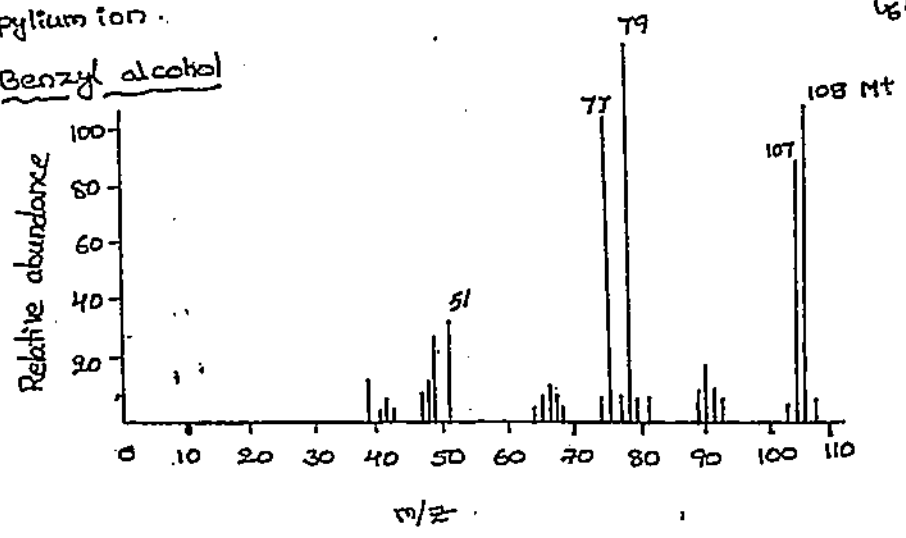


Aromatic alcohols :-

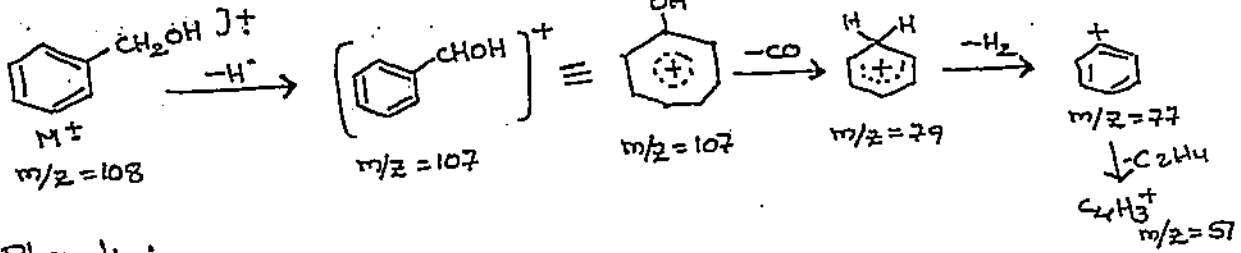
- (i) Aromatic alcohols show fairly intense molecular ion peaks.
- (ii) The fragment ion (M-H) further eliminates CO molecule.
- (iii) During fragmentation, benzyl alcohol can lose one, two and three hydrogen atoms.
- (iv) The M-H fragment of benzyl alcohol undergoes rearrangement to form hydroxy tropylium ion.



Eg: Benzyl alcohol



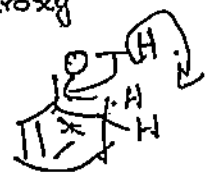
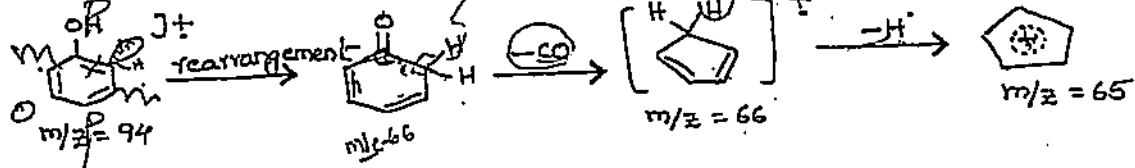
(3)



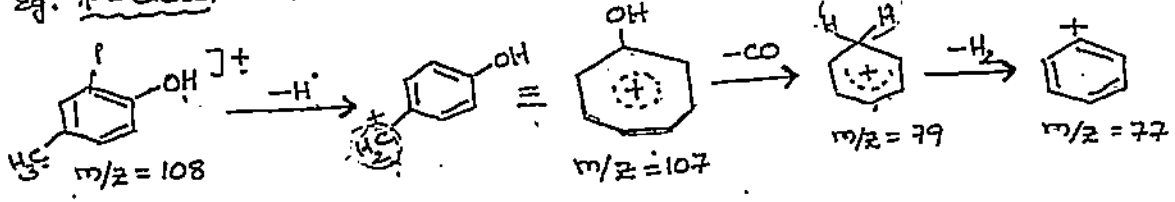
Phenols :-

- (i) The molecular ion peak is intense.
- (ii) The phenol itself the molecular ion peak is the base peak.
- (iii) The common fragmentation is loss of CO (M-28) and CHO (M-29).
- (iv) Phenols with alkyl side chain undergo benzylic fission to give hydroxy tropylium ion.

Eg: Phenol

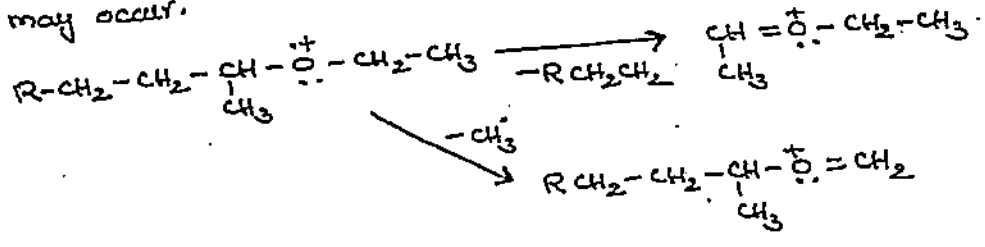


Eg: p-cresol

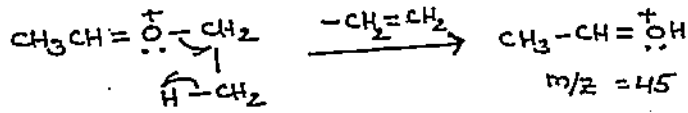


Ethers, Acetals and Ketals :-

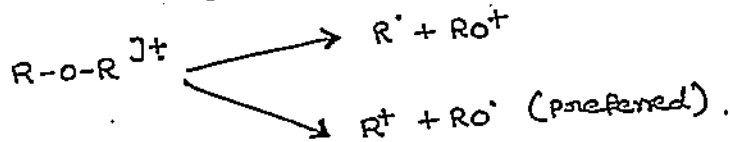
- (i) Their molecular ion peaks are weak.
- (ii) The presence of an oxygen atom can be known from the strong peaks at $m/z = 31, 45, 59, 73$..etc. and these represent the RO^+ and $ROCH_2^+$ fragments.
- (iii) Cleavage of the C-C bond next to the oxygen atom i.e. α -cleavage may occur.



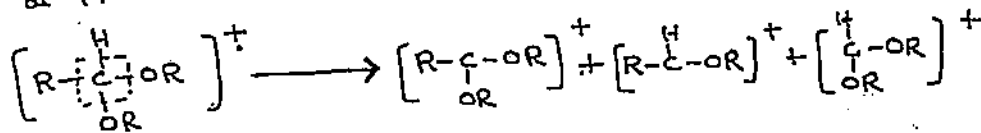
The ion thus produced may fragment further to eliminate an alkene when α -C is substituted and β -hydrogen is available.



(iv) C-O bond cleavage with the charge remaining on the alkoxy fragment.

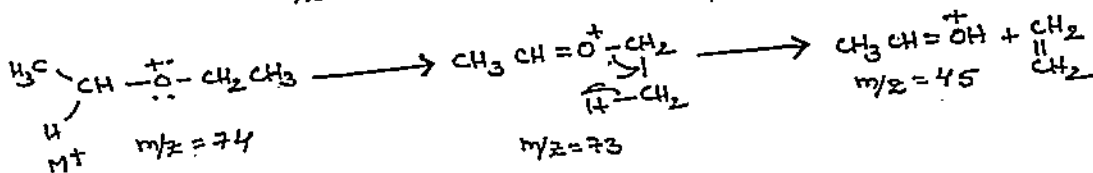
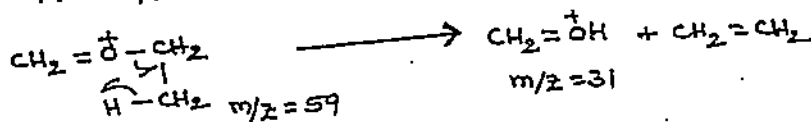
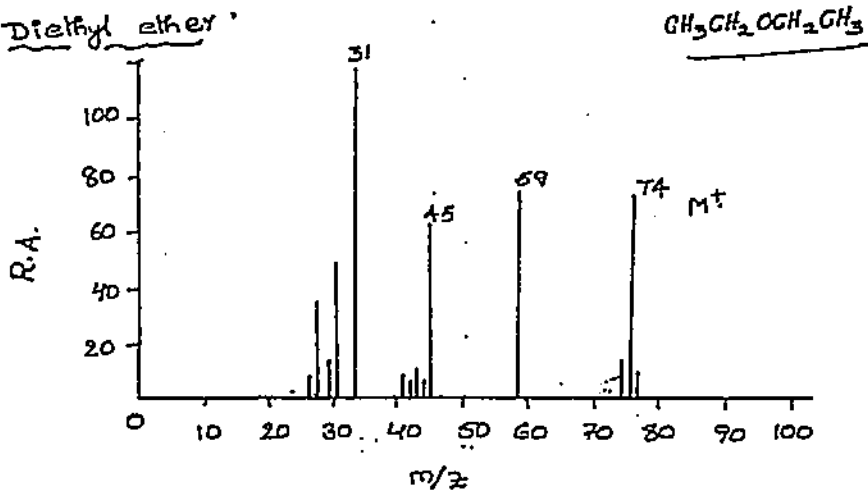


(v) Acetals exhibit prominent peaks at M-R and M-OR and a weak peak at M-H.



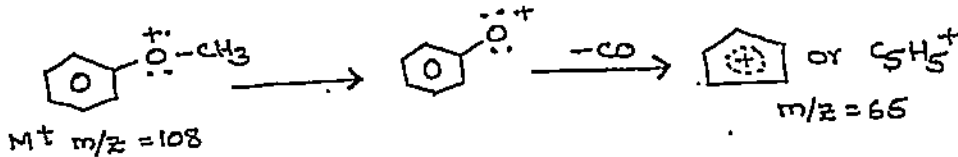
ketals behave similarly.

Eg:- Diethyl ether

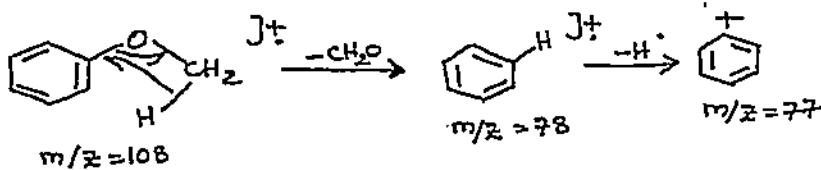


Aromatic Ethers :-

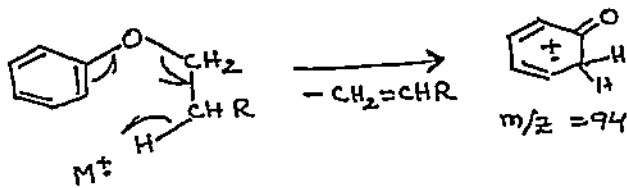
- (i) The molecular ion peak of aromatic ethers is prominent.
 (ii) The primary cleavage occurs at the bond β to the ring and thus formed ion decomposes further.



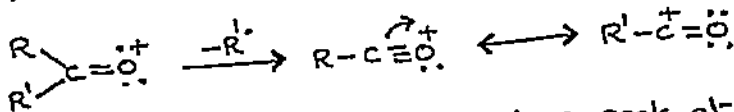
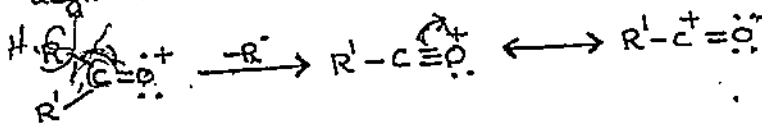
- (iii) The typical aromatic peaks are observed at m/z 78 and at m/z 77 by the loss of HCHO and H radical.



- (iv) In the case of aromatic ethers, when the alkyl group has two or more carbon atoms then fission β to the ring is accompanied by the migration of hydrogen with the elimination of alkene.

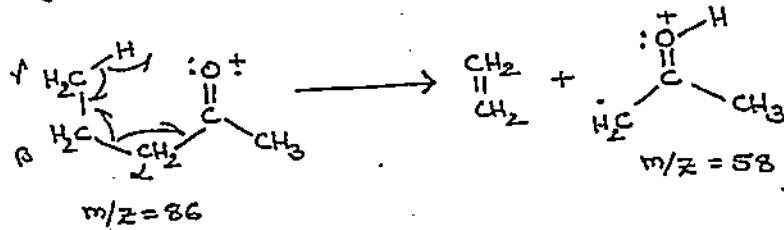
Ketones :-

- (i) The molecular ion peak is prominent.
 (ii) The fragmentation involves the fission of $\text{C}-\text{C}$ bonds adjacent to the oxygen atom. The charge remaining with the resonance stabilized acylium ion.

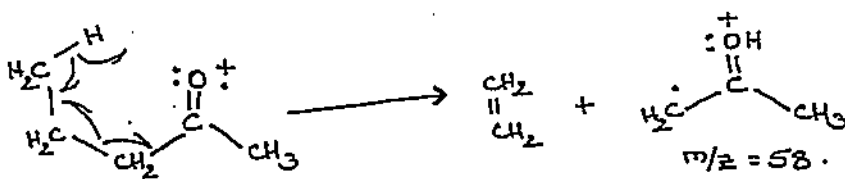
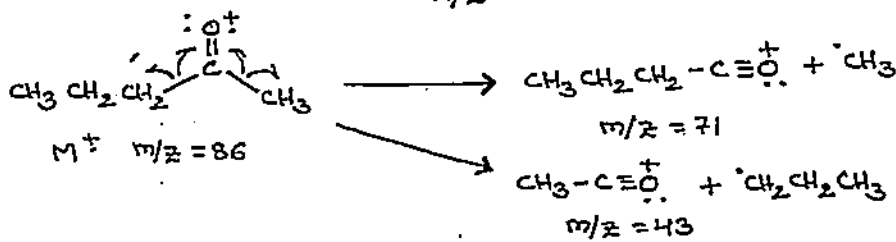
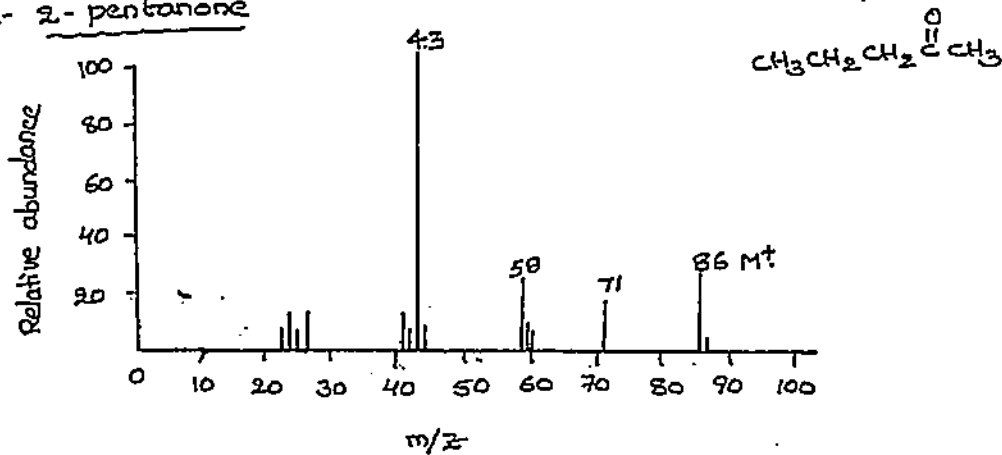


This cleavage gives rise to a peak at $m/z = 43, 57, 71$ etc. The base peak is resulted from this cleavage by the loss of larger alkyl group.

(ii) If one of the alkyl group attached to the carbonyl carbon has a β -hydrogen, Mc Lafferty rearrangement takes place.



Eg:- 2-pentanone

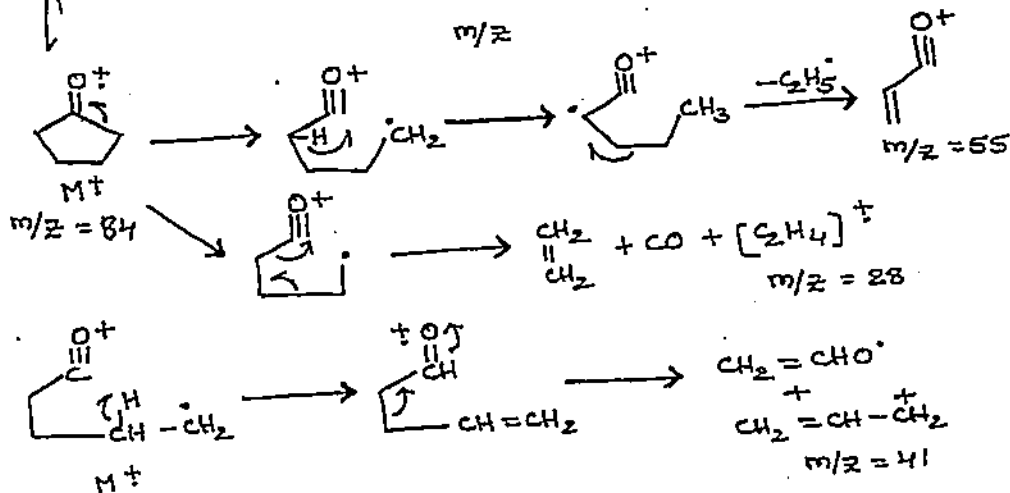
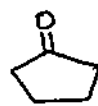
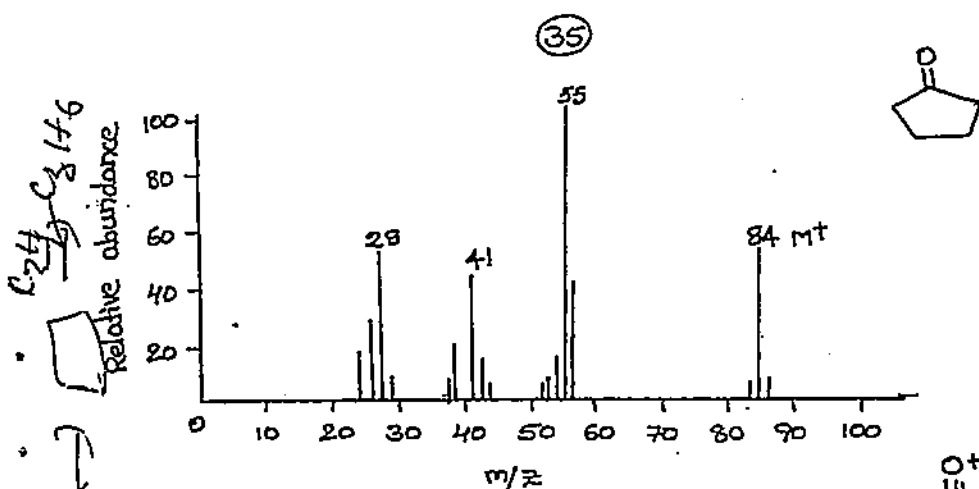
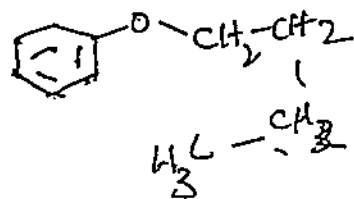


Cyclic Ketones :- (i) The molecular ion peak is prominent.

(ii) The primary cleavage is adjacent to the $C=O$ group which is followed by the hydrogen rearrangement takes place. The rearrangement is accompanied by the loss of alkyl radical to give the base peak.

Eg:- cyclopentanone

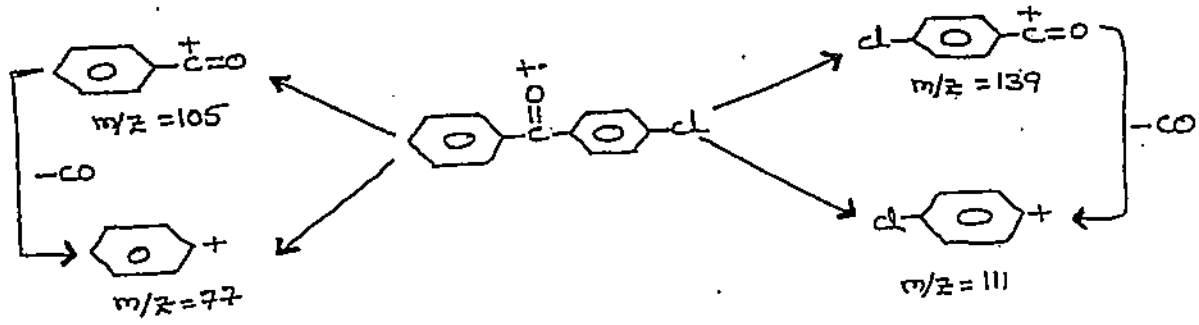
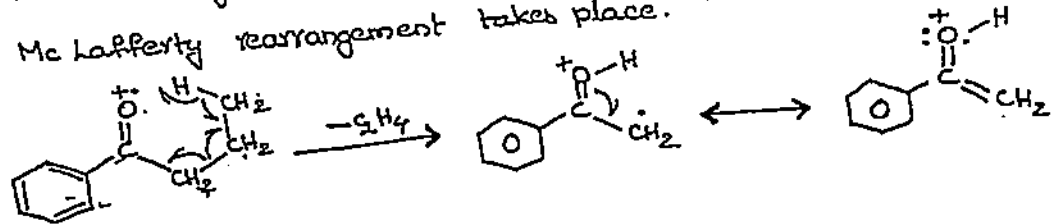
n-Butylphenyl Ether



Aromatic ketones :-

- (i) The molecular ion peak is prominent.
- (ii) The fragmentation is at the bond β to the ring gives a characteristic ArC=O⁺ ion, which is the base peak.
- (iii) Loss of CO from the ArC=O⁺ ion gives the aryl ion.
- (iv) When the alkyl chain is longer i.e. it contains β-hydrogen atom.

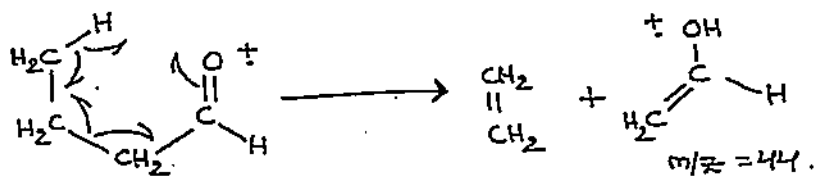
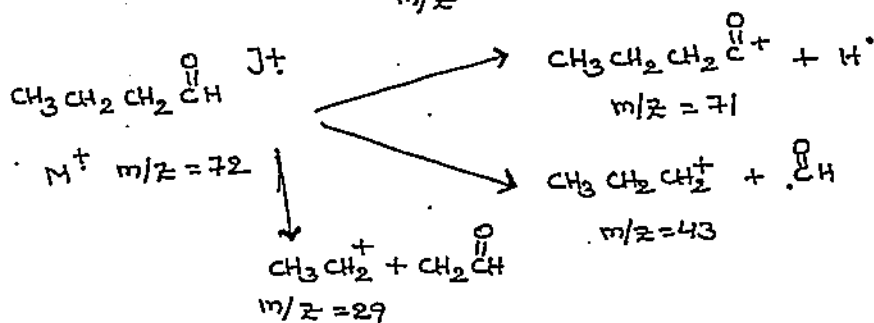
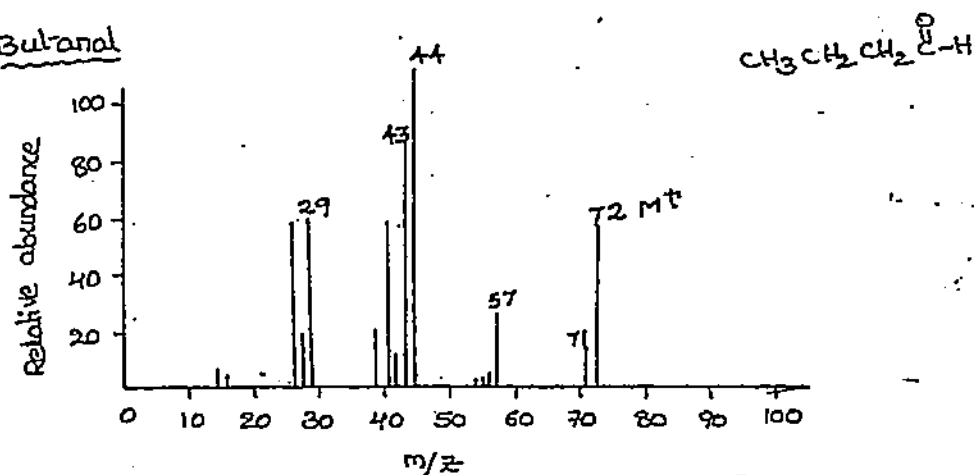
McLafferty rearrangement takes place.

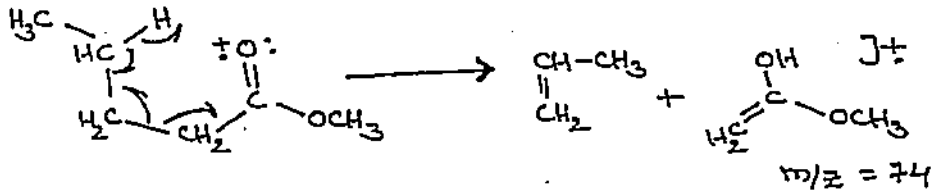
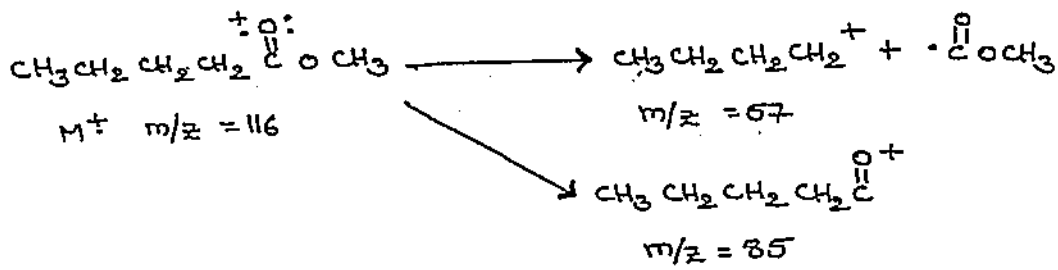


Aldehydes:-

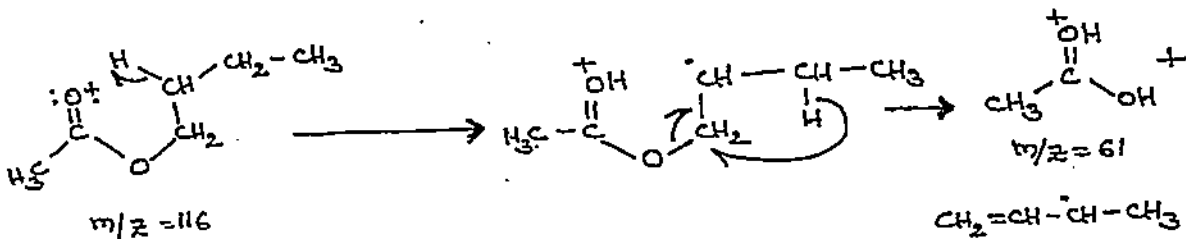
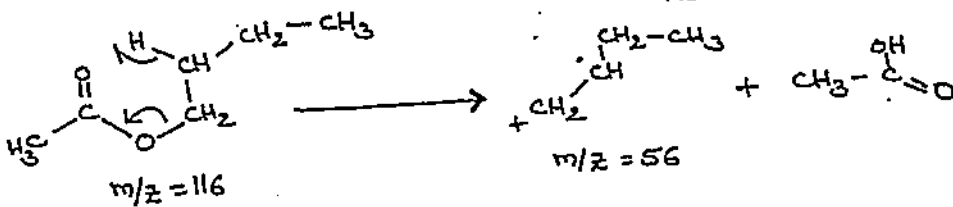
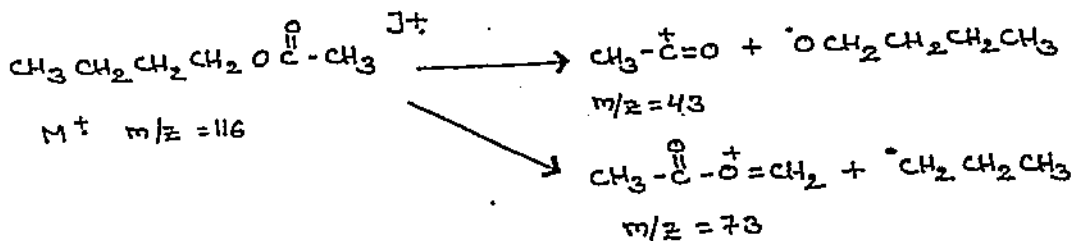
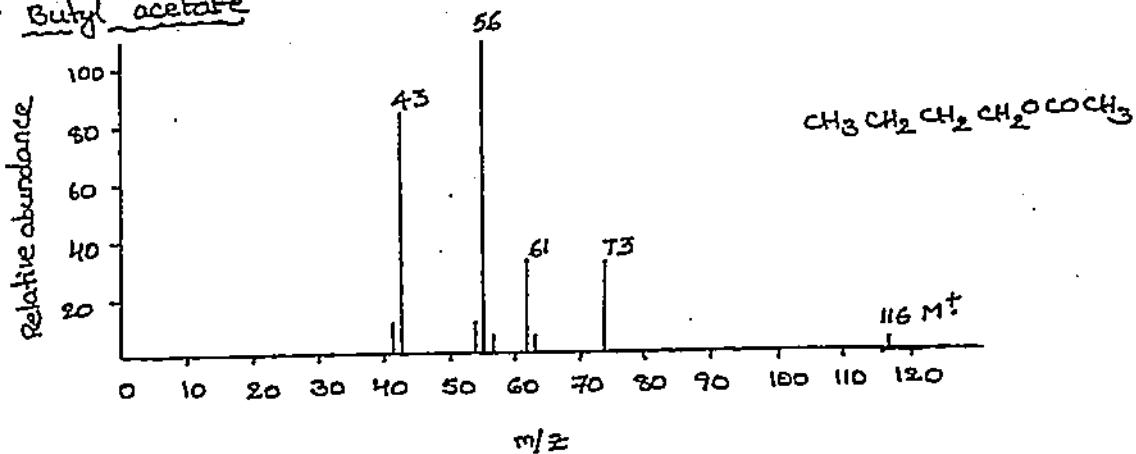
- (i) The molecular ion peak is of low intensity.
- (ii) The cleavage is adjacent to the oxygen i.e. C-H and C-C bonds results in M-1 peak and M-R peak.
- (iii) The M-1 peak is characteristic of aldehydes.
- (iv) When γ -hydrogen is available, Mc Lafferty rearrangement takes place.
- (v) In straight chain aldehydes, the other unique peaks are at M-18 (loss of water), M-28 (loss of ethylene), M-43 (loss of $\text{CH}_2=\text{CH}-\text{O}^\cdot$) and M-44 (loss of $\text{CH}_2=\text{CH}-\text{OH}$).

Eg:- Butanal



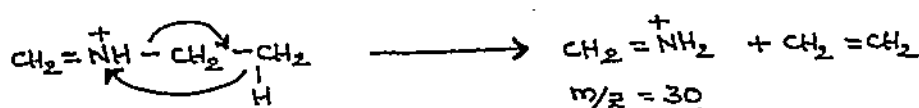


Eg:- Butyl acetate



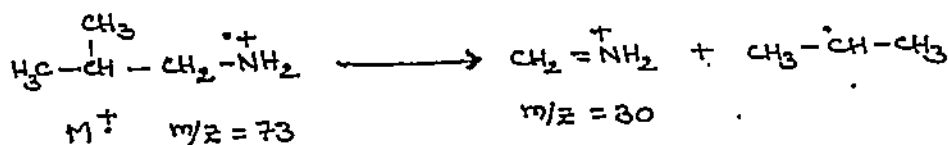
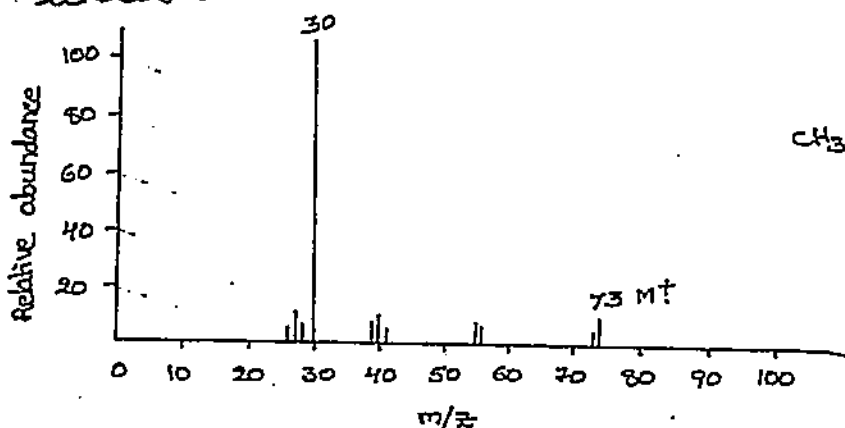
Aliphatic amines :-

- (i) The molecular ion peak is weak.
- (ii) The cleavage of C-C bond next to nitrogen is the characteristic fragmentation mode of amines. The base peak is resulted from this cleavage.
- (iii) For primary amines unbranched at α -carbon, the base peak is at $m/z = 30$.
- (iv) In case of α -substituted amines, loss of largest branch from the α -carbon is preferred.
- (v) The peak at $m/z = 30$ is not conclusive evidence for straight chain amines. The first formed ion in case of secondary amines or tertiary amines undergoes further decomposition gives $m/z = 30$ peak.



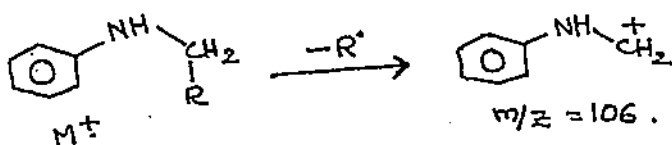
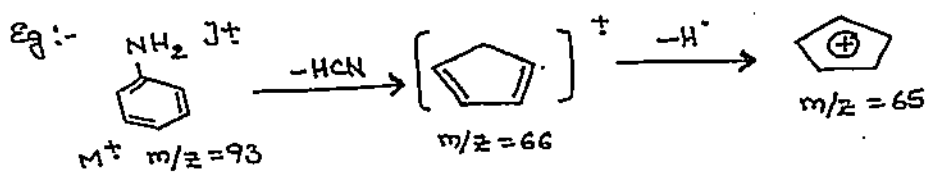
- (vi) Primary straight chain amines show a homologous series of peaks with retention of charge on the N-atom fragment.

Eg:- Iso butyl amine

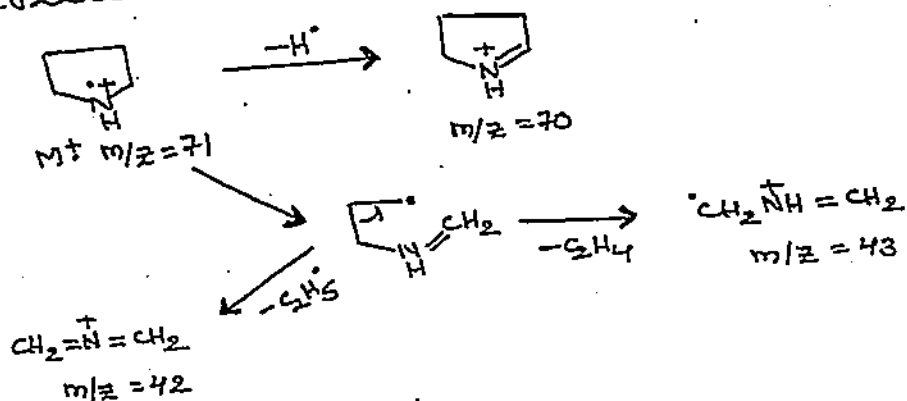


Aromatic amines: (Anilines)

- (i) The molecular ion peak is intense.
- (ii) The loss of one of the amino hydrogen atom gives an intense $M-1$ peak in aniline.
- (iii) Loss of HCN and subsequent loss of a hydrogen atom gives strong peaks at $m/z = 66$ and 65 .
- (iv) In case of alkyl aryl amines, fission of the C-C bond next to the nitrogen atom is predominant.

Cyclic amines:-

- (i) The molecular ion peak is intense.
- (ii) Primary cleavage at the bonds next to N atom leads either loss of α -hydrogen atom to give a strong $M-1$ peak or to opening the ring.
- (iii) The ring opening is followed by the elimination of ethylene gives the base peak.

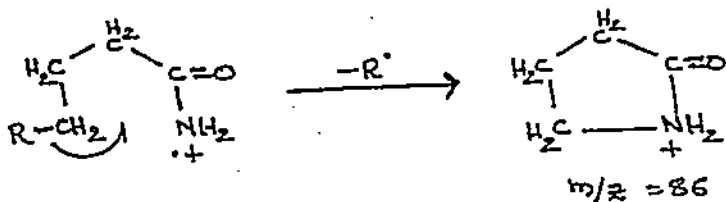
Eg:- Pyrrolidine.

Amides :- (i) The molecular ion peak of straight chain amides is

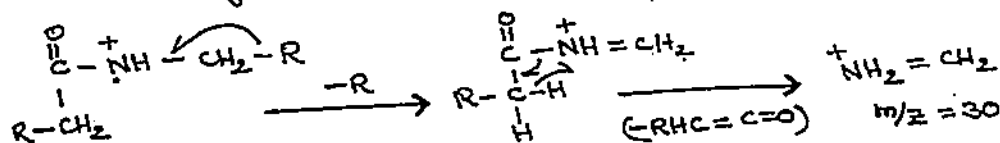
(ii) When β -hydrogen is available McLafferty rearrangement takes place. The base peak in straight chain primary amides higher than propanamide is results from this rearrangement.

(iii) Primary amides (C_1-C_3) gives a strong peak at $m/z = 44$. This is the base peak.

(iv) A moderate peak at $m/z = 86$ results from γ, δ C-C cleavage accompanied by cyclization.

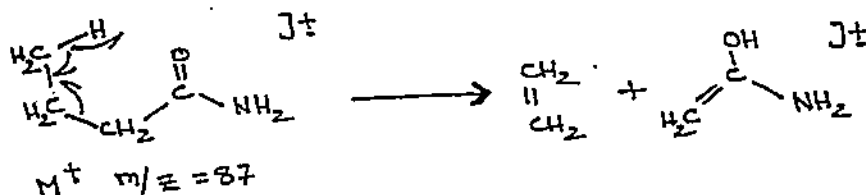
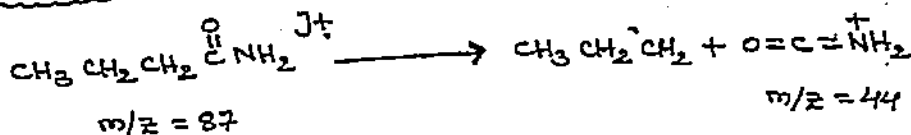


(v) When the N-alkyl groups are C_2 or longer and the acyl moiety is shorter than C_3 another mode of cleavage is predominant. This is the cleavage of the N-alkyl group β to the N-atom and cleavage of the carbonyl C-N bond with migration of an α -hydrogen atom to the acyl moiety.



(vi) Aromatic amide (Eg. benzamide) shows the characteristic peaks at $m/z = 105, 77$ and 44 .

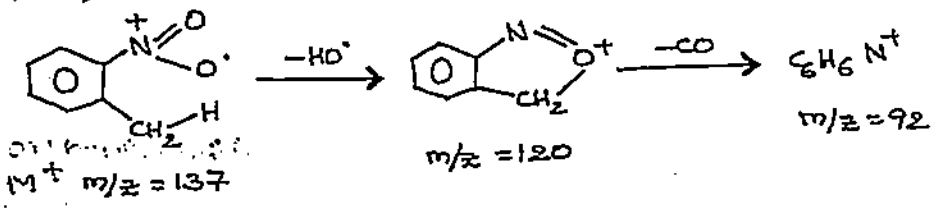
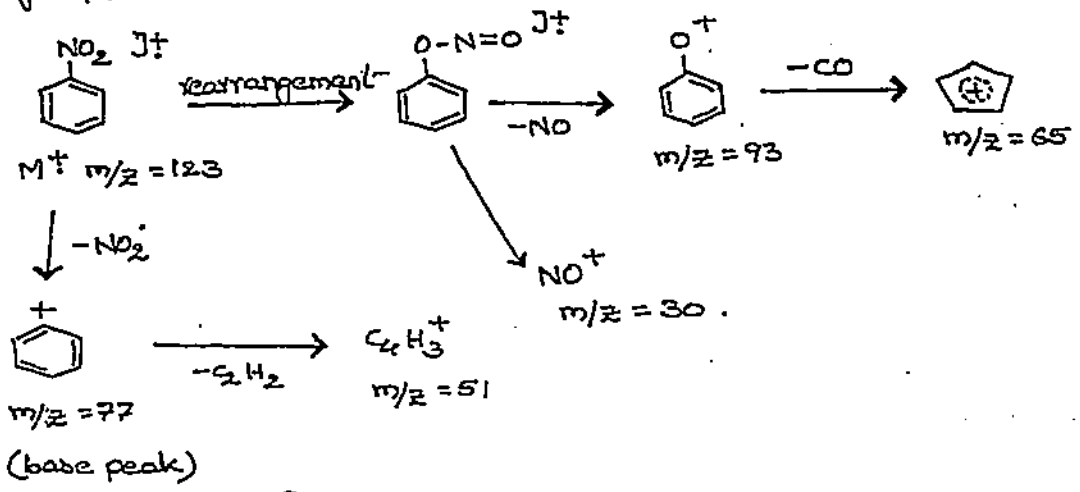
Eg:- butanamide





Nitro compounds :-

- (i) The molecular ion peak in aliphatic nitro compounds is absent, but it is prominent in aromatic compounds.
- (ii) In aliphatic compounds, the signals due to NO^+ and NO_2^+ are observed.
- (iii) In aromatic compounds, the signals due to NO^+ , NO_2^+ , $(\text{M}-\text{NO})$, $(\text{M}-\text{NO}_2)$ are observed.
- (iv) If a hydrogen containing group is also present ortho to the ring group, then $(\text{M}-\text{OH})$ peak is also observed.



Halogen Compounds :-

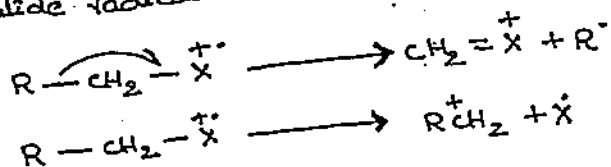
- (i) The molecular ion abundance of a particular alkyl halide increases as the electronegativity of the halogen substituent decreases.
- (ii) The relative abundance of the molecular ion decreases with increase in chain length and increase in branching.
- (iii) Compounds containing chlorine and bromine show characteristic isotope peaks. A compound containing one chlorine atom shows $\text{M}+2$ peak, which is one third in intensity of parent peak.

1:3
 $\text{Cl} = 35.5$
BT-89

(iv) A bromo compound shows $M+2$ peak, which is of the same intensity compared to the parent peak.

(v) In the parent ion, charge resides on the halogen atom.

(vi) Important fragmentation mode is α -cleavage with charge retention by the halogen containing fragment. Another mode leads to the loss of halide radical.



(vii) Aliphatic fluorine compounds show specific peak at $M-HF$ ($M-20$).

(viii) Aliphatic chlorine compounds show $M-36$ (loss of HCl^{35}) and $M-38$ (loss of HCl^{37}). HCl^+ peak may also appear at m/z 36 and 38.

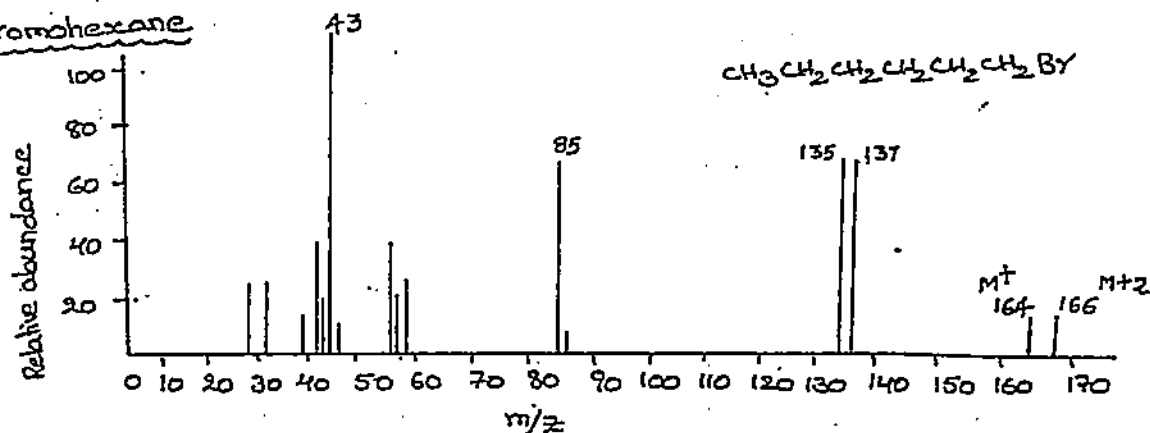
(ix) Loss of chlorine as Cl^+ gives low abundance peaks at m/z 35 and 37 and $M-35$ and $M-37$.

(x) Aliphatic bromine compounds show similar fragmentation as that of chlorine compounds, but loss of Br^+ is the preferred fragmentation.

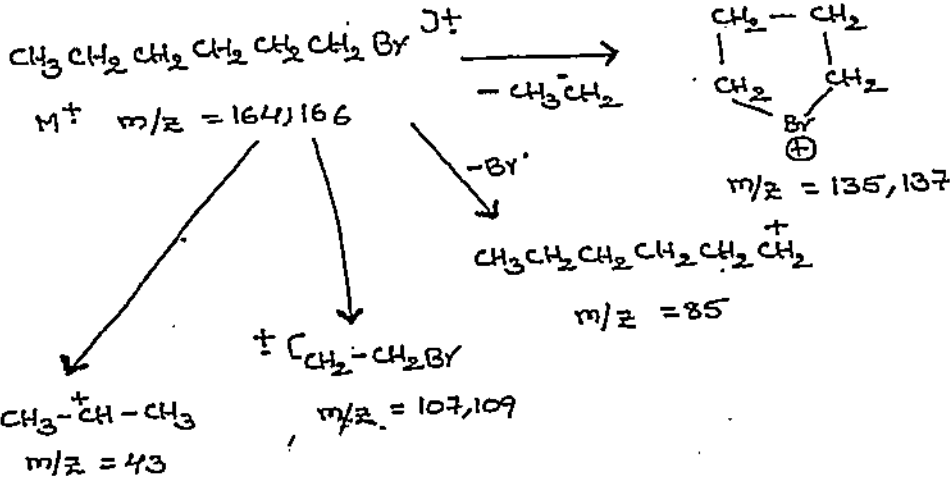
(xi) Aliphatic iodine compounds show peaks corresponding to I^+ (m/z 127), $M-I$ ($M-127$) and $M-\text{H}_2\text{I}$ ($M-129$).

(xii) Aryl halides large $M-X$ peak in which X attached directly to the ring.

Eg: 1-Bromohexane

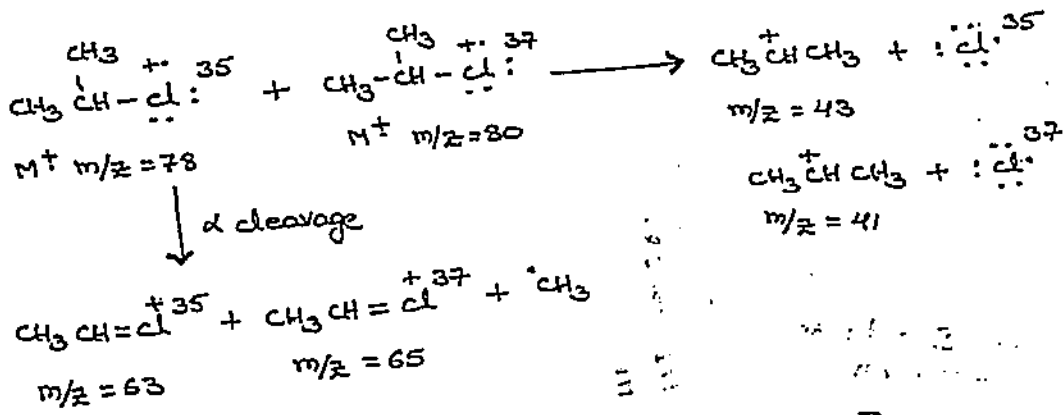
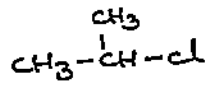
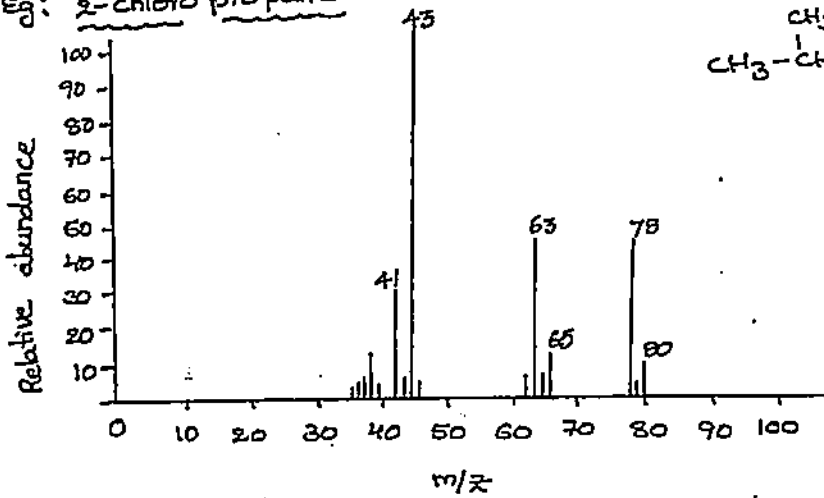


(17)



$\text{Cl} \rightarrow 35 \xrightarrow{+2} 37$
 $\text{Br} \rightarrow 79 \xrightarrow{+2} 81$

Eg: 2-chloro propane



90 78

$\bar{I} = 19$

Paper-I: Organic Spectroscopy-II (R22OC41)

UNIT - III



V.R.S. & Y.R.N. College, CHIRALA

M.Sc (Final), Semester -IV

UNIT-III, Two-Dimensional NMR Spectroscopy

A conventional ^1H NMR spectrum has a frequency axis and an intensity axis, 2D-NMR spectra has two frequency axis and one intensity axis.

The common 2D-spectra are ^1H - ^1H shift correlation in which both frequency axes show ^1H chemical shifts, which is known by the acronym COSY (Correlated Spectroscopy)

Two-dimensional NMR Leads to the development of chemical shifts into two dimensions and to resolve overlap of resonances which enables the correlation of interacting nuclei to be determined. 2D-NMR can thus be applied to complex spectra which are difficult to be analysed by conventional methods.

Two-dimensional NMR spectra which show ^{13}C - ^1H shift correlations are termed HETCOR (Hetero nuclear Correlation) spectra showing ^{13}C - ^{13}C shift correlations are called 2D- ^{13}C INADEQUATE these spectra identify directly bonded carbons. Other spectra involve the Nuclear Overhauser effect (NOESY for very larger molecules; ROESY for medium size molecules). They are employed to determine through space interactions.

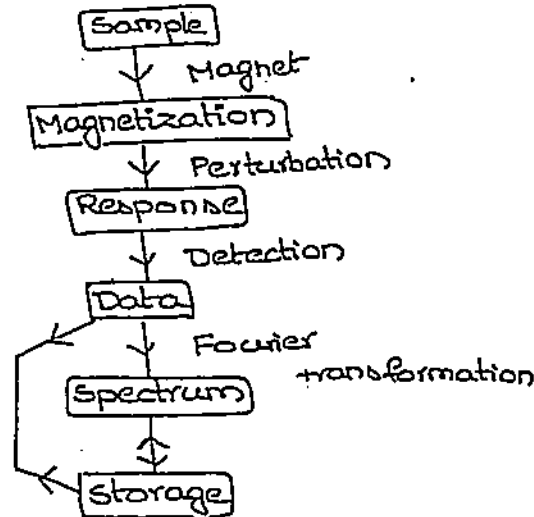
A two dimensional experiment is based on the principle that particular properties of the sample or its spin system can be examined by applying a pulse sequence in which the preparation period is followed by two or more pulses with intervening time intervals, the final pulse being the acquisition pulse. Thus an evolution period is inserted in between preparation and acquisition

(2)

period. Finally the signals are detected in the detection phase.

One-pulse experiment :-

The block diagram of one-pulse experiment is as follows



When a sample is placed in the magnet, the nuclei in the molecule generate a bulk macroscopic magnetization. We disturb the system from equilibrium with a pulse and then monitor the response of the system to the disturbance.

Pulsed NMR is different from most other forms of spectroscopy in that we measure this response rather than directly measuring the absorption or emission of energy. The monitoring process is most conveniently performed with suitable electronic devices which feed information to an on-line digital computer.

We examine first the origin of the magnetization which is induced in the sample by the applied static magnetic field. Once generated, this magnetization can be perturbed by a second field which is oscillating at an appropriate radio frequency; this perturbation of the magnetization generates the nuclear magnetic resonance spectrum.

③

In continuous wave spectroscopy, the disturbance of the magnetization is monitored as either the radio frequency is varied or the applied field is swept; in each case only a single frequency is excited and detected at any one point.

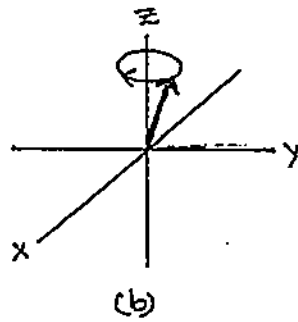
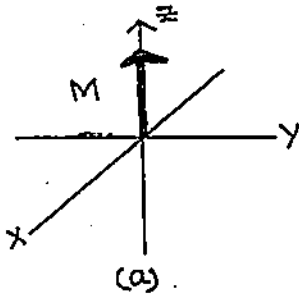
In Fourier transform spectroscopy, the entire spectrum of interesting frequencies is stimulated by a pulse of radio frequency energy and the response of the system is measured as a function of time using a digital computer. The frequency spectrum is generated mathematically in the computer using a Fourier transformation which converts the time domain data into the classical frequency domain spectrum.

The behaviour of the magnetization in a magnetic field can be conveniently described using vector diagrams. We shall discuss the bulk magnetization M , which is the sum of the magnetizations of the individual spins.

Initially, the bulk magnetization will be aligned with the applied field. (as in the figure a) and will remain there unless the system is disturbed in some way. We shall define the direction of the applied field as the z direction.

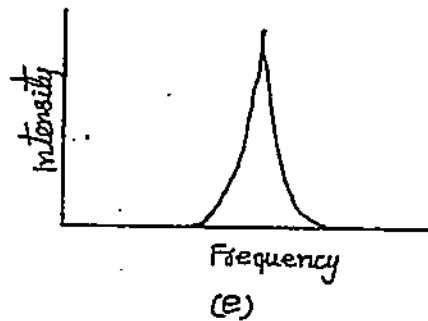
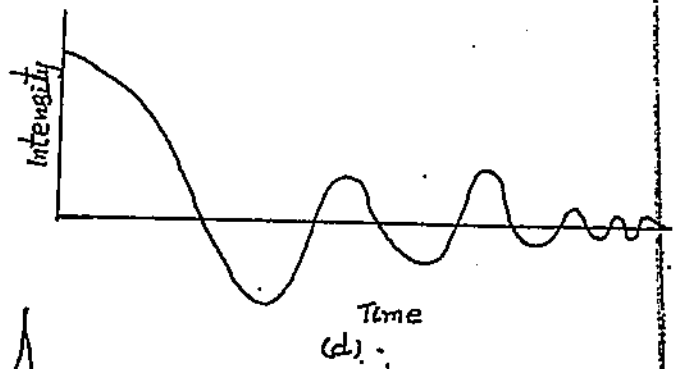
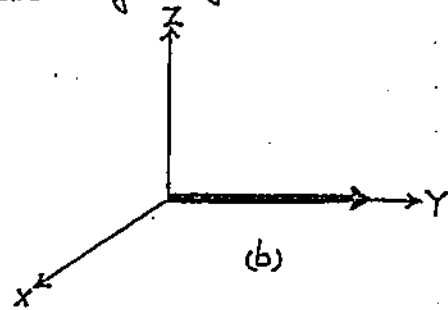
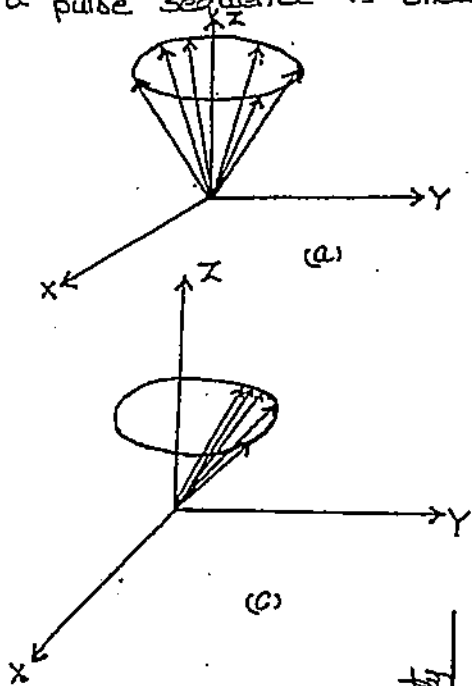
If we could somehow misalign the induced magnetization from the applied field there would be a force developed on M by B_0 . The force generated by B_0 on M will cause M to precess about B_0 (as in the figure b) at a frequency $\gamma B_0 / 2\pi \text{ Hz}$. This motion is known as Larmor precession.

(1)



There is a component of the precessing magnetization in the xy plane. If we were to wind a coil of wire around an axis perpendicular to the B_0 field, the precessing magnetization would induce an oscillating current in the coil. After suitable amplification and analysis, this current would be the NMR signal.

The behaviour of the magnetic moment vectors during a pulse sequence is shown in the following diagrams.



(5)

Figure (a) shows the magnetic moment vectors precessing around an external field in the z-direction. The vectors are randomly distributed around the external field. A 90° pulse is applied by means of a coil with the axis along x, all vectors have been aligned parallel to y (as in b).

After the pulse is terminated, the vectors spiral back towards their original situation (a). An intermediate stage is shown by figure (c). The signal observed by a coil with axis along the x direction (this can be the same coil used to generate the pulse) is shown in (d). Each group of equivalent nuclei leads to a signal similar to that shown but with its characteristic harmonic frequency. The signal received by the coil is the sum of all the signals. After Fourier transformation, the frequency domain signal appears as in (e).

Multiple - pulse Experiment :-

In the above experiment the equilibrium spin system is subjected to a single radio-frequency pulse before acquisition of an FID. The spectra obtained from this one-pulse experiment are equivalent to classical continuous wave spectra.

However with a modern pulse spectrometers we can do far more than simply obtain a spectrum. In which we examine the effects of multiple-pulse sequences and intervening delays on simple spin systems. In the first instance, we look at two methods which can be used to detect the rates at which magnetization returns to equilibrium after perturbation by a pulse.

⑥

At this stage, we discuss these methods purely for the purpose of illustrating how we can manipulate the spectrum. We then consider how population, chemical shift and coupling information, can be transferred between two coupled spins using suitable pulses.

The most common method of measuring spin-lattice relaxation rates is known as an inversion-recovery sequence. The experiment is conceptually simple and serves as a useful introduction to the idea that we can perturb the spin system from equilibrium, allow it to evolve after the perturbation and then detect what happened during the evolution period. In this case the evolution is the relaxation process.

The application of a pulse whose duration is long enough to rotate the magnetization through 180° or π radians, will invert the magnetization from its equilibrium value of M_0 to $-M_0$. As we have seen, this is referred to as a π pulse.

If the pulse is perfect, the magnetization becomes exactly $-M_0$, there is no xy magnetization and hence no signal will appear in the receiver coil; we cannot directly observe the effect of this π pulse. The magnetization will return from $-M_0$ to the equilibrium value of M_0 at the spin-lattice relaxation rate.

If we wish to monitor the relaxation of this magnetization, we must cause a component to appear in the xy plane. This is easily done with a $\pi/2$ pulse which will rotate any z magnetization into the xy plane, producing a signal amplitude A , which is proportional to the magnitude of the remaining z magnetization. This second pulse is a 'read' pulse which transfers information from the

(7)

z-direction, where it is not observable, into the xy plane, where we detect it. We now have a two-pulse sequence in which a π pulse and a $\pi/2$ pulse are separated by a delay over which we have control.

When dealing with more than one pulse in a sequence we have to extend the pulse sequence conventions.

First, the sequence can be written,

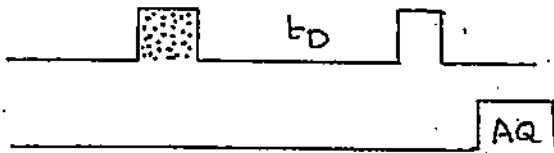
$$\pi - t_D - \pi/2 - \text{Acquire}$$

where, π is a π pulse

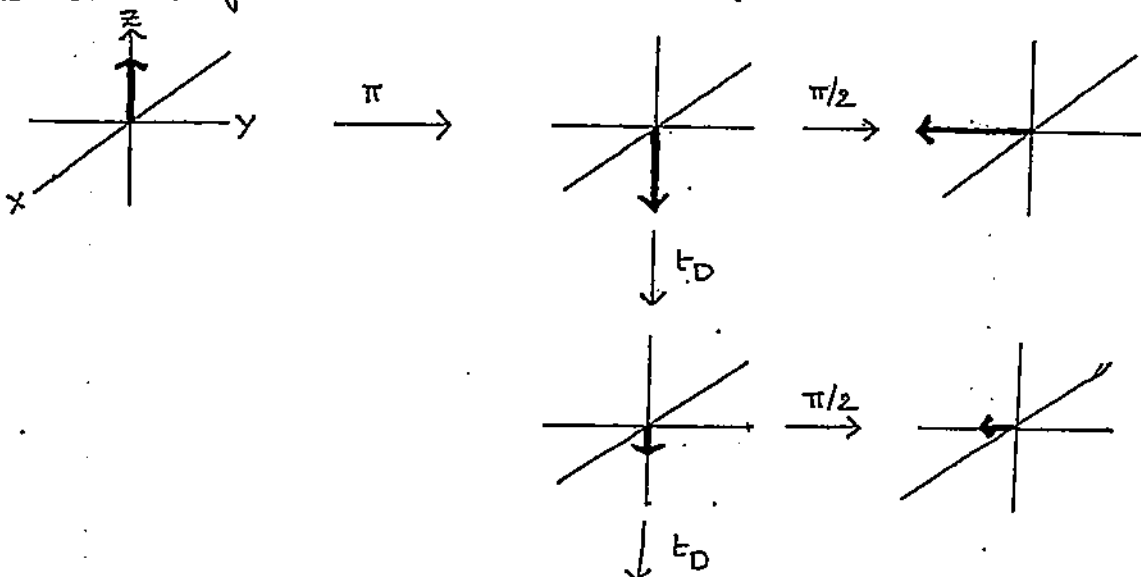
$\pi/2$ is a $\pi/2$ pulse

t_D is a delay which is under the control of the operator.

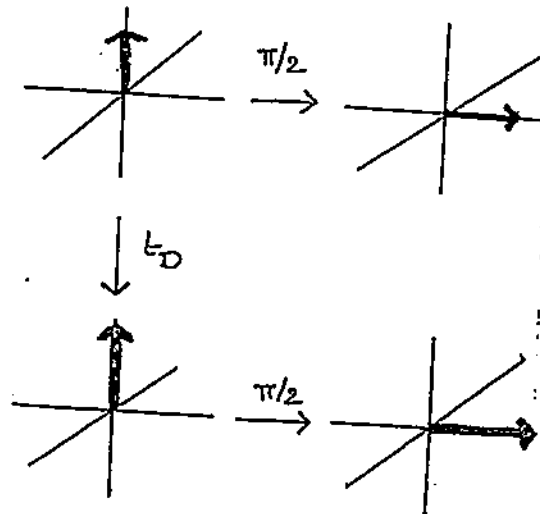
If it becomes necessary to change the relative phases of the pulses, a subscript on the pulse will indicate its phase. For example, $(\pi)_x$ and $(\pi)_{-x}$ are π pulses 180° out of phase with each other. The inversion-recovery pulse sequence is represented diagrammatically as follows.



The vector diagram for the inversion-recovery pulse sequence is as follows.



⑧



The magnetization is initially aligned along the z-axis and is inverted to $-z$ by the pulse. After a short delay, the magnetization will not have recovered to any significant extent and the $\pi/2$ pulse will rotate it to the $-y$ axis. The signal is inverted compared with the signal generated by a $\pi/2$ pulse on the equilibrium magnetization.

If in a separate experiment, we wait a little longer before applying the $\pi/2$ pulse, the magnetization would recover to a point just below the origin. Now a $\pi/2$ pulse will have the magnetization to the $-y$ axis, producing a smaller but inverted signal.

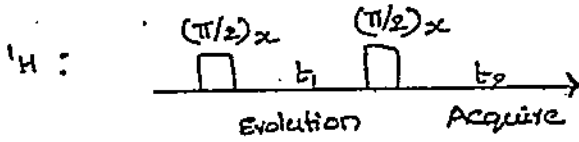
If we wait longer before applying the $\pi/2$ pulse the magnetization will pass through the origin so the $\pi/2$ pulse will generate $+y$ magnetization and a positive signal. If we wait long enough between the pulses, the magnetization will have recovered to its equilibrium value of M_0 .

9

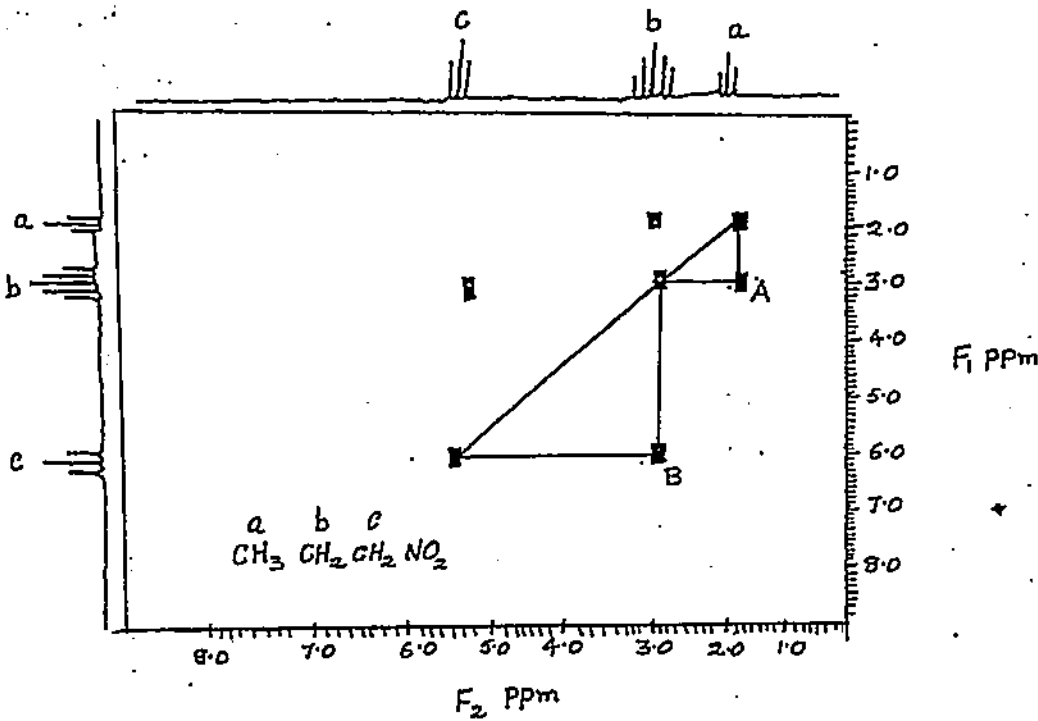
$^1\text{H}-^1\text{H}$ COSY (HOMCOR) :-

The 2D-NMR spectra that show $^1\text{H}-^1\text{H}$ shift correlations is called $^1\text{H}-^1\text{H}$ COSY or HOMCOR.

The basic pulse sequence is



The HOMCOR spectrum of *n*-nitro propane is



The usual one-dimensional ^1H NMR spectrum is plotted on both the x and y axes. To analyse the spectrum, a diagonal is drawn through the dots (peaks) that bisect the spectrum. The dots that are not on the diagonal (A, B) are called cross peaks.

Cross peaks indicates pairs of protons that are splitting each other. For example, if we start at the cross peak labeled A and a straight line is drawn parallel to the y -axis back to the

diagonal, we hit the dot on the diagonal at ~ 2.0 ppm produced by the H_a protons.

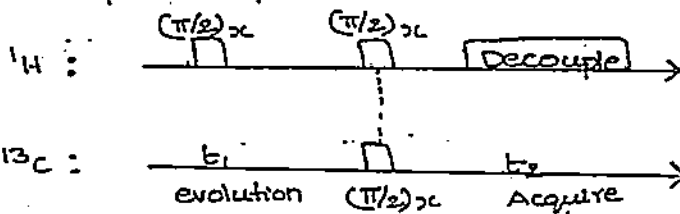
If we then go back to A and draw a straight line parallel to the x-axis back to the diagonal, we hit the dot on the diagonal at ~ 3.0 ppm produced by the H_b protons. This means the cross peak A shows that the H_a and H_b protons are coupled.

If we then go to the cross peak labeled B and draw two perpendicular lines back to the diagonal, we see that H_b and H_c protons are coupled. Notice that we used only cross peaks below the diagonal. The cross peaks above the diagonal give the same information.

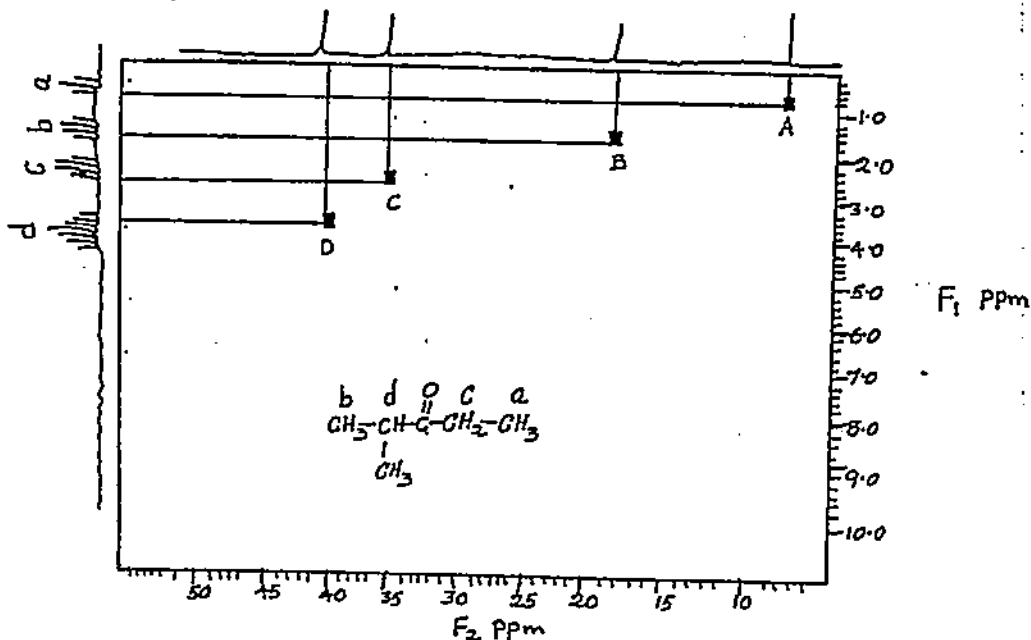
1H - ^{13}C COSY (HETCOR) : 2^{nd}

2-D NMR spectra that show ^{13}C - 1H shift correlations are called HETCOR spectra. HETCOR spectra indicate coupling between protons and the carbon to which they are attached.

The pulse sequence for HETCOR



The HETCOR spectrum of 2-methyl-3-pentanone is



(11)

The ^{13}C spectrum is shown on the x-axis and the ^1H NMR spectrum is shown on the y-axis. In which there is no diagonal. The cross peaks in a HETCOR spectrum identify which hydrogens are attached to which carbons.

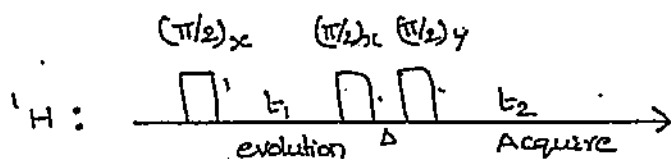
Cross peak A indicates that the hydrogens that show a signal at ~ 0.9 ppm in the ^1H NMR spectrum are bonded to the carbon that shows a signal at ~ 6 ppm in the ^{13}C NMR spectrum.

Cross peak B indicates that the hydrogens that show a signal at ~ 1.0 ppm are bonded to the carbon that shows a signal at ~ 19 ppm. Similarly cross peaks c and d show which hydrogens are attached to which carbons.

Double-Quantum Filtered ^1H - ^1H COSY (DQF COSY) :-

Simply by adding a third $\pi/2$ pulse immediately following the second $\pi/2$ pulse in our simple COSY pulse sequence and there is no change, that gives the DQF ^1H - ^1H COSY experiment. The purpose of the third $\pi/2$ pulse is to remove or filter single quantum transitions, so that only double quantum or higher transitions are present.

The pulse sequence for DQF COSY is

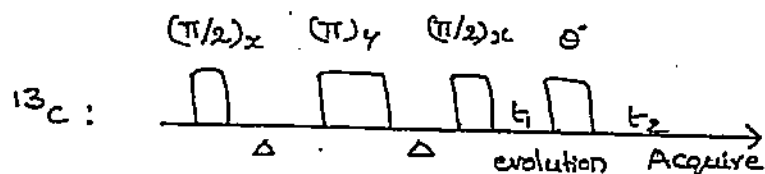


INADEQUATE :-

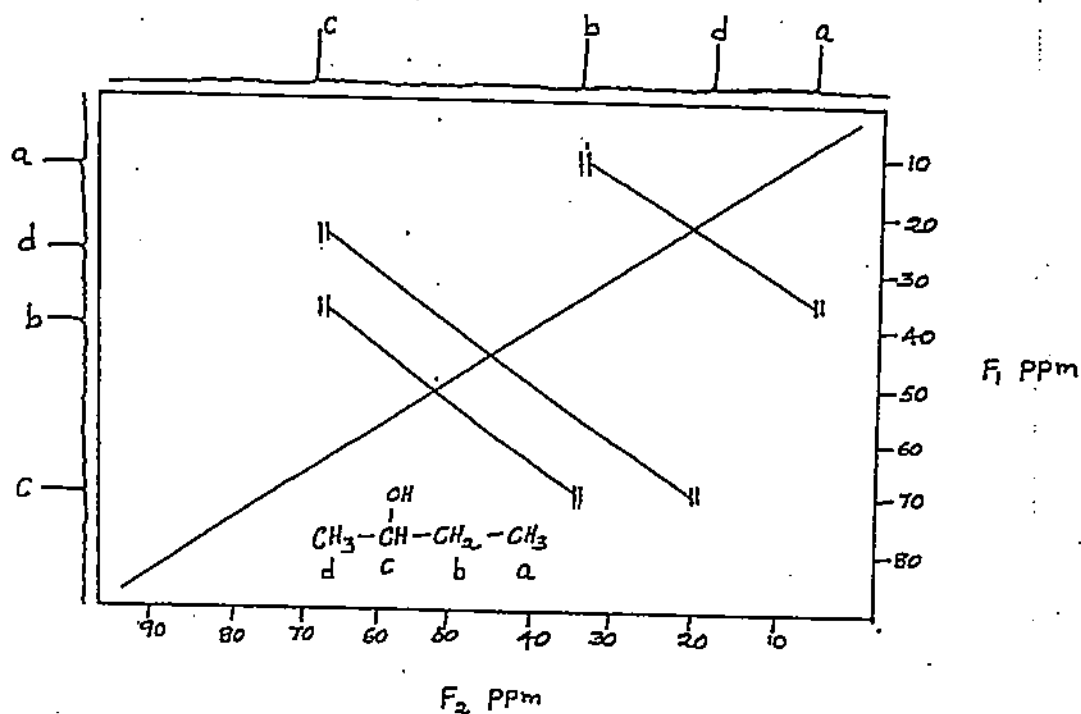
In nature, the amount of NMR active ^{13}C is only about 10^{-2} times that of ^{12}C . This probability of two ^{13}C being adjacent to each other is therefore about 10^{-4} . 2D-INADEQUATE (Incredible natural abundance double quantum transfer experiment)

is a method of analyzing adjacent (coupled) ^{13}C - ^{13}C pairs from the correlation of double quantum transition frequency and chemical shifts.

The pulse sequence for INADEQUATE is



The INADEQUATE spectrum of 2-butanol is



In the spectrum both x and y axes represents the chemical shifts of ^{13}C . The cross peaks corresponding to the adjacent ^{13}C is appear symmetrically with respect to the diagonal line. The carbon frame work of the molecule can be determined simply by taking the signal of one carbon as the origin and successively connecting adjacent carbons.

(18)

Carbon b shows a cross peak with a and c, similarly c shows a cross peak with d. Thus the structure of 2-butanol is determined without much difficulty from the 2D-INADEQUATE.

INEPT:

In assigning carbon signals, multiplicity of the signals along with chemical shift must be known. Off-resonance proton decoupling is used to determine multiplicity but when the molecule is complex determination is not always possible because of overlapping of the signals.

The INEPT (Insensitive nuclear enhancement by polarization transfer) method is very convenient for resolving multiplicity.

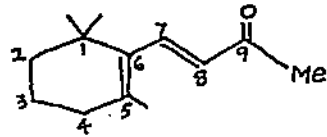
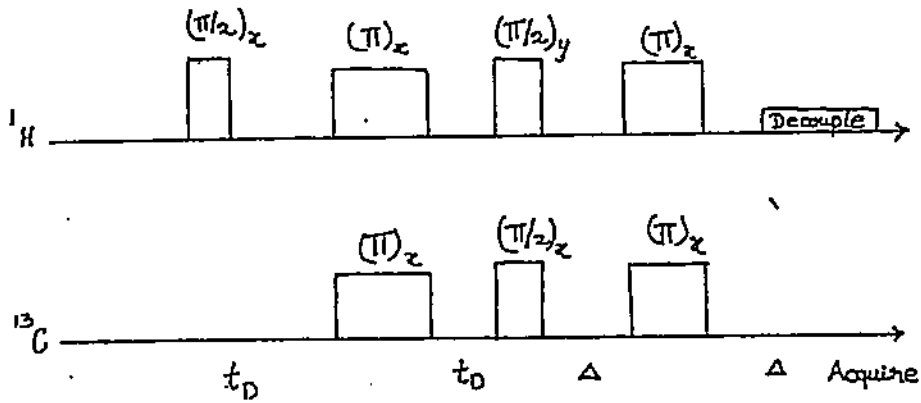
In INEPT, delay time is an important parameter. The normal broad band proton decoupling is shown in the following spectrum (A). When the delay time is $\Delta_3 = \frac{1}{4} J = 2$ milliseconds all carbons with attached protons appear on the positive side, as shown in the spectrum (B) and quaternary carbons show no signal.

When $\Delta_3 = \frac{1}{2} J = 4$ milliseconds only CH carbons appear on the positive side as seen in the spectrum (C). When $\Delta_3 = \frac{3}{4} J = 6$ milliseconds, CH and CH₃ carbons appear on the positive side and CH₂ carbon on the negative side seen in the spectrum (D).

For determining the multiplicity of signals, spectra (A), (C) and (D) are more than adequate and there is no special need for (B). In INEPT, the principle is the transfer of magnetization from sensitive (large difference in Boltzmann distribution) ¹H to ¹³C and adequate results are obtained with less accumulation than for broadband proton decoupling spectrum.

(12)

The pulse sequence for INEPT is

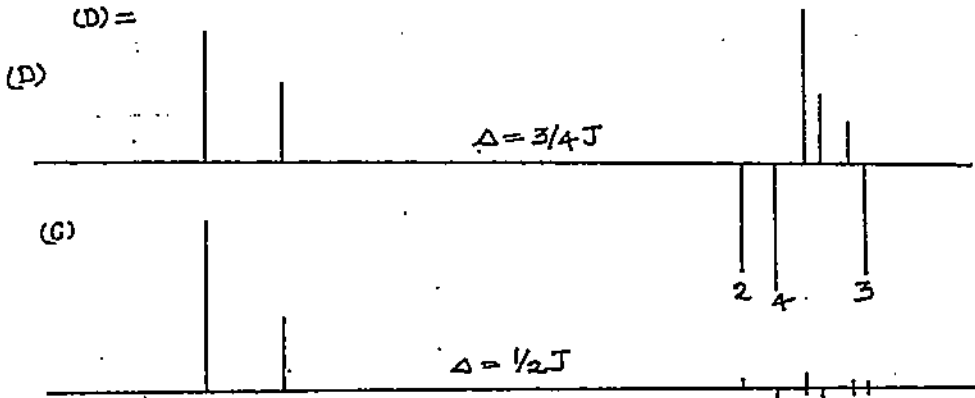


(A) =

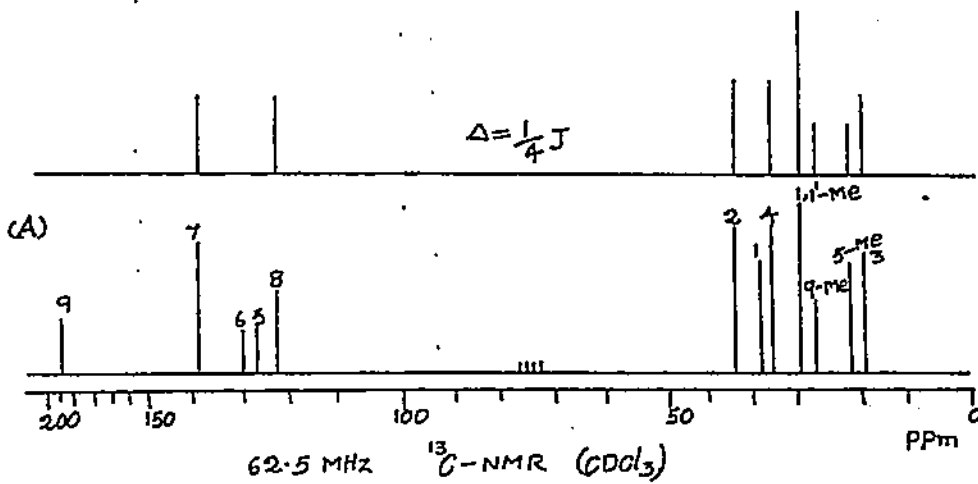
(B) =

(C) =

(D) =



(B)



(15)

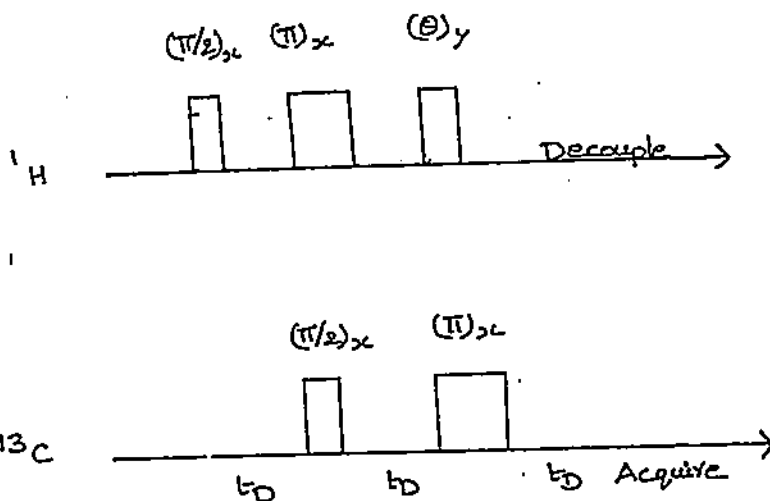
DEPT :- ³¹A

Distortionless enhancement by polarization transfer (DEPT)

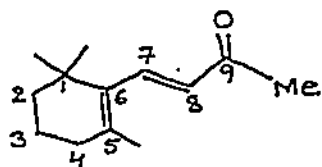
is a modification of INEPT, the increase of signal strength is achieved through polarization transfer. In INEPT, the delay time (Δ) was varied by $\frac{1}{4}J$, $\frac{1}{2}J$ and $\frac{3}{4}J$ before the FID accumulation to distinguish methyl, methylene and methine.

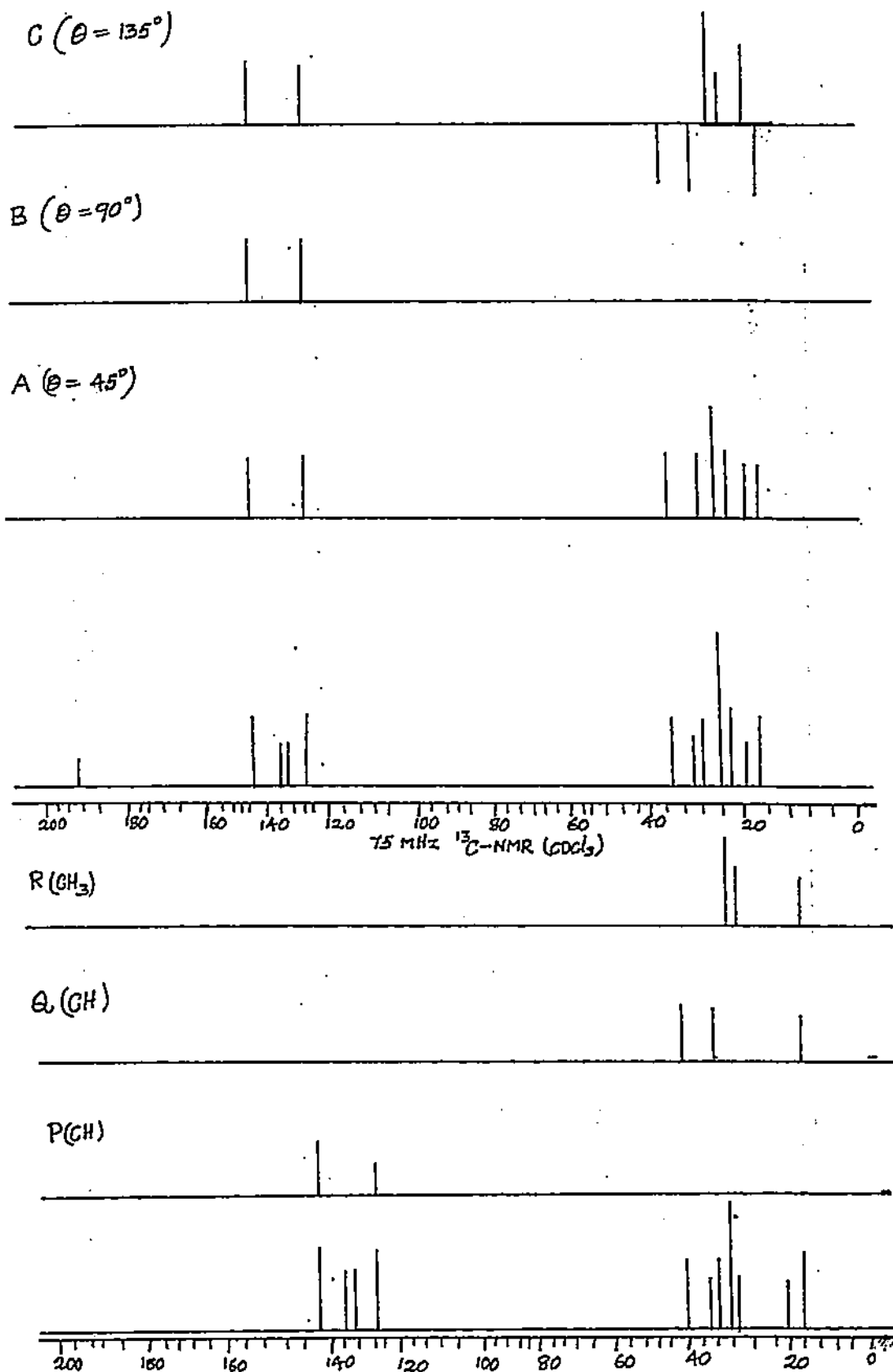
In DEPT, the same spectra are obtained by varying the pulse width (θ) by 45° , 90° and 135° on the third 1H pulse. It can also produce separate carbon sub spectra for methyl, methylene and methine signals.

The pulse sequence for DEPT is



The DEPT spectrum of β -ionone is as follows





(17)

Consider the spectrum (A), in which $\theta = 45^\circ$, all carbons except quaternary carbons are on the positive side. In (B), in which $\theta = 90^\circ$, only CH is on the positive side. In (C) in which $\theta = 135^\circ$, CH and CH_3 are on the positive side and CH_2 on the negative side.

Where DEPT differs from INEPT is in the quantitative character of the signals. By editing the spectrum, carbon can be categorized according to the number of protons. Spectrum P (=B) shows CH only, Q (=A-C) shows CH_2 only and R (=A+C-B) shows CH_3 only. By comparing with broad band proton decoupled spectrum below, multiplicity can be assigned.

NOESY :-

When two protons H_A and H_B are spatially close, saturation of H_A by irradiation, increases the signal strength of H_B . This phenomenon is called the nuclear overhauser effect (NOE).

In 1D spectroscopy, NOE is observed only in protons close to the irradiated proton. NOESY (nuclear overhauser and exchange spectroscopy) was developed to observe NOE 2-dimensionally. By this technique, NOE of spatially close protons can be seen as a cross peak.

The pulse sequence for NOESY is

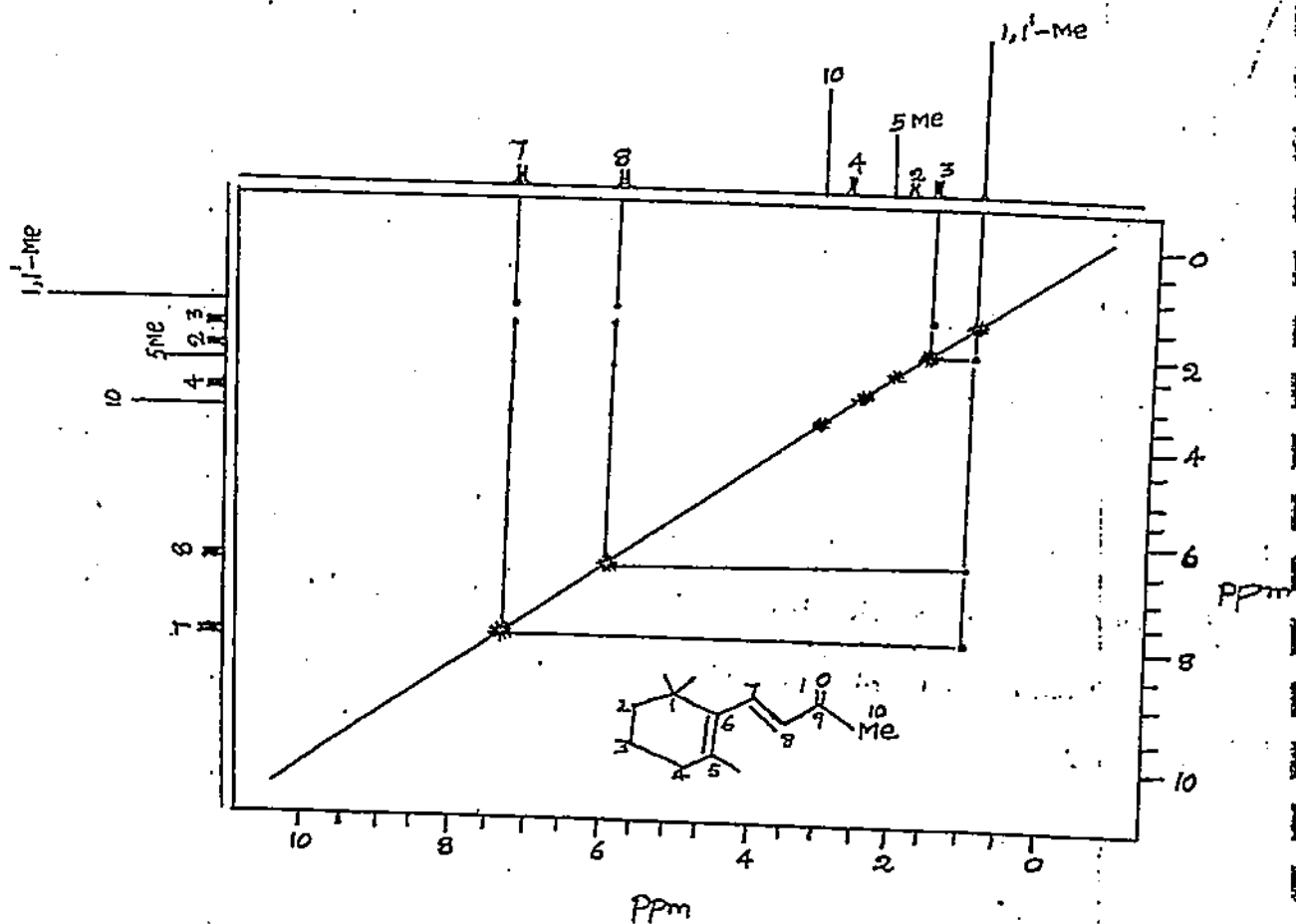


(18)

The important point in the NOESY experiment is the time delay (mixing time) which follows the second pulse i.e. it should be properly set, so that the NOE is as large as possible. The delay time of recovery interval should also be adjusted to allow for complete relaxation.

The spectrum obtained is similar to that of a cosy spectrum but the pulse sequence employed gives rise to cross-peaks only when two nuclei are close together in space.

The NOESY spectrum of β -ionone is as follows.



(19)

In the spectrum of β -ionone both axes are set for ^1H chemical shift. At the centre from top right to bottom left, there is a series of diagonal peaks as in COSY. Peaks off the diagonal are cross peaks due to proton pair showing NOE. (i.e. spatially close protons).

From the high field side of the spectrum, a perpendicular is drawn from $1,1'$ -Me, it first intersects a diagonal peak. As the line is extended it meets cross peak a.

When a line is drawn to the left of a, it meets a diagonal peak. When a perpendicular is drawn upward from that point, it meets 3. This means that 'a' is a cross peak which corresponds to the NOE between $1,1'$ -Me and 3-H.

When the perpendicular is from $1,1'$ -Me is extended, it intersects cross peak b, when the same procedure as in a is applied. It is seen that b is a cross peak between $1,1'$ -Me and 8-H. Similarly, c indicates an NOE between $1,1'$ -Me and 7-H.

When the same procedure is applied to 5-Me and 10-methyl groups show NOE with the following protons.

5-Me : 4-H, 8-H, 7-H

10 : 8-H, 7-H.

The reason why olefinic protons 7-H and 8-H show an NOE with all methyl groups is that the side chain of β -ionone does not have a fixed conformation.

INDOR :

The inter nuclear double resonance (INDOR) is one of the resonance methods to identify coupling systems in complex spectra. The decoupler power used in the INDOR is about one-twentieth of that required for complete decoupling. Consequently the method is highly selective causing minimum perturbation to nuclei with frequencies close to the irradiation frequency.

In this technique, the intensity of a single line is monitored while a decoupler frequency is scanned through the rest of the spectrum. A change in the intensity of the observed line occurs when the decoupler field irradiates a line which has an energy level in common with the observed line.

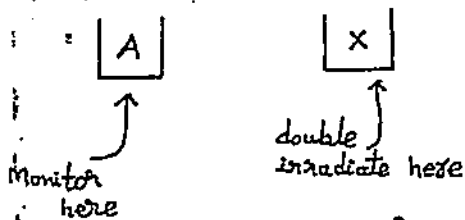
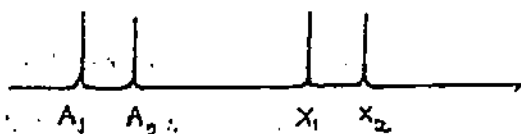
Negative signals are obtained when the irradiated and monitored lines are regressivevely connected and progressively related lines give rise to positive signals.

Consider a simple AX spectrum, we continuously monitor the line intensity of line A₁ and sweep the perturbing irradiation through ν_1 and ν_2 ; at ν_1 the perturbation causes a decrease in the line intensity of A₁, while at ν_2 it causes an increase.

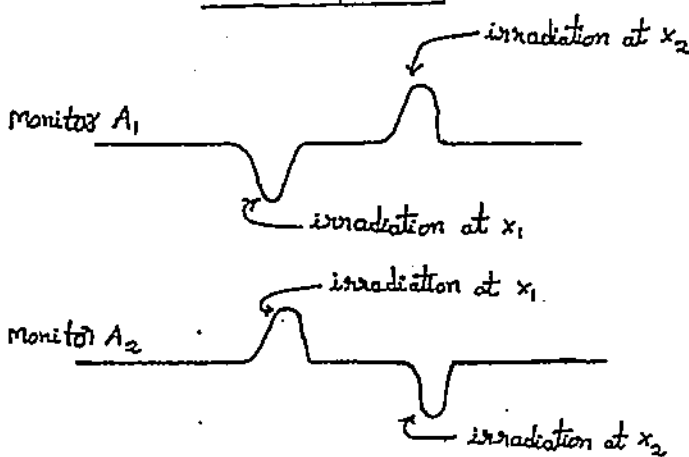
If we monitor line A₂ and repeat the irradiation at ν lines, we get a second INDOR spectrum showing that the line intensity of A₂ increases for irradiation at ν_1 and decreases for irradiation at ν_2 .

(2)

conventional spectrum



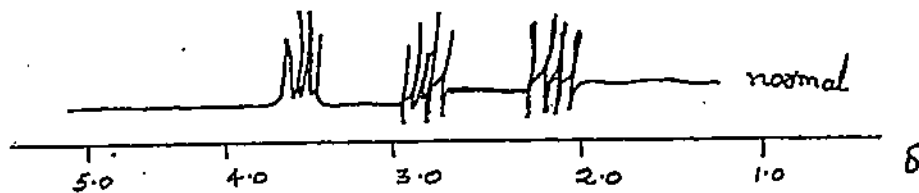
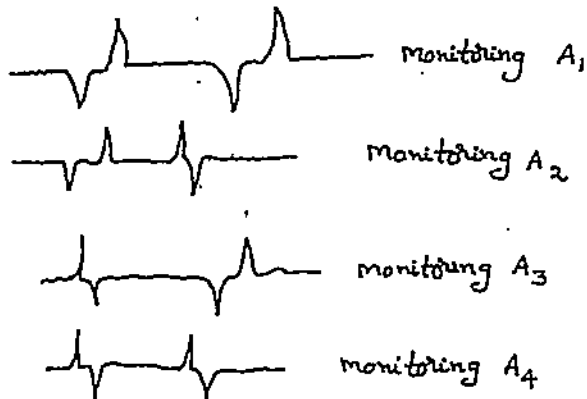
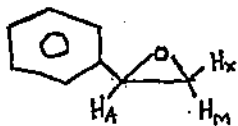
INDOR spectrum



The formation of positive and negative INDOR signals

depends on the populations of the energy levels and the manner in which they change during double irradiation.

Eq :- Styrene oxide

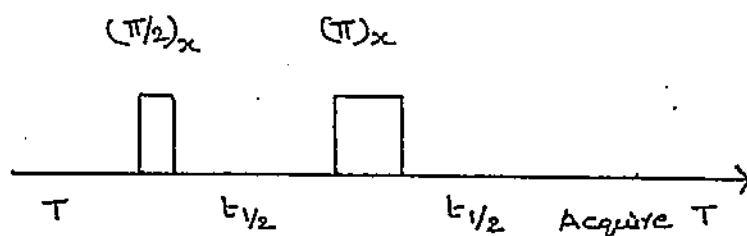


Normal and INDOR NMR spectra of styrene oxide (epoxide ring protons only)

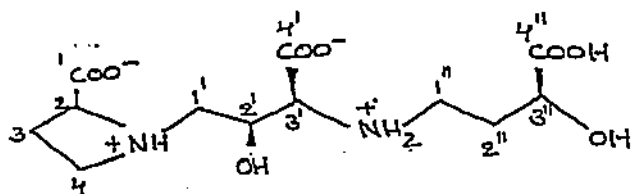
Homonuclear J-Resolved Spectroscopy (HOM 2DJ) :-

This method permits the separation of overlapping signals. In this technique chemical shift is taken on the horizontal axis and spin-spin coupling (J ; Hz) on the vertical axis. With this spectrum, individual chemical shifts and the patterns of splitting are easily seen even when the signals overlap.

The pulse sequence for HOM 2DJ is



The two dimensional J-resolved spectrum of mugineic acid is as follows.



The 1-dimensional spectrum is shown on the horizontal axis.

The signals are those of four protons of $1'$ -H₂ and $1''$ -H₂ and the pattern appears very complex in the 1D spectrum.

In the J-resolved spectrum, contours appear along the vertical axis at sites which correspond to the chemical shifts. These contours are peaks produced by the spin-spin coupling of each proton.

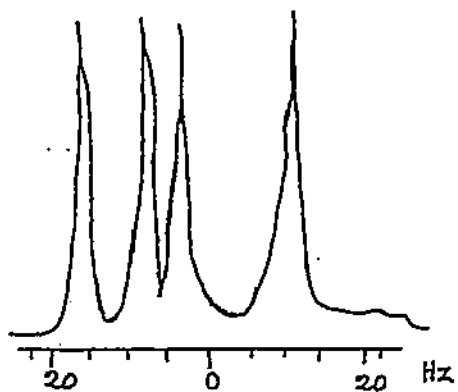
For instance, at 3.55 ppm on the horizontal axis, four peaks are seen along the vertical axis. The cross section of this peak (A) seen that the signals having the 3.55 ppm chemical shift is a doublet

(23)

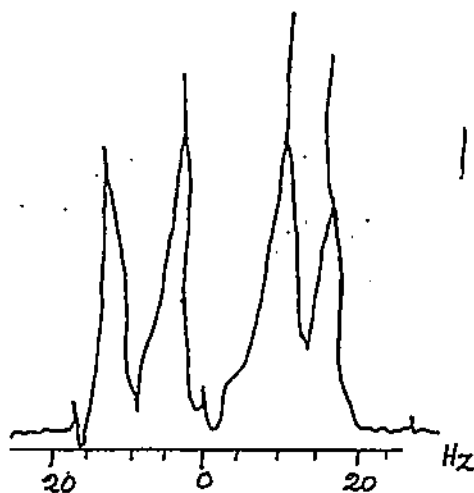
of doublets (dd) of $J = 13, 8 \text{ Hz}$.

When a similar cross section is drawn for the peak at 3.41 ppm (B) being a dd of $J = 13, 3 \text{ Hz}$. These may be assigned to $1''\text{-H}_2$.

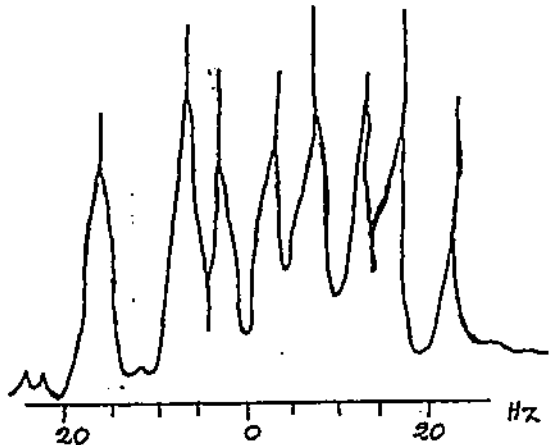
The signals of $1''\text{-H}_2$ in the 1D spectrum appear as complex patterns at 3.14-3.36 ppm. In the J-resolved spectrum, there are signals having chemical shifts of 3.30 ppm and 3.20 ppm and from their cross sections (C) and (D), it is seen that both are ddd of $J = 13, 8, 6 \text{ Hz}$.



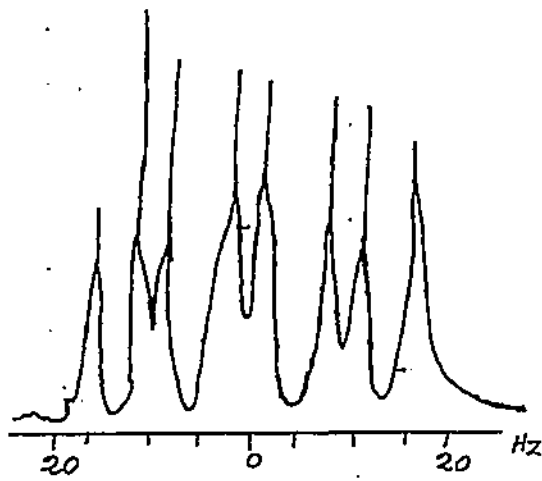
(A)



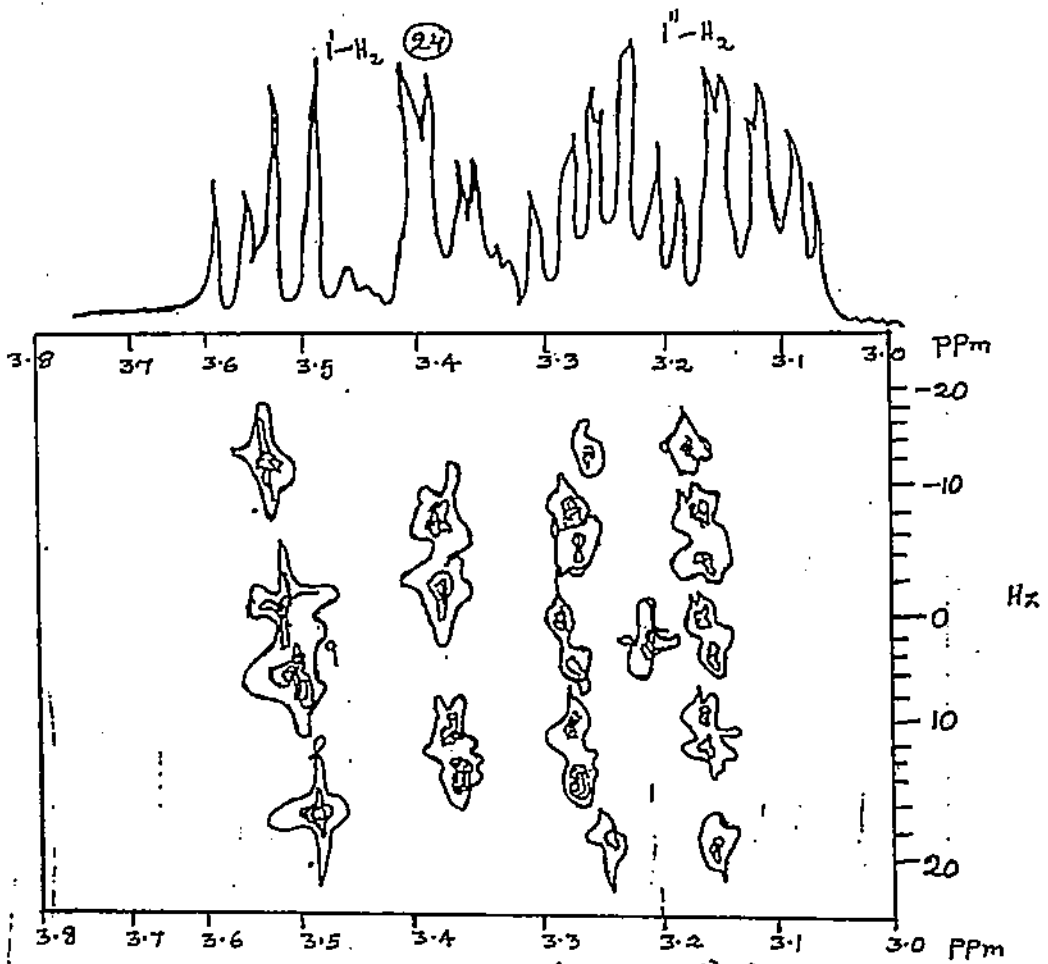
(B)



(C)



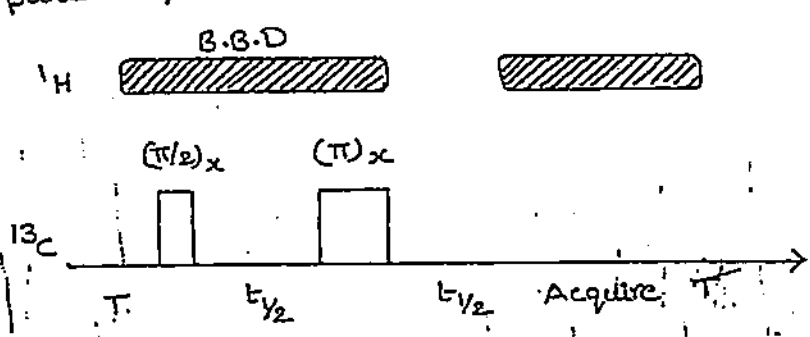
(D)



Heteronuclear J-Resolved Spectroscopy (HET2DJ)

In this technique, the ^{13}C chemical shift is taken on the horizontal axis and the magnitude of ^{13}C - 1H coupling (C-H direct coupling) on the vertical axis.

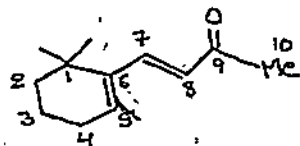
The pulse sequence for HET2DJ is



(25)

The two-dimensional Heteronuclear J-Resolved spectrum of

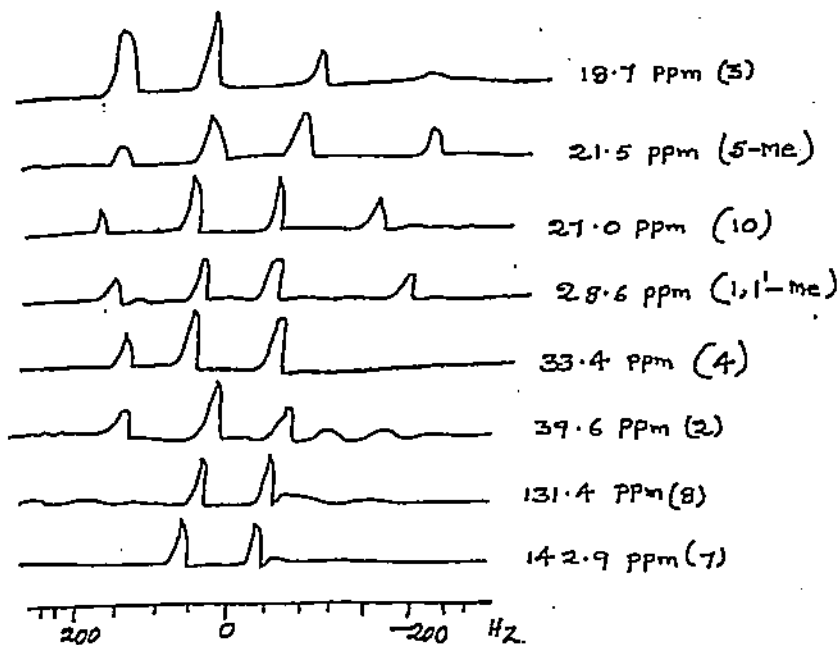
β -ionone is as follows.



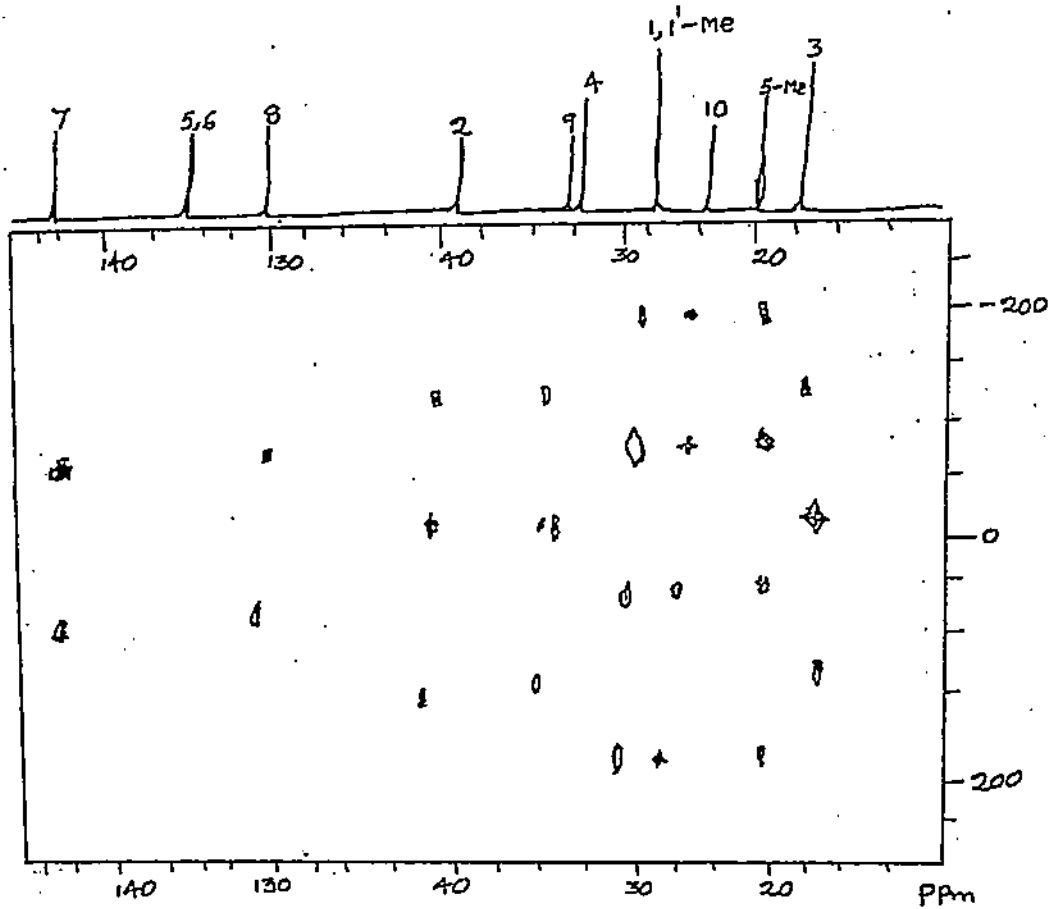
The proton-decoupled spectrum is shown on the horizontal axis. The contour peaks of J-resolved spectrum in numbers corresponding to the number of protons are seen for each ^{13}C signal (CH₃: 4 peaks; CH₂: 3 peaks; CH: 2 peaks).

Where it differs from homonuclear J-resolved spectrum is on the large vertical axis, the maximum width being 500 Hz. This is because J_{CH} is about ten times as large as the $^1\text{H}-^1\text{H}$ J value,

The cross section at each carbon is below.



(P.T.O)



¹³C

Ar — 100 - 150
 C=O — 150 - 200
 alkane — 0 - 50
 C-O, N — 20 - 90
 C=C — 70 - 100

¹H-NMR

C=C — 6 - 7.2
 Ar — 6.8 - 8.0
 C=O — 9 - 10
 H-OH — 10 - 12
 -OH, OR — 3 - 5
 alkane — 3 below

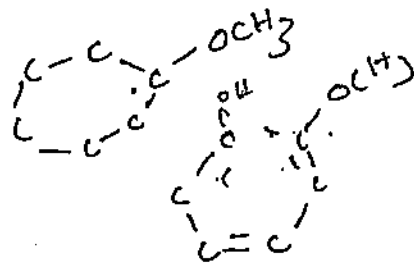
UV

C=O — 250 - 300
 OH & OR — 320 - 380
 CH₂-CH₂-

Paper-I: Organic Spectroscopy-II (R22OC41)

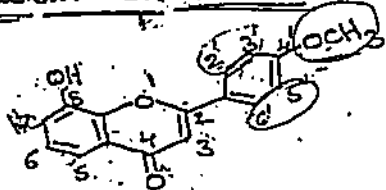
UNIT - IV





Spectral characters and structural elucidation of natural and synthetic compounds involving all the spectral data:

1) H¹, 8 - disubstituted Flavone :-



UV data: generally Flavone appears as yellow or bluish green spots under light they exhibit 2 absorption bands in the range of 377 nm as band-I and 268 nm as band-II. This two bands are due to cinnamoyl group and benzoyl group respectively.

UV data:- λ_{max} 268 nm \rightarrow Band-II (ring A or benzoyl)
(MeOH) 377 nm \rightarrow Band-I (ring B or cinnamoyl)

IR data:- $\nu_{O-H} \rightarrow 3200 - 3500 \text{ cm}^{-1}$ IR: IR spectroscopy is highly useful to notice the nature of various functional groups present in a molecule.
 $\nu_{C=O} \rightarrow 1610 - 1640 \text{ cm}^{-1}$

NMR data:-

Proton	δ (PPM)
H - 2', 6'	7.2 d
H - 3', 5'	6.8 d
H - 3	6.3 s
H - 5	8.0 d
H - 6	6.2 m
H - 7	6.8 d
8 - OH	10.8 s
H - OCH ₃	3.9 s

Note:- The chemical of SH Proton of flavone is strong by the carbonyl and OH group of 8th position. This hydrogen also strongly absorbed. Different hydrogens of aromatic ring are absorbed differentially depend on the nature and no. of substituent.

CMR data:-

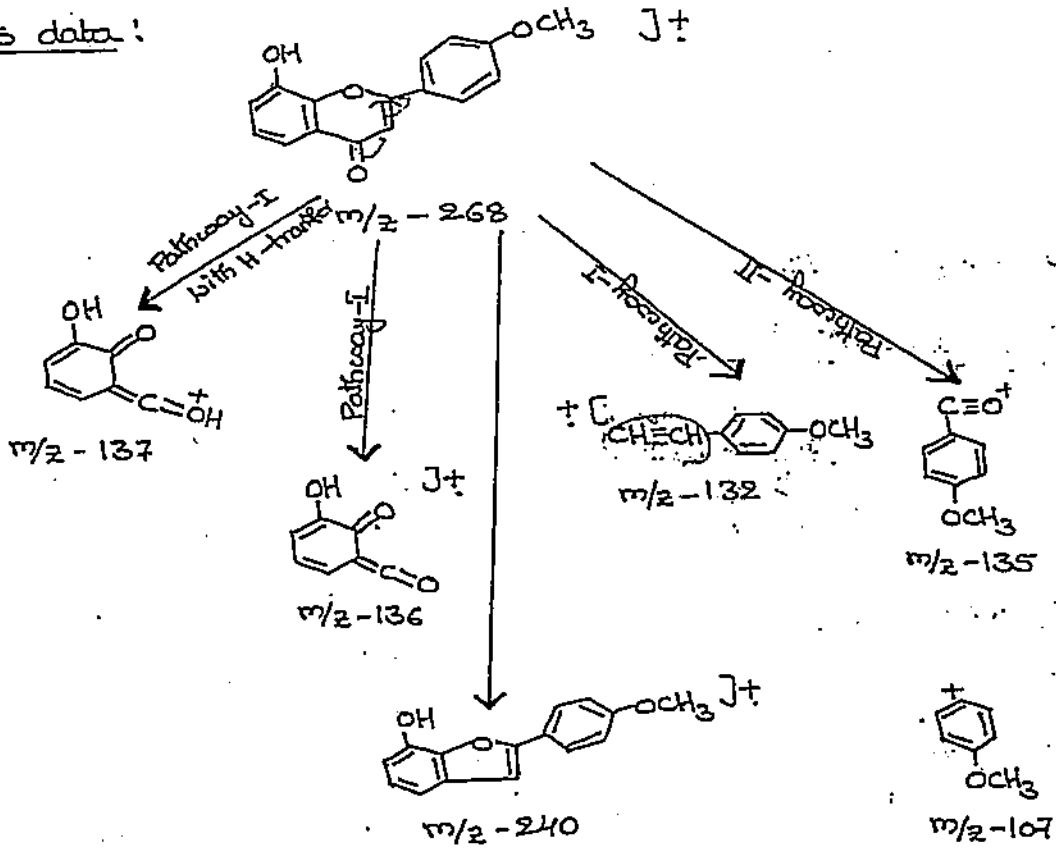
Carbon	δ (PPM)
C ₂	160-165
C ₃	104-107
C ₄	175-179
C ₅ , C ₇	110-120
C ₃ , C ₆	120-140
C ₁ , C ₂ , C ₆	157-167
C ₈ , C ₄	

-OCH₃ - 55-57

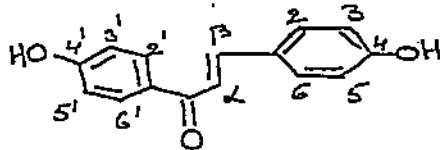
The lack of oxygenation at C₅ position will have marked influence on the carbonyl carbon (C-4) generally the carbonyl carbon is absorbed in the range of 170-180 PPM.

molecular ion peak is generally base peak with other major peaks $m-H^+$, $m-CO^+$ the flavonoids undergo 2-types of retrodiels alder reaction.

MS data:



2) 4,4'-disubstituted chalcone :



UV data:
 chalcone exhibit 2 absorption bands
 major tcm for the chalcones

λ_{max}	230 nm	→ Band II
(Methanol)	348 nm	→ Band I

IR data:

ν_{O-H}	3300 - 3500 cm^{-1}
$\nu_{C=O}$	1610 - 1640 cm^{-1}

Chalcones stretching vibration

(3)

¹H NMR data:

Proton	δ (PPM)
H- α	6.7-7.4 d
H- β	7.3-7.7 d
H-2',6'	7.6 d
H-2,6	7.4 d
H-3',5',3,5	6.5-7.1 dd
4-OH	10.1
4'-OH	10.5

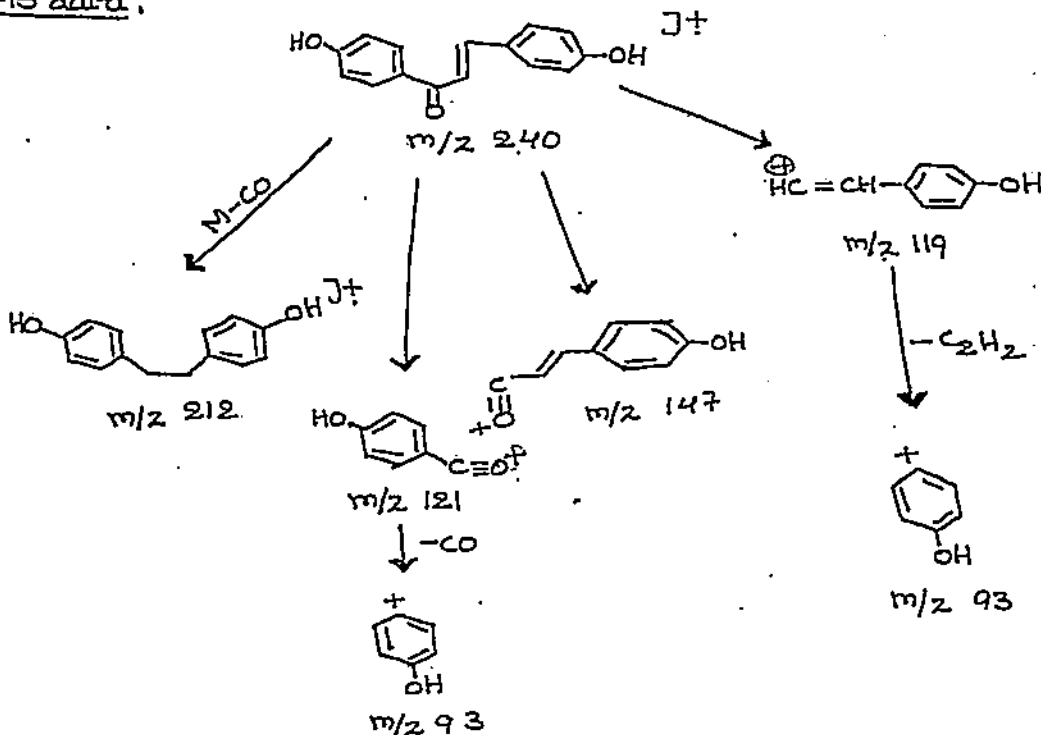
chemical shift of hydrogen on the position of 2',6' is high nearly 7.4-7.6 due to the resonance with carbonyl and double bond

¹³C NMR data:

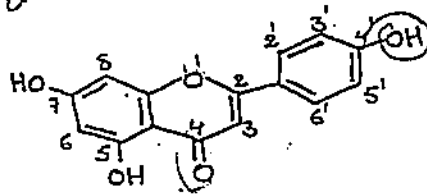
Carbon	δ (PPM)
C- α	120
C- β	126
C=O	175-179
C-2',6'	130
C-3',5'	116
C-4'	160
C-2,6	128
C-3,5	116
C-4	161

" α position (C=O) range 170-180ppm"

MS data:



3) Apigenin :



Carbon 110-1250
(100 - 1250)

UV data: λ_{max} (MeOH) 336 nm — Band I (cinnamoyl)
 major technique for the structural analysis of flavonoids 267, 296 (sh) nm — Band II (benzoyl)

IR data:

In flavonoids the carbonyl stretching is noticed in the range 1620-1650 cm⁻¹

- 3300 cm⁻¹ — ν -OH ✓
- 1646 cm⁻¹ — ν C=O
- 1603 cm⁻¹ — ν C=O of heterocyclic ring
- 1497 cm⁻¹ — Aromatic ν C=C
- 1355 cm⁻¹
- 1240 cm⁻¹ — ν C-O and ν C-O-C
- 1180 cm⁻¹ — δ OH
- 830 cm⁻¹ — δ =C-H out of plane

* P unsat carbonyl cm
1610-1640
Conformation
1710-1720

¹H NMR data:

- | | | |
|----------------|--------------|---|
| δ 7.8 d | (H-2', H-6') | Chemical shift of protons of acyl flavone is strong by the ν ketone group. aromatic protons absorbed in the range of 6-8 ppm. |
| 6.9 d | (H-3', H-5') | |
| 6.5 d | (H-8) | |
| 6.4 s | (H-3) | |
| 6.2 d | (H-6) | |
| 12.4 s | (5-OH) | |
| 10.9 s | (7-OH) | |
| 5.9 s | (4'-OH) | |

CMR data:

Carbon	δ (ppm)
C-2	163.0
C-3	100.2
C-4	131.8
C-5	161.2
C-6	99.7
C-7	164.5
C-8	94.8

Here the carbonyl carbon absorbs the high intensity the carbon at the position δ m absorbed lower

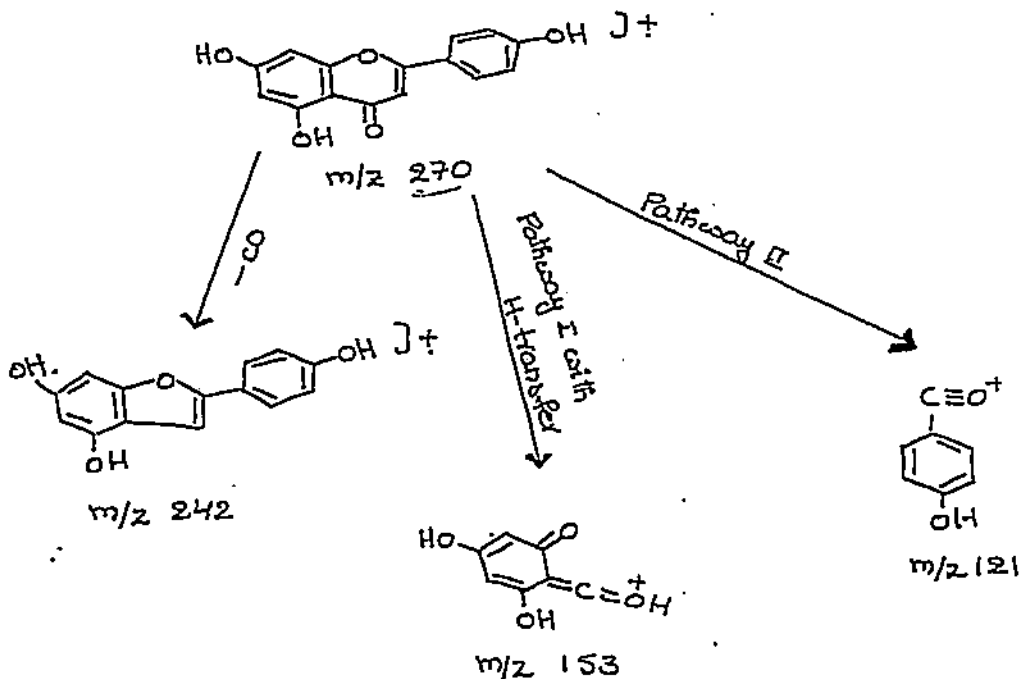
⑤

C-1'	119.1
C-2' & C-6'	121.5
C-3' & C-5'	116.0
C-4'	161.1
C-9	157.0
C-10	103.2

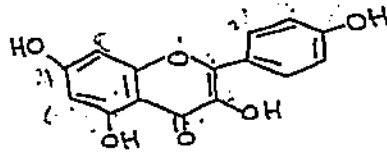
MS data:

270	(M ⁺ , 100%)
269	(M-1)
242	(M-28)
153	
121	

M⁺-H M⁺-60



4) Kaempferol :



UV data: λ_{max} (MeOH) 322 (sh), 367 nm — Band I
 analysis flavonoidy
 cinnomoyl, Benzoyl 253 (sh), 266, 294 (sh) nm — Band II

IR data: 3380 cm^{-1} — ν -OH
 2915 cm^{-1} — chelated ν OH
 1680 cm^{-1} — ν C=O
 1590 cm^{-1} } — Aromatic ν C=C
 1440 cm^{-1} }
 1250 cm^{-1} — ν C-O and ν C-O-C
 1130 cm^{-1} — δ O-H
 835 cm^{-1} — δ C-H out of plane

1H NMR data:

δ	8.14	d	(H-2', H-6')	
	7.04	d	(H-3', H-5')	OH at 5 th position absorbed 6-8 ppm
	6.20	d	(H-6)	
	6.54	d	(H-8)	
	12.22	s	(5-OH)	
	10.9	s	(7-OH)	
	10.02	s	(3-OH)	
	5.9	s	(4'-OH)	

CMR data:

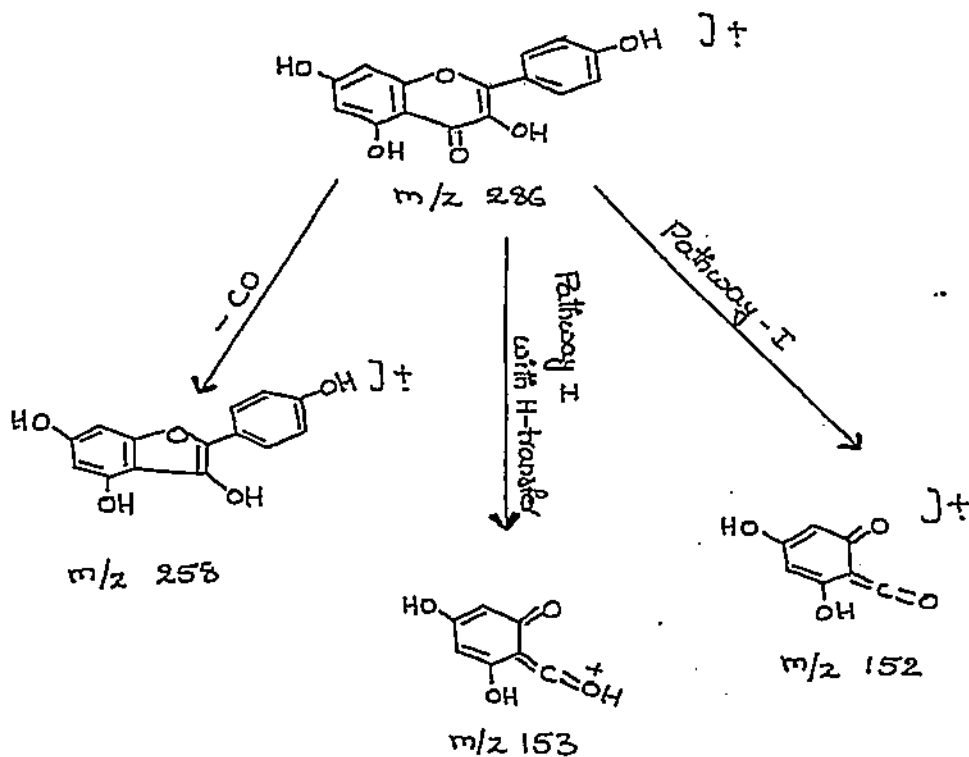
Carbon	δ (ppm)	
C-2	146.8	
C-3	135.6	Carbon 4 th high absorption value & low absorption value
C-4	175.9	
C-5	160.7	
C-6	98.2	
C-7	163.9	
C-8	93.5	

⑦

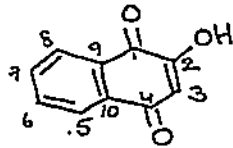
C-9	156.2
C-10	103.1
C-1'	121.7
C-2' & C-6'	129.5
C-3' & C-5'	115.4
C-4'	159.2

MS data: 286 (M⁺)
285 (M-1)
258 (M-28)
153
152
134
124

m-1, m-28 are major peaks



5) Lawson :



(2-hydroxy 1,4 naphtho quinone)

UV data : λ_{max} (EtOH) 242.5, 248, 274, 334 nm

IR data : 3170 cm^{-1} — ν -OH

This is used for the 3077 cm^{-1} — Aromatic ν -H

Identification of the different functional group-OH stre. -C=O Stre

1676 cm^{-1}
1644 cm^{-1} } — ν C=O

1594 cm^{-1}
1580 cm^{-1} } — Aromatic ν C=C

ν OH \rightarrow 1370 cm^{-1} 1476 cm^{-1}

ν C=O \rightarrow 1676, 1644 cm^{-1} 1386 cm^{-1}

ν ArC=C \rightarrow 1594-1476 cm^{-1} 1349 cm^{-1}

ν C-O-C — 1287, 1260 cm^{-1} 1287 cm^{-1}
1260 cm^{-1} } — ν C-O

1122 cm^{-1} — δ O-H

984 cm^{-1}

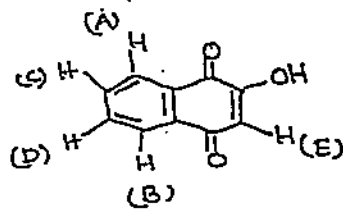
874 cm^{-1}

766 cm^{-1}

724 cm^{-1}

} — δ =C-H out of plane

1H NMR data :



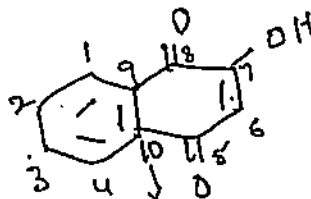
Proton	δ (ppm)
HA	8.004
HB	7.943
Hc	7.85
HD	7.813
HE	6.188
OH	3.8

9

CMR data :

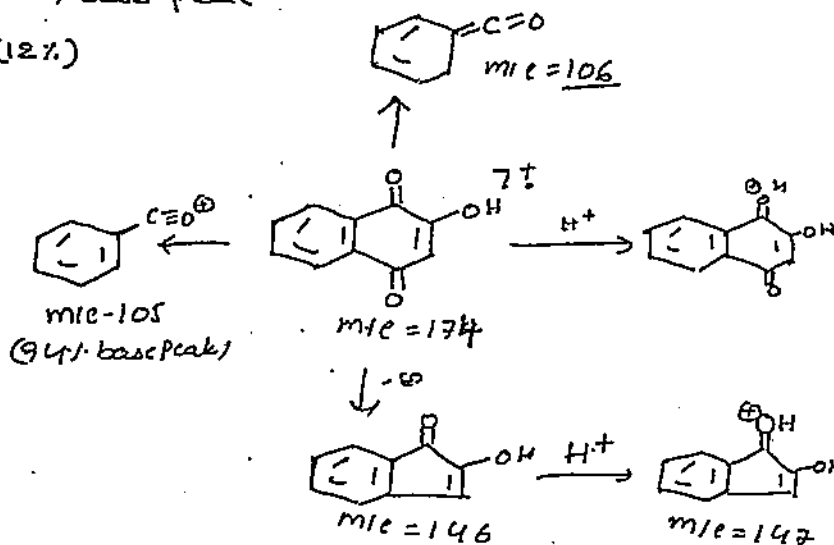
C ₁	181.06
C ₂	159.41
C ₃	110.88
C ₄	134.42
C ₅	125.24
C ₆	133.01
C ₇	134.27
C ₈	125.75
C ₉	130.41
C ₁₀	131.75

The absorption of the carbons of carbonyl group is high and 5rd carbon is less due to its density



MS data :

m/z	174	(M ⁺)	→ base peak
	175	(M+1)	(12%)
	146		(32%)
	147		(4%)
	105		(94%)
	104		(4%)
	106		(4%)
	88		(12%)
	77		(28%)
	76		(20%)
	50		(14%)



Nicotine :-



UV data :-

λ_{max} - 240 nm (2.7) for pyrrolidine ring
 251 nm (3.30)
 256 nm (3.28)
 264 nm (3.17) } for pyridine ring

240
 251
 256
 264

268
 240
 270
 286
 174

IR data :-

3420 cm^{-1}	- $\nu_{\text{N-C}}$ 3040
3030 cm^{-1}	- $\nu_{\text{A-C-H}}$ 3030
2970 cm^{-1}	- $\nu_{\text{C-H}}$ of CH_2 or CH_3 2960 2850
2800 cm^{-1}	
2500 cm^{-1}	- ν_{NH^+} 2500
1600-1400 cm^{-1}	- Aromatic $\nu_{\text{C=C}}$ 1600-1400
1475 cm^{-1}	- $\delta_{\text{C-H}}$ of CH_2 & CH_3 1475
730 cm^{-1}	- $\delta_{\text{C-H}}$ out of plane 726 692
660 cm^{-1}	

Most of the typical bands around 1220 cm^{-1} and 720 cm^{-1} are hidden by solvent absorption.

The band at 2500 cm^{-1} assigned to the NH^+ stretching vibration of the protonated nicotine, which is formed from the traces of HCl always present in the solvent chloroform.

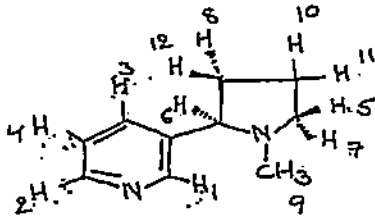
 $^1\text{H-NMR}$ data :-

Assignment of the $^1\text{H-NMR}$ signals is not straight forward. All pyridine protons resonance at δ 6.5 to 9.0. The methyl group gives a singlet at 2.15 ppm.

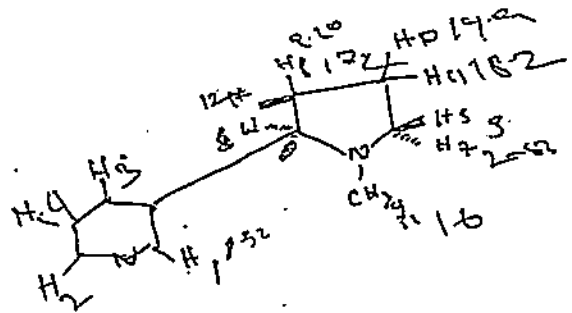
All seven protons of the pyrididine ring exhibit different chemical shifts because the molecule is chiral and therefore the geminal methylene protons are diastereotopic. Assuming first order spectra one would expect the methine proton at lowest field as a doublet or doublets or a triplet if both vicinal coupling constants happen to be equal.

(11)

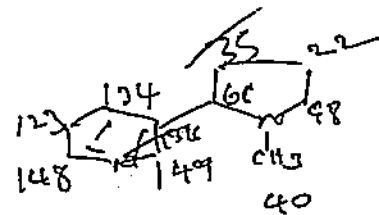
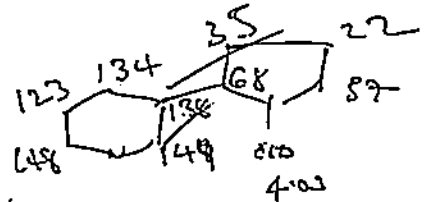
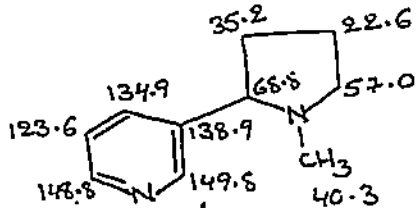
The two methylene protons vicinal to the Nitrogen should follow and exhibit 8 lines (doublet x doublet x doublet). Again depending on the values of the coupling constants the no. of lines may be reduced to anything between 7 and 4.



Proton	δ (PPM)
H ₁	8.54
H ₂	8.48
H ₃	7.71
H ₄	7.25
H ₅	3.23
H ₆	3.08
H ₇	2.30
H ₈	2.20
H ₉	2.16
H ₁₀	1.95
H ₁₁	1.82
H ₁₂	1.72



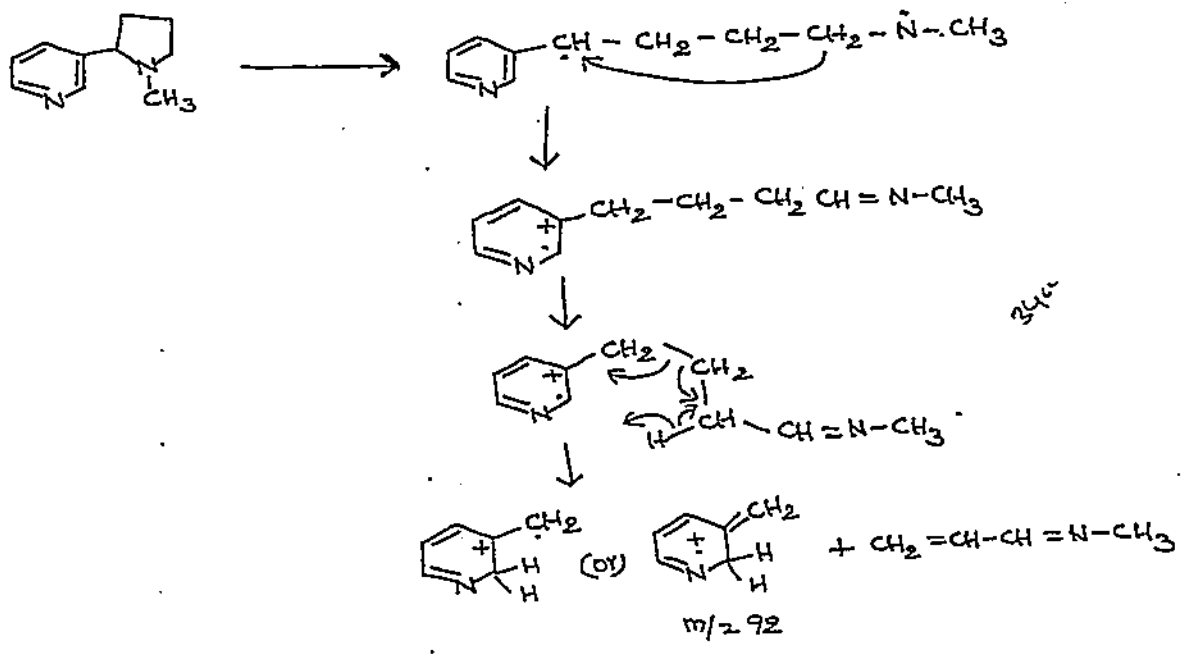
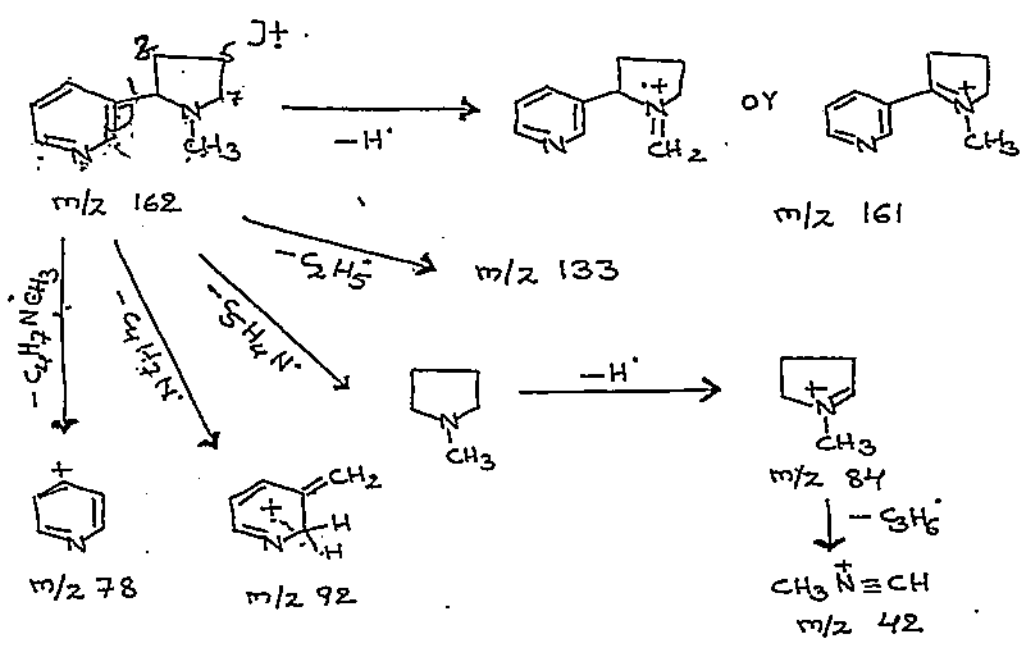
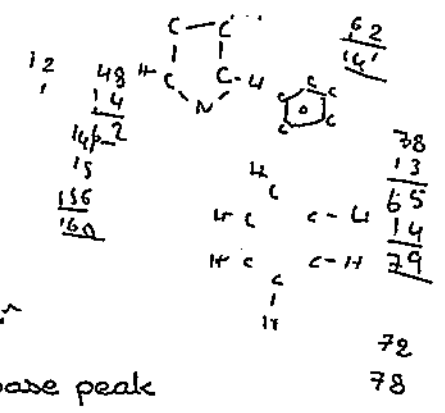
¹³C NMR data:



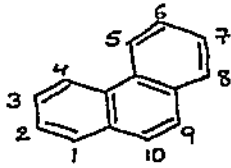
(12)

MS data :-

- m/z 162 (M⁺)
- 161 (M-1)
- 133 (M-C₂H₅)
- 92 (M-70)
- 84 (100%) (M-78) → base peak
- 78 (M-84)
- 42
- 28



(13)

7) Phenanthrene:

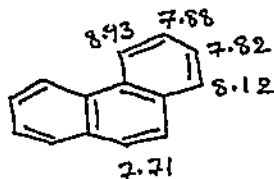
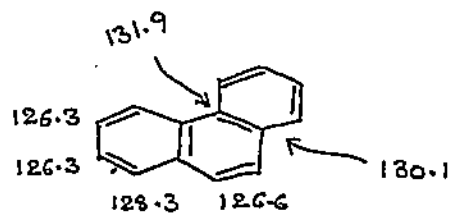
UV data: λ_{max} 252, 293, 330 nm

The absence of a band between λ_{max} 210-235 nm and at λ_{max} 350 nm were shown to be the absence of a hydroxyl or a methoxy group at c-1 and c-8 and at c-4 and c-5.

IR data:

In addition to the normal bands in mono nuclear compounds a strong band at 750 cm^{-1} was observed for the four adjacent hydrogens in terminal benzene rings.

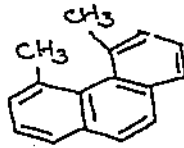
A band at 830 cm^{-1} due to two cis (9,10) hydrogens. In phenanthrene two absorption bands were observed at $1600, 1500\text{ cm}^{-1}$.

 $^1\text{H NMR}$ data: $^{13}\text{C NMR}$ data:MS data:

m/z 179 ($M+1$), 178 (M^+), 177 ($M-1$), 176 ($M-2$), 152, 151, 150, 139, 126, 89 and 76.

(14)

4,5-di substituted phenanthrene : (4,5-dimethyl phenanthrene)

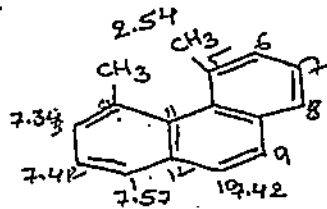


UV data : λ_{max} 257, 298, 335 nm

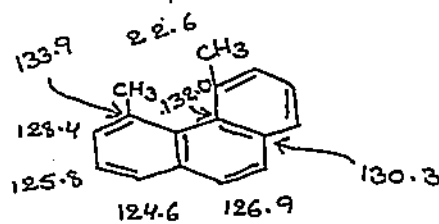
IR data :

3030 cm ⁻¹	—	Aromatic ν_{C-H} .
2980 cm ⁻¹	}	— ν_{C-H} of CH ₃
2895 cm ⁻¹		
1600 cm ⁻¹	}	— Aromatic $\nu_{C=C}$
1500 cm ⁻¹		
920 cm ⁻¹	—	δ_{C-H} out of plane
830 cm ⁻¹	—	δ_{C-H} out of plane of cis (9,10) protons.

¹H NMR data:



¹³C NMR data :



(15)

$$\frac{128}{126} = 1.01587$$
8) Naphthalene :

UV data : λ_{max} 221, 286, 312 nm

The introduction of alkyl groups has little influence on λ_{max} .

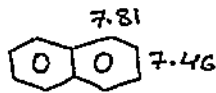
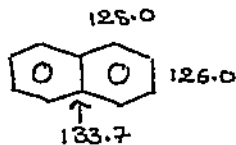
IR data :

The aromatic C-H stretching is in the same region as observed for mononuclear aromatics. The most characteristic bands viz C-H out of plane bending in the region 900-675 cm^{-1} .

C-H out of plane bending in β -substituted Naphthalene:

<u>Substitution pattern</u>	<u>Absorption range (cm^{-1})</u>
Isolated hydrogen	862 - 835
2 adjacent hydrogen atoms	835 - 805
4 adjacent hydrogen atoms	760 - 735

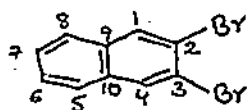
In case of α -substituted naphthalenes the bands due to two adjacent hydrogen atoms in β -substituted compound are replaced by a band for three adjacent hydrogen atoms i.e. 810-785 cm^{-1} .

 1H NMR data :CMR data :

MS data : m/z 130 ($M+2$), 129 ($M+1$), 128: (M^+), 102, 75, 74, 64, 63, 51, 50 and 39.

(16)

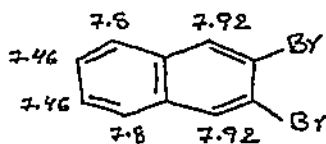
2,3-disubstituted Naphthalene : (2,3-di bromo naphthalene)



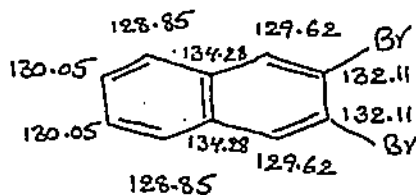
UV data : λ_{max} 210, 252, 314 nm

IR data: 3020 cm^{-1} — Aromatic ν_{C-H}
1580 cm^{-1} } — Aromatic $\nu_{C=C}$
1440 cm^{-1} }
1420 cm^{-1} }
1000 cm^{-1} }
950 cm^{-1} } — $\delta=C-H$ out of plane
880 cm^{-1} }
780 cm^{-1} }
600 cm^{-1} }
490 cm^{-1} }

1H NMR data:

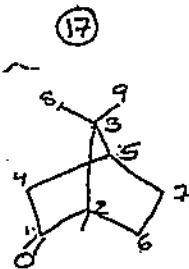
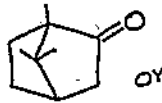


CMR data:



MS data : m/z 286 ($M+2$), 285 ($M+1$), 284 (M^+), 207, 143, 126, 100, 98, 87, 75 and 61.

9) Camphor :



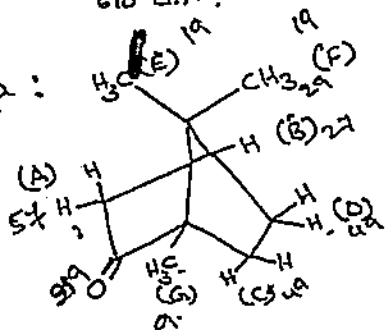
m/z 152

UV data : λ_{max} (CHCl₃) 292 nm — n- π^* of $>C=O$

IR data :

- 3469 cm⁻¹ — overtone of $\nu_{C=O}$
- 2970 cm⁻¹ } — ν_{C-H} of CH₂ and CH₃
- 2825 cm⁻¹ }
- 1740 cm⁻¹ — $\nu_{C=O}$
- 1470 cm⁻¹ } — δ_{C-H} of CH₂ and CH₃
- 1390 cm⁻¹ }
- 1245 cm⁻¹ } — ν_{C-O-C} and δ_{C-O-C}
- 1200 cm⁻¹ }
- 961 cm⁻¹ } — Rocking of gemdimethyl
- 936 cm⁻¹ }
- 751 cm⁻¹
- 610 cm⁻¹

¹H NMR data :

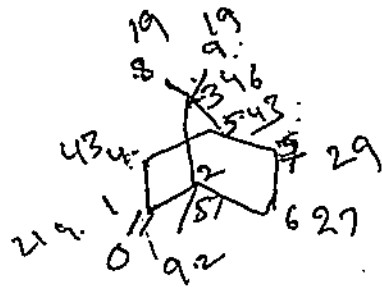


Proton	δ (ppm)
H _A	2.1 (2H)
H _B	1.96 (1H)
H _C	1.65 (2H)
H _D	1.45 (2H)
H _E	1.33 (3H)
H _F	1.2 (3H)
H _G	1.1 (3H)

(18)

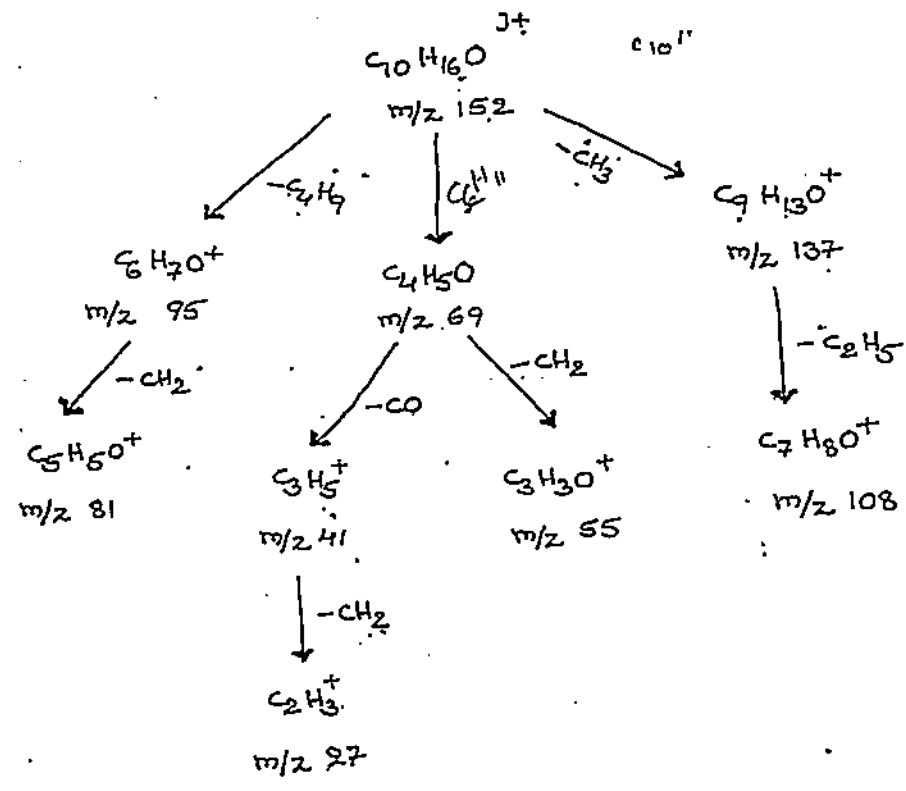
CMR data :

Carbon	δ (ppm)
C ₁	219.3
C ₂	57.65
C ₃	46.76
C ₄	43.29
C ₅	43.09
C ₆	29.95
C ₇	27.08
C ₈	19.77
C ₉	19.15
C ₁₀	9.25



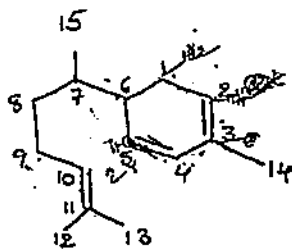
MS data :

m/z 152 (M⁺), 108, **95 (100%)**, 81, 69, 55, 41, and 27.

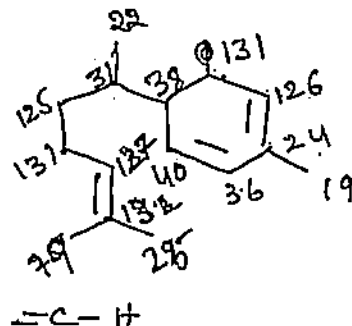


(19)

10) Zingiberene :



204



UV data : λ_{max} (EtOH) 268 nm (2700).

IR data : 3100 cm^{-1} — $\nu=C-H$
 2950 cm^{-1} } — ν_{C-H} of CH_2 and CH_3
 2850 cm^{-1} }

1600-1580 cm^{-1} — $\nu_{C=C}$

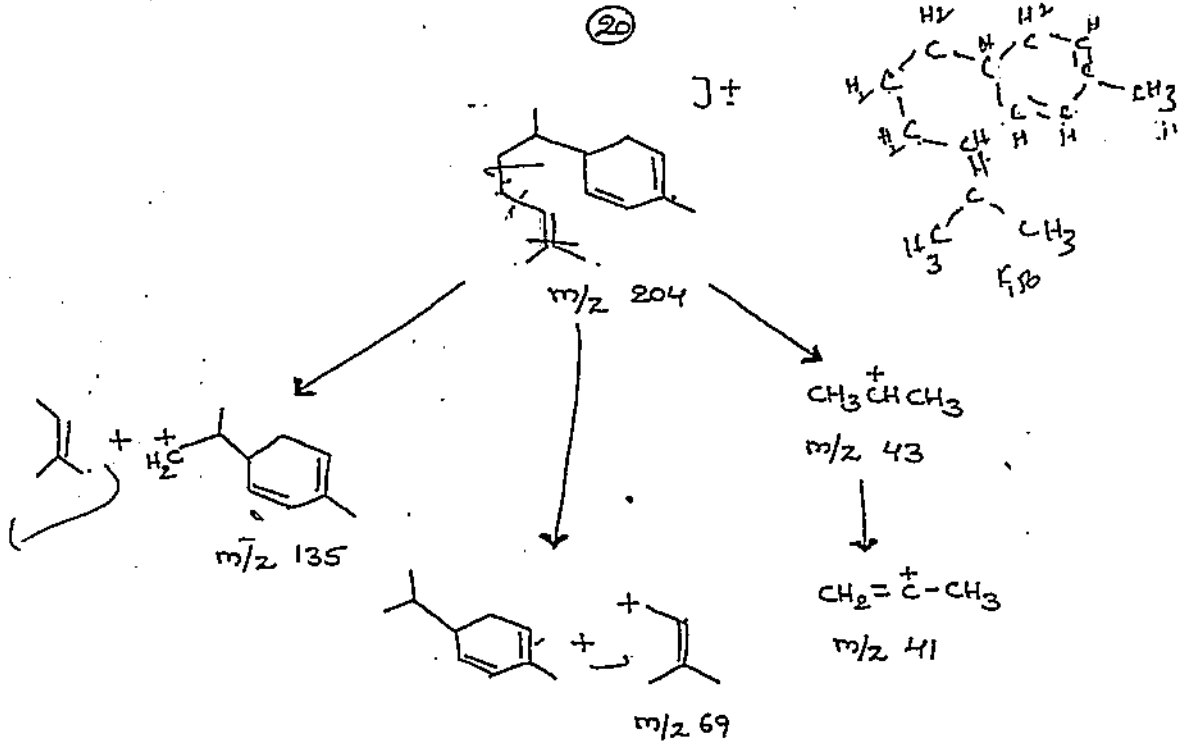
¹H NMR data :

Proton	δ (ppm)	Multiplicity	Integration
H ₁	2.2	t	(2H)
H ₂	5.86	t	(1H)
H ₃	5.86	d	(1H)
H ₅	5.86	t	(1H)
H ₆	3.4	m	(1H)
H ₇	3.2	q	(1H)
H ₈	1.6	t	(2H)
H ₉	1.65	t	(2H)
H ₁₀	5.6	t	(1H)
H ₁₂	1.9	s	(3H)
H ₁₄	1.65	s	(3H)
H ₁₃	1.9	s	(3H)
H ₁₅	1.3	d	(3H)

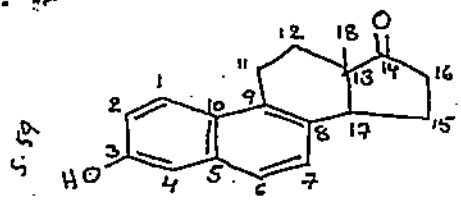
Carbon	δ (ppm)
C ₁	131.4
C ₂	126.7
C ₃	24.8
C ₄	36.0
C ₅	40.1
C ₆	38.3
C ₇	31.4
C ₈	125.7
C ₉	121.1
C ₁₀	127.4
C ₁₁	132.8
C ₁₂	19.6
C ₁₃	25.6
C ₁₄	19.1
C ₁₅	22.4

41510

MS data : m/z 204 (M^+),
 135 ($M - C_5H_9^+$),
 69 ($M - 135$), 53, 43, 41, 27.



✓ 11) Equilenine :



$\delta_{C-H} - 2990$
 δ_{O-H}
 δ_{C-H}

UV data : λ_{max} (EtOH) 231, 270, 282, 292, 325 and 340 nm.

IR data :

3290 cm^{-1}	—	δ_{O-H}
3030 cm^{-1}	—	Aromatic δ_{C-H}
2950 cm^{-1}	}	— δ_{C-H} of CH_2 and CH_3
2920 cm^{-1}		
2860 cm^{-1}		
1730 cm^{-1}	—	$\delta_{C=O}$
1620 cm^{-1}	}	— $\delta_{C=C}$ aromatic
1600 cm^{-1}		
1460 cm^{-1}	}	— δ_{C-H} of CH_2 and CH_3
1390 cm^{-1}		
1220 cm^{-1}	—	δ_{C-O} or δ_{C-C}
1180 cm^{-1}	—	δ_{O-H}
850 cm^{-1}	}	— δ_{C-H} out of plane
830 cm^{-1}		
720 cm^{-1}		

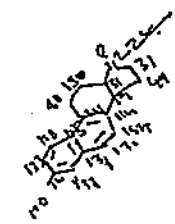
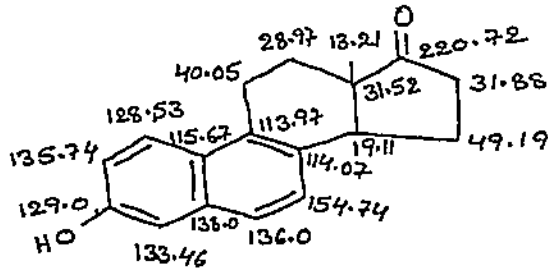
(2)

¹H NMR data :

Proton	δ (PPM)
H ₁	7.66 (d, 1H)
H ₂ & H ₄	7.89 (d, 1H)
H ₆	7.30 (d, 1H)
H ₂	7.24 (d, 1H)
H ₁₁	3.18 (m, 1H)
H ₁₂	2.55 (dd, 2H)
H ₁₅	2.22 (m, 1H)
H _{16'}	3.30 (m, 2H)
H ₁₇	1.94 (m, 1H)
H ₁₈	0.81 (s, 3H)
-OH	5.15 (s, 1H)

116 119
129
C 11 12 13 132 133
C 220
129

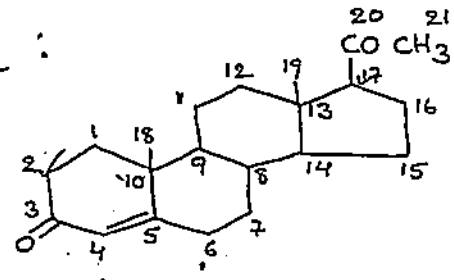
CMR data :



MS data :

m/z	266 (M ⁺) — base peak
267	(M+1)
251	(M-15)
249	(M-OH)
210	(M-56)
195	(M-71)

12) Progesterone :



UV data : λ_{max} 240nm

IR data :

- 3068 cm^{-1} — $\nu=C-H$ —
- 2967 cm^{-1}
- 2952 cm^{-1}
- 2926 cm^{-1}
- 2863 cm^{-1}
- 2850 cm^{-1} } — ν_{C-H} of CH_2 and CH_3
- 1699 cm^{-1} — $\nu_{C=O}$ }
- 1663 cm^{-1} — $\nu_{C=O}$ }
- 1616 cm^{-1} — $\nu_{C=C}$ }
- 1478 cm^{-1} } — δ_{C-H} of CH_3
- 1447 cm^{-1} }
- 1420 cm^{-1} — $\delta=C-H$
- 1386 cm^{-1} — δ_{C-H} of CH_2 ✓
- 1218 cm^{-1} — ν_{C-O-C}
- 1190 cm^{-1}
- 1162 cm^{-1}
- 964 cm^{-1} } — $\delta=C-H$ out of plane ✓
- 671 cm^{-1} }

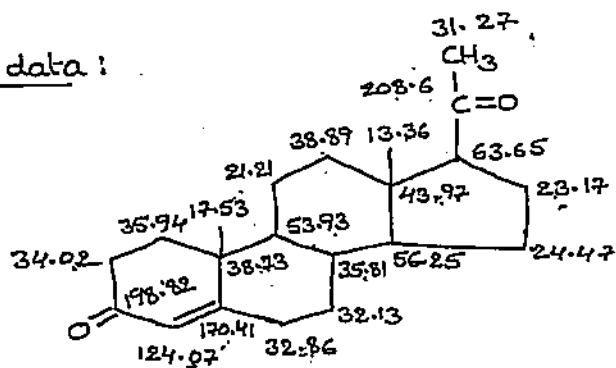
¹H NMR data :

	Proton	δ (ppm)
0.9-1.0	H_1 x H_6	0.9-1.0
2-2.2	H_2	2.0-2.2
5.9	H_4	5.7
1.3-1.5	H_7	1.1-1.3
1.3-1.5	H_8	1.4-1.5
0.9-1.3	H_9	0.9-1.3
1.1-1.3	H_{11}	1.0-1.3
0.9	H_{12}	0.9

(23)

1.2-1.5	H ₁₄	1.2-1.5
0.9-1.8	H ₁₅ & H ₁₆	0.9-1.1
2.0-2.2	H ₁₇	2.0-2.2
1.5-1.7	H ₁₈	1.5-1.7
1.6-1.8	H ₁₉	1.6-1.8
2.8	H ₂₁	2.8

CMR data:



MS data:

m/z 328 (M⁺), 310, 297, 267 (100%), 253, 225, 209,
195, 179, 165, 145, 129, 116, 105, 98, 91, 80, 69, 55, 43,
41 and 29.

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