

Nuclear Magnetic Resonance

NMR

alpha

$\Omega \neq 0$

sigma

$\Omega = 0$ $\Omega =$ Nuclear spin

(paramagnetic nuclei) (anti-magnetic nuclei)

^1H ^2D ^{12}C ^{13}C ^{14}N ^{15}N ^{16}O

I certify that the information given by the candidate Shri/Smt/Kum Rachana Kulkarni Pujarachari has been verified by me with reference to records of the University/Institute.
It is further certified that the said candidate is enrolled for M.Sc (mention the degree/course if M.Sc equivalent) _____ on (mention date/month/year) 1/1/1.
OR

after completing 10+2, the said candidate is enrolled for (mention the degree course) 10+2 M.Sc/2019 on this date/month/year 16/08/2019 and is presently pursuing (mention year/semester, e.g 4th year/7th semester) 3rd/9th and is eligible to appear under Result Awaited since (mention date/month/year) 25/04/23 and is eligible to appear under Result Awaited category as laid down in the eligibility criteria.

Illustrative List of degrees/courses:

(i) B.Sc 4 year program (ii) B.E (iii) B.Tech (iv) B.Pharma (v) MBBS (vi) Integrated BS-MS/Masters M.Sc (vii) M.Sc

Signature of the Head/Dept/Institute
**Department of Physics & General
V.S. University of Technology
Bawali, Samalkhpur
Name: Dr. Dineshwar Singh B.Sc**

Designation: _____

$\Omega = \frac{1}{2}$
 Non quadrupole
 Spherical
 Ellipsoidal
 e.g. ^1H , ^{13}C , ^{15}N , ^{19}F
 ^{31}P
 ^{14}N , ^{30}Si ($T=1$)
 ^{11}B ($I=3/2$)

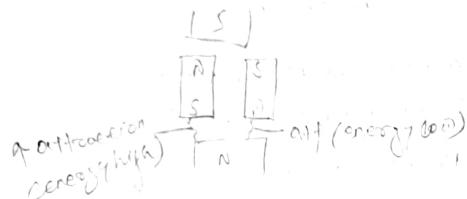
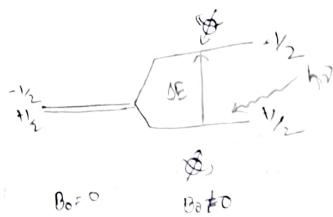
Nucleus \Rightarrow mass no \Rightarrow odd \Rightarrow $\Omega = \frac{1}{2}$ (n)
 Nucleus \Rightarrow mass no \Rightarrow even \Rightarrow $\Omega = 1, 2, 3, \dots$
 (wholeness)

For every nuclear charge Z there exists $2Z$ non degenerate levels $= 2\Omega + 1 = 2 \oplus \oplus$
 no of degenerate levels = $2\Omega + 1$

ANNEXURE-VIII ATTESTATION FORM (For 'Result Awaited' Candidates only)

OR

(For 'Enrolled' Candidates only)



$$\Delta E \propto B_0$$

$$\Delta E = \gamma B_0 t$$

$$\frac{\hbar}{T} = \frac{h}{2\pi}$$

$$\hbar \gamma_R = \frac{\gamma B_0 h}{2\pi}$$

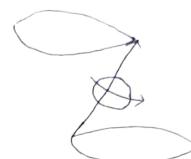
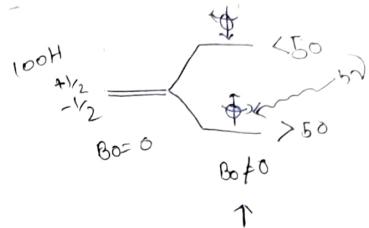
γ - gyromagnetic ratio

Characteristics of molecular nuclei

$$\gamma_R = \frac{\gamma B_0}{2\pi} \quad \gamma_H = 42.59 \text{ MHz/T} \quad \gamma_C = 10.708 \text{ MHz/T}$$

Boltzmann distribution

$$\frac{n_1}{n} = e^{-\epsilon_1/kT}$$



Precessional frequency

$$\omega \propto B_0$$

$$\Rightarrow \omega = \gamma B_0$$

Precessional frequency of nucleus

$$\nu_R = \frac{T}{2\pi} B_0$$

$$\gamma_{B_0} = 2\pi \times \nu_R$$

$$\gamma_p = 2\pi \nu_R$$

Precessional frequency = Radio wave frequency
Resonance

Sensitivity of Nucleus :-



→ less sample required for NMR.

→ less time required



more amount of sample

→ more time required

Sensitivity of Nucleus

→ Natural abundance

→ Gyromagnetic ratio

$$\gamma_H = 42.59 \text{ MHz/T}$$

$$\gamma_C = 10.708 \text{ MHz/T}$$

Higher the value of γ more sensitive the nucleus.

$$\delta = \frac{f_1 - f_0}{B_0}$$

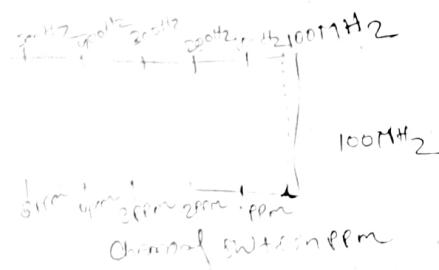
Natural Abundance

Hydrogen	$\frac{1}{6}$	98.9%
Proton	$\frac{1}{6}$	1.1%

Chemical Shift

(you need reference standard)

By using the reference standard the chemical shift becomes applied magnetic field and is converted to ppm. Observe NMR Spectrum. At 100 MHz or 300 MHz the δ value is same for two protons.



$$\delta = \frac{\text{frequency} - \text{frequency}_0}{B_0 \times 10^6} \text{ MHz}$$



$$\delta = \frac{\nu_p}{300 \text{ MHz}}$$

$$1.5 \times 300 \text{ MHz} = \nu_p$$

$$150 \text{ Hz} = \nu_p$$

$$\nu_p = 450 + 300 \times 10^6$$

$$= 3000000 + 450 \text{ Hz}$$

Why TMS is used?

(i) Inert

(ii) Volatile (∴ we can remove the sample)

∴ NMR is non destructive technique.

(iii) 12 equivalent proton

The required amount of added TMS is very very less.

(iv) Highly shielded proton

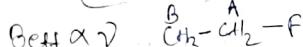
Protons of TMS are highly shielded therefore chemical shift values is very less therefore does not interfere with signal.

Chemical Shift

The chemical shift represents the position of a signal. It also represents the precessional frequency of different proton of a molecule.

$$\text{B}_{\text{eff}} = \text{B}_0 - \text{B}_i$$

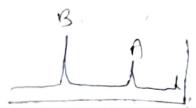
B_i - induced mag field
(due to e^-)



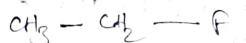
electron density around $\text{H}_a > \text{H}_b$

$$\text{B}_{\text{eff}}(\text{H}_a) < \text{H}_b$$

$$\sqrt{\text{H}_a} < \sqrt{\text{H}_b}$$



electron density $\propto \frac{1}{\sqrt{2}}$ around the nucleus



shielded deshielded

deshielded

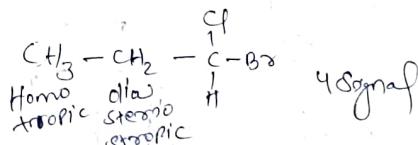
Type of Proton

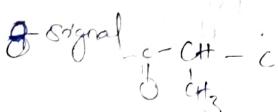
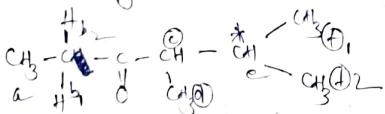
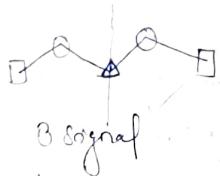
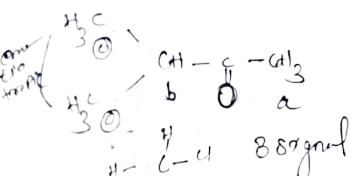
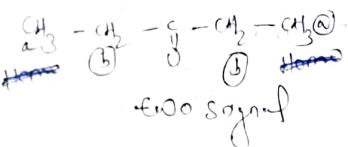
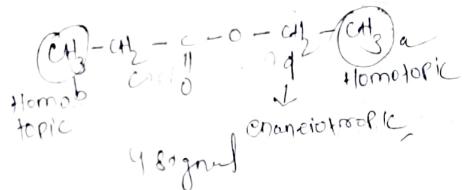
	δ (PPM)
I $\text{C}_{\text{SP}_3} - \text{H}$ (not attached to electronegative substituent)	0.5 - 2.5 ppm
II $\text{C}_{\text{SP}^3} - \text{H}$ (having electronegative substituent)	2 - 5 ppm
III $= \text{C}_{\text{SP}^2} - \text{H}$	5 - 8.5 ppm
IV $\equiv \text{C}_{\text{SP}} - \text{H}$	2 - 3 ppm
V $- \overset{\text{O}}{\underset{\text{H}}{\text{C}}} - \text{H}$ (aldehydic proton)	7.5 - 10 ppm
VI $- \overset{\text{O}}{\underset{\text{H}}{\text{C}}} - \text{OH}$ (carboxylic acid)	10 - 12.5 ppm
# OCH_2	4.0 - 4.5 ppm
	3.5 - 4.0 ppm
VII Alcoholic H ($-\text{OH}$)	4 - 6 ppm

* No of Signals:-

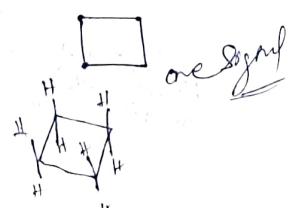
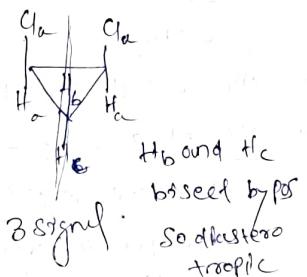
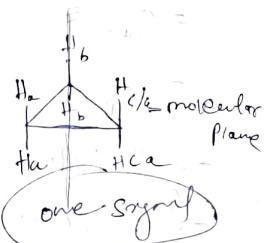
i) chemically equivalent protons give one signal.

Enantiotopic protons \rightarrow equivalent protons
Homotopic protons \rightarrow equivalent protons

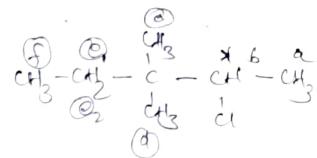
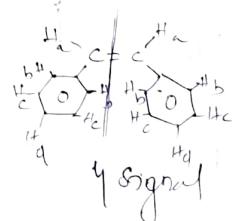
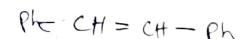
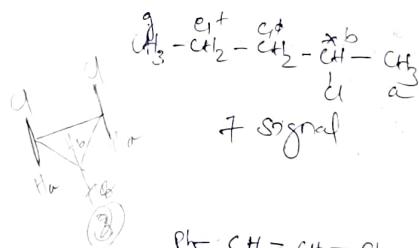
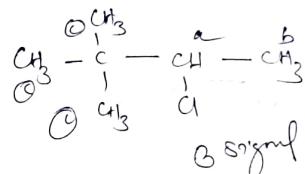
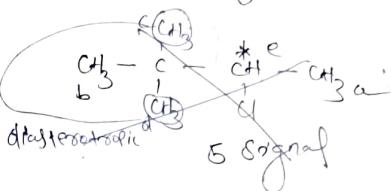




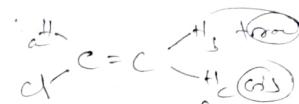
1) POS
 2) asymmetric centers.
 CH_2 → diastereotopic



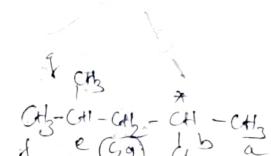
diastereotopic
 $\text{CH}_3 - \text{CH}_2 - \text{C}(\text{H}_3) - \text{CH}_2 - \text{CH}_3$
 a b c d e
 5 signals



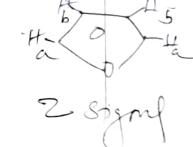
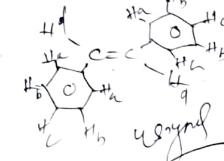
7 signals



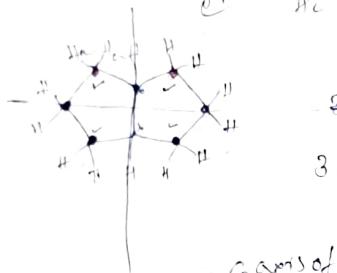
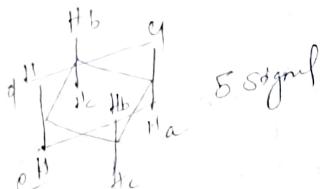
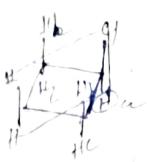
geometrically isomers
 are diastereomers



7 signals



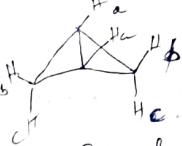
9



C₃ axis of

no asymmetric center

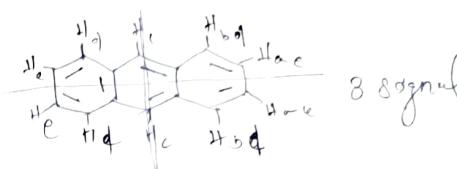
2 signal



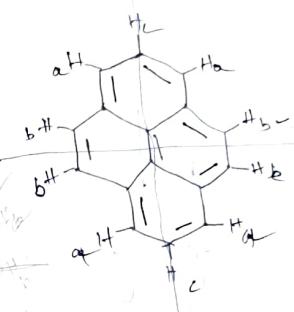
5 Signal



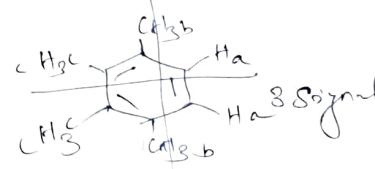
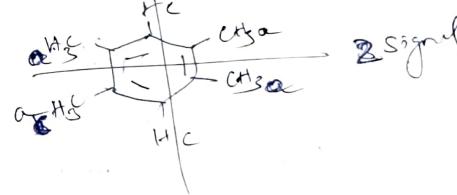
2 signal

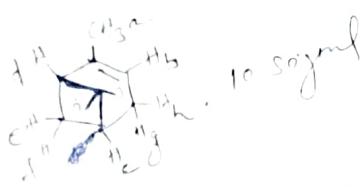


8 signal

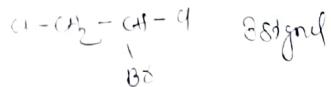


3 signal

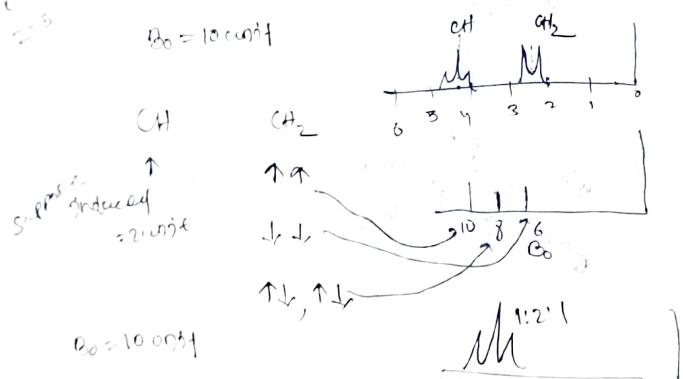




Splitting of signal



BD = 10 count



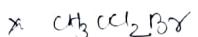
Splitting formulae

$$[2n+1]$$

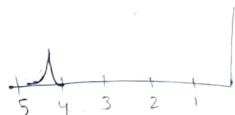
n = no of protons on adjacent carbon or no of protons on surrounding

I = nuclear spin of proton/nucleus which is causing splitting.

$$[n+1] \rightarrow \text{for Proton}$$

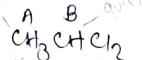


one signal



multiplicity = 1

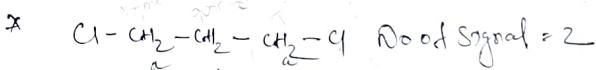
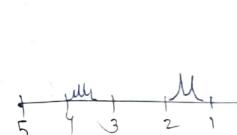
never



Signal = 2

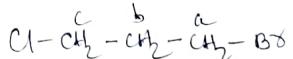
B = quadraplet

A = doubled



multiplicity = 5 : 0

(CH₂^a) quintuplet



(CH₂^c) = Triplets

No of signal = 3

c → multiplicity = 3

a → multiplicity = 3

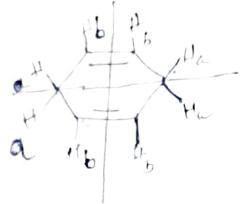
b → multiplicity = $3 \times 3 = 9$ normal
triplets



No of signal = 2

a → triplet

b → triplet.



No of signals = 2

a → triplet

b → ~~quadruplet~~

triplet

etc

chiral

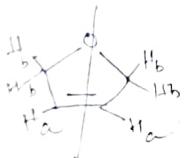


④ 3 signal

a → triplet doublet doublet

b → doublet doublet doublet

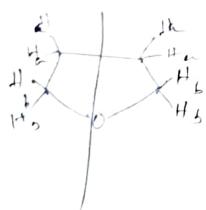
b → doublet doublet



No of signal = 2

a → triplet

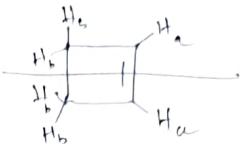
b → doublet



No of signal = 2

a → triplet

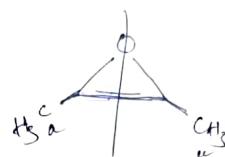
b → triplet



No of signal = 2

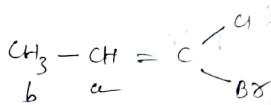
b → doublet

a → triplet



No of signal = 1

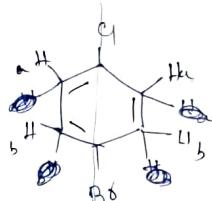
multiplicity = 1



No of signal = 2

b → doublet

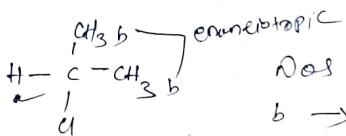
a → quadruplet



No of signal = 2

a → q

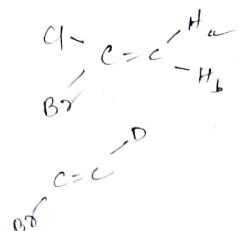
b → q



NoS = 2

b → doublet

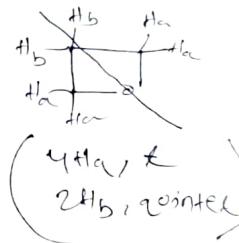
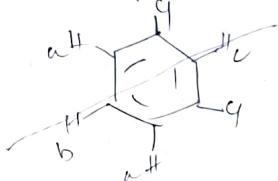
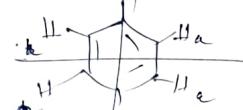
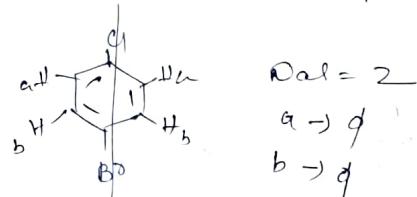
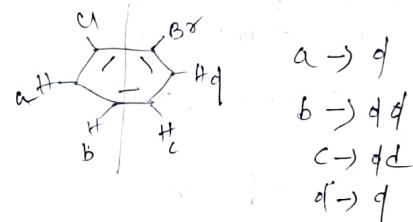
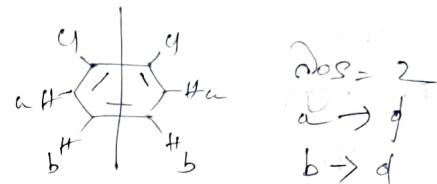
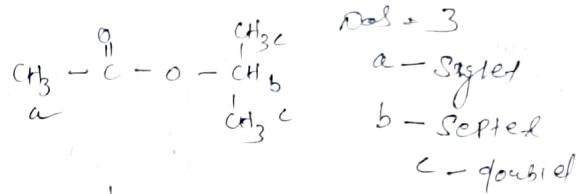
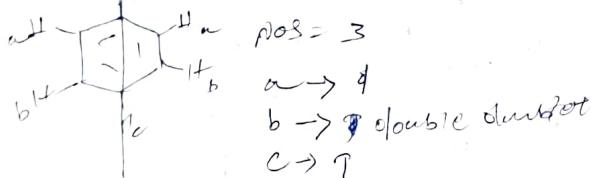
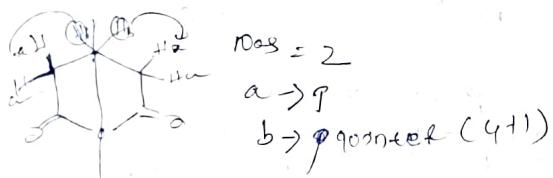
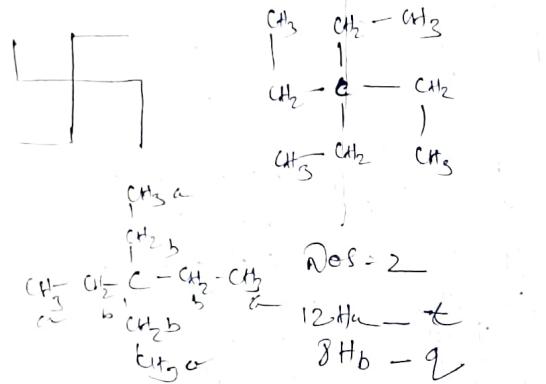
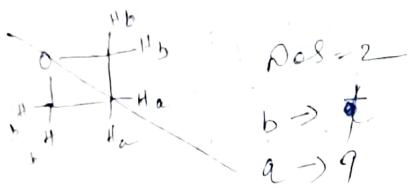
a → septet] diastereop.



NoS = 2

a → q

b → q



Multiplets

Pascal Triangle

Intensity Ratio

$$(2 = \frac{1}{2})$$

Pascal Triangle (ESR)

Coupling constant (J)

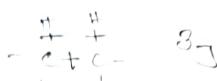
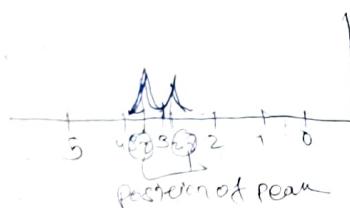
\Rightarrow Standard unit = Hz.

Separation of line of multiplet in one unit of Hz is coupling constant.

① Position of a signal (chemical shift)

② Position of a peak

Position of signal chemical shift



General representation of coupling const.

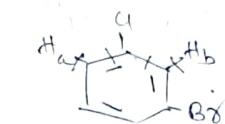
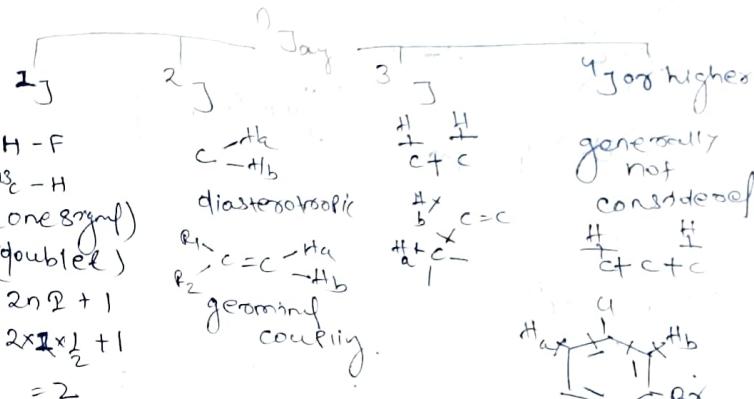
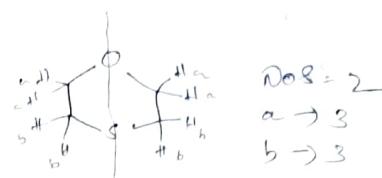
$$= \gamma J_{xy}$$

no at bond between two closely nuclei

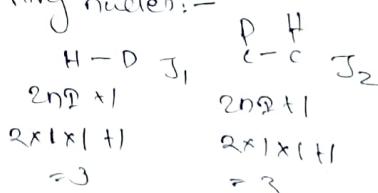
and give coupling const $^3J_{12}$

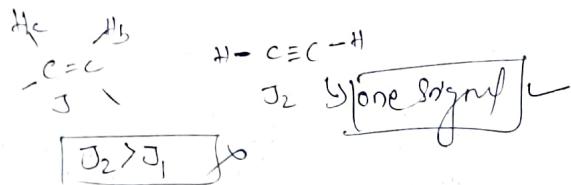
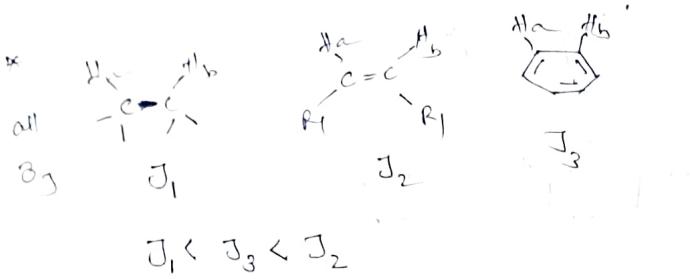
Non-pascal triangle
Intensity Ratio
 $(2 > \frac{1}{2})$

$$\gamma J_{xy} = \gamma J_{yz}$$



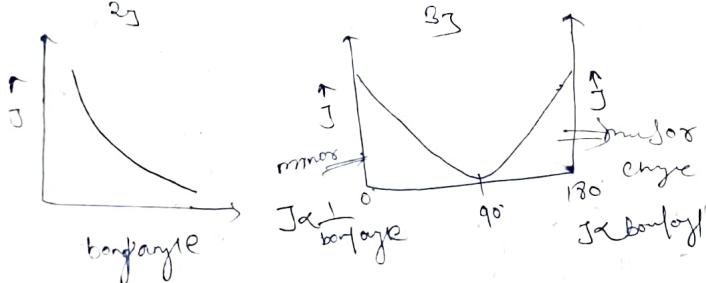
Factors affecting Coupling constant
is comparatively higher
① Bond length / Bond distance b/w coupling nuclei:-





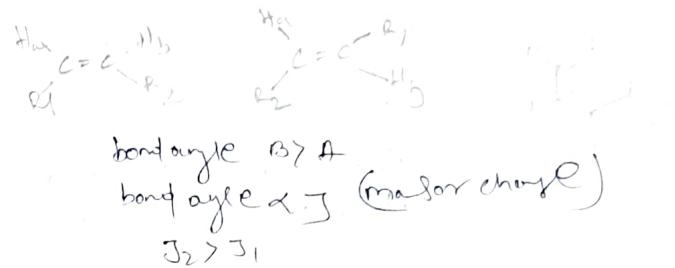
③ Bond angle

Karplus eqⁿ



Bond angle: $\theta_1 > \theta_2 > \theta_3 > \theta_4$

$J_A < B < C < D$



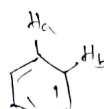
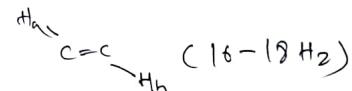
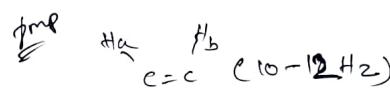
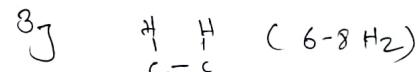
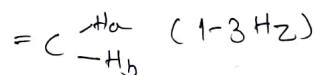
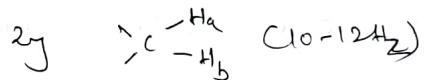
Karplus eqⁿ:

$$J = 8.5 \cos^2 \theta - 0.28 \quad (\theta = 0^\circ - 90^\circ)$$

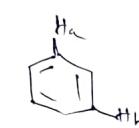
$$J = 9.5 \cos^2 \theta - 0.28 \quad (\theta = 90^\circ - 180^\circ)$$

Value

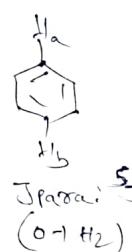
$$^1J \approx 100 \text{ Hz}$$



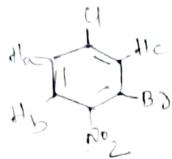
$J_{ortho} {}^3J$
 $7-8 \text{ Hz}$



$J_{meta} {}^3J$
 $(1-3 \text{ Hz})$



$J_{para} {}^3J$
 $(0-1 \text{ Hz})$



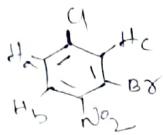
¹H coupling is ignored

H_c → singlet

H_b → doublet (7-3 Hz)

H_a → doublet (7-8 Hz)

¹H coupling is considered

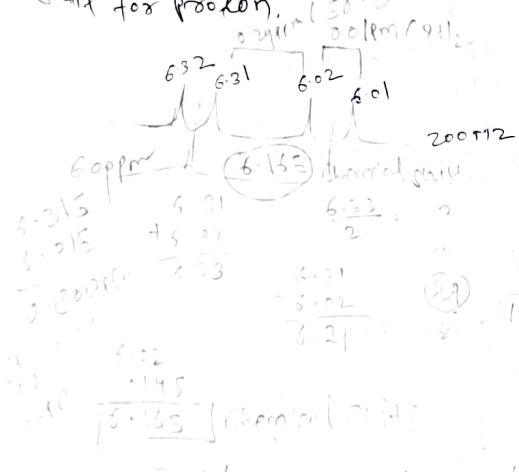


H_c → doublet (7-3 Hz)

H_a → doublet doublet (7 Hz, 2 Hz)

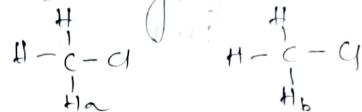
H_b → doublet (2 Hz)

An organic molecule give doublet doublet as shown below for electric proton. At 200 MHz instrument calculate coupling const, chemical shift for proton.



factor affecting chemical shift

① Electronegativity



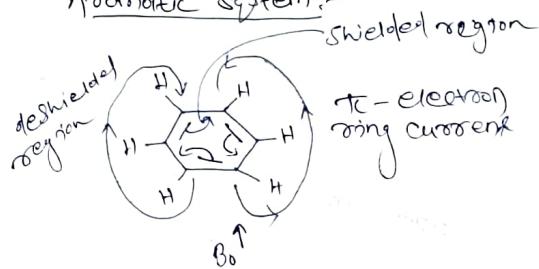
H_a > H_b

Compound	F	C1	B7	P
CH ₃ X	4.3	3.0	2.2	2.2
CH ₂ X ₂	5.4	5.3	5.0	3.9
CHX ₃	7.5	7.25	6.8	4.9

Higher the electronegativity higher is the chemical shift value.

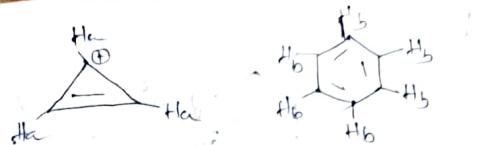
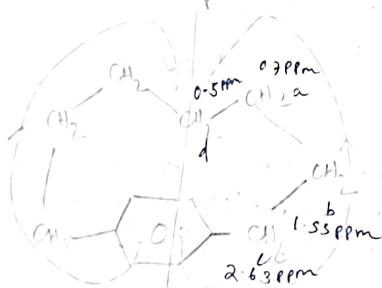
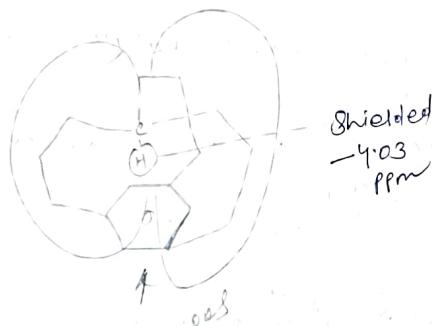
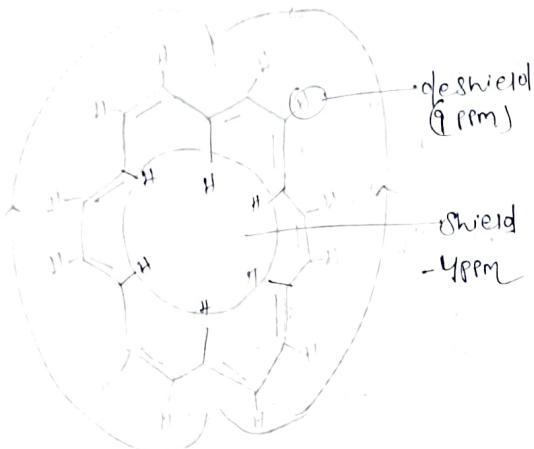
② Anisotropy effect :- direction depended

Aromatic System:-



The π electron ring current of aromatic ring generates an induced magnetic field which is responsible for anisotropy effect.

In case of aromatic system outer proton are deshielded (high δ) inner proton are shielded (low δ)



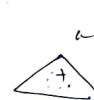
$$\text{Electron density} \propto \frac{1}{\delta}$$

$$[\delta_{\text{Hc}} > \delta_{\text{Hb}}$$

$$\pi\text{-electron density} = \frac{\text{No of } \pi\text{-e}^-}{\text{Total no of proton}}$$

For 3 members

$$\begin{aligned} \text{benzene} \quad \pi\text{-e}^- \text{ density} &= \frac{2}{3} = 0.66 \\ \pi\text{-e}^- \text{ density} &= \frac{6}{6} = 1 \end{aligned}$$



$$\pi\text{-e}^- \text{ density} = \frac{2}{3} = 0.66$$



$$\pi\text{-e}^- \text{ density} = \frac{6}{7} = 0.8$$



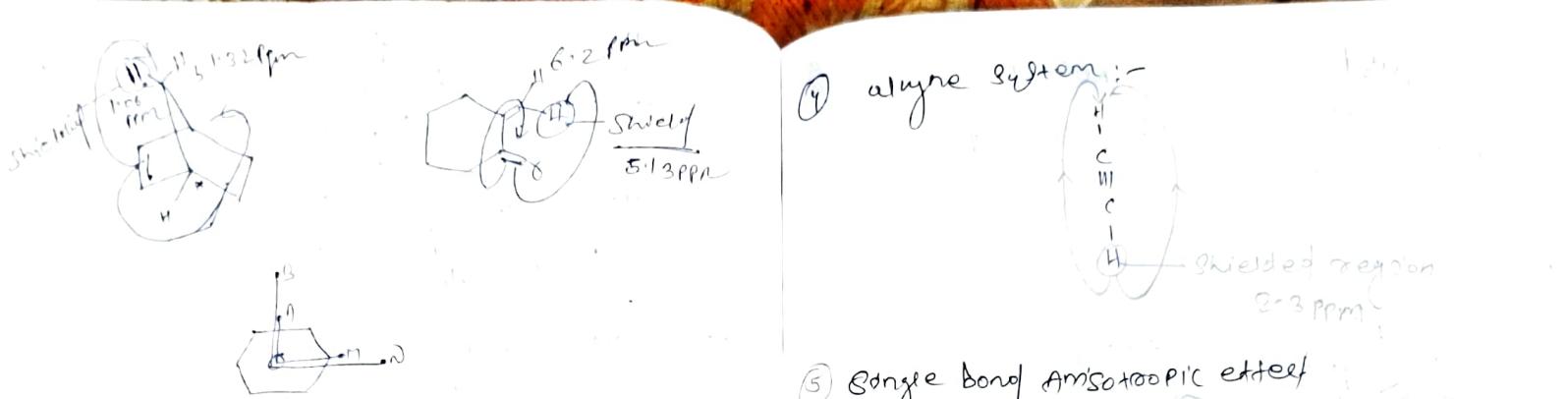
$$\pi\text{-e}^- \text{ density} = 1 \quad \pi\text{-e}^- \text{ density} = \frac{6}{5} = 1.2$$

$$\delta \quad a > b > c > d$$

② olefinic system: carbonyl aldehyde



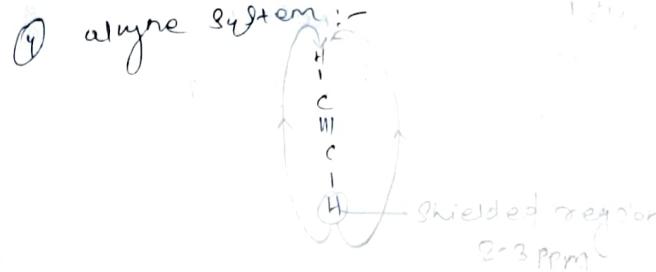
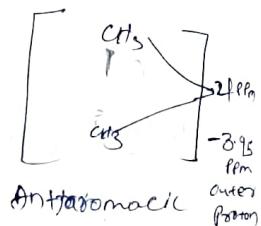
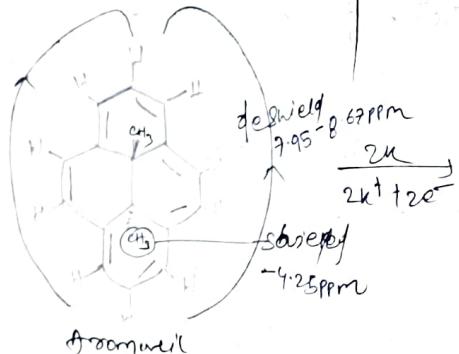
- ① electron deficiency
- ② deshielded region.



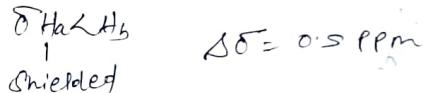
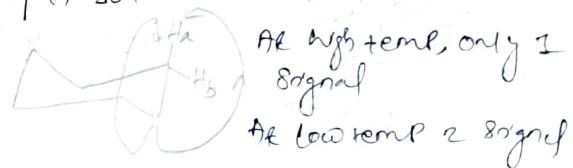
chemical shift: $A < B < N < M$

Aromatic
outer: deshielded
(high δ)
inner: shielded
(low δ)

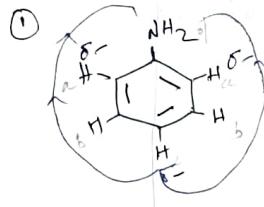
Antiaromatic
outer: shielded (up)
inner: deshielded



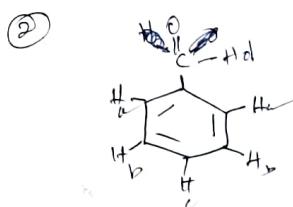
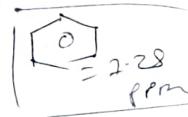
6) Single bond Anisotropic effect



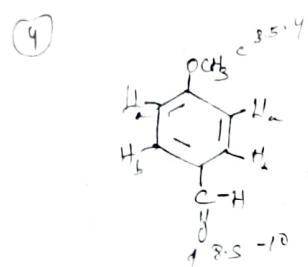
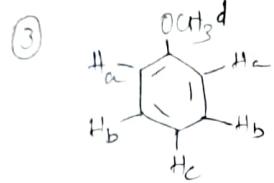
Arrange the following in the increasing order of their chemical shift:



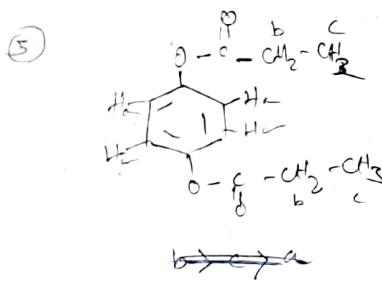
No. of signals = 4
 $\delta_d < a < c < b$
 $\text{NH}_2 < \text{O} < \text{C}_6\text{H}_5$



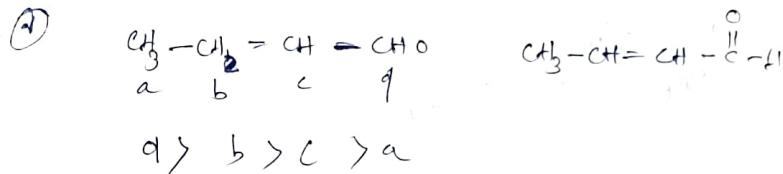
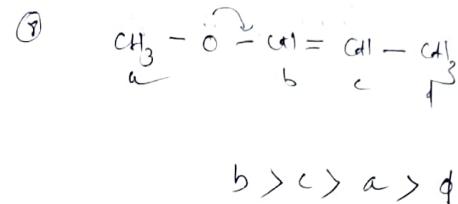
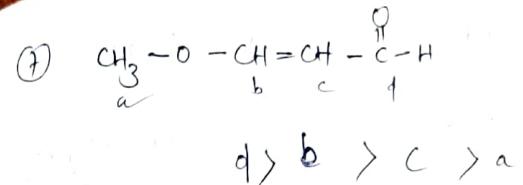
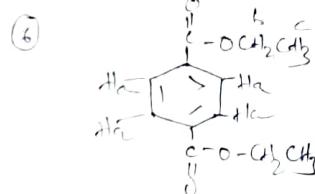
No. of signals = 9
 $\text{H}_d > \text{b} > \text{c} > \text{a}$
 $\text{H}_d > \text{a} > \text{c} > \text{b}$



2④ 2⑤

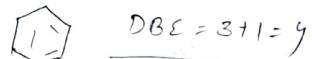
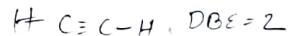
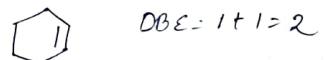


$a > b > c$



Double bond equivalent / Degree of unsaturation

(No. of π -bonds + No of rings / cycles)



$\text{DBE} \geq 4$ (aromatic system)

DBE double bond triple bond ring

$$DBE = \frac{\text{No of tetravalent}}{2} - \frac{\text{No of monovalent}}{2} + \frac{\text{No of trivalent}}{2} + 1$$

C	H	P
δ^-	δ^+	δ^0
Cl, F, Br, I		

C₁₀H₆

$$\begin{aligned} DBE &= 6 - \frac{6}{2} + 1 \\ &= 1 \end{aligned}$$

TMS $\delta^0(\text{CH}_3)_4$

$$\begin{aligned} DBE &= 5 - \frac{12}{2} + 1 \\ &= -2 \end{aligned}$$

C₅H₅N

$$\begin{aligned} DBE &= 5 - \frac{5}{2} + \frac{1}{2} + 1 \\ &= 5 - 2 + 1 = 4 \end{aligned}$$

CyH₆

$$DBE = 4 - \frac{6}{2} + 1 = 0$$



DBE in adamantane system



C₁₀H₁₆

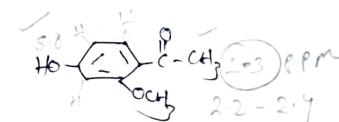
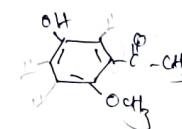
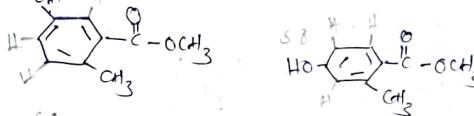
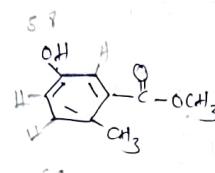
$$DBE = 10 - \frac{16}{2} + 1 = 0$$

Quel C₉H₁₀O₃

DR: 3400, 1680 cm⁻¹

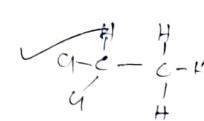
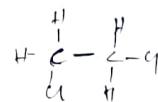
¹H NMR: 7.8 (1H, d, J=8Hz), 7.0 (1H, d, J=8Hz)
6.5 (1H, s), 5.8 (CH, b8S) 3.9 (3H, s), 2.3 (3H, s)

broad
 OCH_3
 OH, NH



Q C₆H₅Cl₂ gives 2 signals: C(0), 2.2ppm, 2.15ppm

$$\begin{aligned} DBE &= (2 - \frac{6}{2} + 1) \\ &= 3 - 3 = 0 \end{aligned}$$



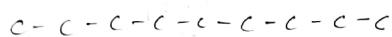
Molecular weight 120

in aromatic at 7.1-7.3 ppm aromatic
doublet at 1.2 ppm
Skeletal III at 2.8 ppm

13/120 @ carbon

$\frac{11}{12}$ quaternary = C
③ quaternary + remainder = H

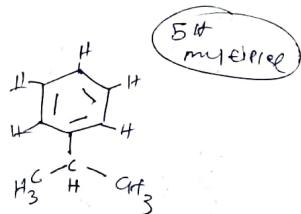
C₉H₁₂



$$DBE = 9 - \frac{12}{2} + 1$$

$$= 9 - 6 + 1$$

④ aromatic



Chemical shift

H₂: dependent on instrument

ppm: independent of instrument

coupling const

H₂: independent

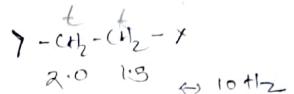
ppm: dependent

spin position

H₂: dependent
ppm: independent



first order
second order (non-first order spectra)



$$2.0 \text{ T.S.} \leftrightarrow 10 \text{ Hz}$$

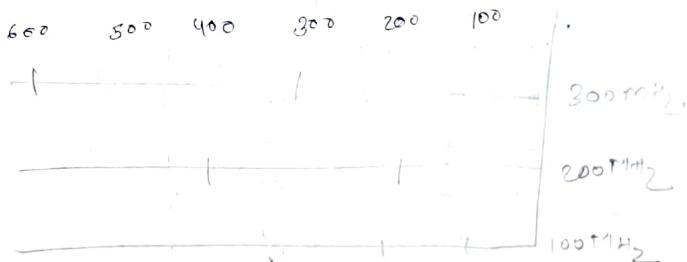
300 T¹H₂

$$\frac{\Delta\delta}{J} = \frac{(8.0 - 1.8) \text{ ppm}}{10 \text{ Hz}}$$

$$= \frac{0.8 \times 500}{10} \text{ Hz}$$

$$= 28 \text{ Hz}$$

300 T¹H₂



1 ppm

2 ppm

Intensity of inner peak
and outer peak decrease \rightarrow other peak merge

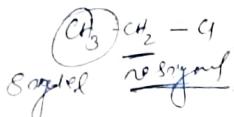
$\frac{\Delta\delta}{J} > 10$ first order spectra (classical triangle)

$\frac{\Delta\delta}{J} \leq 10$ second order spectra (does not follow Pascal triangle)

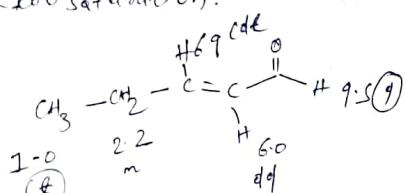
Double irradiation technique

① Selective spin decoupling

double irradiation \Rightarrow saturation



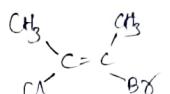
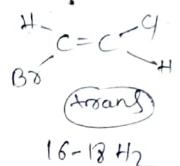
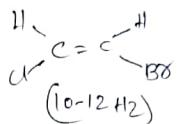
when we selectively double irradiate to the set of equivalent/ non-equivalent nuclei are non signal of this set will disappear due to large proton also disappear due to saturation.



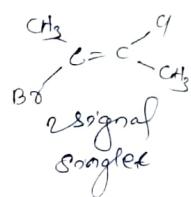
	1.0	2.2	6.0	6.9	9.5	
Normal	t	m	dt	dd	d	
1.0	-	d	dt	dd	d	
2.2	s	-	d	dd	d	
6.9	t	q	-	d	d	
6.0	t	m	t	-	s	
9.5	t	m	dt	d	-	

② NOE & nuclear Overhauser effect

It is used to identify interaction between non equivalent proton through spin.

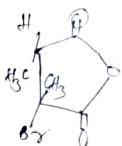
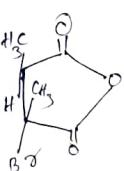


2 signal
singled



2 signal
singled

If two non equivalent proton are far away from each other through the bond but they are very close in space due to their stereochemistry then if we selectively double irradiate, 1 set of equivalent proton the intensity of another set increased.



Under ordinary condition C reacts to air right and water vapour) acid impurity develop in CDCl_3 soln and catalyse the mutual exchange of old proton. The proton is not on the oxygen atom of an individual molecule long enough for it to be affected by CH_2 proton therefore no coupling, so singlet will be obtain.

Rate of exchange can be lowered by

- ① by adding NaClO_3
- ② by lowering the temp.
- ③ by using dilute soln.

^{13}C NMR



↓ dilute

(~1.1%)

$$\text{④ } \gamma_{^{13}\text{C}} = 10.708 \text{ MHz/T}$$

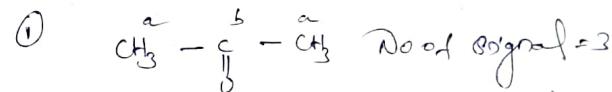
Less sensitive nucleus
Regarding same and
sample amount \rightarrow high



\Rightarrow Concentrated
(~100%)

$$\gamma_H = 42.57 \text{ MHz/T}$$

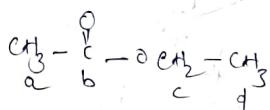
Highly sensitive nuclei



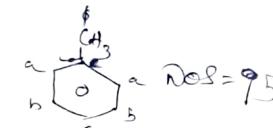
Total No of Signals are not observe from a single molecule it is the average for all the observe molecule.

Brown eye - insect

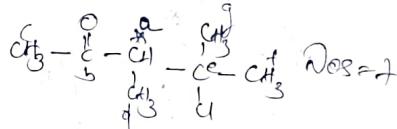
②



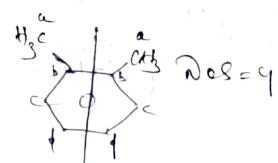
③



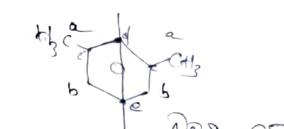
④



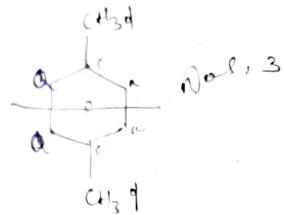
⑤



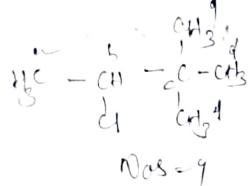
⑥



(7)



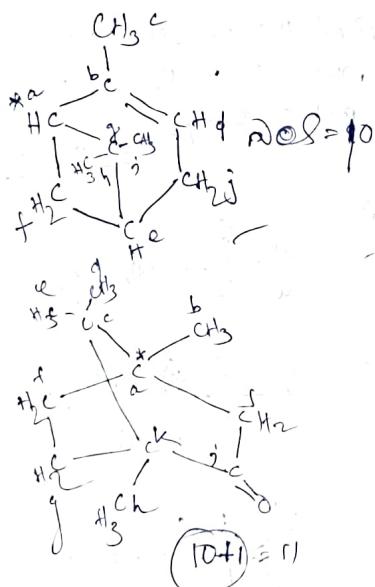
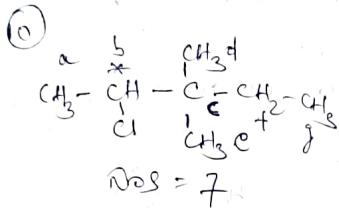
(8)



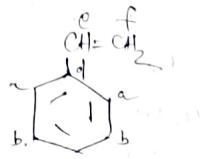
(9)



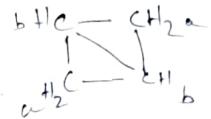
(10)



(11)



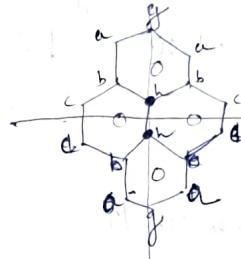
(12)



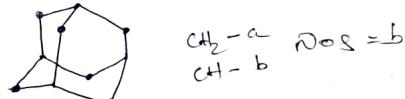
(13)

 $\text{NOS} = 5$ 

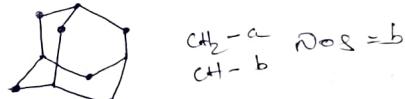
(14)



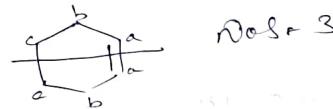
(15)



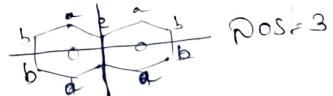
(16)



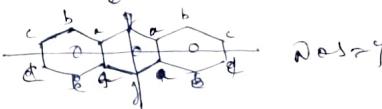
(17)



(18)



(19)



(20)



Chemical Shifts:-

$\text{H-NMR} \rightarrow 0.5 \rightarrow 2 \rightarrow 5 \rightarrow 8 \rightarrow 10.5 \rightarrow 12$

$\text{^{13}C-NMR} \rightarrow 10 \rightarrow 40 \rightarrow 80 \rightarrow 115$
 $100 \rightarrow 150 \rightarrow 220$

$\text{^{13}C-NMR}$ 0 to 12 ppm for aldehyde/ketone
 $(180 \rightarrow 200 \text{ ppm})$

$\text{^{13}C-NMR}$ 10 to 220 ppm

Chemical shift of ^{13}C nucleus will be approximately same as chemical shift of attached proton.

Reason :-

① Hyperfine ratio

$$\gamma_c = 10.705$$

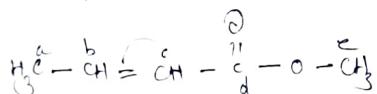
$$\gamma_H = 42.57 \text{ MHz}$$

$$\gamma_H \approx 4\gamma_c$$

② No of electrons

$$H \rightarrow 1$$

$$C \rightarrow 6$$

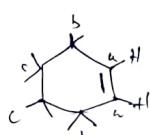
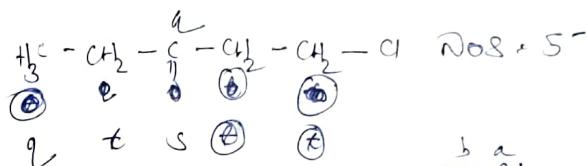


$$a < e < c < b < d$$

Multiplicity of a Signal

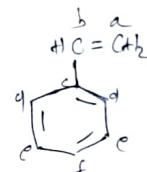
^{13}C - dilute nuclei

only 1J coupling is significant



$$\text{NoS} = 3$$

$$\begin{aligned} a &\rightarrow d \\ b &\rightarrow e \\ c &\rightarrow f \end{aligned}$$



$$\text{NoS} = 6$$

$$\begin{aligned} a &- \text{E} \\ b &- \text{d} \\ c &- \text{s} \\ d &- \text{g} \\ e &- \text{g} \\ f &- \text{g} \end{aligned}$$

* $\text{C}_6\text{H}_5\text{O}$

$^{13}\text{C-NMR}$:

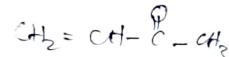
28 ppm, quartet

130 ppm, triplet

188 ppm, doublet

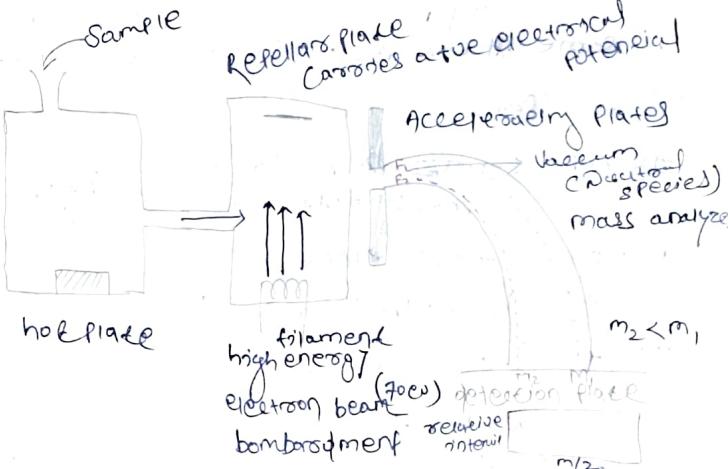
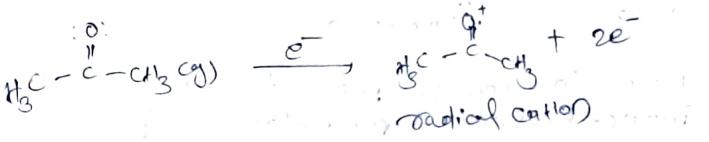
- 188 ppm, singlet

$$\text{DBE} = 4 - \frac{6}{2} + 1 = 2$$



Mass Spectrometry

No radiation is used



Sample introduction → vaporisation → ionisation →
fragmentation → acceleration → deflection →
mass separation → detection

$$\frac{M}{2} \propto \alpha^2 \propto \frac{1}{\text{deflection}}$$

- * which of the following will be deflected max^m and min^m in most spectrometers?

- w) $^{16}\text{O}_2^+$ b) $^{16}\text{O}^{18}\text{O}^+$ c) $^{16}\text{O}_2^{2+}$ d) $^{18}\text{O}_2^{2+}$

$\frac{M}{2} = 32$ 89
less deflection

16 more dedication 18
 $\frac{1}{2}$ x $\frac{1}{2}$ dedication



molecular ion :- peak of disassembled molecular ion peak.

Base peak - Peak having 100% intensity

base peak and molecular ion peak can be same if the molecular ion very stable.

Isotopic Peaks

Isotopes :- atomic no same mass difference

① monoisotopic element :-

e.g. ^{19}F , ^{31}P , ^{127}I

② (± 1) contributions

e.g. C, N, B, H

^{12}C , ^{13}C

^{14}N , ^{15}N

^{11}B , ^{13}B

^{14}N , ^{15}N

^1H , ^2H

③ (± 2) contributions

C: ^{35}Cl and ^{37}Cl

B: ^{11}B , ^{13}B , ^{15}B

④ $(m+1)$ and $(m+2)$ contributions

e.g. ^{16}O , ^{17}O , ^{18}O

^{34}S , ^{35}S , ^{36}S

Relative Natural abundance

$^{12}\text{C} = 100\%$, $^{13}\text{C} = 1.1\%$.

$^{1\text{H}} = 100\%$, $^{2\text{H}} = 0.015\%$.

$^{35}\text{Cl} = 100\%$, $^{37}\text{Cl} = 33\%$.

$^{14}\text{N} = 100\%$, $^{15}\text{N} = 0.32\%$.

$^{32}\text{S} = 100\%$, $^{33}\text{S} = 0.8\%$, $^{34}\text{S} = 4.4\%$.

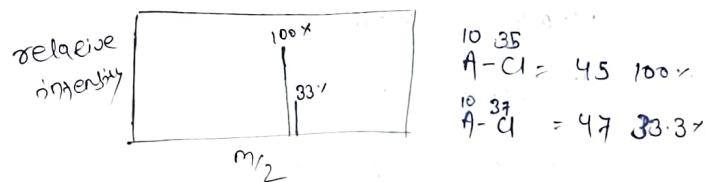
$^{28}\text{Si} = 100\%$, $^{29}\text{Si} = 5.1\%$, $^{30}\text{Si} = 3.4\%$.

$\checkmark 79\text{ Br} = 100\%$, $^{81}\text{Br} = 97.5\%$.

^{12}C , ^{13}C

Natural abundance 98.92% , 1.08% .

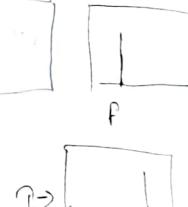
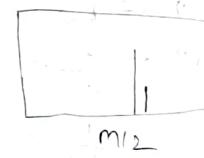
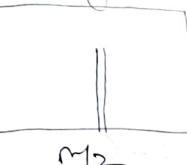
Relative natural abundance $\frac{98.92}{98.92} \times 100 = 100\%$, $\frac{1.08}{98.92} \times 100 \approx 1.1\%$.

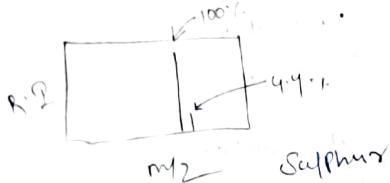


Halogen containing compound = Br

Relative abundance

m/z



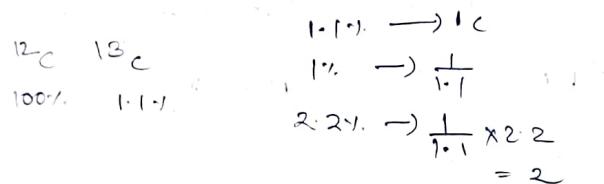


Q.10 Intensity of M^+ = 100%.

$$(M+1)^+ = 2.2\%$$

Calculate the no. of odd carbon atoms.

Ans



for saturated hydrocarbons molecular peak

at $\frac{M}{2} = 84$ with relative intensity of

8.63% and $(M+1)$ peak of intensity 2.06%.

What is the molecular formula?

m : $M+1$ Molecular ion
81.63% 2.06% Peak = 84

$$\frac{81.63}{81.3} \times 100\% = \frac{2.06}{81.3} \times 100$$

$$= 100\% = 6.38\%$$

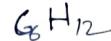
m $M+1$

$1.1\% \rightarrow 1\%$

$1\% \rightarrow \frac{1}{1.1}\%$

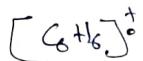
$$6.38 \rightarrow \frac{1}{1.1} \times 6.38 \approx 6$$

Rel. no. of carbons = 6



* calculate the intensity ratio of isotopic signal ($M+1$) and ($M+2$) w.r.t. molecular ion of benzene.

Ans



$m : M+1 : M+2$

Lee $\eta = 100\%$.

$M = 100\%$

$$M+2 = (6 \times 1.1) + (6 \times 0.015)$$

$$= 6.6 + 0.090$$

$$= 6.69\%$$

$$M+1 = 6.69$$

$$M+2 = 0.006\%$$

$$\boxed{M+2 = 0.006\%}$$

$\eta = \text{no. of carbon atoms}$

$$= 0.006 \times 6^2$$

$$= 0.006 \times 36$$

$$= 0.216\%$$

$M : M+1 : M+2$

$$100 : 6.69 : 0.216$$

$$\frac{100}{0.216} : \frac{6.69}{0.216} : \frac{0.216}{0.216}$$

$$462.9 : 31 : 1$$

* calculate $\eta : M+1 : M+2$ for standard reference of $^1\text{H-NMR}$.

Chloro SiF_3 = 100% + $^{29}\text{Si} = 5.1\%$, $^{31}\text{Si} = 34\%$)



$M = 100\%$

$M+1 = 4 \times 1.1\%$

$$+ 12 \times 0.015$$

$$+ 5.1\%$$

$$= 4.4 + 5.1 + 0.180$$

$$= 9.68\%$$

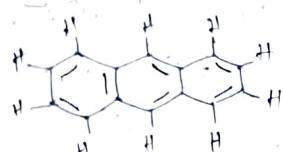
$M+2 = 3.1\%$ (carbon neglected)

$$100 : 9.68 : 3.4$$

$$\frac{100}{3.4} : \frac{9.68}{3.4} : \frac{3.4}{3.4}$$

$$30 : 3 : 1$$

Calculate the intensity ratio of $M_1/M_1 + M_2$ of anthracene.



$C_{14}H_{10}$

$$\eta = 100\%$$

$$M_1 = 14 \times 1.1 + 10 \times 0.005$$

$$= 15.4 + 0.15$$

$$= 15.55\%$$

$$M_2 = 0.006 \times (14)^2$$

$$= 0.006 \times 196$$

$$= 1.176$$

$$100 : 15.55 : 1.176$$

$$100 : 15 : 1$$

Catalytic intensity ratio $M_1/M_1 + M_2$ for See

$$M = 100\% \quad M_1 : M_2$$

$$M_1 = 1.1 \times 60 \approx 66.0\%$$

$$100 : 66 : 21.6$$

$$100 : 66 : 22$$

$$5 : 3 : 1$$

$$M_2 = 0.006 \times 60\%$$

$$= 21.6\%$$

When no of carbon in molecule are high the probability of two Carbon atom at the same time in the molecule increases.

The contribution of two carbon β^2 at the same time will be provided to the M_2 signal of will be equal to $0.006 n^2\%$.

Compound containing halogen:-

If $\eta =$ total no of halogens

then no of isotopic signals $S = \frac{\eta}{2}$

$$\eta = 1 \quad M_1 \quad M_2$$

$$\eta = 2 \quad M_1 \quad M_1 + 2 \quad M_2 \quad M_2$$

$$\eta = 3 \quad M_1 \quad M_1 + 2 \quad M_1 + 4 \quad M_2 \quad M_2 + 4$$

201



Intensity Ratio

case of only ^{37}Cl is present

$$\frac{^{35}\text{Cl}}{^{37}\text{Cl}} : \frac{^{37}\text{Cl}}{^{37}\text{Cl}}$$

$$100\% : 33\% : 1$$

case If 2 CI are present

M M+2 M+4

35CI	37CI	35CI
35CI	37CI	37CI

$3 \times 3 : (1 \times 3) + (3 \times 1) : 1 \times 1$

9 : 6 : 1

case If 3 CI are present

M M+2 M+4 M+6

35CI	35CI	35CI	37CI	37CI	35CI	37CI
35CI	35CI	37CI	37CI	35CI	37CI	37CI
35CI	37CI	35CI	37CI	35CI	37CI	37CI

$3 \times 3 \times 3 : (3 \times 3 \times 2) + (3 \times 3 \times 1) + (3 \times 3 \times 1) : (1 \times 1 \times 3)(1 \times 1 \times 3) + (1 \times 1 \times 1)$

27 : 27 : 9 : 1

case-10 only one B8 present

M M+2

B8 : B8

100 : 97.5

1 : 1

case If two B8 are present

M M+2 M+4

79B8	79B8	81B8	81B8
79B8	81B8	79B8	81B8

$1 \times 1 : (1 \times 1) + (1 \times 1) : 1 \times 1$

1 : 2 : 1

case If three B8 are present

M M+2 M+4

79B8	79	81	79	81	81	79	31
79B8	79	79	81	79	81	81	81
79B8	81	79	79	79	81	81	81

$1 \times 1 \times 1 : 1 + 1 + 1 : 1 + 1 + 1 : 1 \times 1$

1 : 3 : 3 : 1

4B8 : 1 : 4 : 6 : 4 : 1

SB8 : 1 : 3 : 10 : 10 : 3 : 1

follows
Pascal triangle

case If 1CI and 1B8 are present

No 2 isotopic signals = 2

M M+2 M+4

35CI 35CI 37CI 37CI

79B8 81B8 79B8 81B8

$(B8 \times 1) : (3 \times 1) + (1 \times 1) : 1 \times 1$

8 : 4 : 1

for 3 isotopic signals = 3

case if 2Cl and 1Br is present

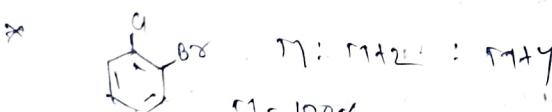
71	71+2	71+4	71+6
35	35 33 35	37	35 37 37
35	35 33 33	37	37 35 32
29	81 79 79	79	81 81 81

$$(8 \times 3 \times 1) : (3 \times 3 \times 1) + (1 \times 3 \times 1) + (3 \times 1 \times 1) : 1 + 3 + 3 : 1 \\ 9 : 18 : 7 : 1$$

case if 2Br and 1Cl is present

71	71+2	71+4	71+6
71	81 79 79	81 81 79	81
71	79 81 79	81 79 81	81
35	35 35 37	35 37 37	37

$$[3 : 7 : 5 : 1]$$



$$71 = 100\%$$

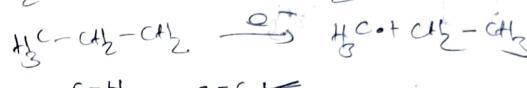
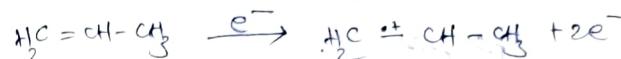
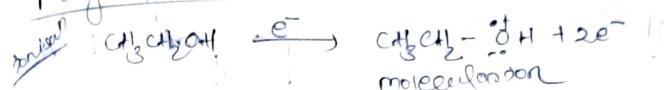
$$71+2 =$$



71	71+2	71+4
35	35 33	37
29	81 79	81

$$(8 \times 1) : (3 \times 1) + (1 \times 1) : 1 \times 1 \\ 3 : 4 : 1$$

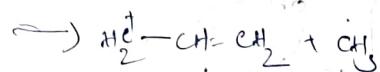
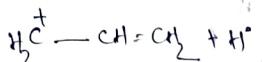
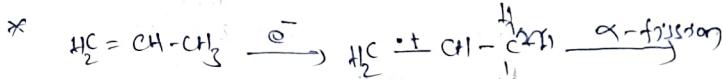
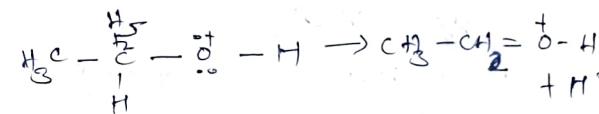
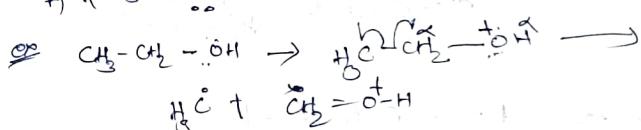
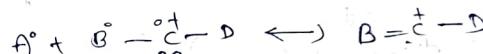
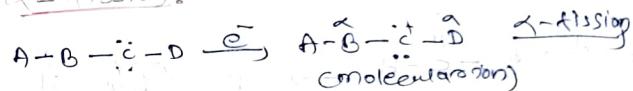
Fragmentation:-

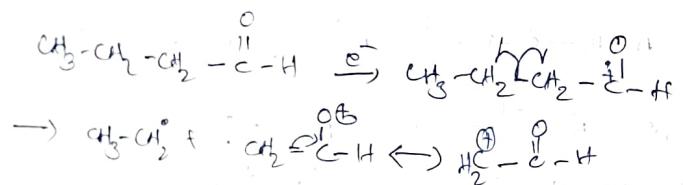
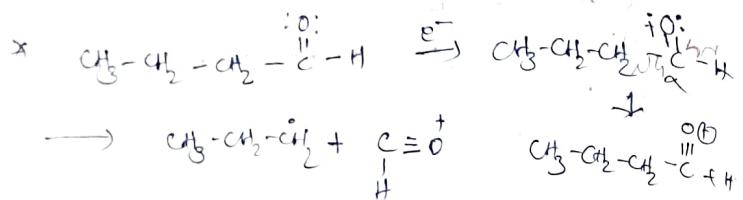
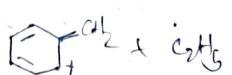


Both radical are generated.

Fragmentation on π bond and nonbonding electron containing system

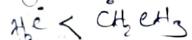
(i) α-fission:-





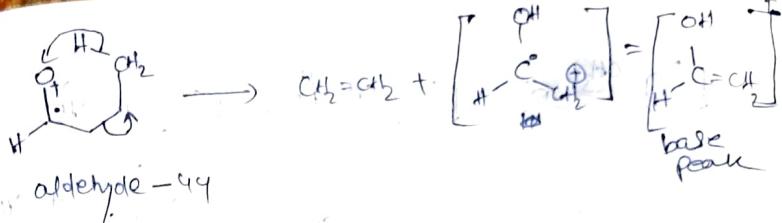
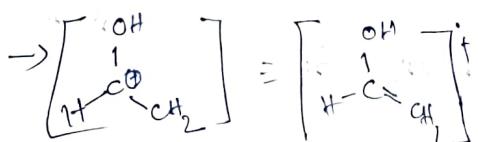
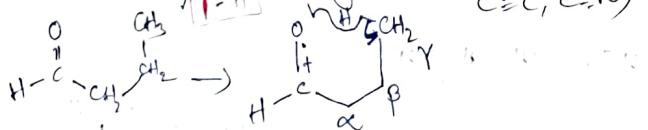
Rules

① Br_nY radical base preferred



② more stable cation fragment should be formed.

③ McLafferty Rearrangement ($\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{CO}_2\text{Na}$, $\text{C}_2\text{H}_5\text{CN}$)



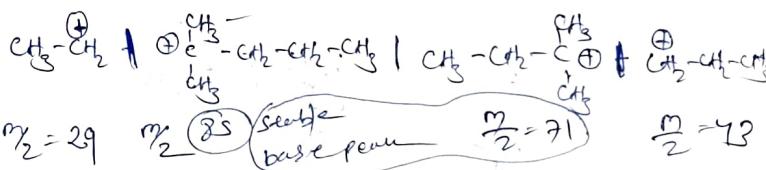
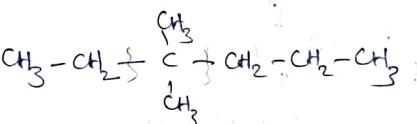
Note

- * Carbocation should be stable
- * If both carbocations are equally stable then the fragment having more fully branched will be preferred.

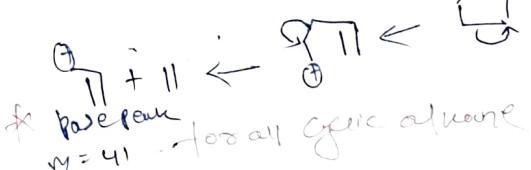
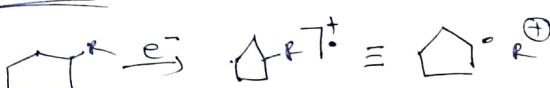
Branched alkane

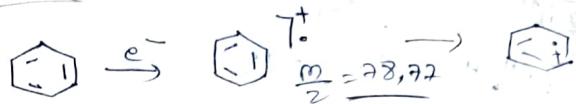
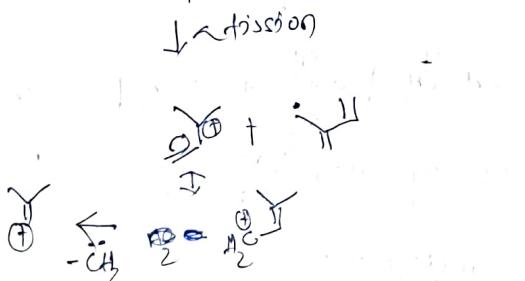
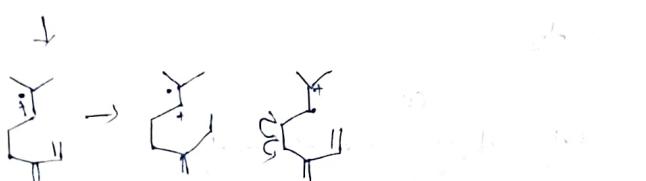
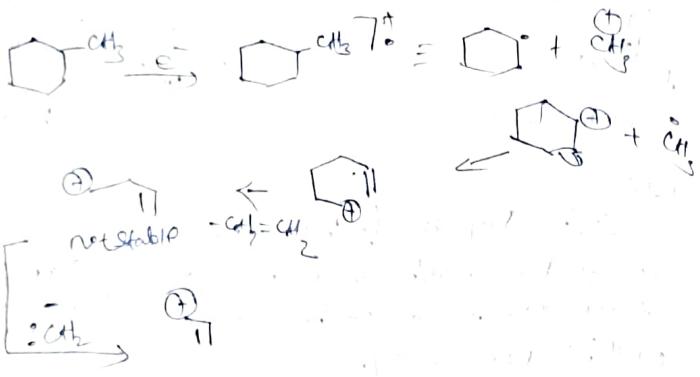
* deprotonation from the most branched carbon.

* C₈H₁₈

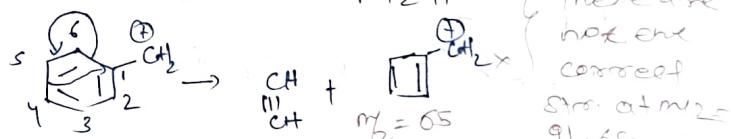
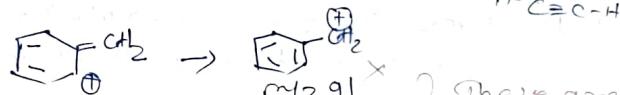
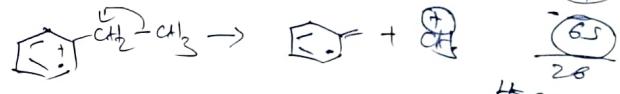


cyclic alkane



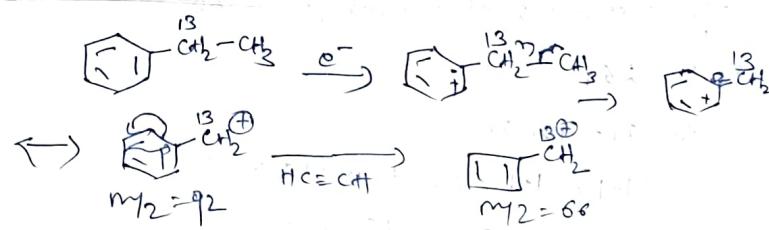


Mono Substituted Benzene:-

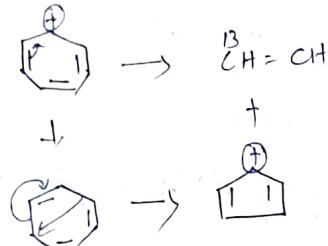
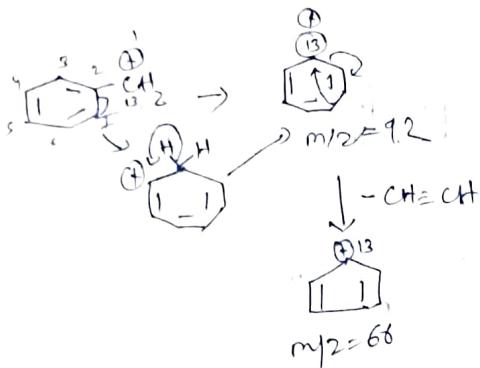


These are
not the
correct
steps at my
91, 65.

Experimental proof



Pearns 92, 68, 68 -



Ans:

- Q1. In the mass spectrum of dodecaheptane ($\text{C}_{20}\text{H}_{20}$) approximate ratio of the peak at m/z 280 and 261 is :-

- ① 1:1 ② 6:1 ③ 10:1 ④ 20:1

Ans $\text{C}_{20}\text{H}_{20}$

$$M = 12 \times 20 + 20 \times 1 = 240 + 20 = 260$$

$$M+1 = 261$$

$$\% M = 100\%$$

$$M+1 = 1.1 \times 20 + 0.015 \times 20$$

$$= 22.0 + \frac{15}{100} \times 20$$

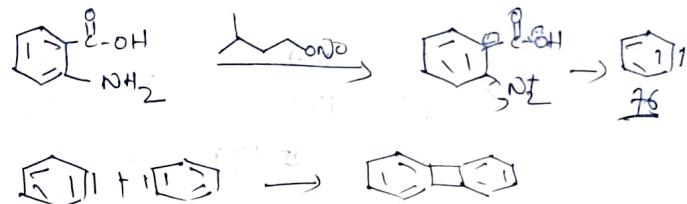
$$= 22.0 + 0.30 = 22.30$$

$M: M+1$

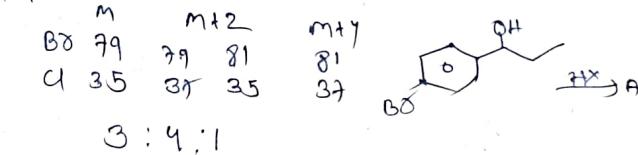
100: 22.3

$$\frac{100}{22.3} : \frac{22.3}{22.3} = 8:1$$

Q2 Anthranilic acid on treatment with isoamyl nitrite furnished a product which displayed a strong peak at 76 (m/e) in its mass spectrum. The structure of the product is

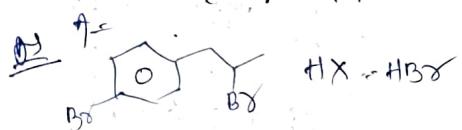


Q3 The mass spectrum of product A, formed in following reaction, exhibited $M, M+2, M+4$ peak in the ratio of about 1:2:1. The reagent HX and product A are?

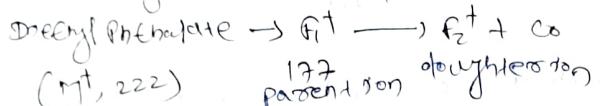


B8	79	81	79	81
B8	79	91	81	81

1:2:1



Q4 The mass of metastable ion produced during decomposition of F_1 in the following mass fragmentation sequence is

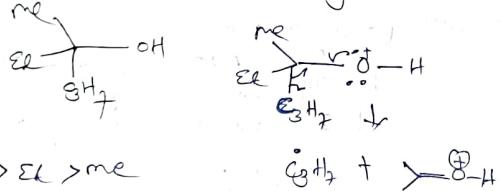


- (A) 141.2 (B) 125.4 (C) 45.0 (D) 210.2

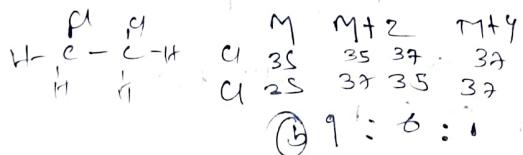
\Rightarrow mass of metastable ion = (mass of daughter ion) / mass of parent ion

$$\begin{aligned}\text{F}_1^+ &= 177 \\ \text{F}_2 &= 177 - 28 \\ &= 149 \end{aligned} \quad \frac{(149)^2}{177} = 124.5$$

Q5 In the mass spectrum of the compound given below, during α -cleavage, the ordered preferential loss of group (I) is



Q6 In the mass spectrum of 1,2-dichloroethane, approximate ratio of peaks at m/z 98, 100, 102 will be



Statement: 5-Bromopyrromoline ($\text{C}_9\text{H}_9\text{BrN}_2$) exhibits two prominent peaks in the mass spectrum at m/z 112 and 160 in the ratio of 1:1

Reason: There are two basic centers in the molecule which are protonated.

Assumption: There are two isotopes of bromine ($^{79}\text{Br}, ^{81}\text{Br}$) that occurs in the ratio of 1:1.

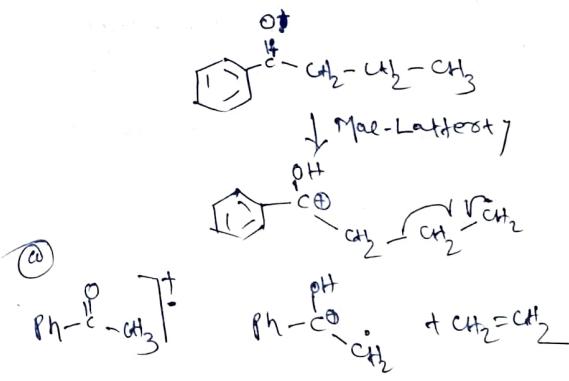
Assumption is correct but reason is wrong.

Q7 Among the isomers given below,

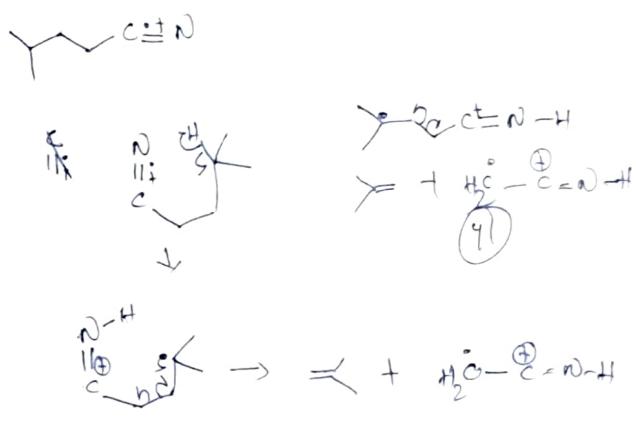
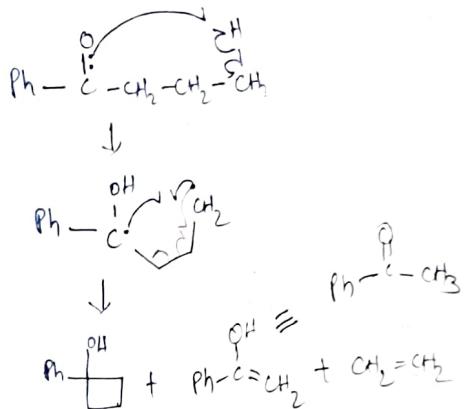


The isomer that can be separated uniquely by mass spectrometry alone is — McLafferty rearrangement

Q8 for butyrophenone ($\text{PhCOCH}_2\text{CH}_2\text{CH}_3$). The most probable fragmentation observed in the electron impact ionization mass spectrometry is:



Q.10 For butyrophenone ($\text{PhCOCH}_2\text{CH}_2\text{C}_6\text{H}_5$). Photo
irradiation leads to the following set of
products: —



Q.11 The ratio of relative intensities of the two
molecular ion peaks of methyl bromide (CH_3Br)
in the mass spectrum is

	m	$m+2$
Br	79	81

✓ 1:1

Q.12 The m/z value of the detectable fragment from
by Metathesis like rearrangement of the following
compound in mass spectrometer is —



Absorption Spectroscopy
microwave radiation ($\lambda = 0.9 - 25 \text{ cm}$)

McLafferty rearrangement

Compound type . substituent $\text{^77} \text{Cl}$ Peak

Aldehyde	-H	44
methyl ketone	-CH ₃	58
Amide	-NH ₂	59
Acid	-OH	60
enyl ketone	-CH ₂ -CH ₃	72
methyl ester	-OCH ₃	74

Aldehyde

