Unit - 2

Mass spectrometry

* we supply energy in the form of light (UV, IR, NMR) absorption takes place so these are called spectroscopy techniques.

Where as in mass instead of light we supplied high energetic electronic been 70 eV.

Hence it is called spectrometry. It is an instrumentation word.

* Advantages:

* Less quantity of sample is required remaining all the above 3 times.
* Molecular weight of the compound is identified
* Approximate No. of carbons can be identified.

To identified the preferable position of the fragmentation.

It is used to the explanation of the reaction mechanism.

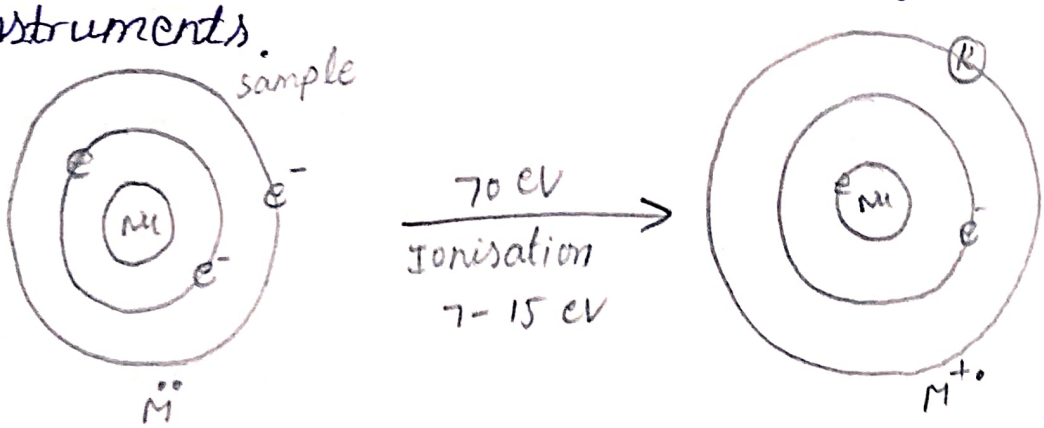
It is used identified to the extra elements.

Drawbacks

* sample can't reproduce. It involves in fragmentation.
* The sample must be taken it vapour state.
* Compounds having high melting point or B.P detection of sample is difficult.

Principle

when this supply high energetic electronic beam to our sample if removes an electron from if outermost shell to give position ion. These positive ions are analyzed by mass instruments.



Ionization Energy for most of the organic compounds is 7 to 15 eV.

The remaining energy is used further fragmentation.

$$\ddot{M} \xrightarrow[(7 \text{ to } 15 \text{ eV})]{70 \text{ eV}} \overset{+\cdot}{M} \xrightarrow{70 - (7 \text{ to } 15)} \text{fragmentation} \rightarrow m_1^{\cdot}, \; m_2^{+}, \; m_3^{+\cdot}, \; m_4^{-}$$

Ionisation Molecular ion — Radical cation — Fragment ions Daltel ions.

Generally, mass instrument recognize +ve ions with their corresponding m/z values.

Here, m = mass of the substance

z = charge of the ion

Charge in the sense removal of one electron.

Therefore z = 1.

10M Mass instrument consists of five major parts,

1. Inlet system :- samples are inserted into the ionisation chamber in vapour phase, samples are placed in an ampoule connected to the ionisation chamber by heating the Ampoule. By heating the Ampoule the sample can be diffused to the sinter into the ionisation chamber.

Solid sample with lower vapour pressure are inserted directly to the ionisation chamber through insertion probe. (10^{-6} mm of Hg).

2. Ionisation chamber :-

Electron impact method is the common technique used to bombardment of the sample with the high energetic electronic Bean (70 e^- volts), 1 electron is eleminated from outermost shell of the compound. Forming a Radical cation which is known as molecular ion (or) parent ion.

For ionisation only 7 to 15 e^- volts required the remaining energy is used for the further Fragmentation of the molecular ion. After the fragmentation the formed dather ions (or)

fragment ions are repelled by accelerated plates and they down to ion tube.

3. Ion Tube :- Behavior of ions in ion Analyzer :-

Ions are repelled by accelarated plates donot have identical kinetic energy. They have passed through the ion tube between two curved plates which are electrostatically charged. Behaviour of ions in electricfield can be calculated by using the equation.

Centrifugal force $\frac{mv^2}{r} = zE$

$$mv^2 = rzE \longrightarrow (1)$$

at the time potential energy = kinetic energy

$$zV = \frac{1}{2}mv^2$$

$$2zV = mv^2 \longrightarrow (2)$$

from equation (1) & (2)

$$rzE = 2zV$$

$$rE = 2V$$

$$\boxed{r = \frac{2V}{E}}$$

Thus radial part followed by ions of given velocity is independent of m & z values

When the ions are repelled by electric field the potential energy is converted into

kinetic energy.

$$zV = \tfrac{1}{2} mv^2$$

$$2zV = mv^2$$

$$\frac{2zV}{m} = v^2 \longrightarrow (3)$$

The ions repelled by electric field whatever may be their m/z values and they couple with magnetic ioniser to resolve m/z values.

when ions are shoot into magnetic field they have circular motion and the centrifugal force is equal to magnetic field.

$$\frac{mv^2}{r} = zBv$$

$$v = \frac{zBr}{m}$$

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

v^2 value substitute in eq (3)

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

$$2V = \frac{zB^2r^2}{m}$$

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

By varying B (or) V the focusing of ions

can be regulated. These double focussed spectrometer can attain resolutions of 1 in 16,000.

4. Detector (or) Reflector :

The focused ions bean pass through the collecter slit to detector which converds the positively charged ions into electrical pulse. This are amplified and recorded to give the spectrum.

Mass spectral Analysis of Butane :

$$CH_3 - CH_2 - CH_2 - CH_3 \xrightarrow{70 e^- V} CH_3 - CH_2 - CH_2 - CH_3^{+\cdot}$$

$M^{+\cdot} = 58$

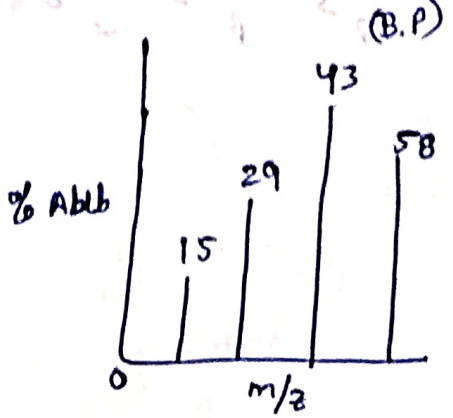
$-\dot{C}H_3$: $CH_3 - \overset{\oplus}{C}H - CH_2$ (H shift) ; m/z = 43 ; $1^\circ C^\oplus$

$-\dot{C}_2H_5$: $CH_3 - \overset{\oplus}{C}H_2$; m/z = 29 ; $1^\circ C^\oplus$

$-\dot{C}_3H_7$: $\overset{\oplus}{C}H_3$; m/z = 15

H-shift ⟷

$CH_3 - \overset{\oplus}{C}H - CH_3$; $2^\circ C^\oplus$



SM

Mac. Lafferty.

Mc. Lafferty rearrangement takes place in unsaturated centres which contain γ-hydrogen in this mechanism involves 3 steps.

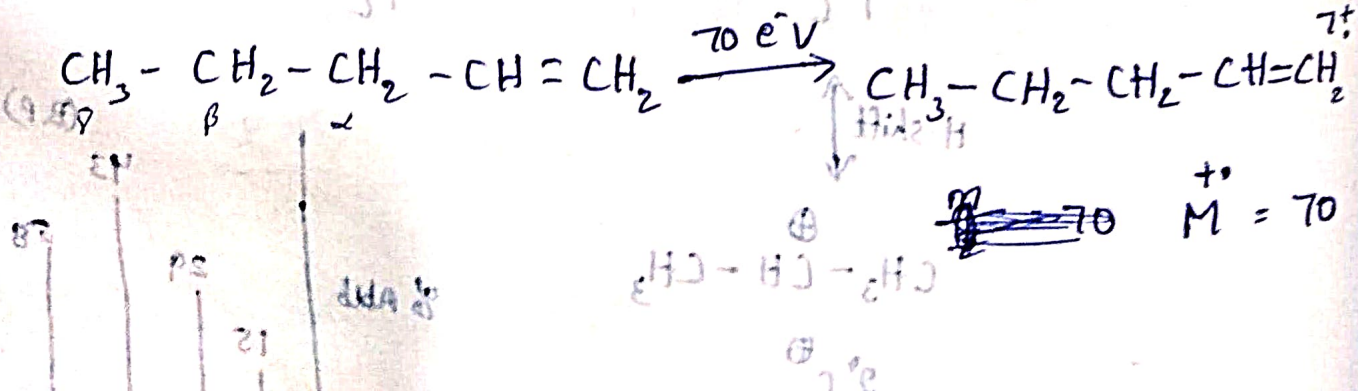
Step-1:- γ-hydrogen transfer to unsaturated centre.

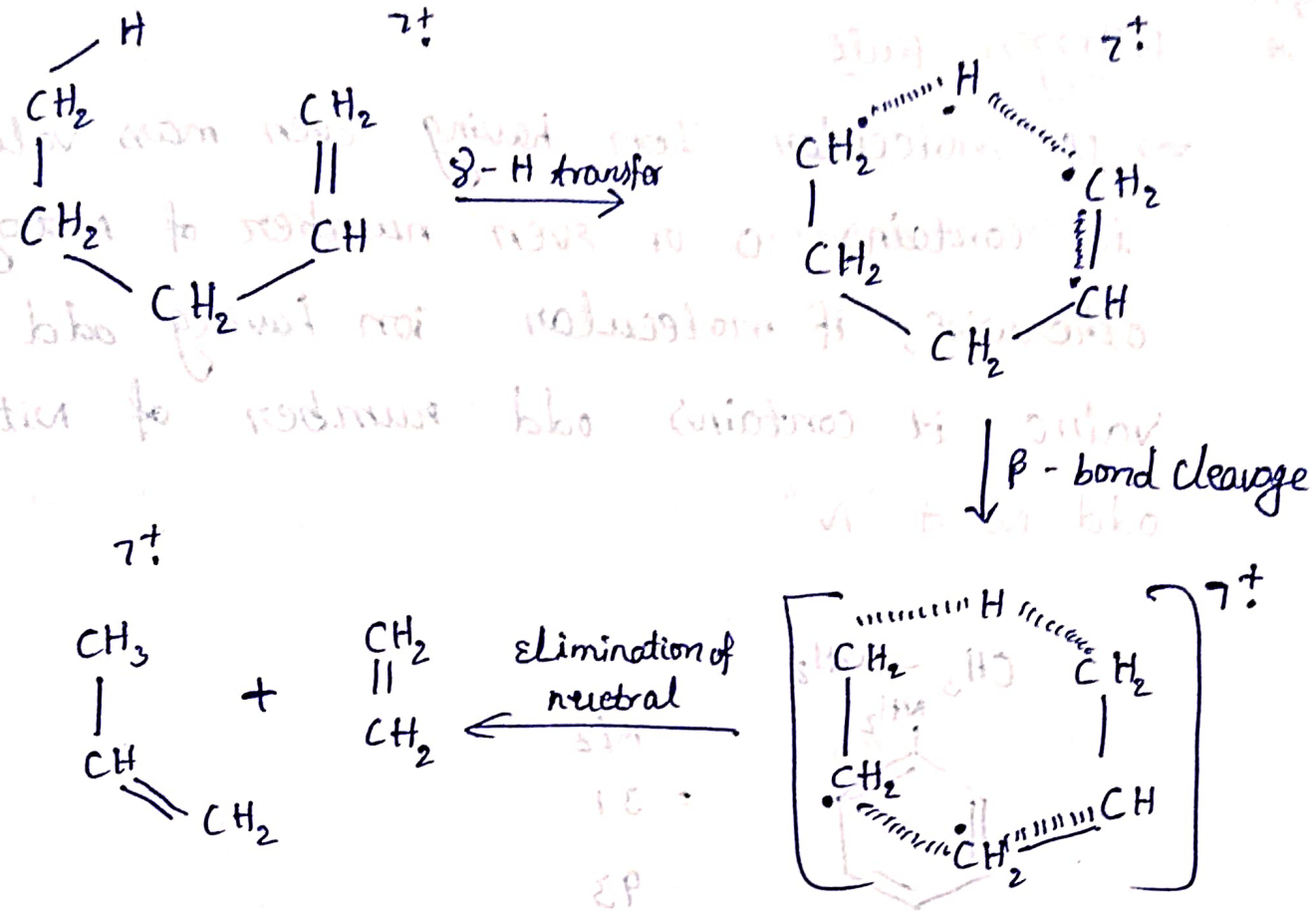
Step-2:- Followed by β-bond cleavage.

Step-3:- A neutral molecule is eliminated to form radical cation.

The formed radical cation is called (M.R. ion) in this mechanism 6 membered cyclic transition ~~stage~~ state is operated.

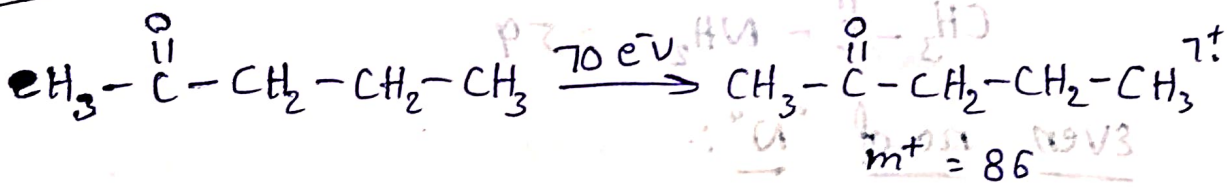
Ex:- 1-pentene

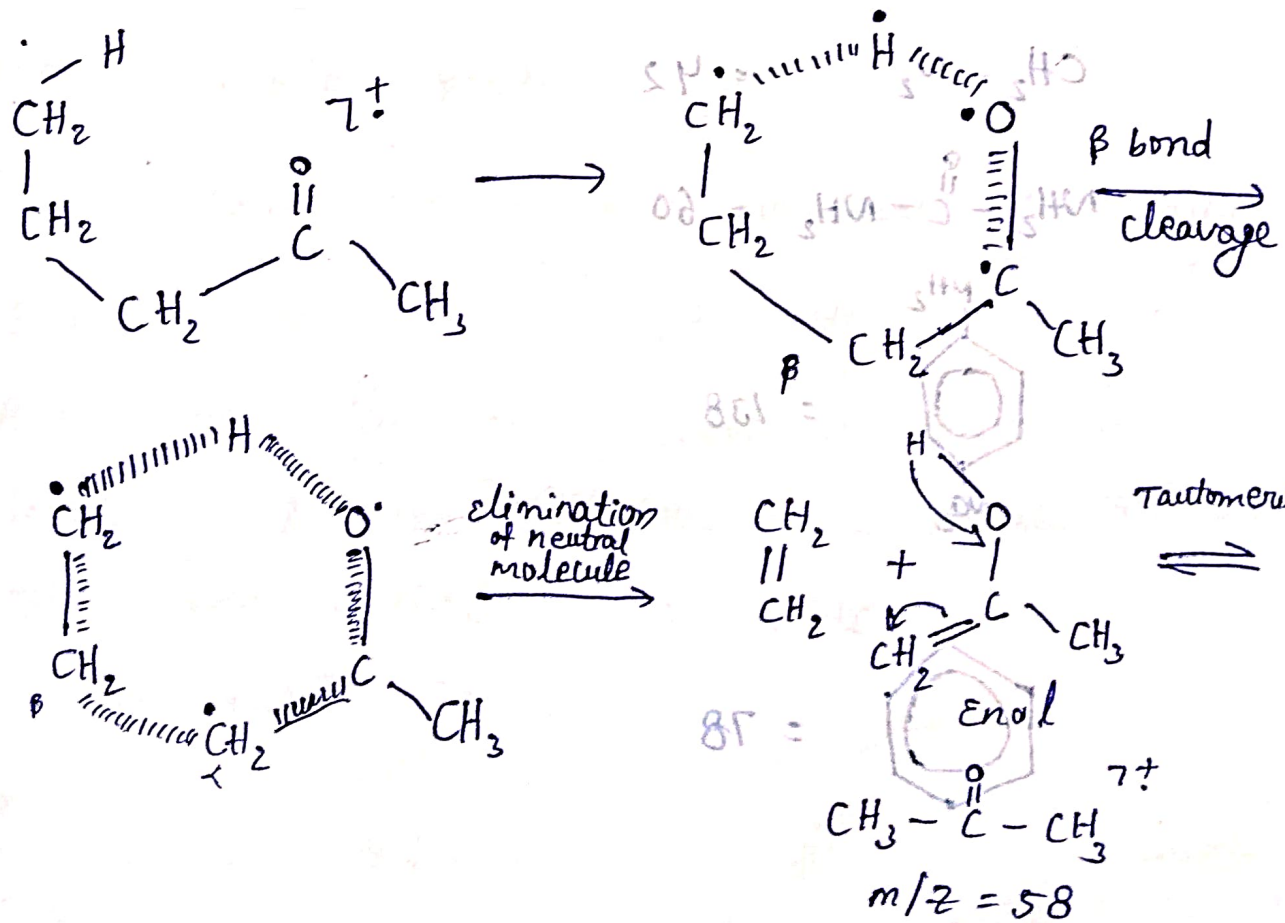



γ- H transfer
β - bond cleavage
elimination of neutral

Ex :- 2

6 MCTs


70 eV
m+ = 86


β bond cleavage
elimination of neutral molecule
Tautomerism
Enol
m/z = 58

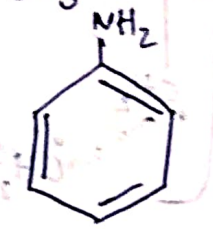
SM

* Nitrogen Rule

⇒ If molecular Ion having Even mass value it contains 0 or even number of Nitrogens otherwise, if molecular ion having odd mass value it contains odd number of Nitrogens.

odd No: of "N":

$CH_3 - NH_2$ m/z = 31



= 93

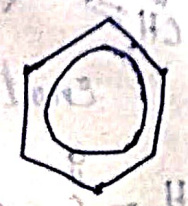
$CH_3 - \overset{O}{\overset{\|}{C}} - NH_2$ = 59

Even no. of "N":

$CH_2 - N_2$ = 42

$NH_2 - \overset{O}{\overset{\|}{C}} - NH_2$ = 60

= 138

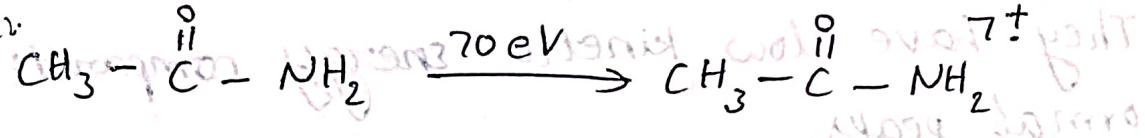


= 78

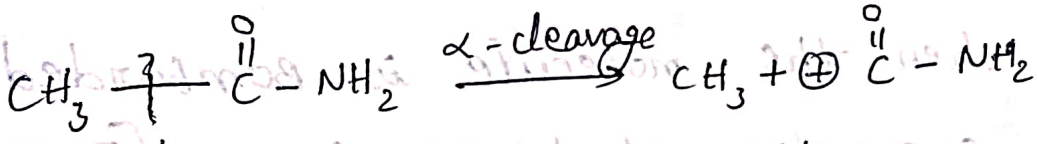
Corolary

⇒ If molecular Ion having even mass value undergo fragmentation. The fragment ion having odd mass value & all the Nitrogens must be present in it & viceversa.

Ex:



$M^{+\cdot} = 59$



m/z = 44

No. of Nitrogens	M^+ ions	Fragment ion mass
zero/even	Even	odd
odd	odd	Even

SM *

Meta - stable peaks or ions

Mass spectra of a molecule generally Exhibit sharp peaks at integral m/z values. But occasionally some diffused Broad low intensity & non-Integral m/z values are occurs. These are called meta-stable peaks or meta stable ions.

*

* Characteristics

⇒ Meta stable peaks are low intensity much broader & appear at non-Integral values.

⇒ Meta stable peaks exhibit abnormal transition energy.

⇒ They have low kinetic energy comparitive normal peaks.

* Formation:

When the molecule is bombarded with high energetic electronic beam [70eV] molecular Ion is produced. It is fragmented into daughter ions.

$$M^{+\cdot} \xrightarrow{\text{Fragmentation}} m^{+} + \dot{m}$$

This reaction takes place in ionization chamber. It gives normal peaks with their broad peaks with non-Integer m/z values. These are called metastable peaks.

Calculation of mass of meta stable ions

$$m^{*} = \frac{m^2}{M^{+\cdot}}$$

m^{*} = mass of meta stable ion

m = mass of fragment ion.

$M^{+\cdot}$ = mass of molecular ion.

1. $CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{70\ eV} CH_3-\overset{O}{\overset{\|}{C}}-NH_2^{+\cdot}$

$m^{+\cdot} = 59$

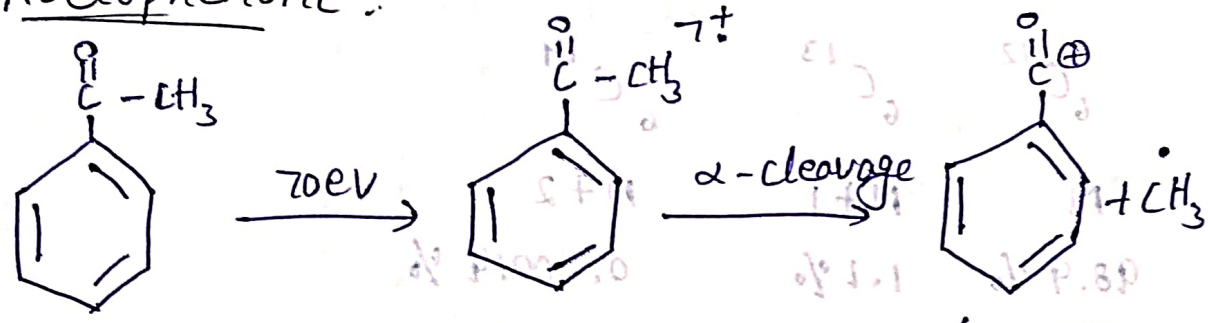
↓ α cleavage

$\dot{C}H_3 + \oplus \overset{O}{\overset{\|}{C}} - NH_2$

$m/z = 44.$

$$m^* = \frac{m^2}{m^{+\cdot}} = \frac{44 \times 44}{59} = \boxed{32.81}$$

Acetophenone :



$m/z = 105$

$$m^* = \frac{m^2}{m^{+\cdot}}$$

$$= \frac{105 \times 105}{120}$$

$$= \boxed{91.87}$$

* Isotope abundence

Species having same atomic number different masses numbers are called isotopes. Many elements occurs naturally as the mixture of isotopes.

All elements are not isotopically pure. As among halogens F^{19}, I^{127} are monoisotopics

where as, Cl, Br exist as Cl^{35}, Cl^{37} and Br^{79}, Br^{81}.

Some elements and their isotopes with abundance are listed below.

$_1H^1$; H^2 , H^3

M	M+1	M+2
99.99%	0.00016%	7.1×10^{-17}

$_6C^{12}$ $_6C^{13}$ $_6C^{14}$

M	M+1	M+2
98.9%	1.1%	0.00014%

$_{17}Cl^{35}$ $_{17}Cl^{37}$

M	M+2
75%	25%

$_{35}Br^{79}$ $_{35}Br^{81}$

M	M+2
99.9%	98%

In most of the cases to delete halogens by using mass spectra.

For compound containing Cl (or) Br the M+2 isotopic peak is important.

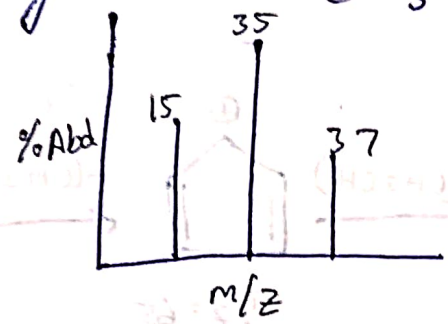
The M+2 isotopic peak is due to the

Presence of Cl about 33% of the molecular ion peak. ~~There fore~~ ratio

∴ ratio of intensity M & M+2 be 3:1 respectively. The M+2 isotopic peak is due to the presence of Br about 98% of the molecular ion peak.

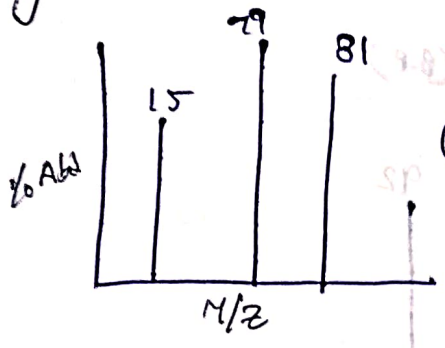
∴ Ratio of intensity of M & M+2 will be 1:1 respectively.

Ex:- Methyl chloride (CH_3Cl)



3:1 ratio
so it is chlorine.

Methyl Bromide (CH_3Br)



(1:1 ratio)

no. of Cl / Br increases

CH_2Cl_2

Cl^{35}
Cl^{35}
M

Cl^{35}, Cl^{37}
M+2

Cl^{37}, Cl^{37}
M+4

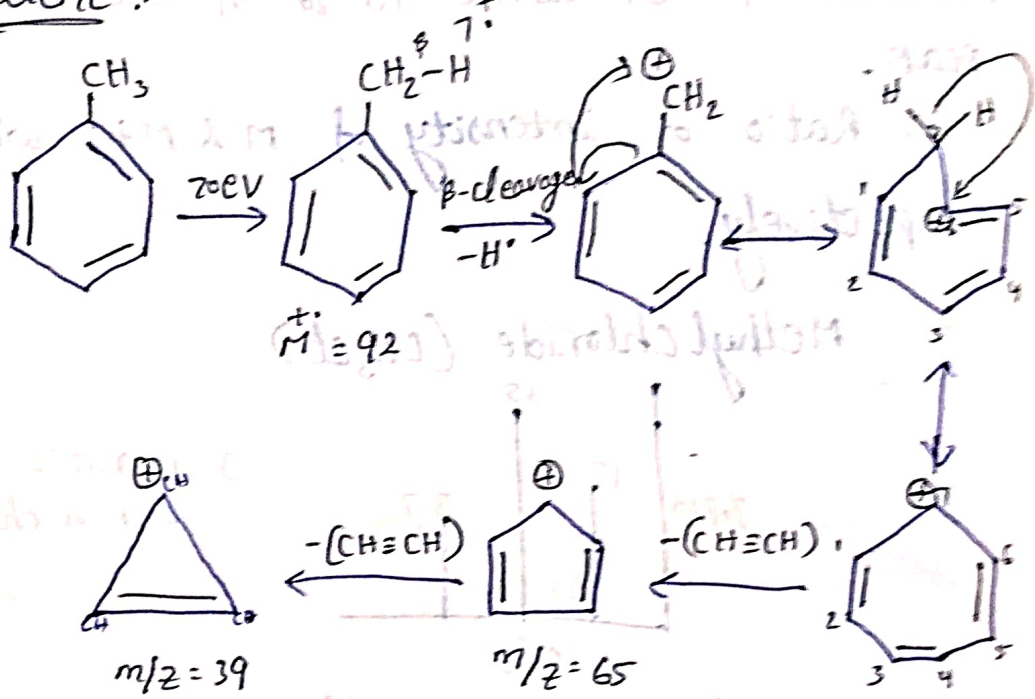
$(a+b)^n = a^2 + b^2 + 2ab$

$(3+1)^2 = (3)^2 + (1)^2 + 2(3)1$

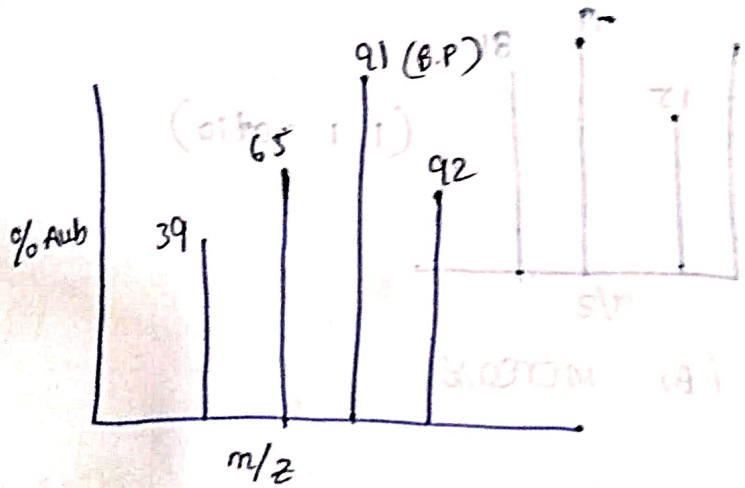
$= 9 + 1 + 6$

$= 9 : 6 : 1$

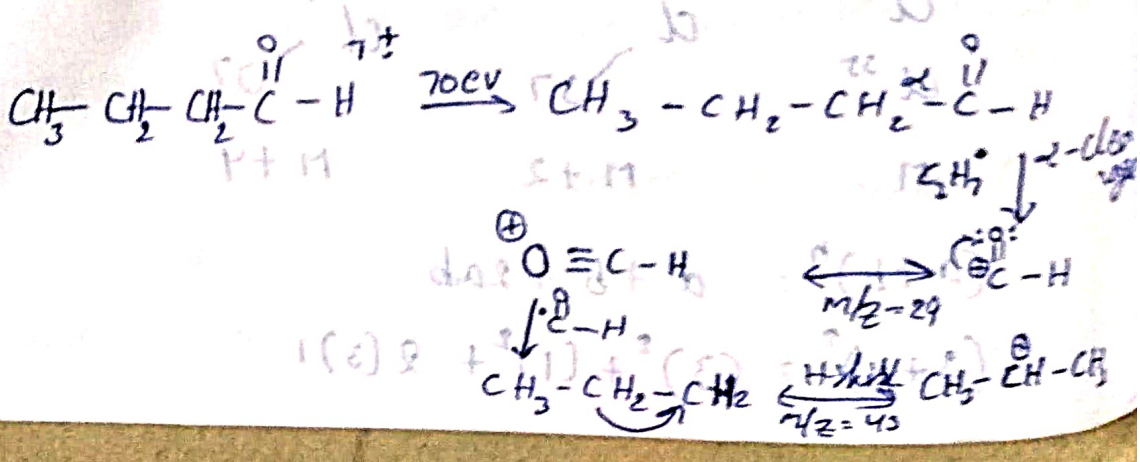
Toulene :-

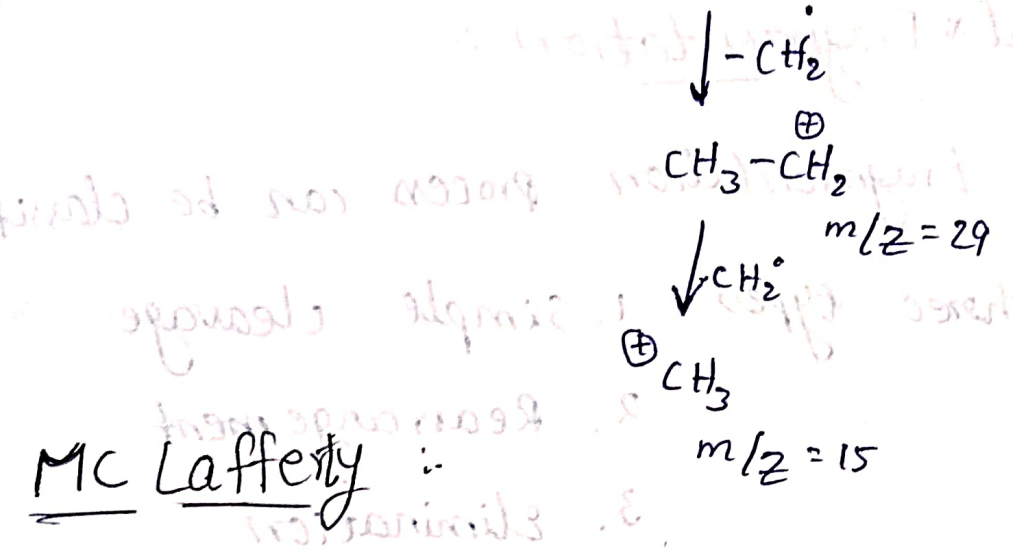


Tropyllium cation
(or)
Cyclo hepta trienyl cation

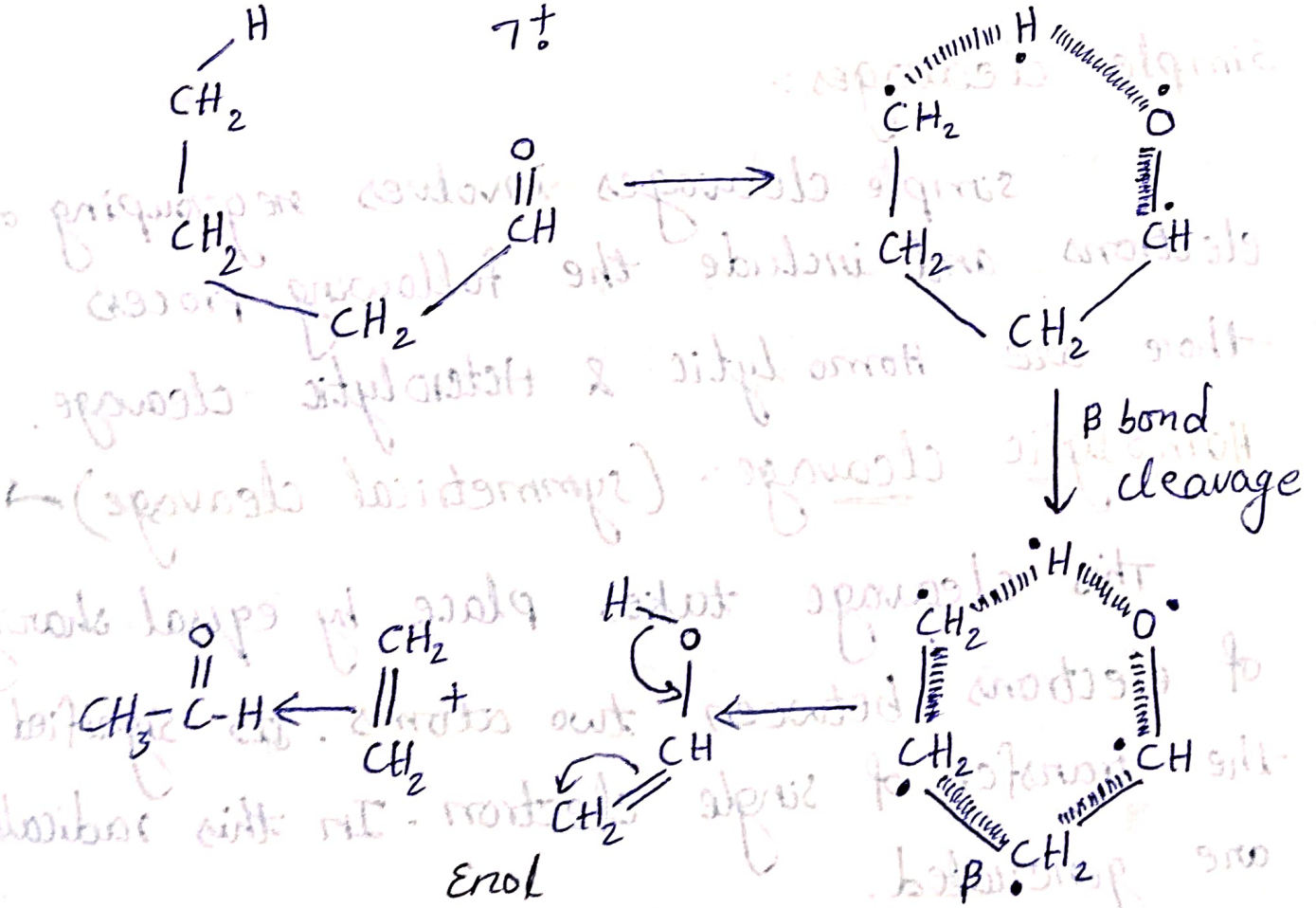


Ex: **Butanaldehyde**




- CH2
CH3 - CH2
m/z = 29
CH2
CH3
m/z = 15

Mc Laffery :-


H
CH2
CH2
CH2
O
CH
7+
β bond cleavage
Enol
β

* General x Modes of Fragmentation :-

Fragmentation process can be classified into three types :
1. simple cleavage
2. Rearrangement
3. Elimination

Simple cleavages :-

simple cleavages involves regrouping of electrons and include the following process those are Homolytic & Heterolytic cleavage.

Homolytic cleavage :- (symmetrical cleavage) →

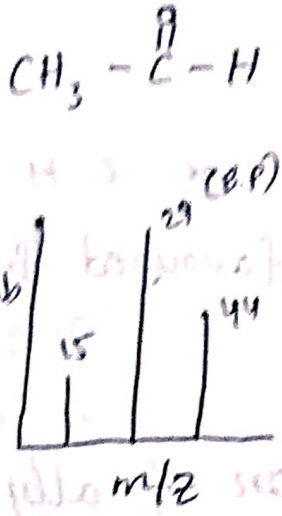
This cleavage takes place by equal sharing of electrons between two atoms. Its signified the transfer of single electron. In this radicals are generated.

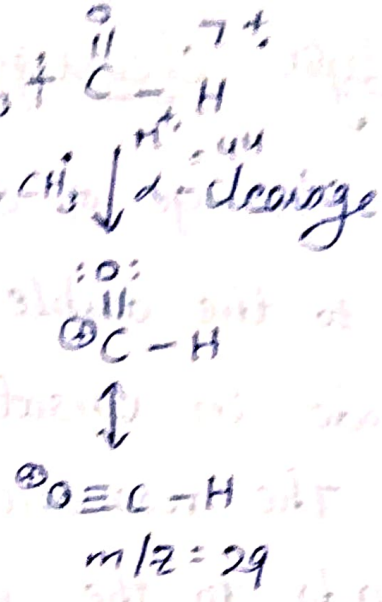
It is further classified into 4 types They are
- α - cleavage
- β - cleavage
- Allylic - cleavage
- Benzylic cleavage

α - cleavage :-

Hetero atom is linked to carbon with double bond α - cleavage is preferable.

Ex:



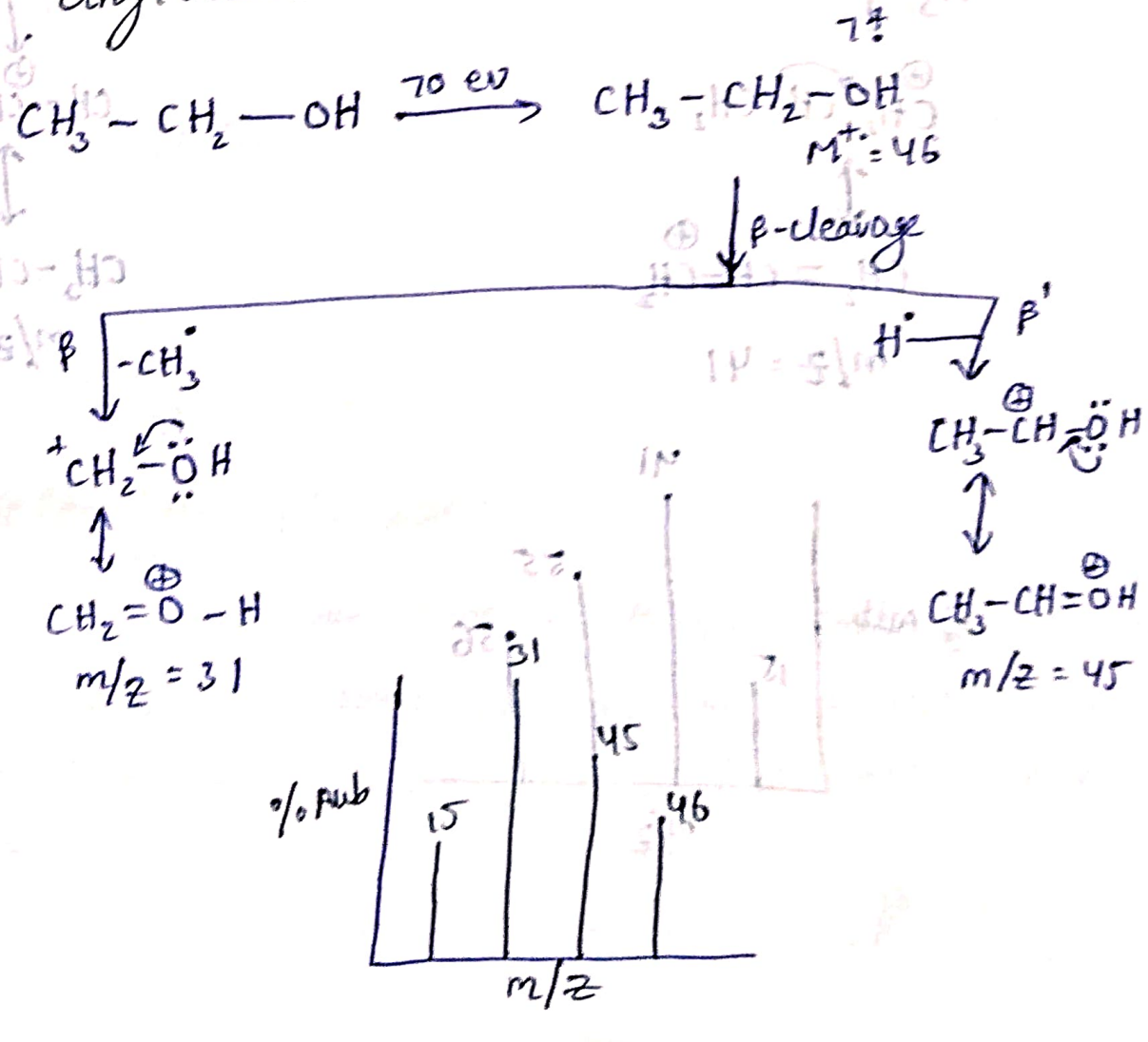


β - cleavage:

Hetero atom is linked to carbon with single bond β-cleavage is preferable.

It generally takes place in alcohols, Alkyl halide, Amine.

Ex: Ethyl alcohol



Allylic cleavage:

Cleavage of a C-C bond or C-H bond, β to the double bond is a favoured fragment mode in unsaturated

The resonance stabilization of allylic cation leads to the probability of β-cleavage.

Ex:- 1-Butene $CH_3-CH_2-CH=CH_2$

$$CH_3-CH_2-CH=CH_2 \xrightarrow{70eV} CH_3-CH_2-CH=CH_2^{+\cdot}$$

$M^{+\cdot} = 56$

Allylic cleavage

β

$-CH_3$ β

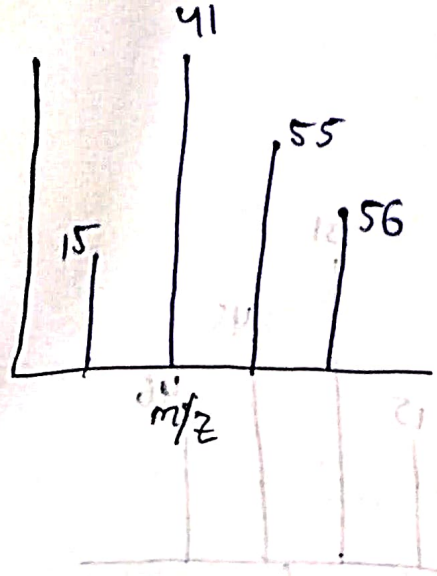
$H-$ β'

$CH_2-CH=CH_2^{\oplus} \leftrightarrow CH_2=CH-CH_2^{\oplus}$

$m/z = 41$

$CH_3-CH=CH-CH_2^{\oplus} \leftrightarrow CH_3-CH^{\oplus}-CH=CH_2$

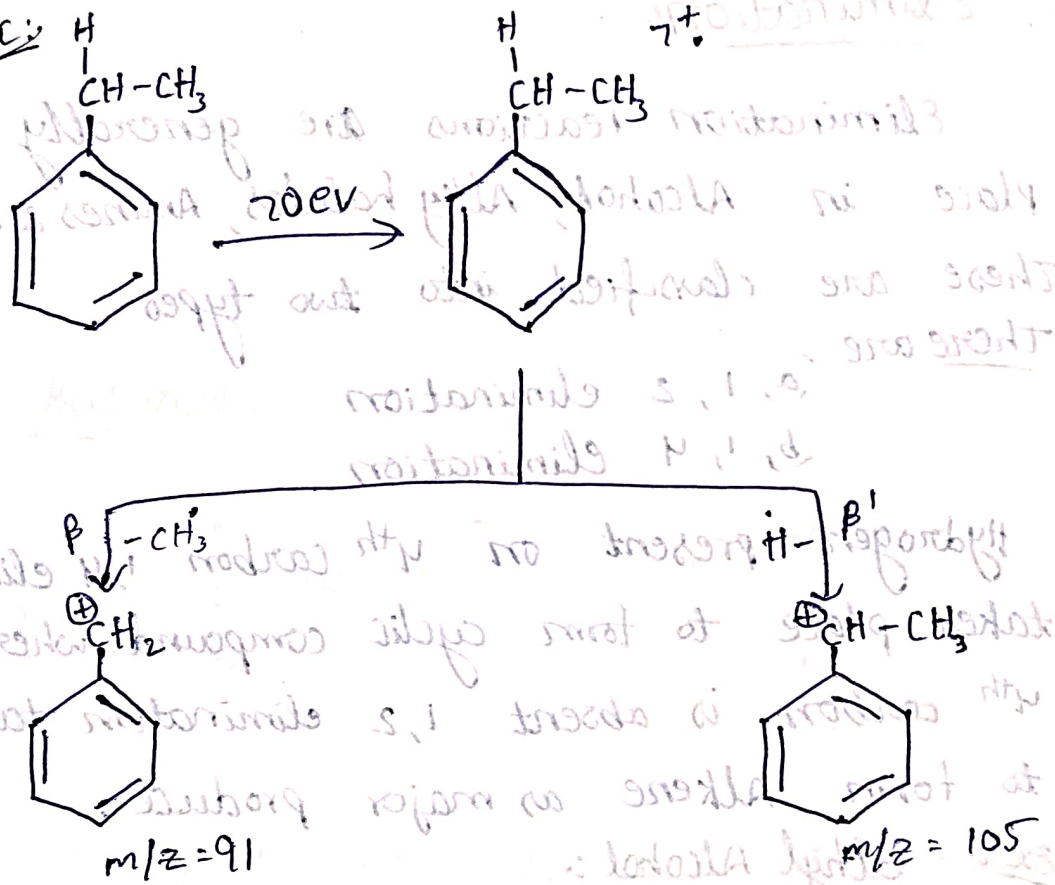
$m/z = 55$

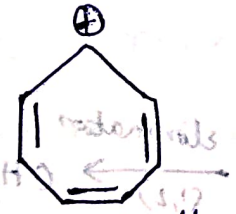


Benzyllic cleavage:-

cleavag of a C-C bond (or) C-H bond β to the aromatic ring it is an energyfically prefered fragmention.

Ex:-





Tropyllium cation.

Heterolytic cleavage:-

In this type of cleavage both the electrons of a bond are taken over by one of the atom then fragment ions are even electron cation under radical.

Ex:-

$$CH_3-X \xrightarrow{70\,ev} CH_3-X^{7+} \longrightarrow CH_3^{\oplus} + X^{\bullet}$$

2. Rearrangement :-

i. Hydrogen
ii. Mc Lafferty

3. Eliminations :-

Elimination reactions are generally takes place in Alcohol, Alky halides, Amines & esters. These are classified into two types.

There are :-

a. 1, 2 elimination
b. 1, 4 elimination

Hydrogen present on 4th carbon 1,4 elimination takes place to form cyclic compound. where as 4th carbon is absent 1,2 elimination takes place to form Alkene as major product :-

ex :- Ethyl Alcohol :-

$$CH_3 - CH_2 - OH$$

$$CH_3-CH_2-OH \xrightarrow{70\ eV} CH_3-CH_2-\overset{+\cdot}{O}H \xrightarrow[(1,2)]{\text{elimination}} CH_2=CH_2^{+\cdot}$$

$M^{+\cdot} = 46$ $\qquad m/z = 28$

$[M^{+\cdot} - 18]$

$-CH_3^{\cdot}$ ↓ β-cleavage

$$CH_2 \leftarrow \ddot{O}H \quad \leftrightarrow \quad CH_2=\overset{\oplus}{O}H$$

$m/z = 31$

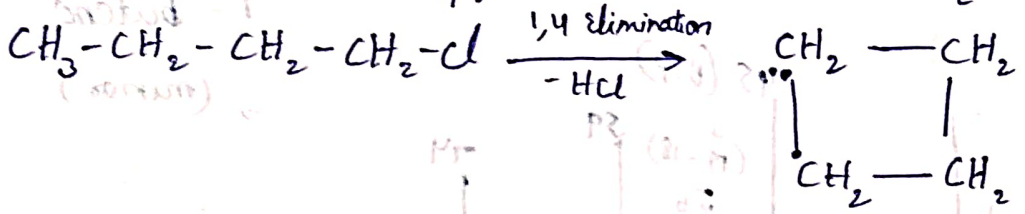
1 - chloro butane :-

$CH_3-CH_2-CH_2-CH_2-Cl \xrightarrow{70\ eV} CH_3-CH_2-CH_2-CH_2-Cl^{+\cdot}$

$M^{+\cdot} = 92\ (94)$

$-C_3H_7^{\cdot}$ ↓

CH_2-Cl^{+}

$CH_3-CH_2-CH_2-CH_2-Cl^{+\cdot} \xrightarrow[-HCl]{1,4\ \text{elimination}}$ 

2 - Butanol :- .

$CH_3-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 \xrightarrow{70\ eV} CH_3-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3^{+\cdot}$

$M^{+\cdot} = 74$

In this preferable cleavage is β-cleavage to form oxonium ion as base peak. and it undergo elimination of water molecule to form alkene. $(M^+ - 18)$.

$CH_3-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 \xrightarrow{70\ eV} CH_3-CH_2\overset{\beta}{-}\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}\overset{\beta'}{-}CH_3^{+\cdot}$

$-C_2H_5^{\cdot}$ ↓

$\overset{\oplus}{C}H-CH_3$ ↔ $CH=CH_3$ (OH)$^{\oplus}$

$m/z = 45$

$-CH_3^{\cdot}$ ↓

$CH_3-CH_2-\overset{\oplus}{C}H$ ↔ CH_3-CH_2-CH (OH)$^{\oplus}$

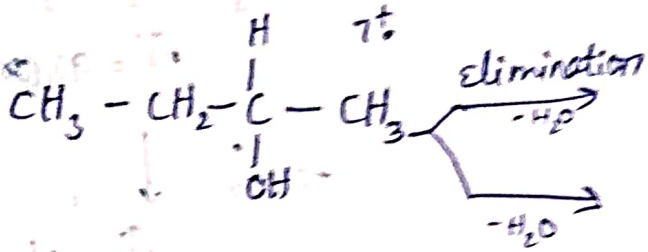
$m/z = 59$

$-H^{\cdot}$ ↓

$CH_3-CH_2-\overset{\oplus}{C}-CH_3$ ↔ $CH_3-CH_2-C(=OH^{\oplus})-CH_3$

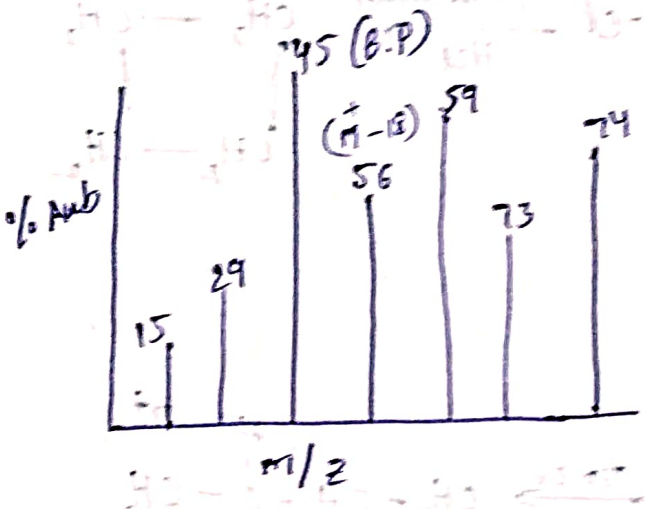
$m/z = 73$

Elimination :-



$CH_3-CH_2=CH-CH_3$
2-butene (major) stable

$CH_3-CH_2-CH=CH_2$
1-butene
(minor)



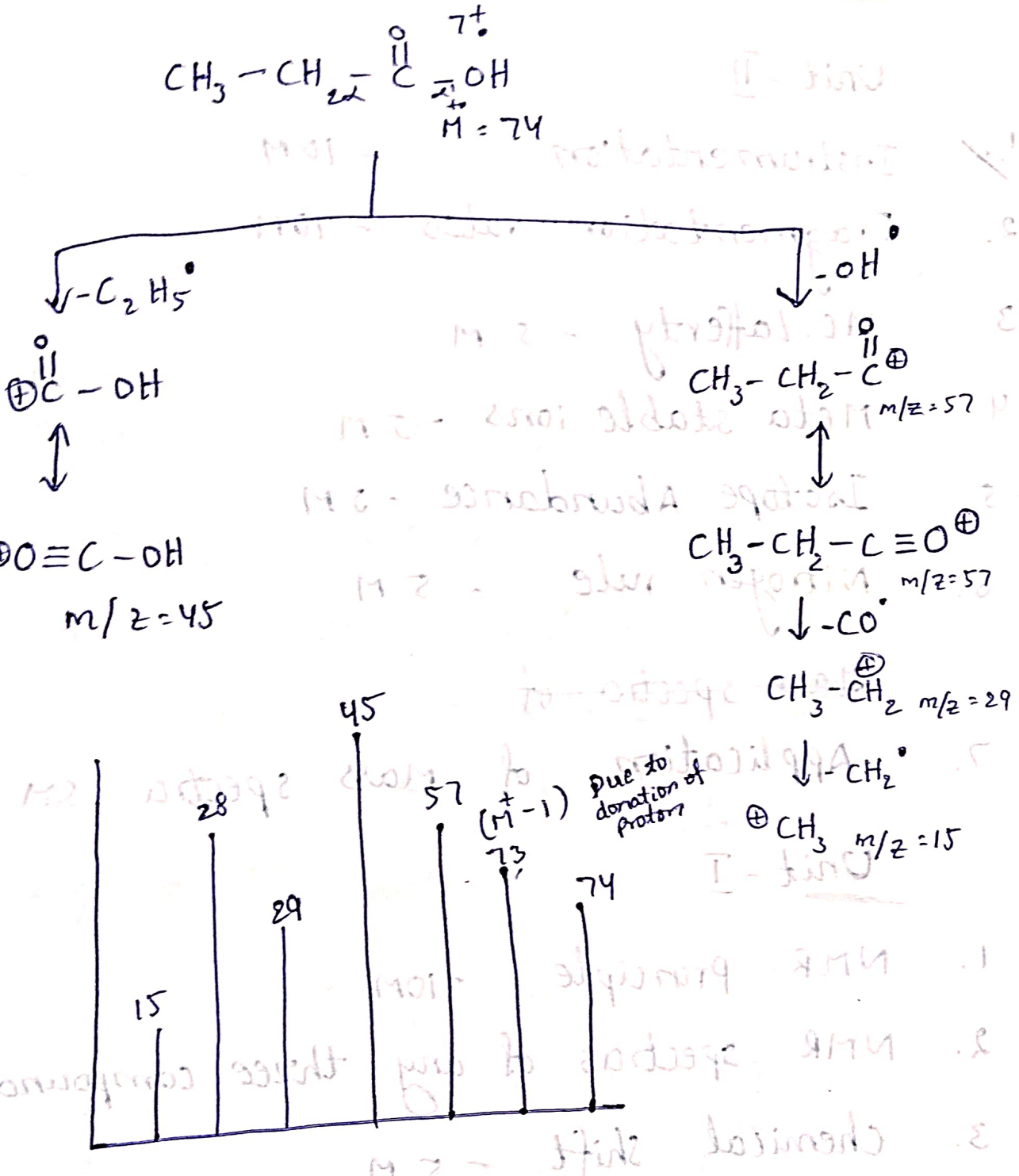
Proponoic acid :-

$CH_3 - CH_2 - COOH$

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{70\ eV} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH^{+\cdot}$$

$M^{+\cdot} = 74$

In this hetero atom linked to the carbon with double bond then preferable cleavage is α-cleavage to give acid ($COOH$) m/z value 45 is base peak.


$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$
$M^{+\cdot} = 74$
$-C_2H_5^{\cdot}$
$-OH^{\cdot}$
$\oplus C(=O)-OH$
$\oplus O\equiv C-OH$
m/z = 45
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}\oplus$
m/z = 57
$CH_3-CH_2-C\equiv O\oplus$
m/z = 57
$-CO^{\cdot}$
$CH_3-\oplus CH_2$ m/z = 29
$-CH_2^{\cdot}$
$\oplus CH_3$ m/z = 15
45
28
57
(M^+-1) Due to donation of proton
73
74
29
15