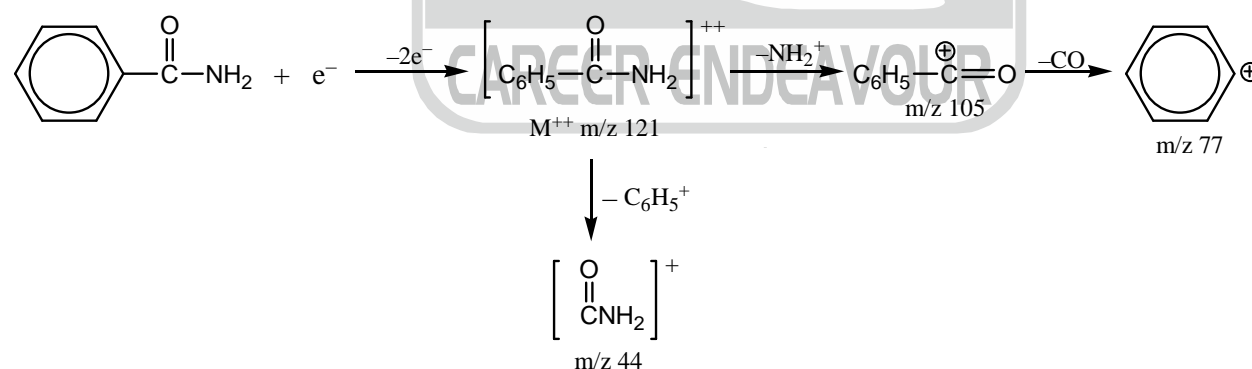# MASS Spectrometry

Introduction:

In the commonly used electron-impact (EI) mode, a mass spectrometer bombards molecules in the vapour phase with a high-energy electron beam and records the result of electron impact as a spectrum of positive ions separated on the basis of mass/charge (m/z); most of these ions are singly charged. The mass spectrum of

benzamide $\left(C_6H_5 - \overset{\overset{O}{\|}}{C} - NH_2 \right)$ is presented as a computer-plot bar graph of abundance (vertical peak

intensity) versus m/z. The positive ion peak at m/z 121 represents the intact molecule (M) less one electron removed by the impacting beam and is designated the molecular ion, M^{++}. The molecular ion in turn produces a series of fragment ions as shown for benzamide:

Mass Spectrometry (MS) in sufficient detail to appreciate its application to organic structure determination.

- Molecular weight can be obtained from a very small sample.
- It does not involve the absorption or emission of light.
- A beam of high-energy electrons breaks the molecule apart.
- The masses of the fragments and their relative abundance reveal information about the structure of the molecule.

**The main use of Mass spectrometry in organic chemistry is:**

- Determine the molecular mass of organic compounds.
- Determine the molecular formula of organic compounds.

How do we achieve this?

- Persuade the molecule to enter the vapor phase (can be difficult)
- Produce ions from the molecules that enter the gas phase
- Separate the ions according to their mass-to-charge ratios (m/z))
- Measure and record these ions
- Isotopes: present in their usual abundance.
- Hydrocarbons contain 1.1% C-13, so there will be a small M^{+1} peak.
- If Br is present, M^{+2} is equal to M^+.
- If Cl is present, M^{+2} is one-third of M^+.
- If iodine is present, peak at 127, large gap.
- If N is present, M^+ will be an odd number.
- If S is present, M^{+2} will be 4% of M^+.

A Mass Spectrometer: A mass spectrometer is designed to do three things

- Convert neutral atoms or molecules into a beam of positive (or negative) ions
- Separate the ions on the basis of their mass-to-charge ratio (m/z)
- Measure the relative abundance of each ion.
- Electron Ionization MS in the ionization chamber, the sample is bombarded with a beam of high-energy electrons collisions between these electrons and the sample result loss of electrons from sample molecules and formation of positive ions
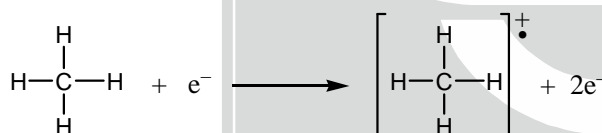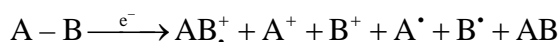

Molecular ion
A radical cations

- **Mass spectrum:** a plot of the relative abundance of each ion versus mass-to-charge ratio
- **Base peak:** the most abundant peak; assigned an arbitrary intensity of 100 .
- The relative abundance of all other ions is reported as a % of abundance of the base peak
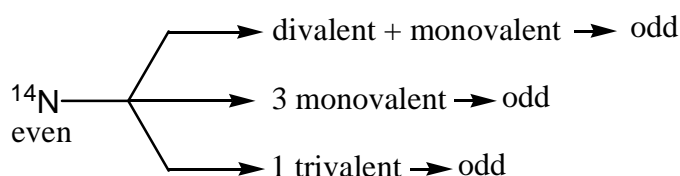
Fragmentation by electron impact:

$$A \overset{\bullet}{\underset{\bullet}{-}} B \xrightarrow[\text{gas phase}]{70 \text{ eV}}$$
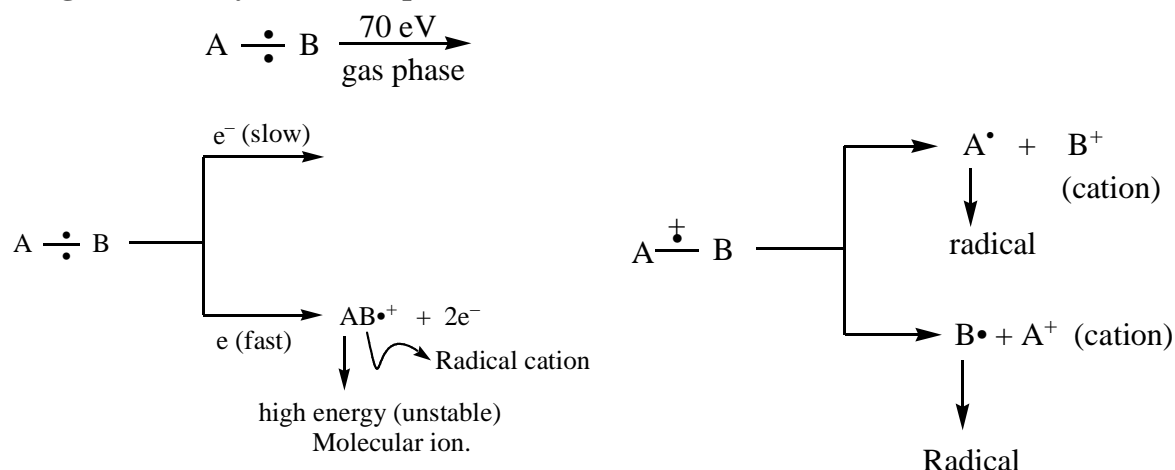
Overall process is:

$$A - B \xrightarrow{e^-} AB_{\bullet}^+ + A^+ + B^+ + A^{\bullet} + B^{\bullet} + AB$$

NITROGEN RULE

- Monovalent mass odd
- Divalent mass even
- Trivalent mass should odd → only N is a trivalent having odd mass.
- Tetravalent mass even.

Three possibilities are possible, with N.

$$^{14}N \text{ even} \begin{cases} \longrightarrow \text{divalent + monovalent} \longrightarrow \text{odd} \\ \longrightarrow \text{3 monovalent} \longrightarrow \text{odd} \\ \longrightarrow \text{1 trivalent} \longrightarrow \text{odd} \end{cases}$$

EFFECT OF 'N' RULE :

1. If 'N' atom is absent in molecule then

all radical cation = even mass

all cations = odd mass.

Problem: A molecule containing Carbon, Hydrogen & Oxygen has mole. wt 120. In mass spectrum shows peaks at 120, 100, 105, 76, 59, 43. Find out the even e^- and odd e^- species among these.

OR, Classify as radical cation, cation, EES and OES.

Soln.

Radical cation	120, 100, 76	EES → even electron species.
Cation	105, 59, 43	OES → Odd electron species.
EES	105, 59, 43	
OES	120, 100, 76	

2. **If one 'N' atom present in molecule then**

Two type of fragments are

(a) having N atom in each fragment

odd mass species = radical cation

even mass species = cations

(b) having not 'N' atom in the species.

odd mass species = cation

even mass species = radical cation

FRAGMENTATION OF HYDROCARBONS

Alkanes	Alkenes	Alkynes	Aromatic
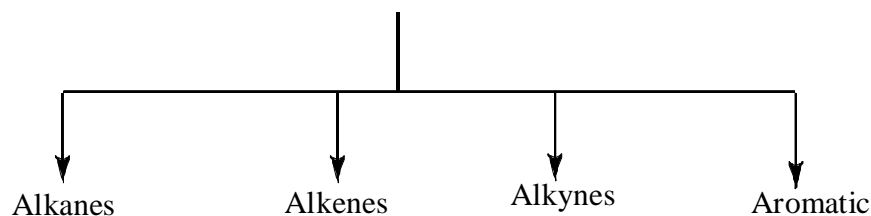
Fragmentation of saturated aliphatic hydrocarbons (alkenes)

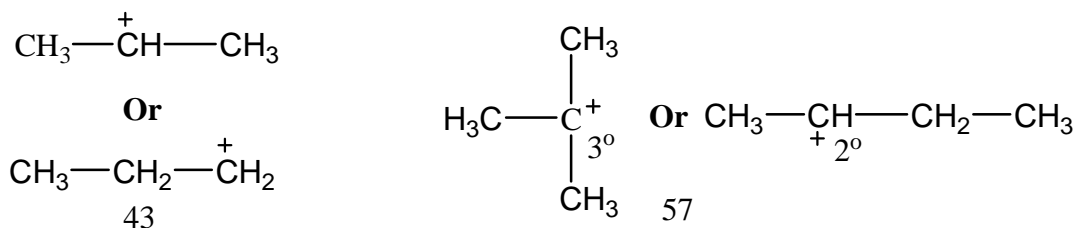$$C \overset{\bullet}{\underset{\cdot}{—}} C \qquad C —— H$$

- The characteristic property of mass spectrum of alkanes is group of peaks at 14 mass apart (difference of CH_2 (14)

Most intense peak at 43 – 57.

- Most intense peak is known as Base peak.

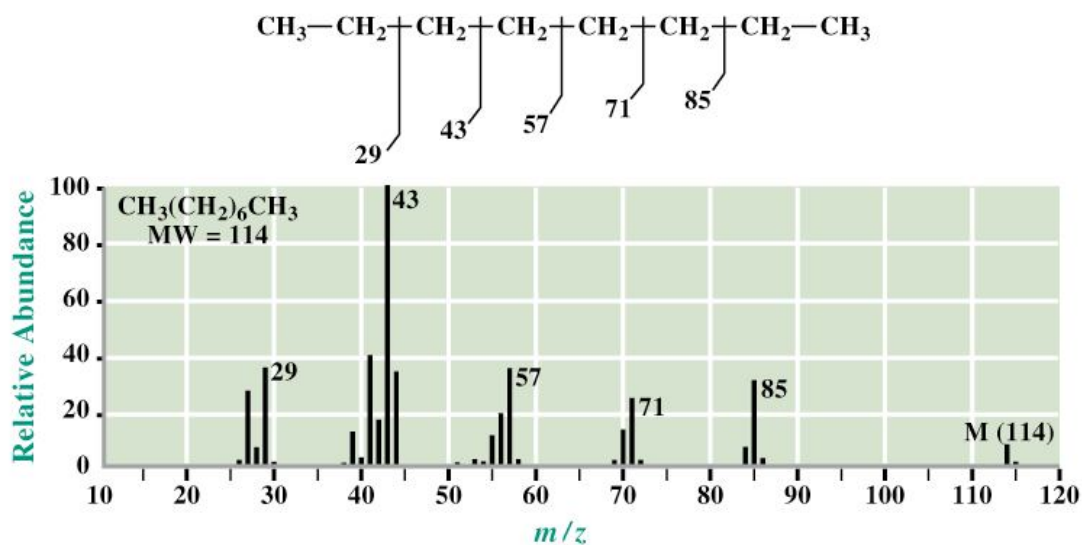• The peak which show molecular mass known as molecular ion peak. (radical cation) may be less/more intense.
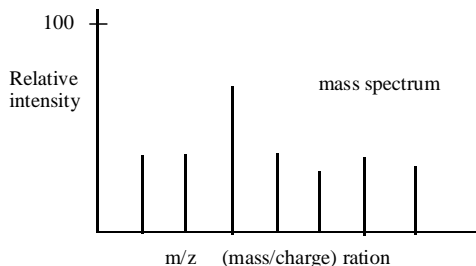
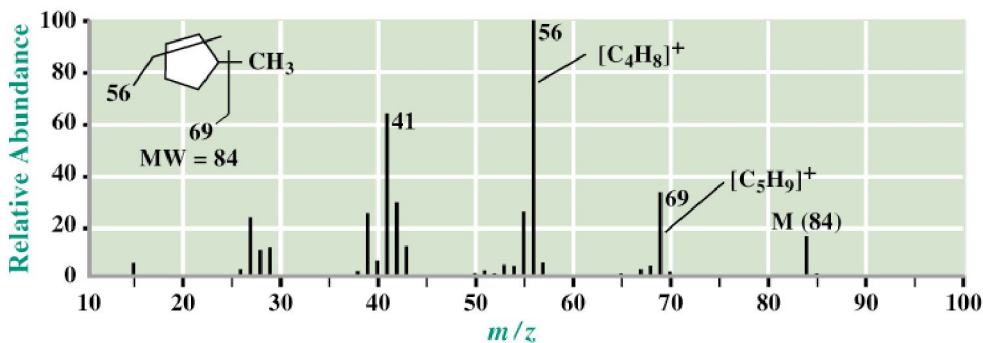
• The most intense peak appears at m/z 43 and 57.

$$CH_3—\overset{+}{CH}—CH_3$$

Or

$$CH_3—CH_2—\overset{+}{CH_2}$$
43

$$H_3C—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C^+}}\ 3°$$
57

Or $CH_3—CH—CH_2—CH_3$
$\overset{+}{}\ 2°$

• The intensity of these peaks depend on the stability of carbocation formed. allyl $> 3° > 2° > 1° > CH_3^+$.

Mass spectrum of octane:

$$CH_3—CH_2{+}CH_2{+}CH_2{+}CH_2{+}CH_2{+}CH_2—CH_3$$

29   43   57   71   85

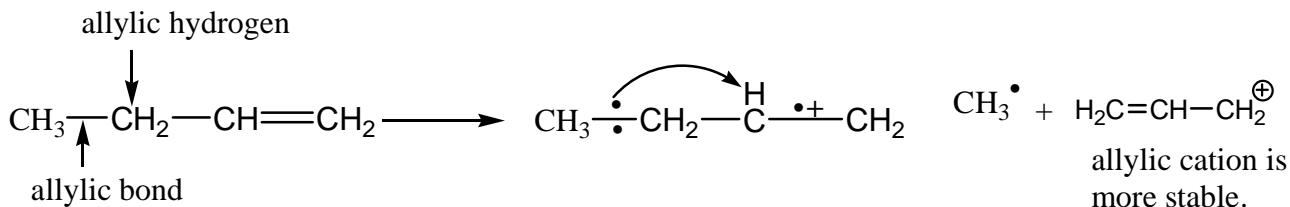**Mass spectrum of methylcyclopentane:**

FRAGMENTATION OF ALKENE

Alkenes:
• Alkenes characteristically show a strong molecular ion peak
• They cleave readily to form resonancestabilized allylic cations

1. **Allylic Fission :** $CH_3-CH_2-CH=CH_2]^{\bullet+}$

(a) Normal :

allylic hydrogen

$CH_3-CH_2-CH=CH_2 \longrightarrow CH_3-CH_2-C-CH_2$ $CH_3^{\bullet} + H_2C=CH-CH_2^{\oplus}$

allylic bond

allylic cation is more stable.

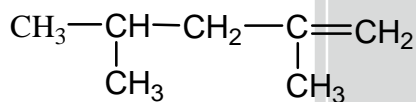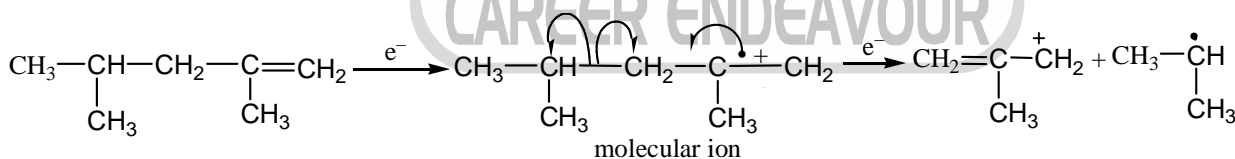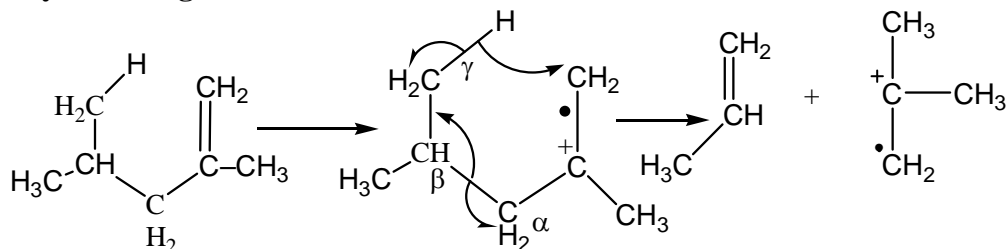**(b) Mclafferty Rearrangement :** If γ-H is present in the alkene the MR fragment will be the base peak. the Mclafferty rearrangement is β fission followed by γ-H transfer.

Radical cation

Radical cation (even mass)
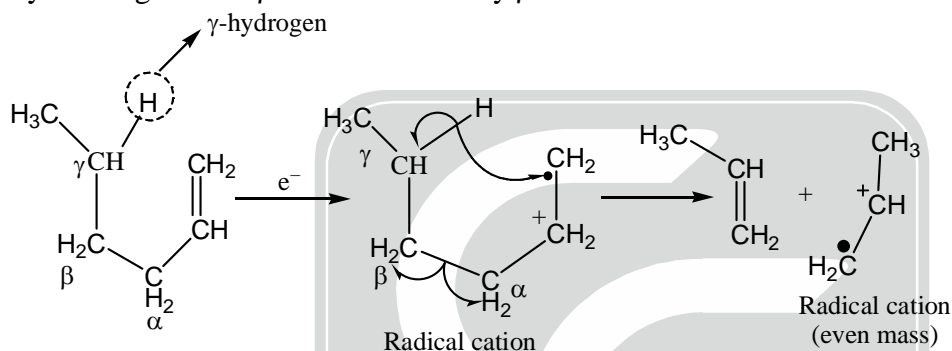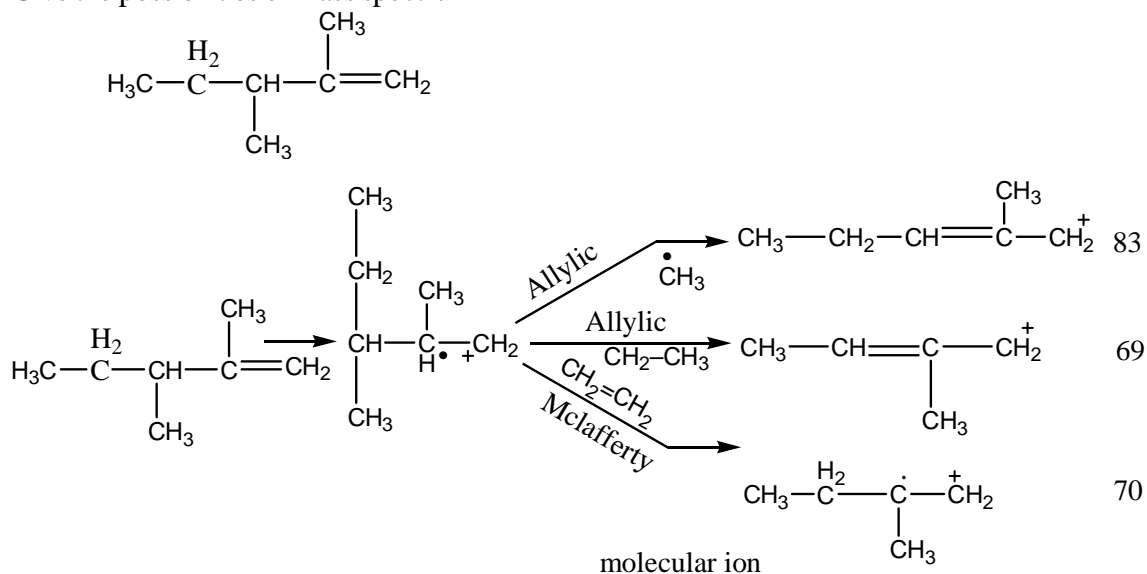
Problem: Give the allylic fission and MR in the given alkene.

2. **Allylic Cleavage :**

molecular ion

3. **Mclafferty Rearrangement :**

EXAMPLES

1.   Give the possibilities of mass spectrum in
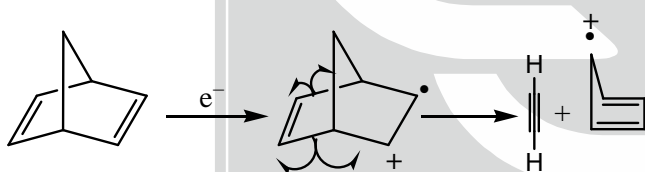

Note: When 2 or more possibility for allylic fission the bulky group preferentially goes as radical.
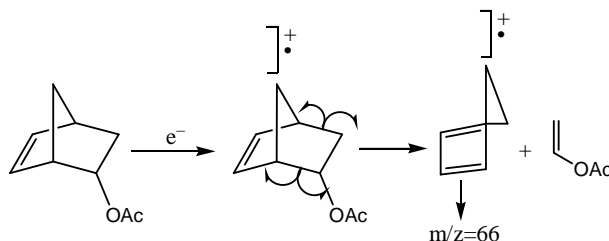
(c) Cyclohexene and its derivative : This type of Alkene shows fragmentation by Retro-diels alder reaction.
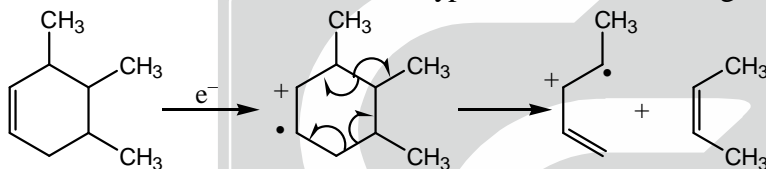
2.   Explain the peak, at m/z 66 and 26. in the ratio 5 : 1 for the mass spectrum of norbarene?

3.   The compound gives m/z 66 in its mass spectrum explain.

4. How can you differenciate 1-hexene, 2-hexene and 3-hexene on the basis of mass spectrum?

$$H_2C=CH-CH_2-CH_2-CH_2-CH_3 \text{ (one hexene)}$$

Now,

$$H_3C-\underset{H}{C}=CH-CH_2-CH_2-CH_3 \text{ (2-hexene)}$$

Now,

$$H_3C-CH_2-\underset{H}{C}=CH-CH_2-CH_3 \xrightarrow{e^-} H_3C-\underset{\beta}{CH_2}-\underset{\alpha}{CH}-\overset{\oplus}{CH}-CH_2-CH_3$$

$$\overset{\cdot}{C}H_3 + H_2C=CH-\overset{\oplus}{CH}-CH_2-CH_3$$
m/z=69
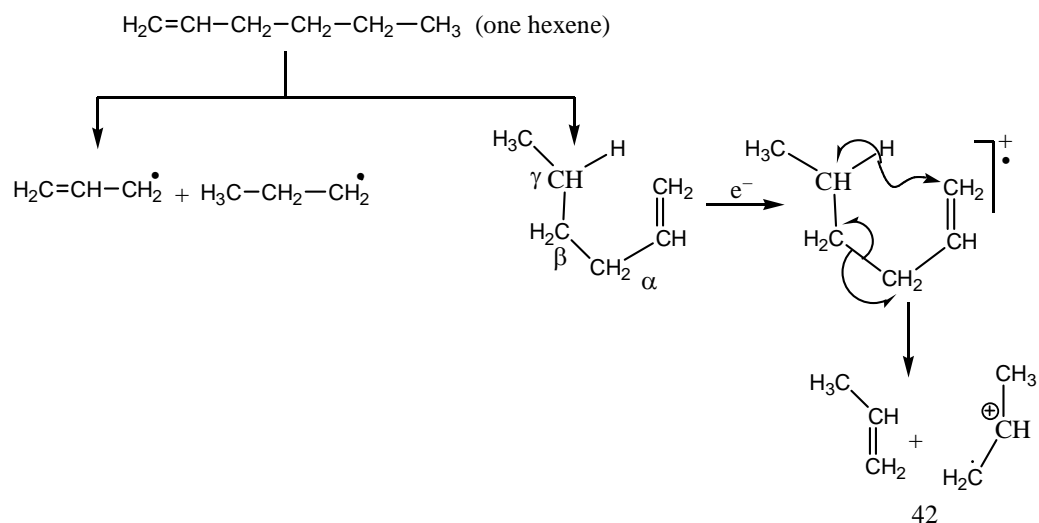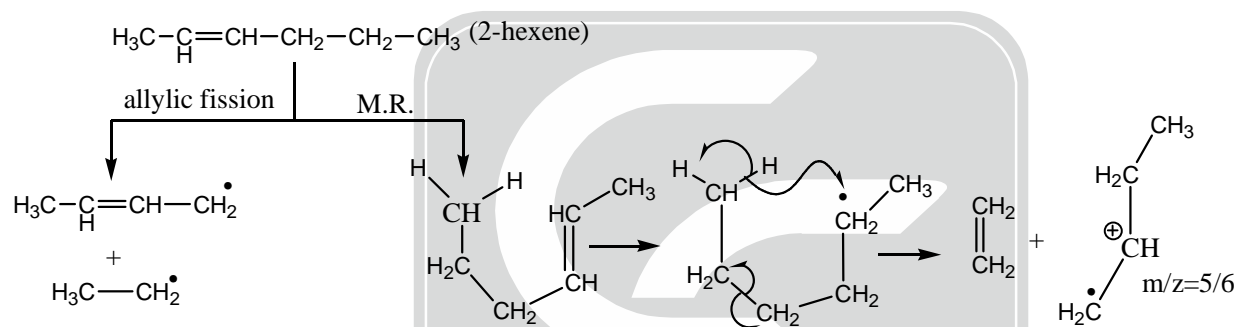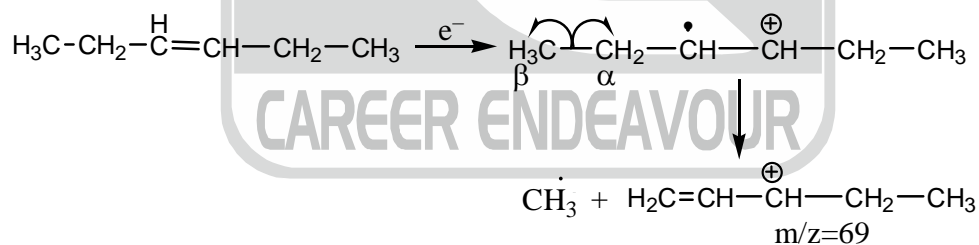
3-hexene will not give MR because it has no γ-H atom.

AROMATIC HYDROCARBON

FRAGMENTATION OF BENZENE:
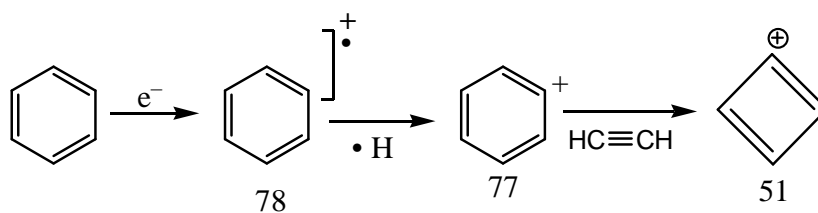
Fragmentation of alkyl Benzene

(a) Benzylic Fission : All alkyl Benzene without $\gamma - H$ gives the base peak by Benzylic fission. The fission is similar to the allylic fission of alkene.

m/z=91   m/z=91   Tropolium ion

       m/z=91
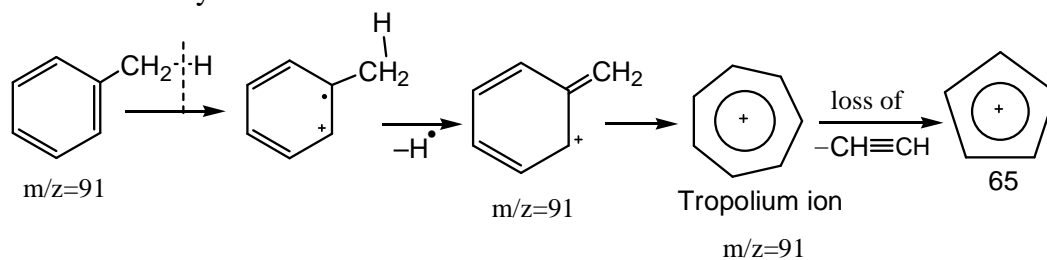
Note: Bulky group will go as radical preferentially from benzene ring.

methyl tropolium ion.

ethyl tropolium.
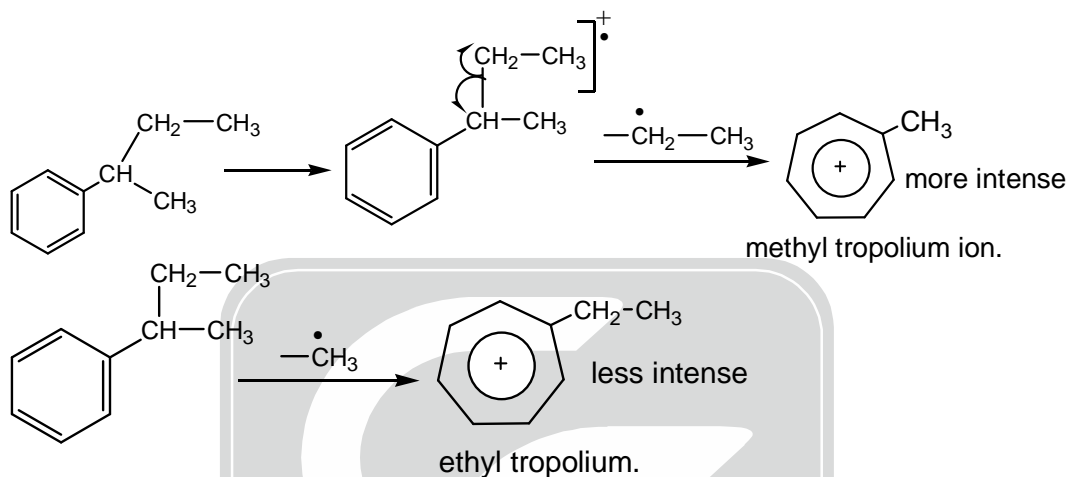
(b) M.R. fragmentation : Alkyl benzene having $\gamma - H$ shows base peak by Mc Lafferty rearrangement.

Note: If ortho position is filled by any other group then MR is not possible.
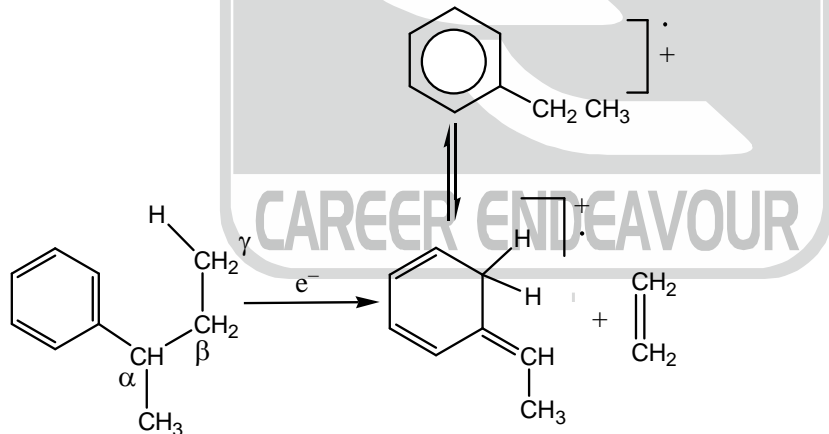
Problem: How fragmentation occur in this molecules :

$CH_2-CH_2-\overset{H_2}{C}-\overset{}{\underset{H}{C}}=CH_2$ having

(1)   Alkyl benzene
(2)   Alkene part
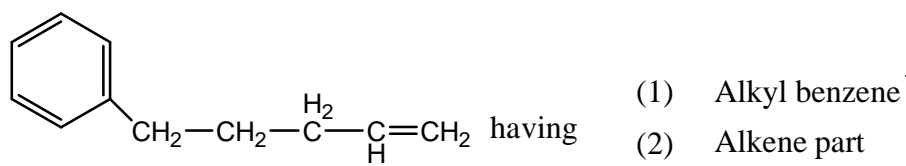
Fragmentation through
1. Allylic fission   2. Benzylic fission

3. MR of alkyl-benzene   4. MR of alkene

1.   Allylic Fission :

Benzylic fission :

65   91
Cyclo pentadienyl cation Tropolium ion

M.R. of alkyl Benzene:

92

M.R. of Alkene :

radical cation
42
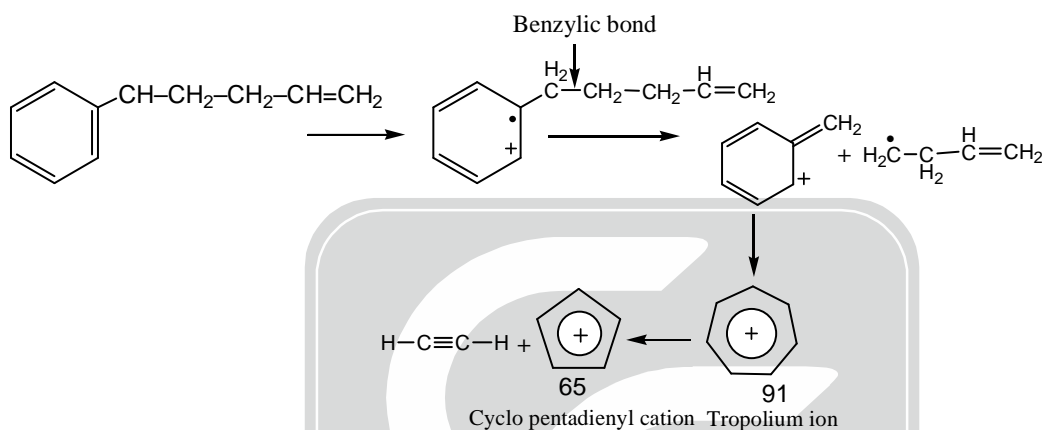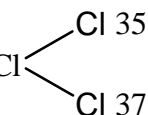
FRAGMENTATION OF HALOGEN COMPOUND

1. The presence of halogen atom Cl^-, Br^- and I^- can be identified easily by the mass spectrum

$R - Cl$ $R - Br$ $R - I$

Cl^+ Br^+ $I^+ (127)$
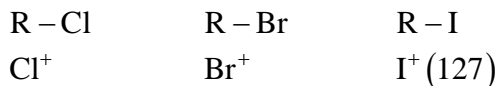
CH_3Cl give 2 peak. due to isotope of $Cl \Big\langle \begin{matrix} Cl\ 35 \\ Cl\ 37 \end{matrix}$

Cl^{35} Cl^{37}

3   1

100 mole   75%   25%

75   $CH_3 - Cl^{35} \big]^{+\cdot} = 50$ $\boxed{M}$ peak hight ratio 3 : 1

25   $CH_3 - Cl^{37} \big]^{+\cdot} = 52$ $\boxed{M+2}$

Presence of I : The iodine compound shows fragmentation by a loss of I^+ cation at 127 m/z. This peak is characteristic for compounds having iodine atom.

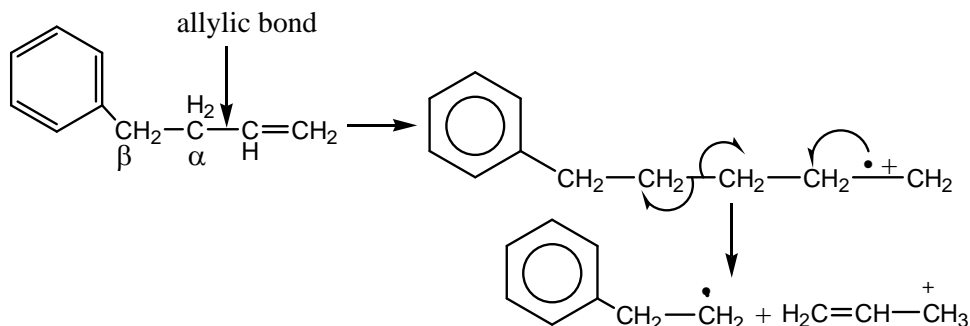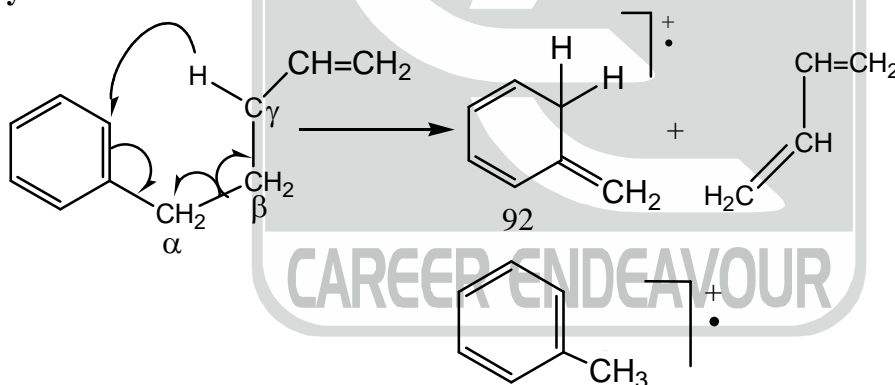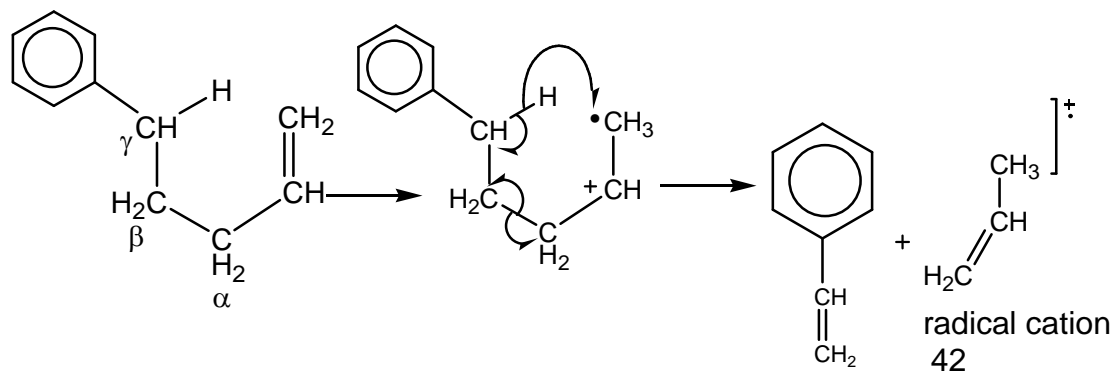**Presence of Cl :** Presence of Cl^- can be identify easily by the mass spectrum due to isotopic abundance of 2 isotope Cl^{35} & Cl^{37} in the ratio 3 : 1.

If the fragment has 1 Cl atom then the intensity ratio of M & M + 2 peak will be 3 : 1.

eg : CH_3Cl molecular ion peak 50 & 52 will appear in the intensity ratio 3 : 1

$1\,Cl \longrightarrow 2$ peak $M : M + 2$ $3 : 1$

$2\,Cl \longrightarrow 3$ peak $M : M + 2 : M + 4$ $9 : 6 : 1$

$3\,Cl \longrightarrow 4$ peak $M : M + 2 : M + 4 : M + 6$ $27 : 27 : 9 : 1$

Example: CH_2Cl_2, $H - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} - H$

There are 3 posibilities
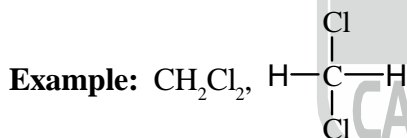
$\boxed{\begin{matrix} 35 \\ 35 \end{matrix}}$	$\boxed{\begin{matrix} 35 \quad 37 \\ 37 \quad 35 \end{matrix}}$	$\boxed{\begin{matrix} 37 \\ 37 \end{matrix}}$
3	3 1	1
×	× + ×	×
3	1 3	1
‾	‾‾‾	‾
9	6	1

So, the ratio is 9 : 6 : 1.

CHCl$_3$:

$Cl - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} - H$

Chloroform :

3 Cl ⟶ 4 peak   M : M + 2 : M + 4 : M + 6
There are 4 possibilities.

M	M+2			M+4			M+6
35	35	35	37	35	37	37	37
35	35	37	35	37	37	35	37
35	37	35	35	37	35	37	37

$$
\begin{array}{cccccccc}
3 & 3 & 3 & 1 & 3 & 1 & 1 & 1 \\
\times & \times & \times & \times & \times & \times & \times & \times \\
3 & 3 & 1 & 3 & 1 & 1 & 3 & 1 \\
\times & \times & \times & \times & \times & \times & \times & \times \\
3 & 1 & 3 & 3 & 1 & 3 & 1 & 1 \\
\hline
& & + & & & + & & \\
\hline
\end{array}
$$

27   9 + 9 + 9   3 + 3 + 3   1
27 :   27   :   9   :   1

So the ratio is 27 : 27 : 9 : 1.

Presence of Br : The two isotope of Br are ^{79}Br and ^{81}Br are present in the nature 1 : 1 means 50% + 50% Hence the presence of 1 Br atom in a fragment can be identified easily by the intensity of M and M + 2 peak in the ratio 1 :1.

CH₃Br : $CH_3Br]^{+\bullet} \longrightarrow$ m/z 94   intensity ratio 1 :1
                                                        m/z 96

CH₂Br₂ :

$$CH_2Br]^{+\bullet}$$

M	M+2		M+4
79	79	81	81
79	81	79	81

$$
\begin{array}{ccc}
1 & 1 \quad 1 & 1 \\
\times & \times \; + \; \times & \times \\
1 & 1 \quad 1 & 1 \\
\hline
1 & 2 & 1
\end{array}
$$

So the ratio is 1 : 2 : 1

CH₃Br₃:

$$CH_3Br_3]^{+\bullet}$$

M	M + 2			M + 4			M + 6
79	79	79	81	79	81	81	81
79	79	81	79	81	79	81	81
79	81	79	79	81	81	79	81

$$
\begin{array}{cccccccc}
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\times & \times & \times & \times & \times & \times & \times & \times \\
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\times & \times & \times & \times & \times & \times & \times & \times \\
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\hline
1 & & 3 & & & 3 & & 1
\end{array}
$$

1 :   3   :   3   :   1

FRAGMENTATION OF HALOGEN COMPOUNDS

1. α **-Fission :**

$$R—CH_2—CH_2—\ddot{\underset{\cdot\cdot}{X}}: \xrightarrow{e^-} R—\underset{\beta}{CH_2}—\overset{H_2}{\underset{\alpha}{C}}—\overset{+\cdot}{X} \xrightarrow[\text{fission}]{\alpha} R-\overset{\bullet}{C}H_2 + H_2C=\overset{\oplus}{X}$$

If $\alpha-$C having H^+ then it will also leave.

$$R—CH_2—\underset{R_1}{\overset{R_2}{\underset{|}{\overset{|}{C}}}}—X \xrightarrow{\alpha \ \text{fission}} \text{Bulky group will go as radical preferentially.}$$
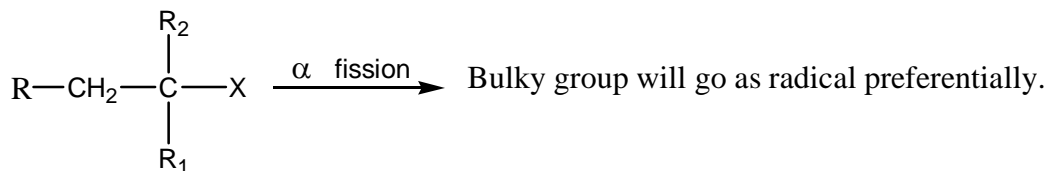
2. **M -1 Peak : M** -1 peak appear due to loss of H- atom from α position. This peak appear in different halogen compound in this order. R–F > R–Cl > R – Br > R–I
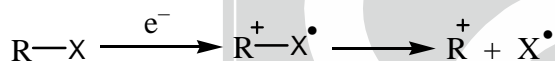
3. **Loss of X$^+$ Cation :** This peak appears by loss of alkyl part as radical.

$$R—X \longrightarrow R—\overset{\bullet}{X^+} \longrightarrow R^\bullet + X^+$$
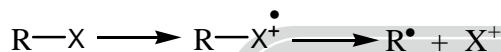
The order is RI > R – Br > RCl > R – F
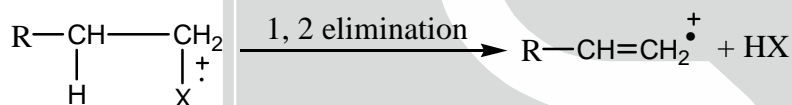
Hence the presence of I_2 atom in the molecule can be identify by a peak at 127 m/z ratio

4. **Loss of Halide Radical :**

$$R—X \xrightarrow{e^-} \overset{+}{R}—\overset{\bullet}{X} \longrightarrow \overset{+}{R} + X^\bullet$$
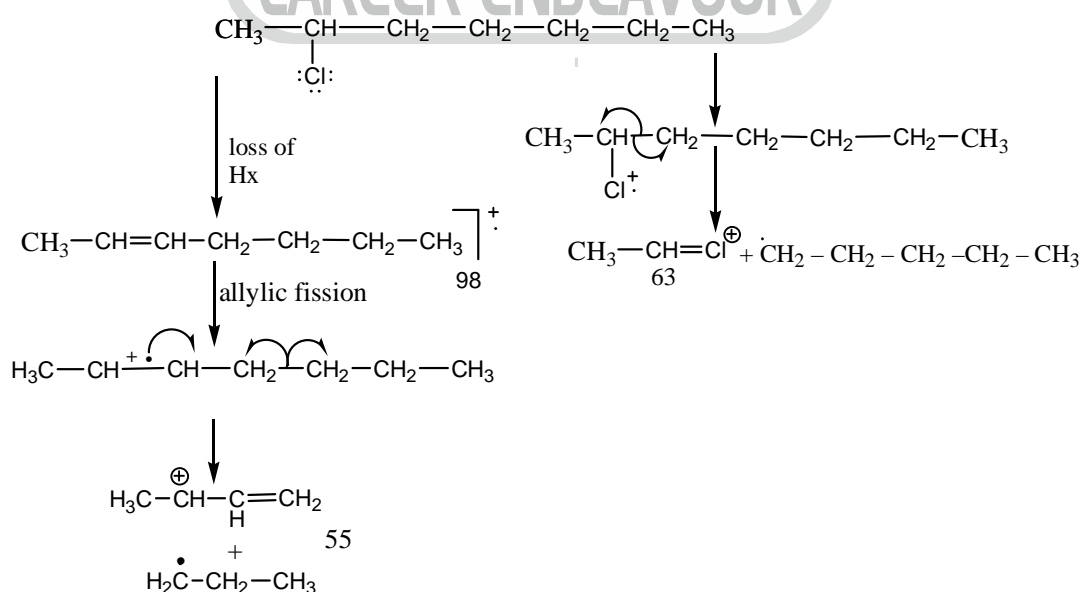
Due to loss of this radical the mass fragment peaks of alkanes like pattern may appear.

5. **Loss of Hydrogen Halide (HX):** (Which is important for fluoride and chloride.
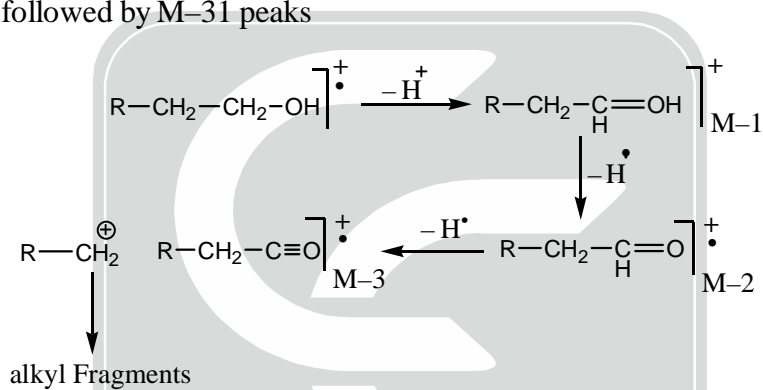
$$R—\underset{H}{\overset{|}{CH}}——\underset{\underset{\cdot\cdot}{\overset{|+}{X}}}{CH_2} \xrightarrow{1, 2 \ \text{elimination}} R—CH=CH_2^{\overset{+}{\bullet}} + HX$$

Problem: Explain the mass peaks at 56, 55, 63 and 98 for 2-chloroheptane.

$$CH_3—\underset{:\overset{\cdot\cdot}{Cl}:}{\overset{|}{CH}}——CH_2—CH_2—CH_2—CH_2—CH_3$$

loss of Hx

$$CH_3—CH=CH—CH_2—CH_2—CH_2—CH_3 \ \Big]^{\overset{+}{\cdot}} \quad 98$$

allylic fission

$$H_3C—\overset{+\bullet}{CH}—CH—CH_2—CH_2—CH_2—CH_3$$

$$H_3C—\overset{\oplus}{CH}—\underset{H}{\overset{|}{C}}=CH_2 \quad 55$$
$$+$$
$$H_2\overset{\bullet}{C}-CH_2—CH_3$$

$$CH_3—\overset{|}{\underset{\overset{|+}{\underset{\cdot\cdot}{Cl}}}{CH}}—CH_2—CH_2—CH_2—CH_2—CH_3$$

$$CH_3—CH=\overset{\oplus}{Cl} + \overset{\bullet}{C}H_2 – CH_2 – CH_2 –CH_2 – CH_3 \quad 63$$

$$CH_3-\overset{\bullet}{C}H-CH_2-CH_2-CH_2-CH_2-CH_3$$
$$\underset{Cl^+}{|}$$

loss of HX

α fission

$$CH_3-CH=CH-CH_2-CH_2-CH_2-CH_3$$
98

$$CH_3-\overset{H}{\underset{\overset{|}{Cl}\,{}_+^{\bullet}}{C}}-CH_2-CH_2-CH_2-CH_2-CH_3$$

$$CH_3-\underset{\overset{||}{Cl}}{\overset{\oplus}{C}H} + \overset{\bullet}{C}H_2-CH_2-CH_2-CH_2-CH_3$$
63

H₃C—CH H   HC—CH₃

H₂C   CH

C
H₂

$$\underset{CH_2}{\overset{H_3C}{\underset{||}{C}H}} + \underset{\overset{\bullet}{H_2C}}{\overset{\overset{CH_3}{|}}{\underset{\overset{|}{+}}{CH_2}}}$$ 56

AROMATIC HALIDES

CH₂—Cl

$$\overset{\oplus}{C}H_2 \quad + \quad \overset{\bullet}{Cl}$$

$$\overset{Cl\rceil^{+\bullet}}{} \xrightarrow{\text{loss of halogen radical}} \overset{\oplus}{} + \overset{\bullet}{Cl} \xrightarrow{-H-C≡C-H} \overset{\oplus}{\square}$$
m/z 51

ALCOHOLS

1. α-**Fission :**

$$CH_3-CH_2-CH_2-OH \longrightarrow CH_3-CH_2\,CH_2-\overset{..+}{O}H \longrightarrow CH_3-\overset{\bullet}{C}H_2 + CH_2=\overset{+}{O}H$$

31 m/z

31 mass peak characteristic of OH group.

Problem: How we can differentiate the 3 isomeric the basis of α -fission.

n-pentanol	Iso-pentanol	Neo-pentanol

$$CH_3-CH_2-CH_2-CH_2-OH$$

$$CH_3-CH-CH_2-CH_3$$
$$\quad\quad\;\; |$$
$$\quad\quad\;\; OH$$

$$CH_3$$
$$\quad |$$
$$H_3C-C-OH$$
$$\quad |$$
$$CH_3$$

$\downarrow$

$$[CH_3-CH_2-CH_2-CH_2-OH]^{\overset{\bullet}{+}}$$

$\downarrow \alpha$–fission

$$CH_3-CH_2-\overset{\bullet}{C}H_2 + CH_2=\overset{+}{O}H$$
$$\qquad\qquad\qquad\qquad 31$$

$\downarrow$

$$[CH_3-CH-CH_2-CH_3]^{\overset{\bullet}{+}}$$
$$\qquad\;\; |$$
$$\qquad\;\; OH$$

$\downarrow \alpha$–fission

$$CH_3-CH=\overset{+}{O}H + \overset{\bullet}{C}H_2CH_3$$
$$\qquad\qquad 45$$

$\downarrow \alpha$ fission

$$H_3C-C=\overset{+}{O}H + \overset{\bullet}{C}H_3$$
$$\quad\;\; |$$
$$\quad\;\; CH_3 \quad 59$$
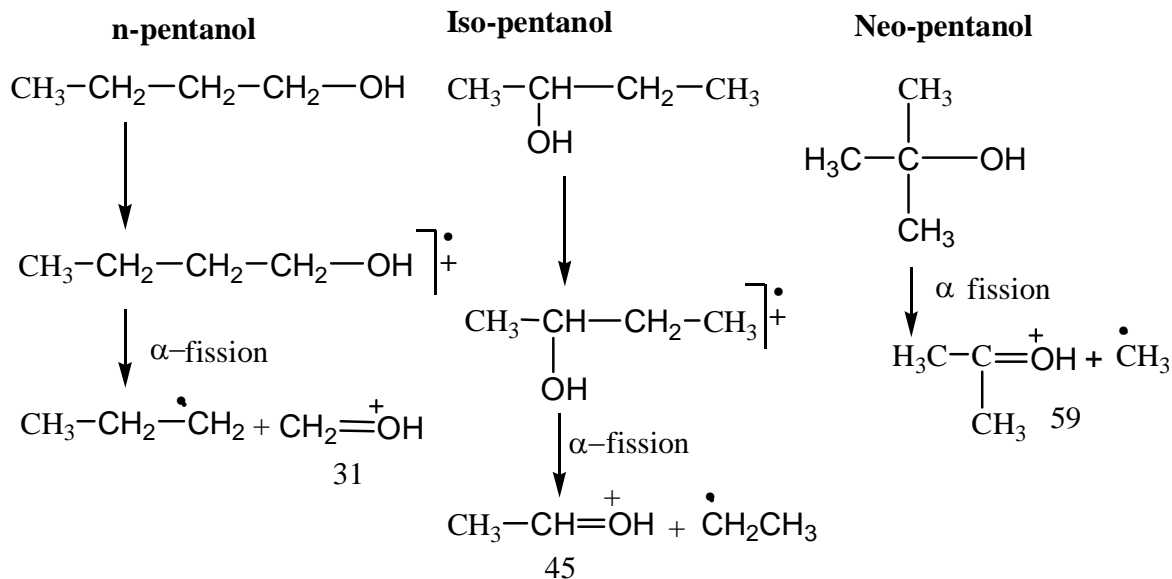
2.   M–1, M–2, M–3 followed by M–31 peaks

$$[R-CH_2-CH_2-OH]^{\overset{\bullet}{+}} \xrightarrow{-\overset{+}{H}} [R-CH_2-\underset{H}{\overset{|}{C}}=OH]^{+} \; M-1$$

$\downarrow -\overset{\bullet}{H}$

$$R-\overset{\oplus}{C}H_2 \qquad [R-CH_2-C\equiv O]^{\overset{\bullet}{+}}_{M-3} \xleftarrow{-\overset{\bullet}{H}} [R-CH_2-\underset{H}{\overset{|}{C}}=O]^{\overset{\bullet}{+}}_{M-2}$$

$\downarrow$

alkyl Fragments

AROMATIC ALCOHOLS

Benzylic alcohol

$$C_6H_5-CHO \longrightarrow C_6H_5-C\equiv O^{+} \xleftarrow{-2\overset{\bullet}{H}}$$

$$C_4H_3 \xleftarrow{-[C_2H_2]} C_6H_5 \xleftarrow{-CO}$$
$$\text{m/z } 51 \qquad \text{m/z } 77$$

$\xrightarrow{-\overset{\bullet}{H}}$ Hydroxy Tropylium ion

Problem:

1-Phenylethanol   m/z 107   m/z 79   m/z 51

hydroxytropylium ion

FRAGMENTATION IN PHENOL

1. M–1 peak is most important for phenol.
2. M–28 peak is characteristic for loss of CO.
3. Phenols, thiophenols, aniline etc. exhibits similar type of fragmentations by loosing M–CS,

$$\underbrace{M - CSH}_{} \; , \; \underbrace{M-CNH, \; M-CNH_2}_{}$$

e.g.

FRAGMENTATION OF ALDEHYDE

1. α- fission : (α–to oxygen) :

2. β – **fission :**

3.   M.R. Peak :
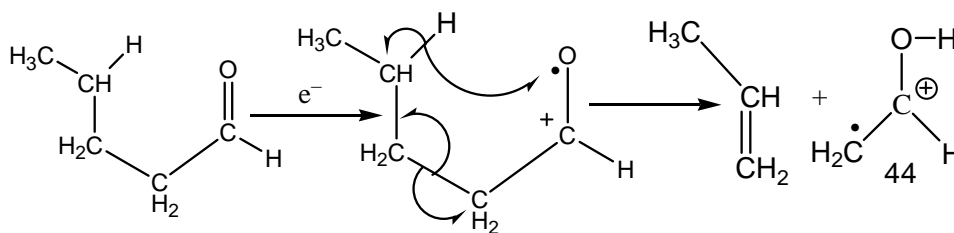
Problem: Explain the mass peak of hexanol 44, 56, 57, 29, 8, 72.

H_3C—CH_2—CH_2—CH_2—CH_2—CHO

α-clevage

$$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{CH_2} + H\text{-}C\equiv O^+$$

β-Fission:

β-fission

$$H_3C\text{-}CH_2\text{-}CH_2\text{-}\overset{\bullet}{CH_2} + \left.H_2C=\overset{|}{\underset{H}{C}}=O\right]^+$$

FRAGMENTATION OF KETONES

CH_3—CH_2—CH_2—$\underset{\underset{O}{\|}}{C}$—$CH_2$—$CH_3$
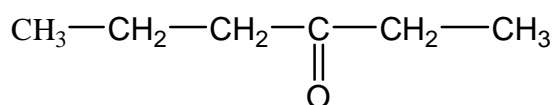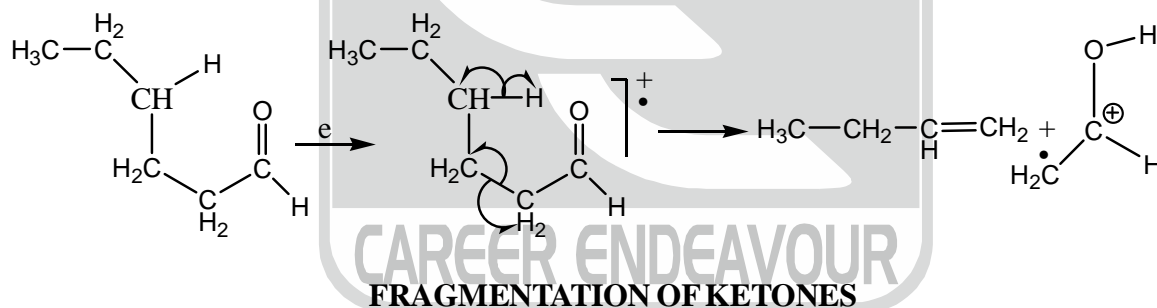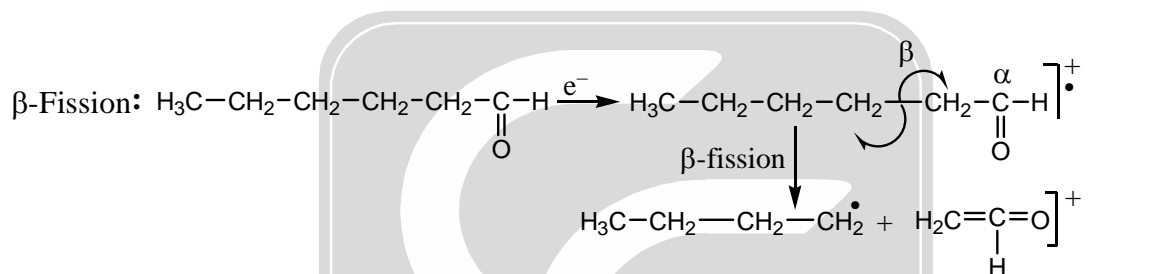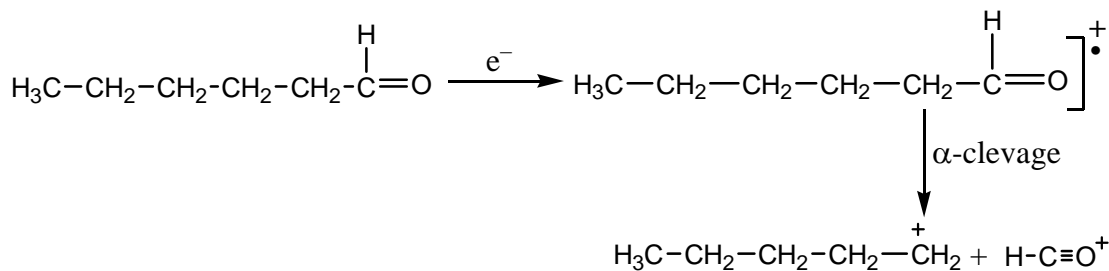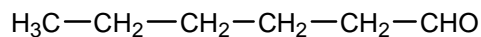
α – fission : 2 possibilities:

β – fission : 2 possibilities :

M.R. → 1 possibility

e.g. : CH_3—CH_2—CH_2—$\underset{\underset{O}{\|}}{C}$—$CH_2$—$CH_3$

(a) α – fission :

(b) β – **fission :**

β – **fission :**

(a)

(b)

M.R. :
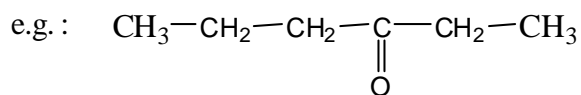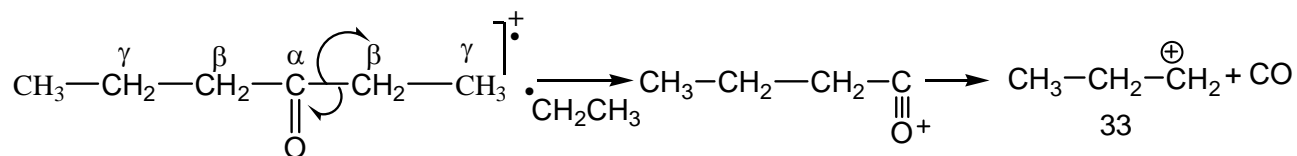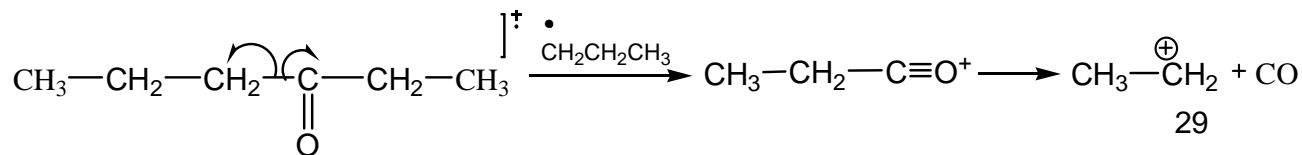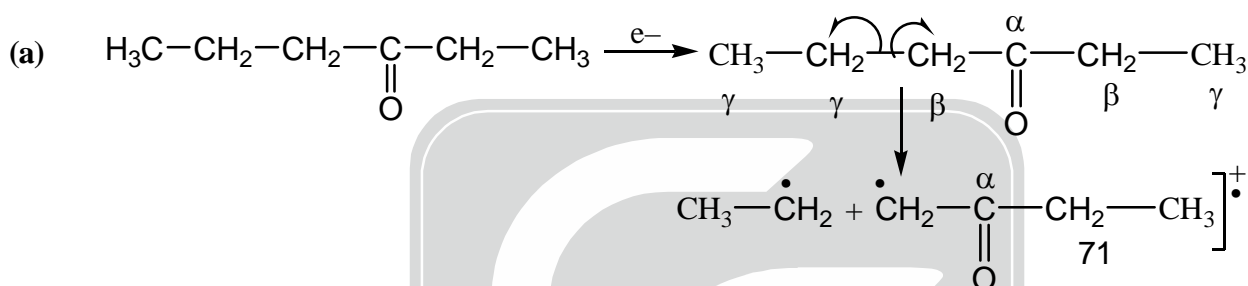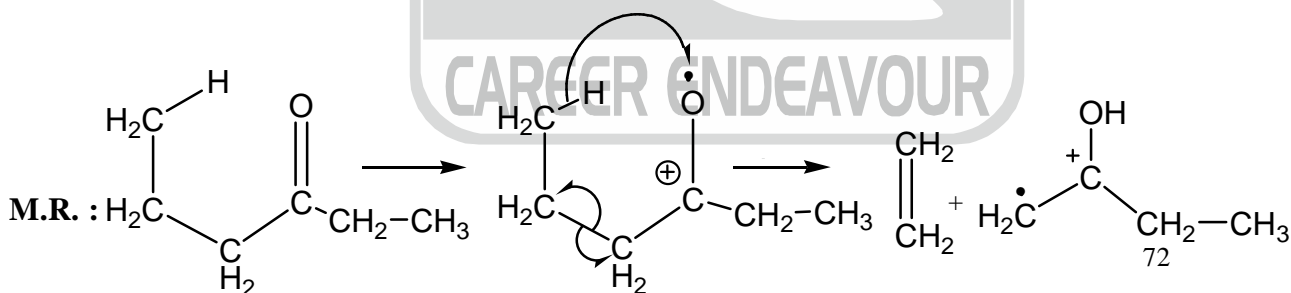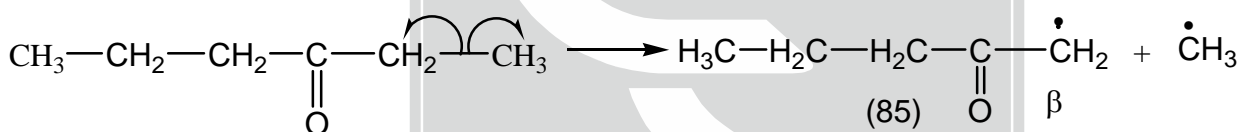
Note: (i) Methyl group at γ position can not migrate for MR.

(ii) Secondary γ Hydrogen migrates more preferentially than primary. (in MR).

Problem. Explain mass peak and 91, 92 & 58 for 1 phenyl 5 Hexanone.

Benzylic :

Tropolium ion
91

M.R. Two type :

(a)

(b)

92
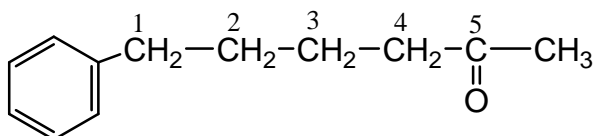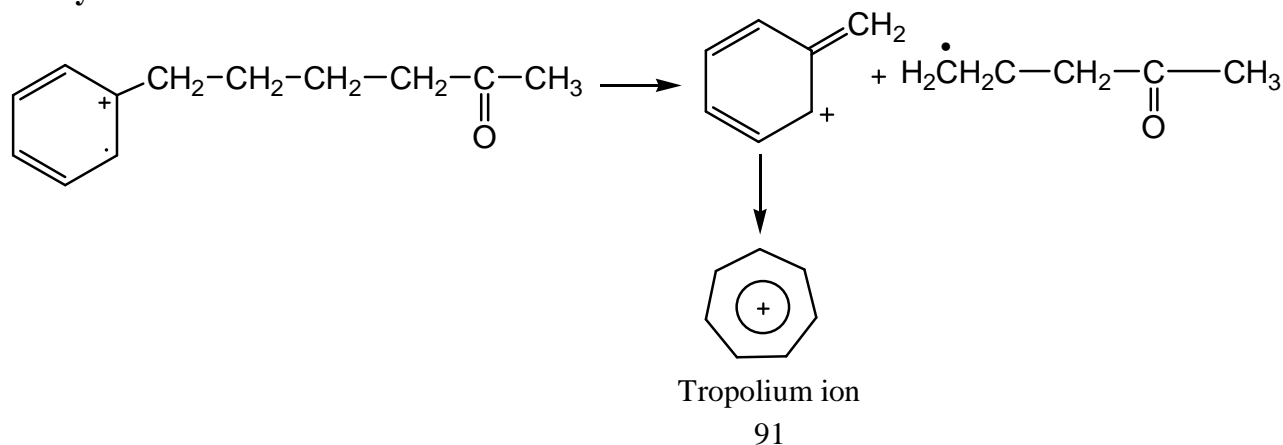
AROMATIC ALDEHYDE/KETONE
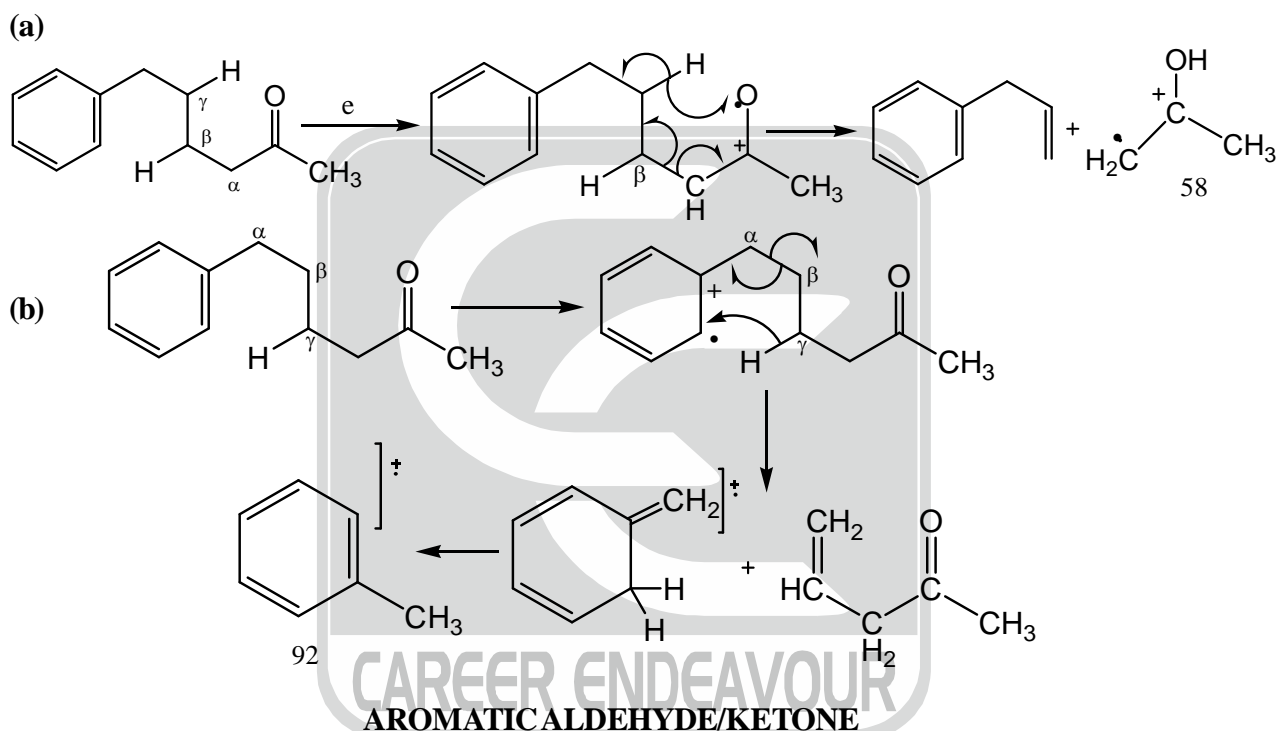
ESTER

Some important features of the mass spectrum of esters are:

(a) The moleclar ion peak is weak.

(b) The fragment ion due to α-cleavage is usually observed.

(c) In methyl esters, peaks due to R–CO$^+$, R$^+$, CH$_2$O$^+$ and CH$_3$OCO$^+$ (m/z 59) are observed.

(d) The methyl esters not substituted at the α-carbon atom show McLafferty rearrangement.

Problem:

$H_3CO-C{\equiv}O^{\oplus}$
m/z = 59

m/z 74

$H_3C-\overset{\oplus}{C}H-CH_3$
m/z 43

$\overset{+}{O}CH_3$
m/z 31
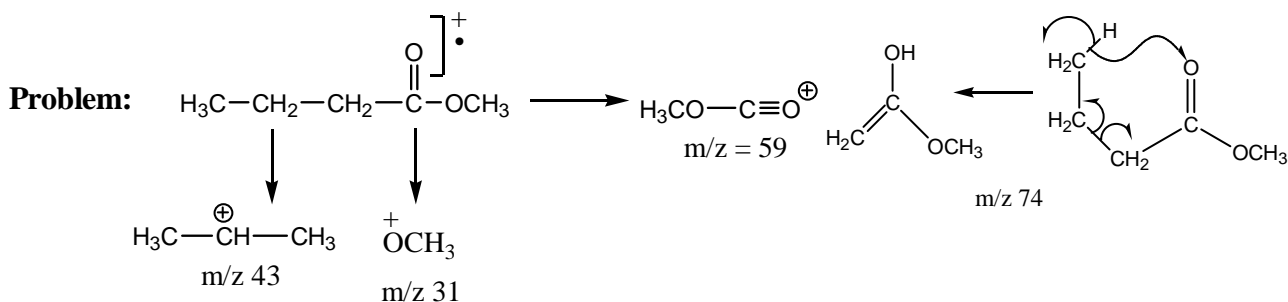
M.R. :
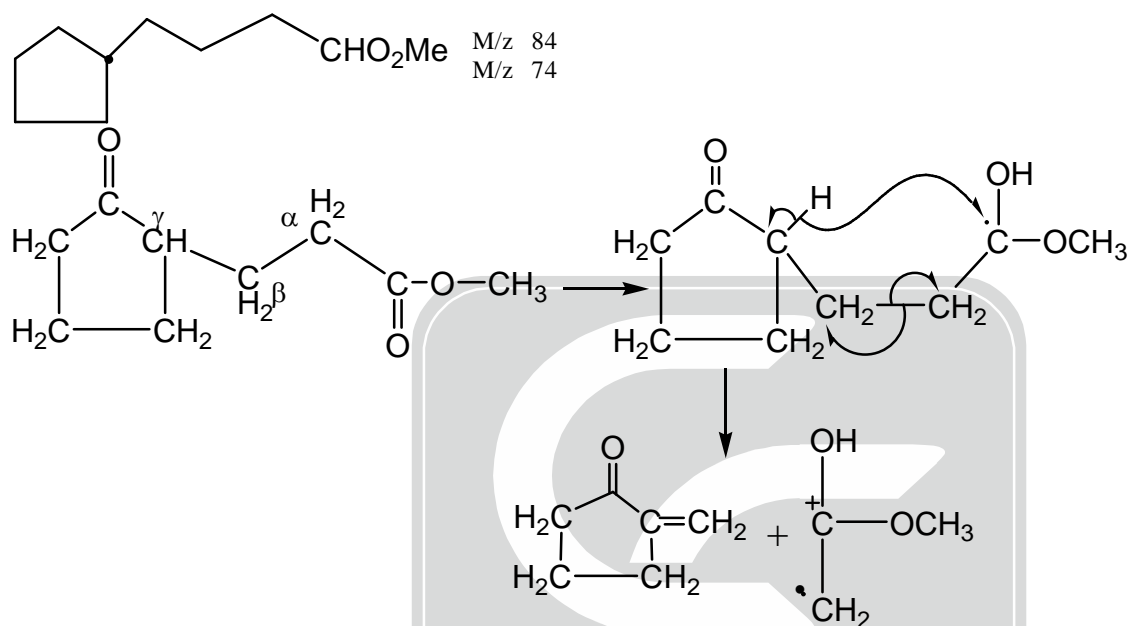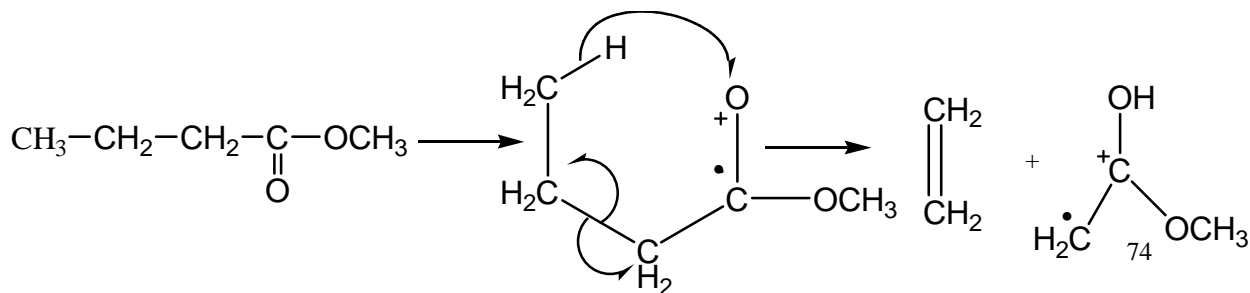
AROMATIC ESTER

Aromatic ester give intense peak by loss of alkoxy radical followed by removal of CO.
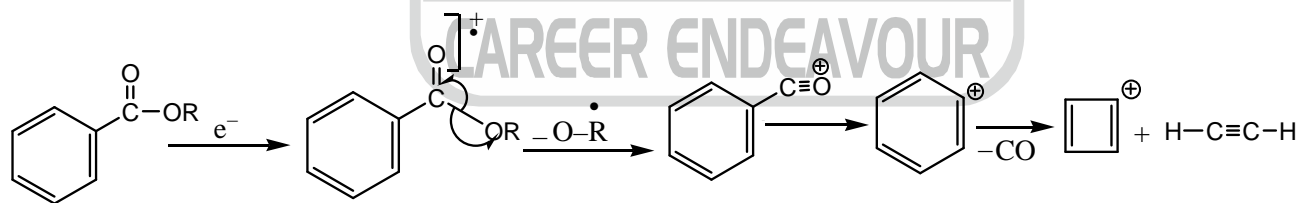
Substitution of para and meta position does not alter. This fragmentation but methyl group at O–position to the ester function lead to the elimination of alcohol.
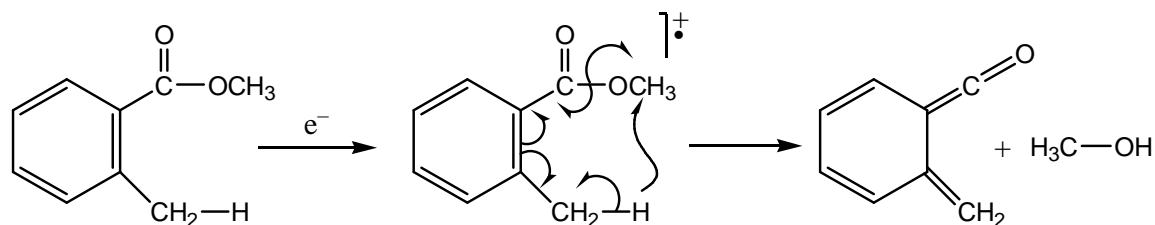
CARBOXYLIC ACID

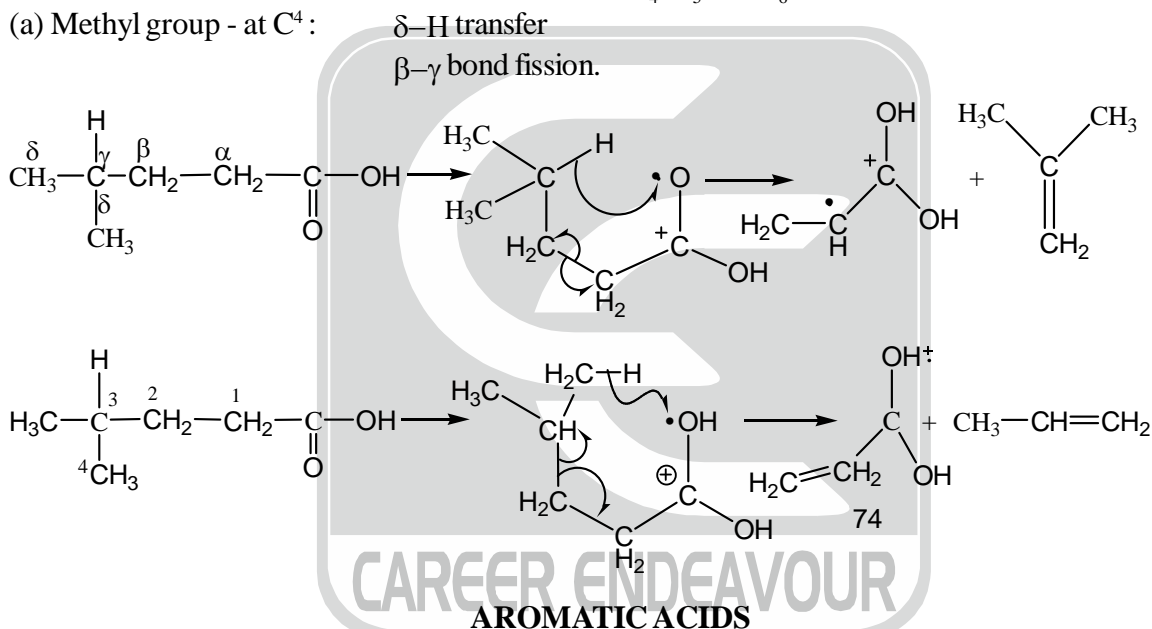The most important feature of acid is mass fragment at m/z 60 if $\gamma-H$ to C=O is present.
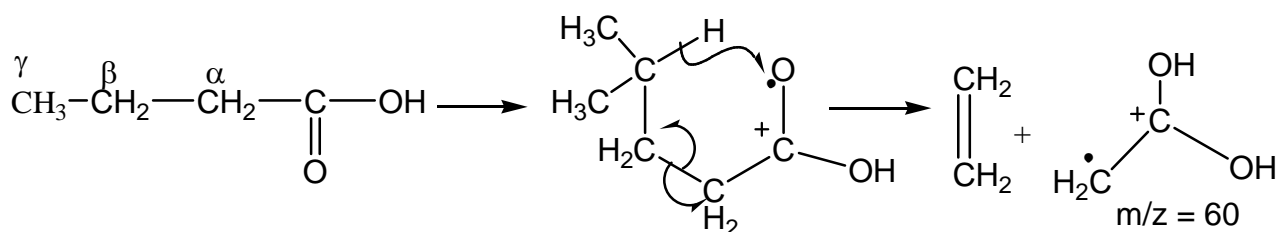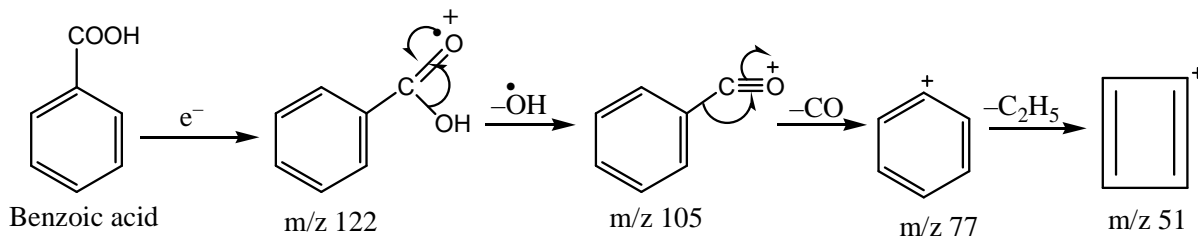

In lower acid α-fission to $C = O$ lone pair is most important.
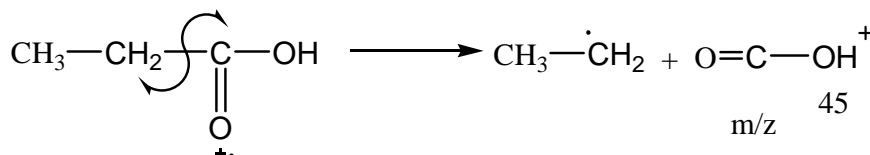
• Straight chain acids containing a methyl group at C_4, C_5 and C_6 gives a special type of fragmentation.

(a) Methyl group - at C^4 : $\delta-H$ transfer

$\beta-\gamma$ bond fission.

AROMATIC ACIDS

• In aromatic acids parent peak ion is intense.

• Some other prominent peak are M–17 and M–45

• If an alkyl group is present or any other hydrogen bearing group is present ortho to COOH group, then a signal due to M–18 (loss of water molecule) is also observed.
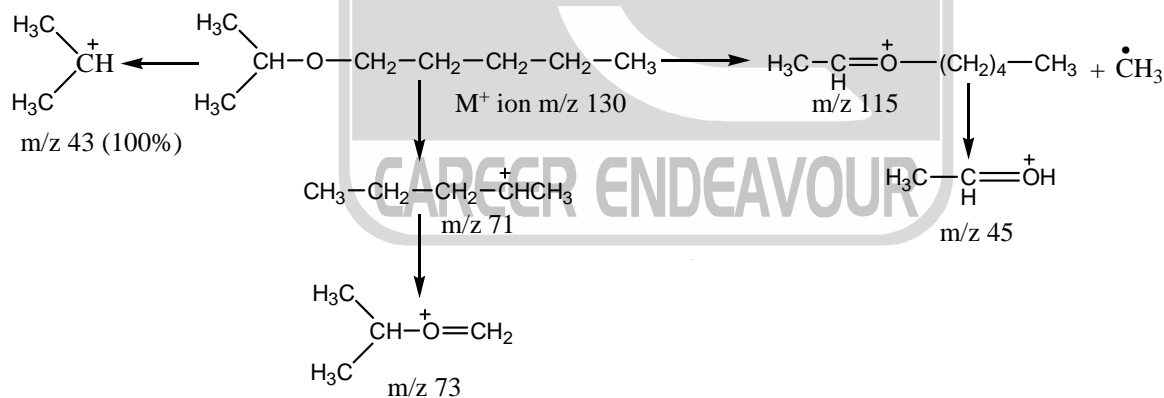

Benzoic acid   m/z 122   m/z 105   m/z 77   m/z 51

M^+ m/z 138 $\xrightarrow{-H_2O}$ m/z 120

ETHERS

Some impotant features of the mass spectrum of Aliphatic ethers are:
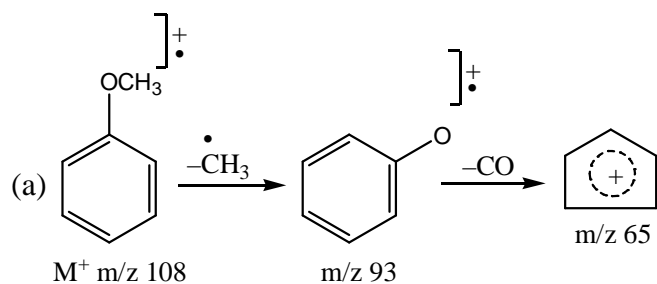
(a) They show molecular ion peak almost of negligible abundance.

(b) The presence of oxygen atom in ethers can be known from strong peaks at m/z 31, 45, 59etc. and these peaks represent $\overset{+}{R}O$ and $\overset{+}{ROCH_2}$ fragments.

(c) The most characteristic fragmentation mode is the loss of one of the alkyl groups to form an oxonium ion $\overset{+}{R}O$ or the alkyl cation.
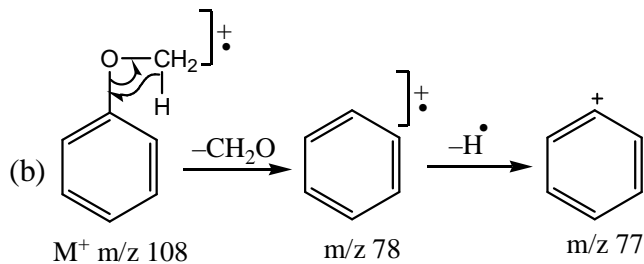

$$H_3C-\overset{+}{\underset{H}{C}}=OH \longleftarrow H_3C-CH_2-O-CH_2-CH_3 \longrightarrow H_2C=\overset{+}{O}H$$

m/z 45   m/z 31

$$\overset{\bullet}{C}H_3 + H_2C=\overset{+}{O}-CH_2-CH_3$$

m/z 59
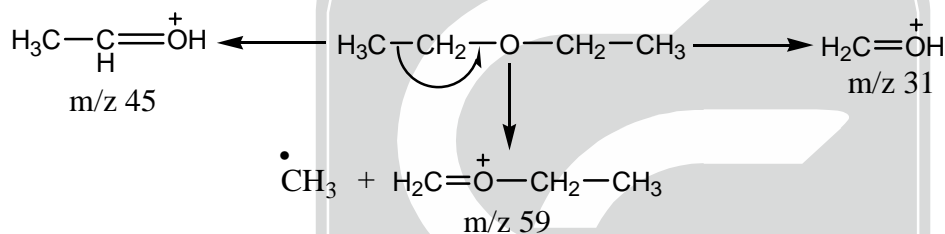
Its various fragmentation modes are:

$$\overset{H_3C}{\underset{H_3C}{>}}\overset{+}{C}H \longleftarrow \overset{H_3C}{\underset{H_3C}{>}}CH-O-CH_2-CH_2-CH_2-CH_2-CH_3 \longrightarrow H_3C-\overset{+}{\underset{H}{C}}=\overset{+}{O}-(CH_2)_4-CH_3 + \overset{\bullet}{C}H_3$$

m/z 43 (100%) M^+ ion m/z 130   m/z 115

$$CH_3-CH_2-CH_2-\overset{+}{C}HCH_3$$

m/z 71

$$H_3C-\overset{+}{\underset{H}{C}}=OH$$

m/z 45

$$\overset{H_3C}{\underset{H_3C}{>}}CH-\overset{+}{O}=CH_2$$

m/z 73

Aryl Ethers:

(a) M^+ m/z 108 $\xrightarrow{-\overset{\bullet}{C}H_3}$ m/z 93 $\xrightarrow{-CO}$ m/z 65

(b)

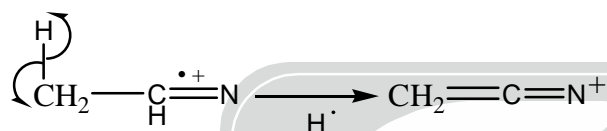M$^+$ m/z 108 →(−CH$_2$O)→ m/z 78 →(−H$^\bullet$)→ m/z 77
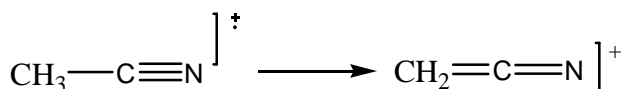
ALIPHATIC NITRILES

(1) Alkyl nitrile of lower molecular wt. show intense

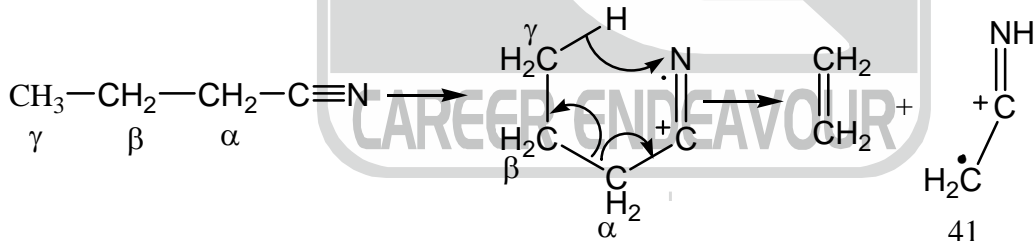M−1 peak by loss of H$^\bullet$

$CH_3—C≡N$]$^{+}$ → $CH_2=C=N$]$^{+}$

$CH_2—C≡N$ →(−H$^\bullet$)→ $CH_2=C=N^+$

(2) Up to C$_3$ (−CH$_2$—CH$_2$—C≡N) M − 27 due to loss of HCN is the base peak.

Molecular ion
radical cation (OES)

$CH_2=CH_3$]$^{+}$ + HCN ←(HCN)— $H_3C—H_2C—C≡N$ → $CH_3—CH=C=N$]$^{+}$

28   55   cation 54
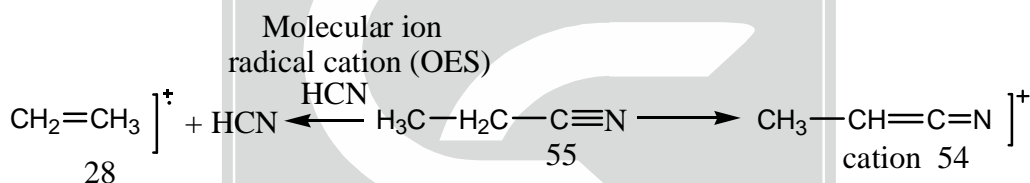
(3) If γ−H is present to the C = N then MR fragmentation give the base peak.
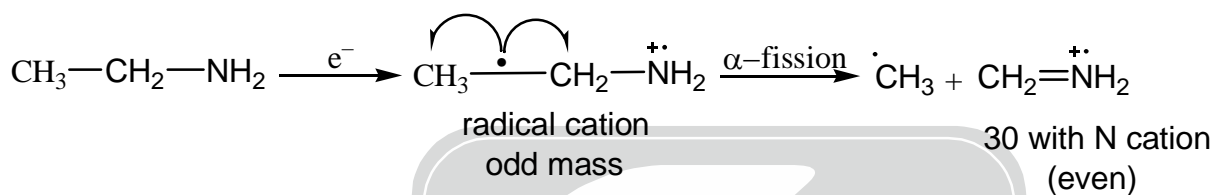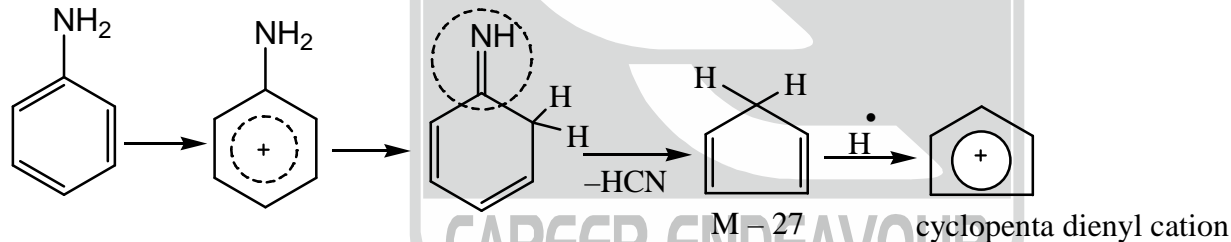
$CH_3—CH_2—CH_2—C≡N$ →
γ   β   α

41

ARYL NITRILES :

+ HCN
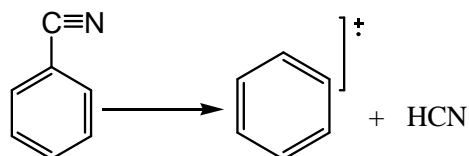
(1) Aryl nitrile shows base peak as M −HCN (M − 27) by using the ortho Hydrogen.
(2) If alkyl group are present then other characteristic fragmentation also possible.

(1) Fragmentation of Ar–CN

(2) Fragmentation of alkyl benzene.

(1) Fragmentation of alkyl benzene

(2) Fragmentation of alkyl nitile.

AMINES :

(1) α–fission :

radical cation
odd mass
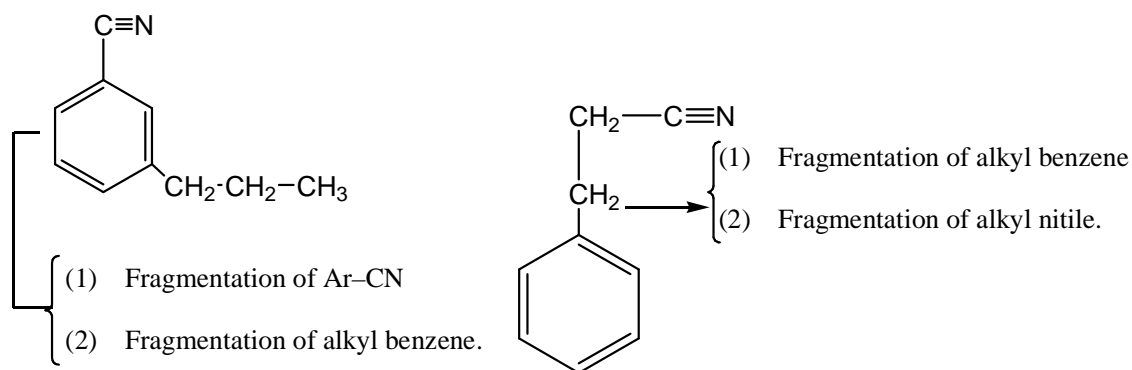
30 with N cation
(even)

(2) **M – 1 peak :**

Due to loss of α–H

(3) The fragments related to the alkyl group.

AROMATIC AMINES :

–HCN

M – 27

cyclopenta dienyl cation

NITRO COMPOUNDS :

Aliphatic nitro compound shows characteristics peak at

m/z, 30 due to NO^+

m/z, 46 due to NO_2^+

$$CH_3—CH_2—N(O)(O) \longrightarrow CH_3—\overset{+}{CH_2} + NO_2^+ + \overset{+}{NO}$$

29   46   30
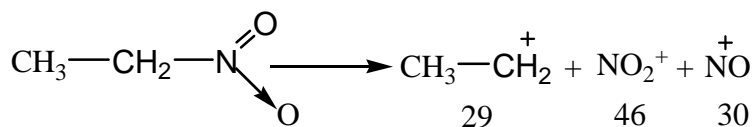
If the long alkyl chain is present the characteristic fragment of alkyl chain also exist.

ARYL NITRO COMPOUND :

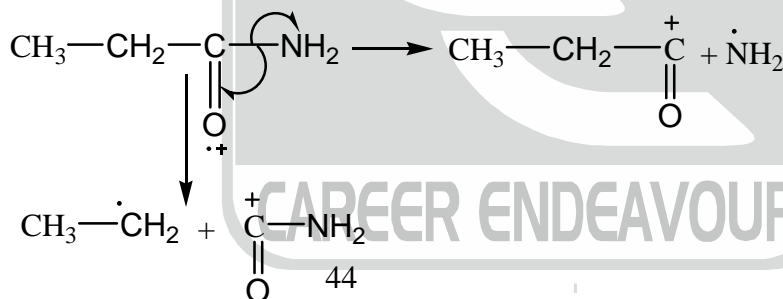(1) NO^+ (2) NO_2^+ (3) M – NO   (4) M – NO_2 (5) M – OH (ortho effect)
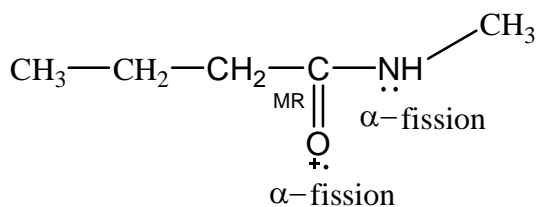

65
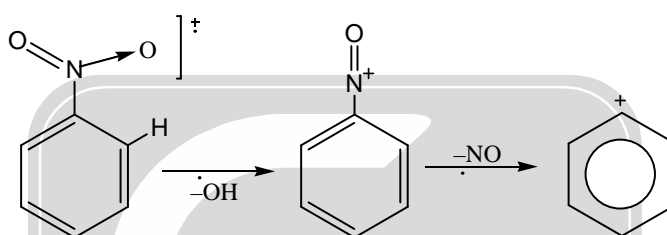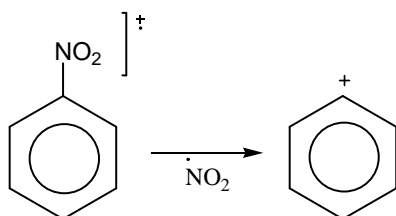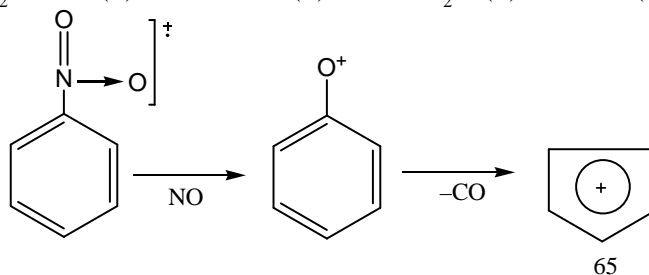
AMIDES :

(1) α−fission :

Giving alkyl gp. as radical preferentially

44

more intense

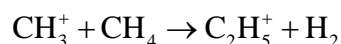The carbonyl group of Amide can give MR rearrangement if $\gamma - H$ is present.
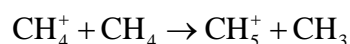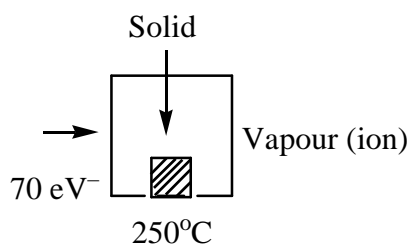
INSTRUMENTATION

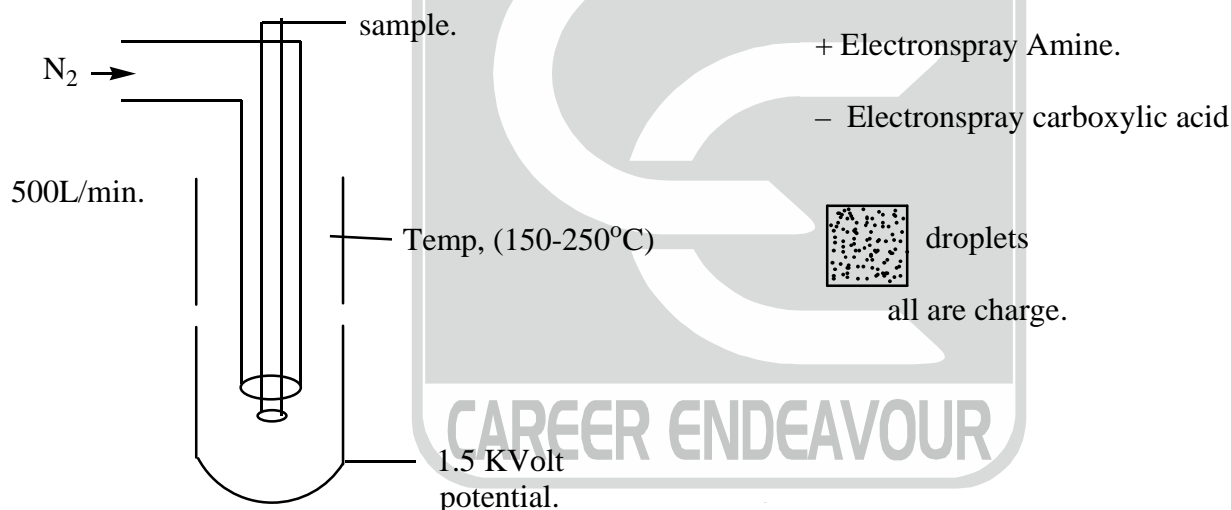| Ion-Formation | | ion separation | | Detection |

ION FORMATION :

1. Chemical ionisation (CI)
2. Electrons pray ionization (ESI)
3. Fast atom bombardment (FAB)
4. Matrix assisted laser desorption ionization (MALD)

Solid

→ Vapour (ion)

70 eV⁻

250°C

$$CH_4 + 70eV \rightarrow CH_4^+$$
$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$$
$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

ELECTROSPRAY : The technique use for those solid which not change in ions at 250°C . they are dissolve in solvents like CH_3OH, C_2H_5OH, THF, H_2O.

$N_2 \rightarrow$

sample.

500L/min.

Temp, (150-250°C)

1.5 KVolt potential.

+ Electronspray Amine.

− Electronspray carboxylic acid

droplets

all are charge.

If we give +ve charge then all droplets will be + charged.
If we give –ve charge then all droplets will be –vely charged.

on bursting
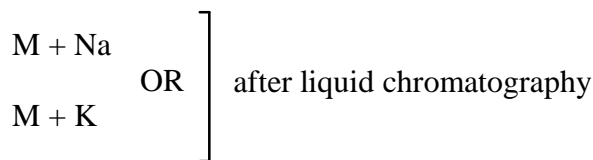form small droplet
density increases.
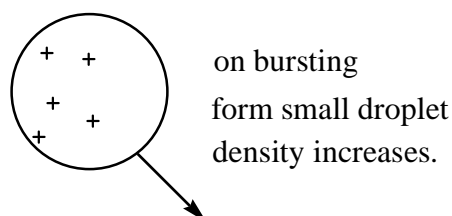
M + 1   or M+ solvent.

To increase ionisation we use formic acid.
LCMS : Liquid chromatograph Mass Spectroscopy.
To increase ionisation we use formic acid.
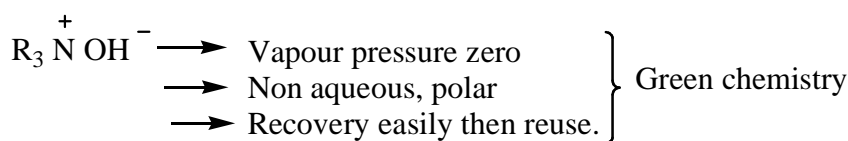**LCMS :** Liquid chromatograph Mass Spectroscopy.

$$\left.\begin{array}{l} M + Na \\ \\ M + K \end{array}\right\} \text{OR} \quad \text{after liquid chromatography}$$

GCMS : Gas chromatography Mass spectroscopy.

Fast Atom Bombardment (FAB)

$$M + 1 \ \& \ M - 1.$$

for special compound.

MALDI : Ionic liquids - B.P. high, liquid.

$$R_3 \overset{+}{N} OH^- \longrightarrow \left.\begin{array}{l} \text{Vapour pressure zero} \\ \text{Non aqueous, polar} \\ \text{Recovery easily then reuse.} \end{array}\right\} \text{Green chemistry}$$

Comp + ionic liquid $\longrightarrow$ ion of comp. only

ION SEPARATION :
(1) Magnetic/Electrostatic sector $\quad \Rightarrow \quad$ High resolution, exact mass.
(2) Quadrupole $\quad\quad\quad\quad\quad \Rightarrow \quad$ Unit mass resolution, fast scan
(3) Time of fight (TOF) $\quad\quad\quad \Rightarrow \quad$ Unit mass System
(4) Ion Cyclotron resonance. $\quad \Rightarrow \quad$ Very High resolution, exact mass

Time-of-flight mass analysers:

The time-of-filight (TOF) mass analyzer is based on the simple idea that the velocities of two ions, created at the same instant with the same kinetic energy, will vary depending on the mass of the ions – the lighter ion will have a higher velocity. If these ions are travelling towards the mass spectrometer's detector, the faster (lighter) ion will strike the detector first. Examining this concept further, the kinetic energy of an ion accelerated through an electrical potential V will be

$$zV = \frac{mv^2}{2} \qquad\qquad\qquad\qquad\qquad \text{... (i)}$$

and the velocity of the ion is the length of the flight path L divided by the time 't' it takes the ion to travel over that distance.

$$v = \frac{L}{t} \qquad\qquad\qquad\qquad\qquad\qquad \text{... (ii)}$$

Replacing this expression for v in equation (i)

$$zV = \frac{mL^2}{2t^2} \qquad\qquad\qquad\qquad\qquad \text{... (iii)}$$

Thus, it follows that,

$$\frac{m}{z} = \frac{2Vt^2}{L^2} \qquad\qquad\qquad\qquad\qquad \text{... (iv)}$$

Metastable peak:

The metastable peaks in the mass spectrum greatly contribute to structure elucidation. From the positions of the parent ion and the daughter ion, the position of the metastable ion can be calculated. For example, in the spectrum of toluene, the formation of less intense metastable peak at 46.4 lends weight to the structure of toluene. It is due to the fragmentation of $C_7H_7^+$ ion to $C_5H_5^+$ ion in the second field free region.

Problem: Calculate the position of metastable peak in case of toluene

Soln. Mass spectrum of toluene exhibits two strong peaks at m/e 91 and at m/e 65. The peak at m/e 91 is due to the formation of tropylium cation (stable) which loses a molecule of acetylene (26 mass units) to give $C_5H_5^+$ (m/e 65).
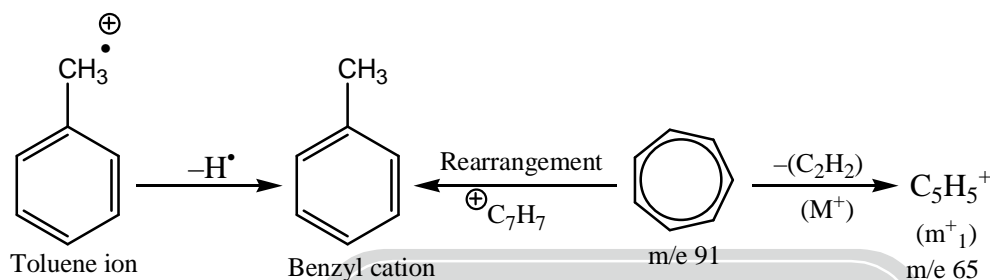

Suppose the transition $C_7H_7^+$ (91) to $C_5H_5^+$ (65) occurs in the second field free region, then a metastable peak is formed. The position of the broad metastable peak is determined as

$$m^* = \frac{m_1^2}{M_1} = \frac{65 \times 65}{91} = \textbf{46.4}$$

A metastable peak in case of toluene appears at 46.4 in the mass spectrum.

$$\textbf{Metastable peak} = \frac{(\textbf{Daughter ion})^2}{(\textbf{Parent ion})}$$

Problem: The m/z value of the detectable fragment formed by McLafferty like rearrangement of the following compound in mass spectrometer is _____

Soln.
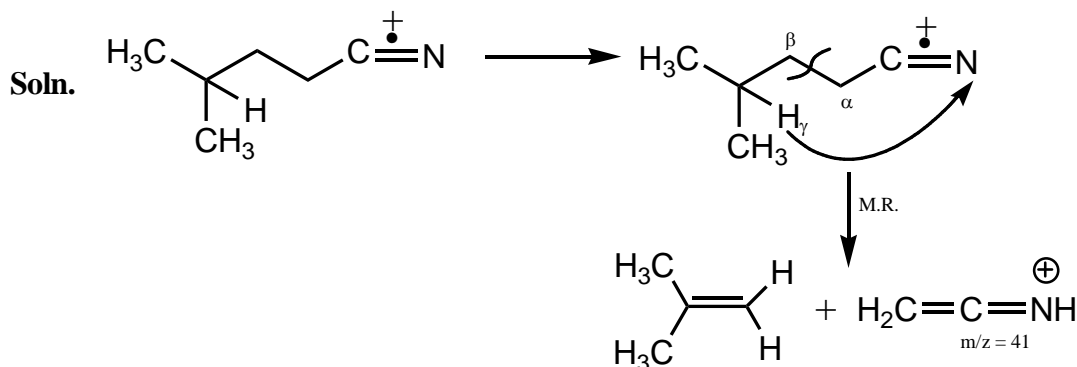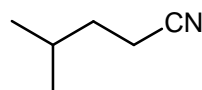
Correct answer is (41).

Problem: Mass fragment of $[IrCl]^+$ in mass spectrometry shows three mass peaks at m/z = 226, 228, and 230. Given that natural abundances of ^{191}Ir, ^{193}Ir, ^{35}Cl and ^{37}Cl are 37%, 63%, 76%, and 24% respectively, the intensities of the mass peaks are in the order

(a) 49.5 : 100 : 26.6   (b) 100: 49.5: 26.6   (c) 26.6: 100: 49.5   (d) 26.6: 49.5: 100

Soln.

$$^{191}Ir : {}^{193}Ir \quad + \quad {}^{35}Cl : {}^{37}Cl$$

Natural abundance

$$37\% : 63\% \quad + \quad 76\% : 24\%$$
$$x \qquad y \qquad\qquad a \qquad b$$

$$(3.7x + 6.3y)^1 (7.6a + 2.4b)^1$$

$$= 3.7 \times 7.6\, xa + 6.3 \times 7.6\, ya + 3.7 \times 2.4\, xb + 6.3 \times 2.4\, yb$$

$$= 28.12 \frac{xa}{M} + 47.88 \frac{ya}{M+2} + 8.88 \frac{xb}{M+2} + 15.12 \frac{yb}{M+4}$$

$$= 28.12 M + 56.76 (M+2) + 15.12 (M+4)$$

$$= 28.12 \times 1.76 M + 56.76 \times 1.76 (M+2) + 15.12 \times 1.76 (M+4)$$

$$= 49.49 M + 100 (M+2) + 26.6 (M+4)$$

$$= 49.5 M + 100 (M+2) + 26.6 (M+4)$$

$$M \quad : M + 2 : M + 4$$
$$49.5 : 100 \qquad 26.6$$

Correct option is (a)