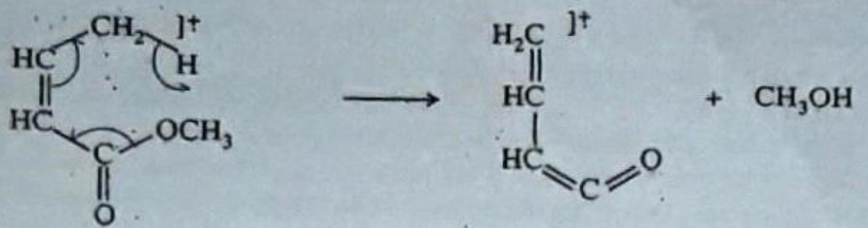


Such an elimination distinguishes (*i*) between cis and trans isomers and (*ii*) ortho substituted compound from meta and para substituted isomers.

4. McLafferty rearrangement ion. This rearrangement involves the cleavage of a β-bond followed by a γ-hydrogen transfer. The mechanism involves a six membered transition state (For details, see page 277).

7.10 Important Features of the Mass Spectra of Hydrocarbons

(*a*) **Alkanes (saturated hydrocarbons).** Some important features of the mass spectra of alkanes are as follows:

(*i*) The relative height of the parent peak decreases as the molecular mass increases in the homologous series.

(*ii*) Groups of peaks in the mass spectrum are observed 14 mass units apart. The most abundant peaks correspond to $C_nH^+_{2n+1}$ ion.

(*iii*) The most intense peaks are due to C_3 and C_4 ions at m/e 43 and m/e 57 respectively.

(*iv*) There is no preferred charge stabilisation site to favour any specific cleavage.

(*v*) The peaks corresponding to $C_nH^+_{2n+1}$ ions are also accompanied by $C_n\ H^+_{2n}$ and $C_n\ H^+_{2n-1}$ ions in much less abundance.

The mass spectrum of dodecane ($C_{12}H_{26}$) is shown below:

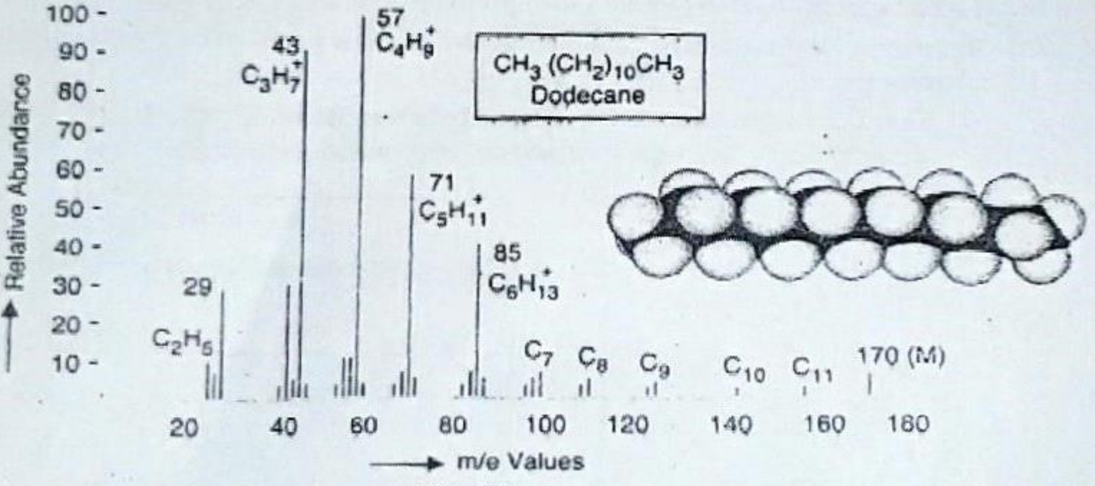


Fig. 7.7

It is very important to note that relative abundance of the ion (fragment ion) formed depends upon the (*i*) stability of the ion formed and also (*ii*) the stability of the radical which is lost.

Note. The stability of the carbocation has the order

allylic > tertiary > secondary > primary > methyl. The stability of the free radical lost depends upon:

(*i*) The length of the straight chain since it allows greater dispersal of the odd electron. Greater the dispersal of odd electron, greater is the stability of the free radical. *n*-butyl free radical is more stable than *n*-propyl free radical. Greater the stability, easier the formation.

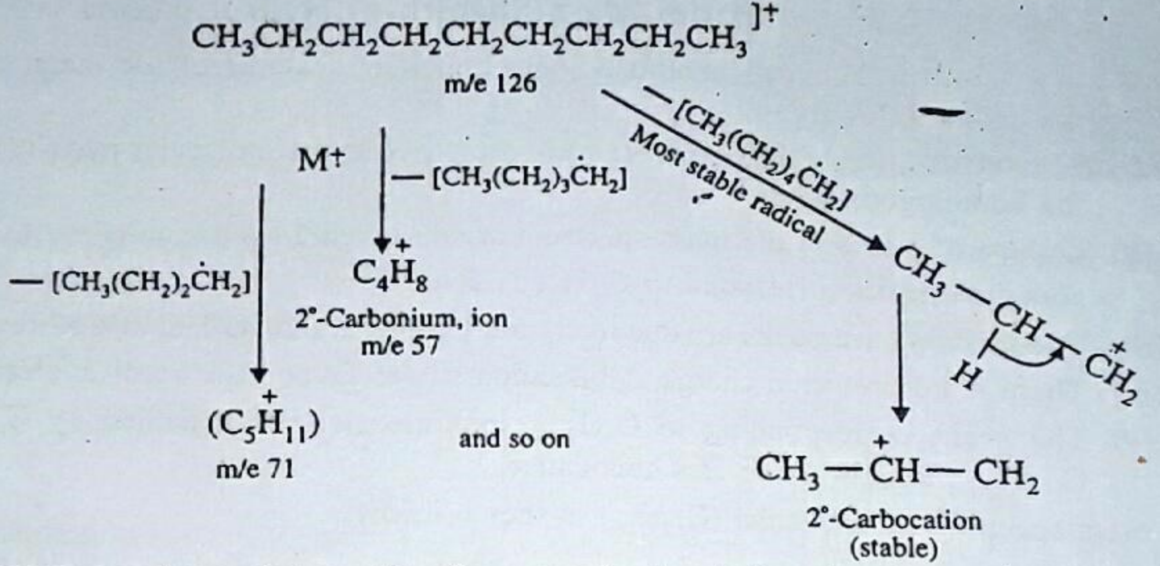
(*ii*) The nature of the free radical, whether primary, secondary or tertiary.

Explanation of the mass spectrum of dodecane. The $C_4H_9^+$ ion (m/e 57) is the base peak (100% abundance). It is due to the formation of the most stable secondary carbonium ion and the elimination of the most stable secondary free radical. As expected, the peaks are formed at 14 mass units apart with decreasing abundance. $C_3H_7^+$ ion peak is much abundant for the same reasons. The relative abundance goes on decreasing from m/e 57 to 71 to 85 and so on. As expected, the molecular ion peak is much less intense.

Also, we notice small peaks for $C_n\ H_{2n-1}^+$ and $C_n\ H_{2n}^+$ ions.

Exercise. Draw the mass spectrum of *n*-nonane (C_9H_{20}).

Hints. The M^+ and $M^+ + 1$ peaks are formed at m/e 128 and 129. The other signals which appear in the spectrum are m/e 43, 57, 71, 85, 99 alongwith other less intense peaks.



In the mass spectrum, also mention the approximate relative abundance of each fragment ion.

(*b*) **Branched chain alkanes.** Some important features of the mass spectra of branched chain alkanes are:

(*i*) Bond cleavage takes place preferably at the site of branching. Due to such cleavage, a more stable secondary or tertiary carbonium ion results.

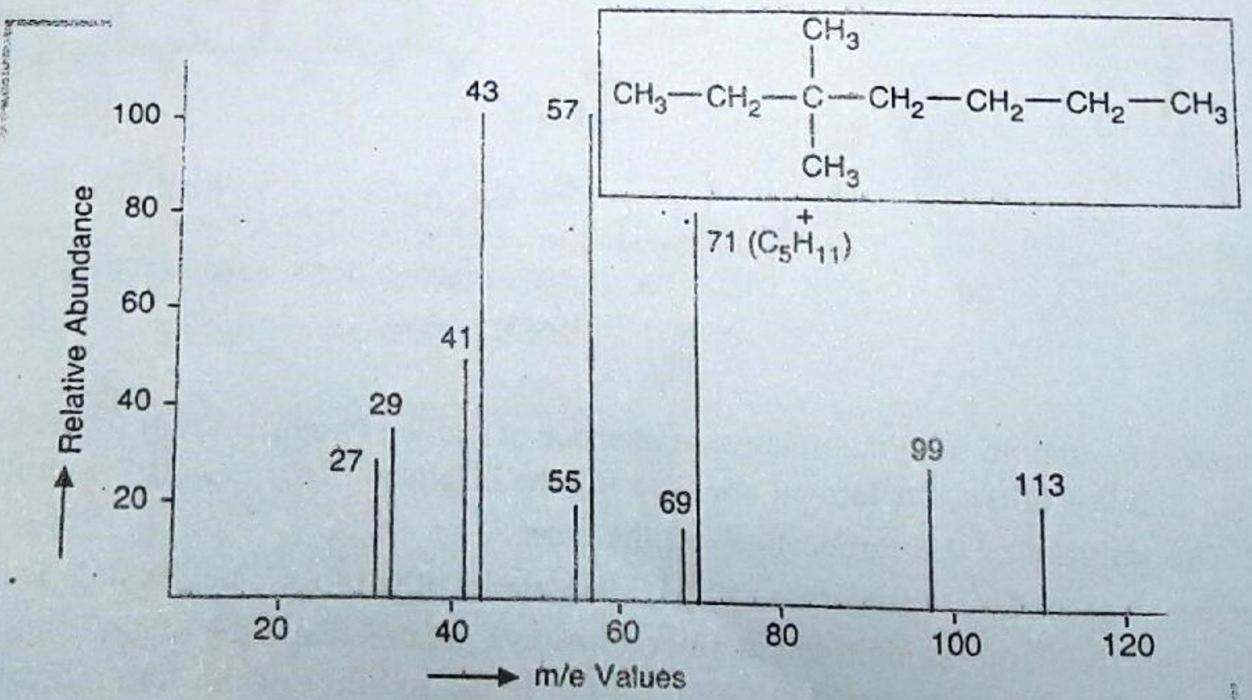


Fig. 7.8. Mass spectrum of 3, 3-Dimethyl heptane.

(*ii*) Generally, largest substituent at a branch is eliminated readily as a radical. The radical achieves stability by the delocalisation of lone electron.

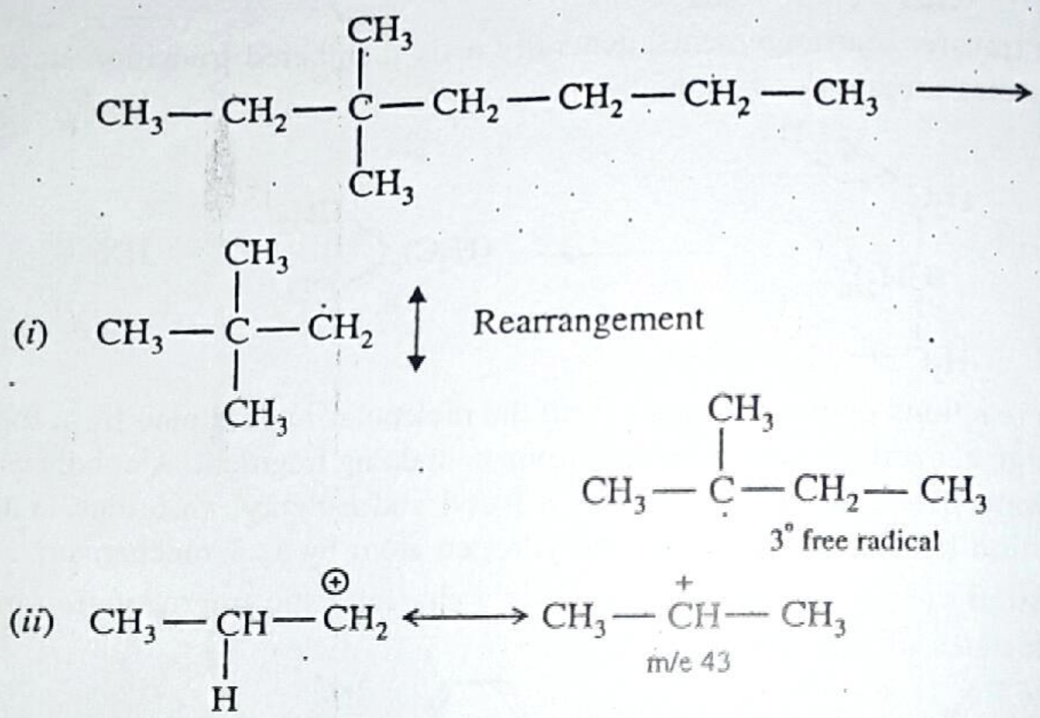
(*iii*) The relative abundance of the parent ion is least and is mostly not observed.

(*iv*) Great number of fragments result from a branched chain compound compared to the straight chain compound. It is due to greater pathways available for cleavage.

(*v*) The signals corresponding to $C_n H_{2n+1}^+$ ions follow weak signals which appear 2 units below them. Consider the mass spectrum of 3, 3-dimethyl heptane (Fig. 7.8).

Explanation. As expected, the loss of tertiary free radical forms a peak due to $C_4H_9^+$ ion at m/e 57. Also the loss of *n*-butyl free radical results in the formation of tertiary carbonium ion at m/e 71 in much abundance. The peak at m/e 71 is formed due to the loss of methyl radical in less abundance. **As expected, the branched chain compound does not form any molecular ion.**

The much abundant peak at m/e 43 ($C_3H_7^+$) is formed due to the loss of most stable free radical.



$$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-CH_2-CH_3 \longrightarrow$$

$$(i)\quad CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\dot{C}H_2 \;\updownarrow\; \text{Rearrangement} \qquad CH_3-\overset{CH_3}{\dot{C}}-CH_2-CH_3$$

$$(ii)\quad CH_3-\underset{H}{CH}-\overset{\oplus}{C}H_2 \longleftrightarrow CH_3-\overset{+}{C}H-CH_3$$

Also small peaks are formed due to the formation of alkenyl cation.

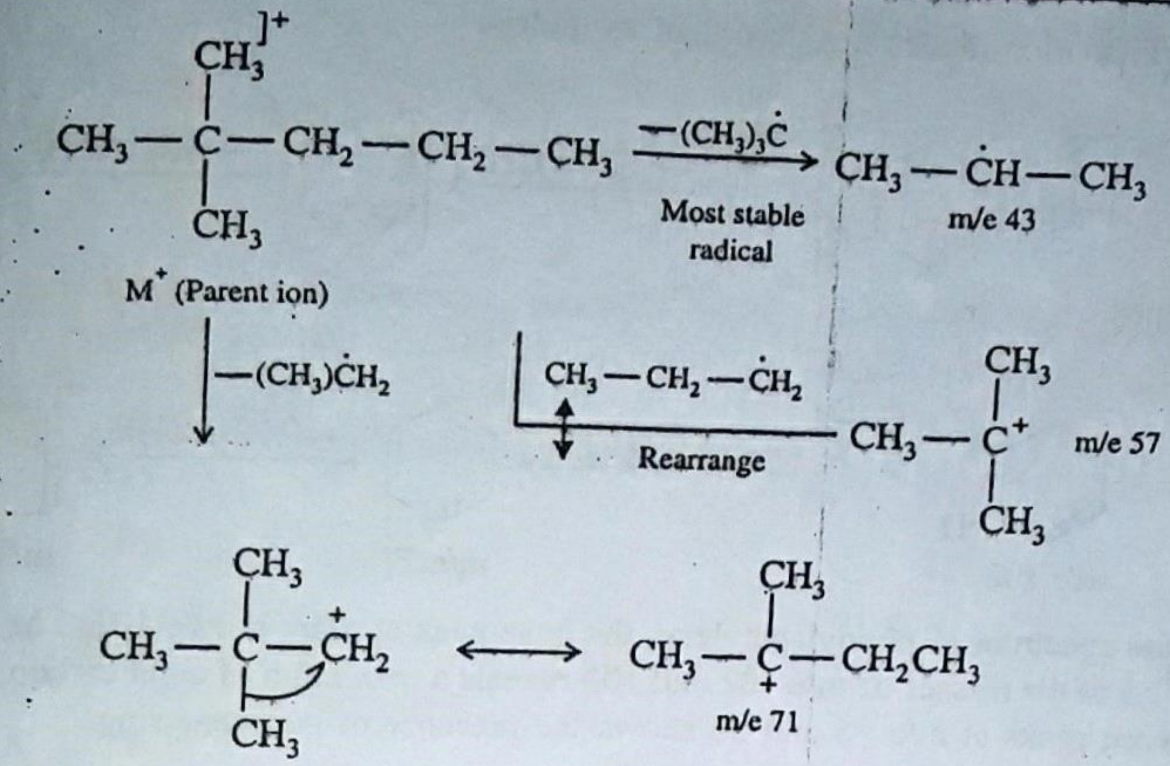
Note. The compounds in which parent ion peak (M^+) is formed, we also notice ($M^+ + 1$) peak whose relative abundance will be N × 1.1% of the abundance of C^{12} containing ion. Here N is the number of carbon atoms. In *n*-nonane, the M^+ (parent ion peak) ion is formed at m/e 128. The $M^+ + 1$ ion is formed in 9 × 1.1 = 9.9% of the abundance of m/e 128. The peak at m/e 44 is 3.3% of the abundance of m/e 43. Clearly, the signal at m/e 44 is not due to $C_3H_8^+$ ion.

Let us consider the mass spectrum of 2, 2 dimethyl pentane. Some important peaks of this spectrum can be predicted as follows:

(*i*) No parent ion (M^+) peak is expected in this compound.

(*ii*) Peaks due to $C_3H_7^+$ ion, $C_4H_9^+$ ion at m/e 43 and 57 are formed in substantial abundance due to the removal of most stable radical.

A much abundant peak at m/e 71 is also expected due to the formation of tertiary carbonium ion. The peak at m/e 57 due to tertiary carbonium ion ($C_4H_9^+$) follows a less abundant peak at m/e 41 ($C_3H_5^+$) due to the loss of methane molecule. Some less abundant peaks (peaks with less percentage of relative abundance) are also expected due to $C_nH_{2n-1}^+$ ions (alkenyl ions).



Exercise. Draw the mass spectrum of 2,2-dimethyl pentane.

Exercise. Draw the mass spectra of (*i*) *n*-Heptane and (*ii*) 2,2-dimethyl hexane. Also predict he approximate relative abundance of each peak.

11A Alkenes (Olefins)

Some important features of the mass spectra of olefins are:

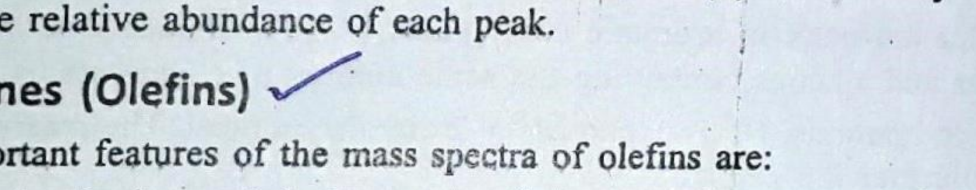
(*a*) The molecular ion peak in the spectra of unsaturated compounds is more intense than the orresponding saturated analogues. The reason is the better resonance stabilisation of the charge n the cation formed by the removal of one of the π-electrons. Mono-olefines contain $C_n\,H_{2n-1}^+$ ions their mass spectra.

(*b*) The relative abundance of the molecular ion peak decreases with increasing molecular ass.

(*c*) A cyclic olefine also shows group of peaks which are 14 mass units apart.

(*d*) The general mode of fragmentation induced by a double bond is the allylic cleavage.

(*e*) The C_nH_{2n} ions (fragments) formed by McLafferty rearrangement are more intense. For ample, Mc Lafferty rearrangement ion is formed at m/e 42 from 1-pentene due to the loss of ylene molecule.



1B Acetylenes (Alkynes)

For 1-Butyne and 2-Butyne, the molecular peak is the base peak. The relative abundance of molecular ion peak decreases as the molecular mass of the alkyne increases. In alkynes, the ment ions are generally formed by the loss of alkyl radicals. Thus, M^+-15, M^+-29 etc. peaks generally noticed in the mass spectra of alkynes.

7.11C Cycloalkanes

Some important characteristics of the mass spectrum of cycloalkanes are:

(*i*) The relative abundance of the molecular ion of cycloalkane is more as compared to the corresponding alkane.

(*ii*) It favours cleavage at the bond connecting the ring to the rest of the molecule.

(*iii*) Fragmentation of the ring is usually characterised by the loss of two carbon atoms as C_2H_4 (28 mass units) and $C_2H_5^+$ (29 mass units).

(*iv*) The stability of the fragment ion depends upon the size of the ring.

(*v*) Fragment ions are commonly observed by the loss of alkenes or alkenyl ions. The side chain on the ring breaks and the lone or odd electron remains on the ring.

Consider the mass spectrum of *n*-propylcyclohexane.

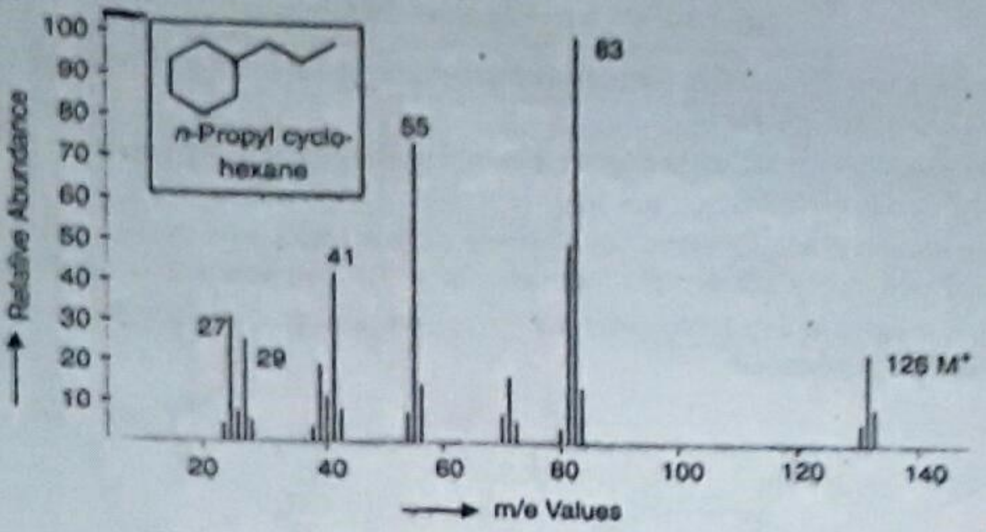


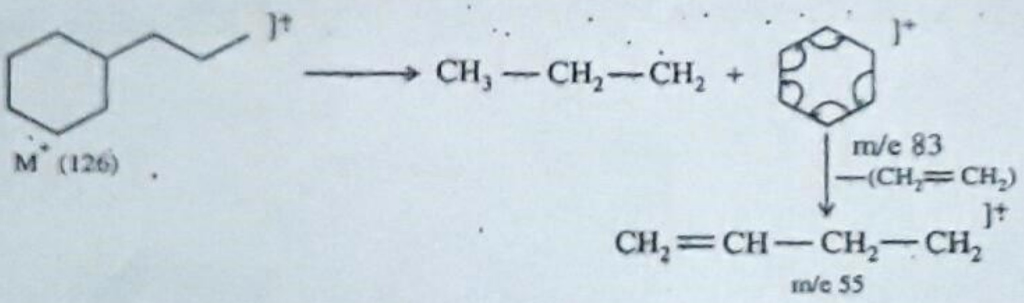
Fig. 7.9. Mass spectrum of *n*-propylcyclohexane.

(*a*) The peak m/e 128 is the molecular ion peak and is quite abundant.

(*b*) The largest peak (base peak) at m/e 83 is formed by the loss of the side chain. The lone electron remains on the ring. This positively charged ion radical appears at m/e 83.

(*c*) The ion radical shows retro-Diel's-Alder reaction and a fragment ion is formed at m/e 55. The abundance of this ion is very large.

The various fragmentation modes are described as under:



Exercise. Draw the mass spectrum of *n*-propylcyclobutane and also write the related abundance of ions formed in its mass spectrum.

7.11D Cycloalkenes and Cycloalkynes

(*a*) **Cycloalkenes.** A double bond in the alicyclic ring introduces a possible pathway involving retro Diels-Alder reaction. Consider the mass spectrum of cyclohexene.

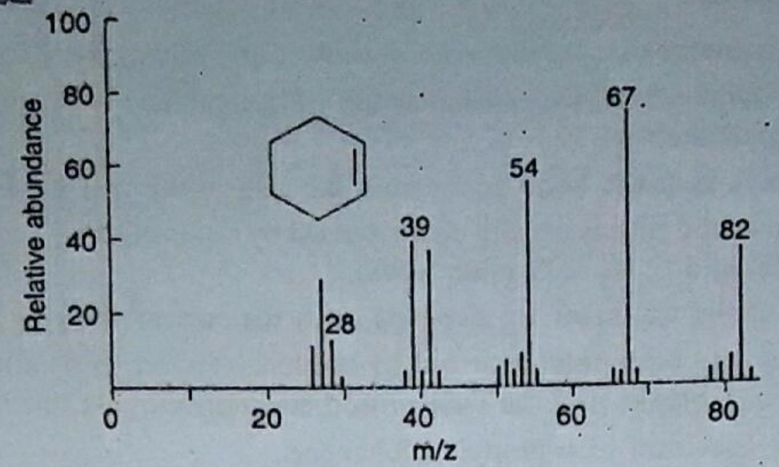


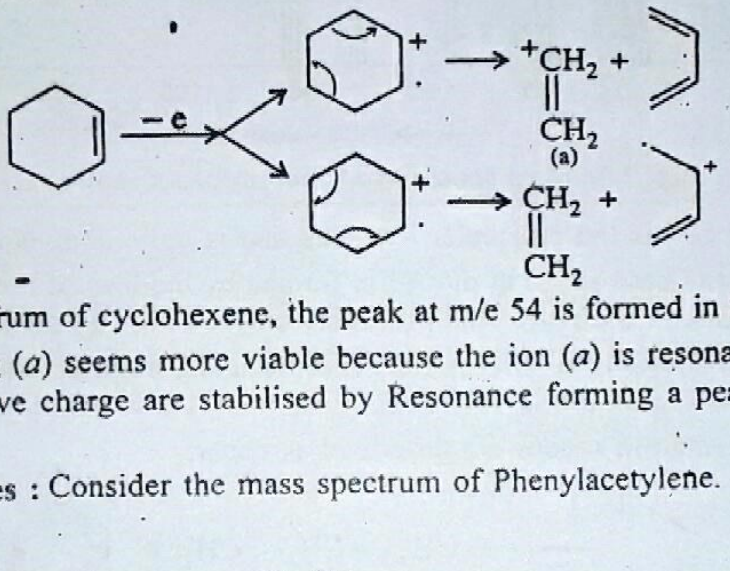
Fig. 7.10. Mass Spectrum of Cyclohexene.

Cyclic olefines usually show a distinct molecular ion peak. A unique mode of cleavage is a type of retro-Diels-Alder reaction.

The retro-Diels-Alder reaction is an example of a multicentered fragmentation mode which is characteristic of cyclic olefines.

The fragmentation mode involves the cleavage of two bonds of a cyclic system resulting in the formation of two stable unsaturated fragments in which two new bonds are formed.

This does not involve any hydrogen transfer rearrangement. Consider the retro-Diels-Alder reaction in case of cyclohexene.



In the mass spectrum of cyclohexene, the peak at m/e 54 is formed in fairly high abundance.

The path forming (*a*) seems more viable because the ion (*a*) is resonance stabilised *i.e.*, the radical and the positive charge are stabilised by Resonance forming a peak at m/e 54 which is intense.

(*b*) **Cycloalkynes :** Consider the mass spectrum of Phenylacetylene.

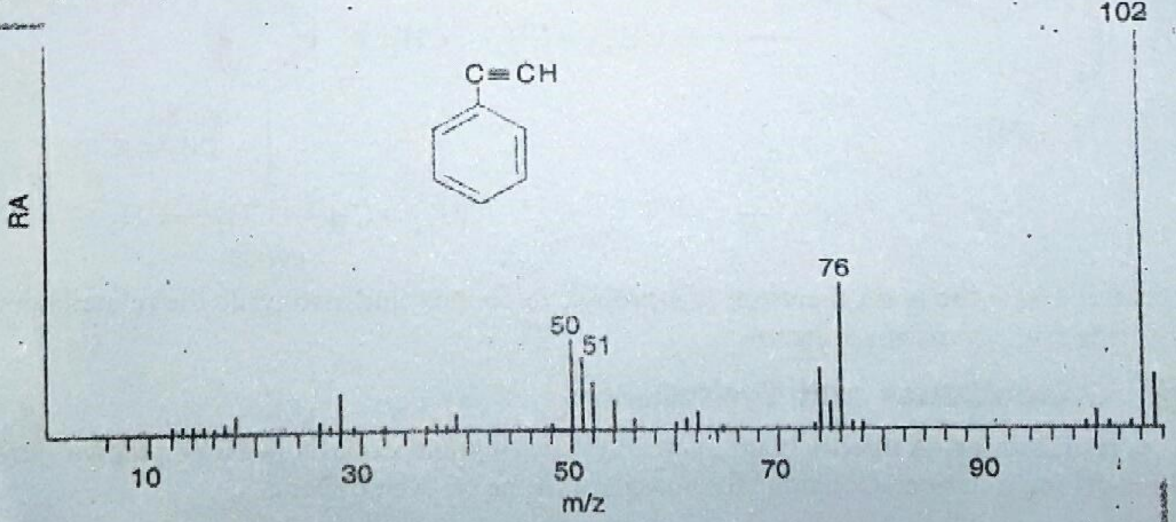
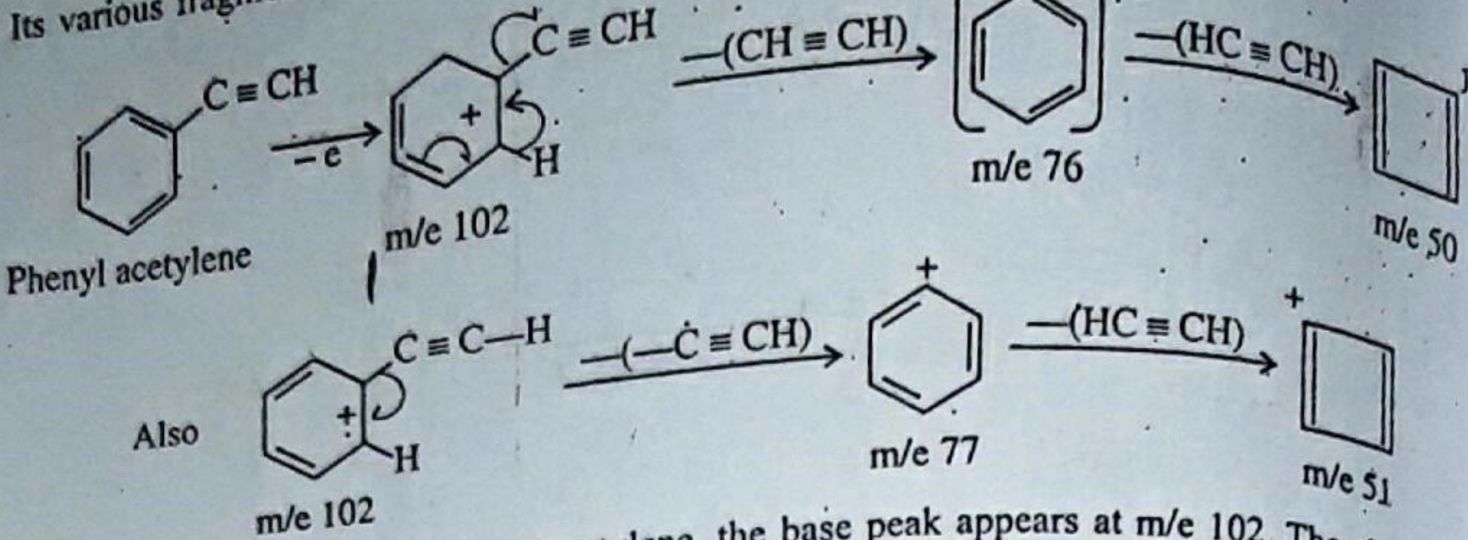


Fig. 7.11. Mass spectrum of Phenylacetylene.

Its various fragmentation modes are described as under :



In the mass spectrum of phenylacetylene, the base peak appears at m/e 102. The abundance ratio (about 9%) of the masses of m/e 102 and 103 reveals a maximium of eight carbon atoms. The relatively intense peaks at m/e 76 and 50 shows the presence of benezene ring.

7.12 Aromatic Compounds

Some important features of the mass spectra of aromatic compounds are:

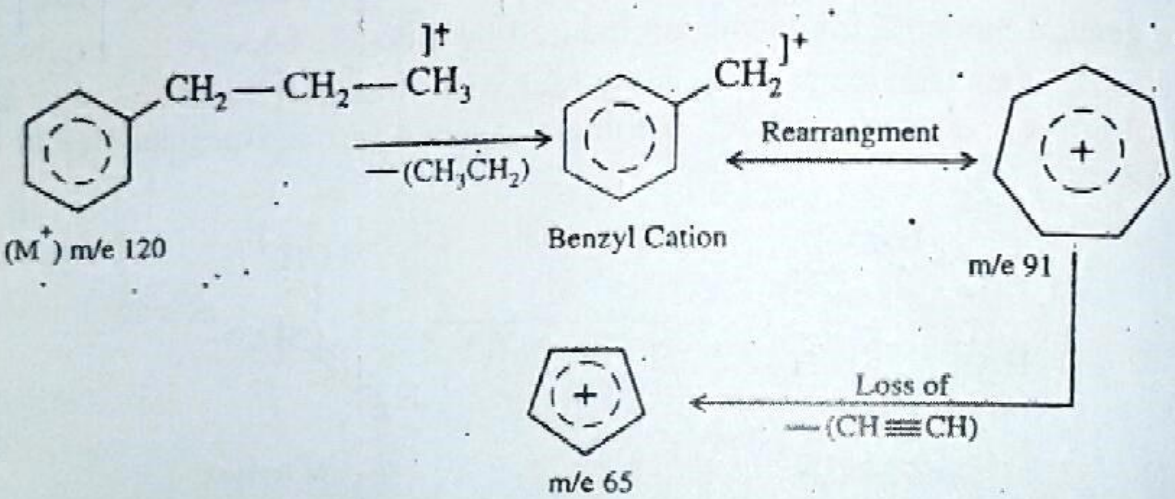
(*i*) The molecular ion peak in aromatic compounds is fairly abundant as compared to the corresponding alkanes and alkenes containing the same number of carbon atoms.

(*ii*) In aromatic compounds, $M^+ + 1$ and $M^+ + 2$ are also noticed. The reason is fairly large abundance of the molecular ion peak.

(*iii*) In case of polynuclear hydrocarbons, doubly or triply charged ions (M^{2+}, M^{3+} ions) are possibly formed. Doubly charged molecular ions (m/2e) appear at integral m/e values.

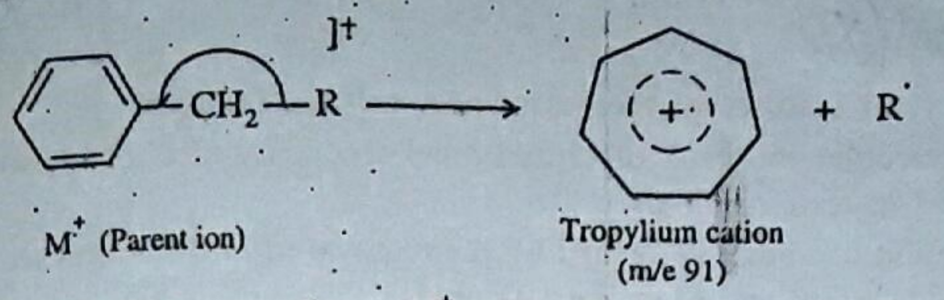
(*iv*) If the aromatic ring is substituted by an alkyl group, a prominent peak is formed at m/e 91. Here benzyl ($C_6H_5\overset{+}{C}H_2$) cation formed rearranges to tropylium cation ($C_7H_7^+$).

The fragmentation pattern of *n*-propyl benzene is shown below:



The benzyl cation formed rearranges to more stable tropylium cation which appears at m/e 91. Tropylium cation in turn loses a molecule of acetylene to form $C_5H_5^+$ at m/e 65.

Cleavage of a carbon-carbon bond which is in the β-position to the aromatic ring is an energetically favoured fragmentation mode.



The mass spectrum of ethyl benzene has a (M^+—CH_3) peak in large abundance. The fragment ion appears at m/e 91 and it is a base peak. Tropylium cation, then loses a molecule of acetylene, *i.e.*, 26 mass units to form a peak at m/e 65.

The mass spectrum of ethyl benzene is shown below:

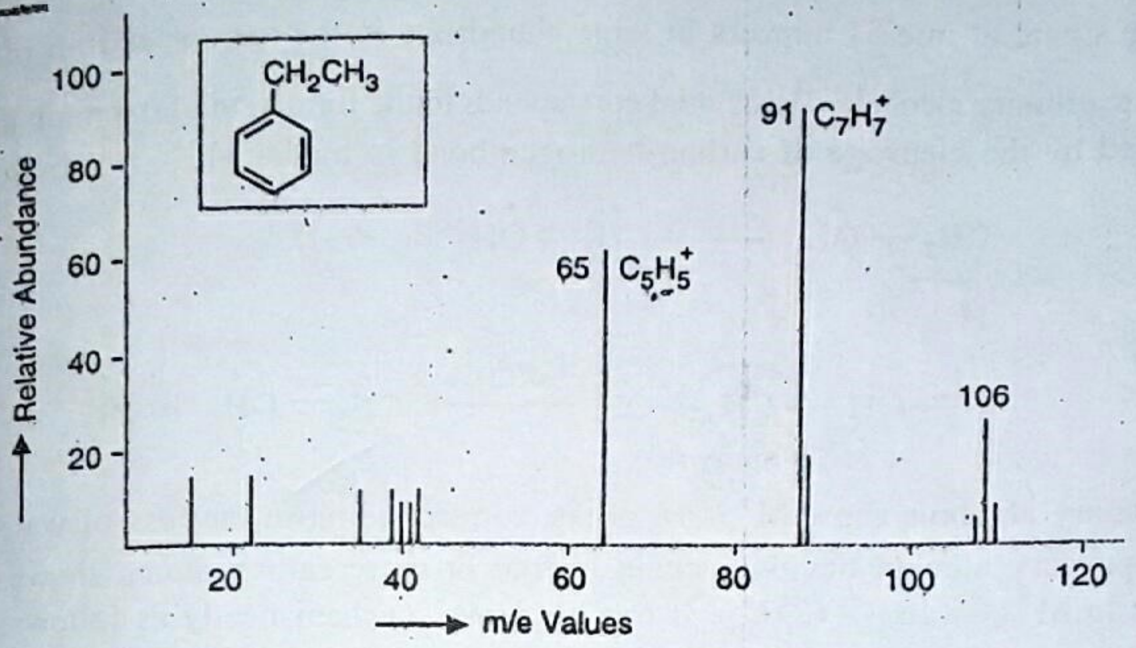


Fig. 7.12. Mass spectrum of Ethyl benzene.

Note. In the absence of an easily cleaved side chain, aromatic molecules give abundant molecular ions. For example in the mass spectrum of naphthalene (10 π electron system), $C_{10}H_8$, the molecular ion is highly abundant. The mass spectrum of Naphthalene is shown below:

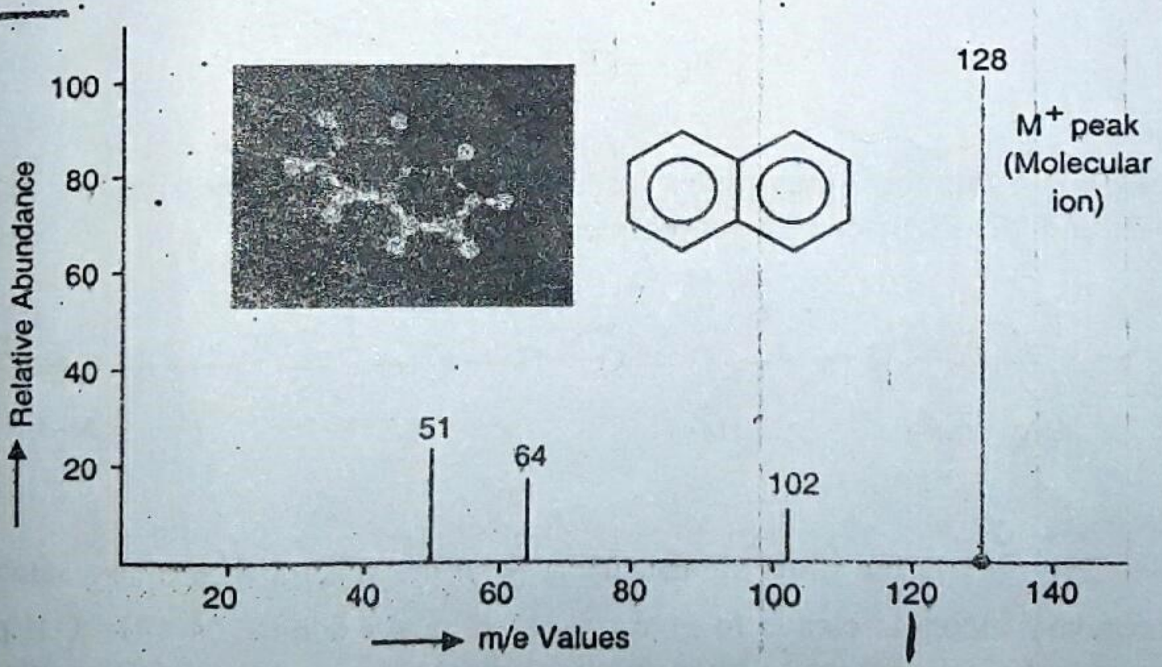


Fig. 7.13. Mass spectrum of Naphthalene.

The mass spectrum of *m*-xylene is shown below (Fig. 7.13): In this case also, the base peak appears at m/e 91 due to the formation of Tropylium cation. Thus, like alkyl benzenes, Xylenes also involve easy loss of alkyl group $(M—CH_3)^+$ ion.

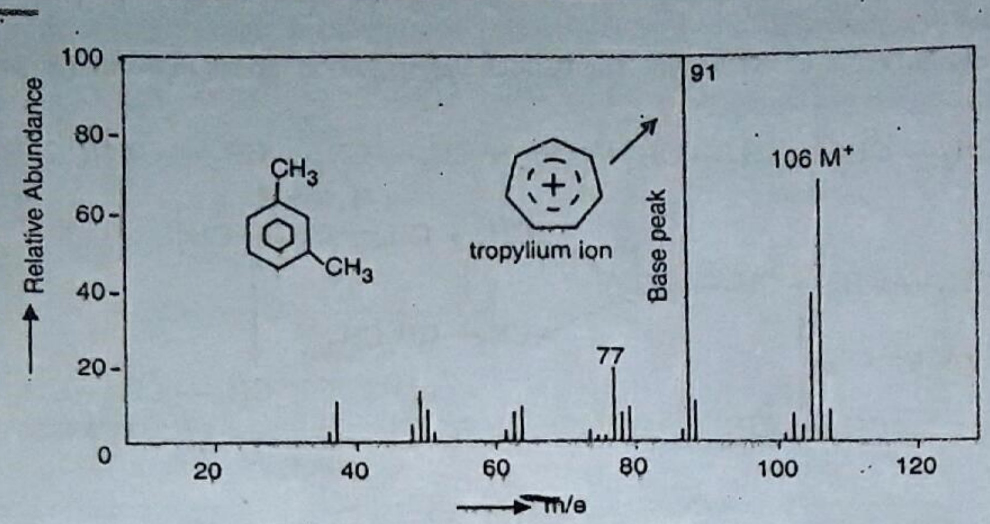


Fig. 7.14. Mass spectrum of m-Xylene.

In the spectrum of *n*-butyl benzene, characteristic peaks at m/e 91 and 65 are obtained which are typical of alkyl benzenes due to tropylium ion and cyclopentadienyl cation. Also a peak at m/e 92 in fair abundance is due to McLafferty rearrangement ion.

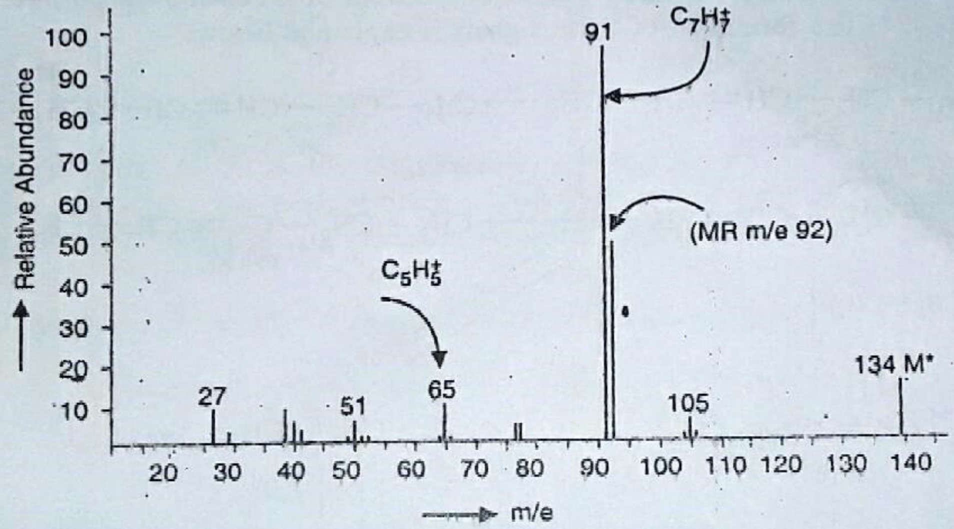
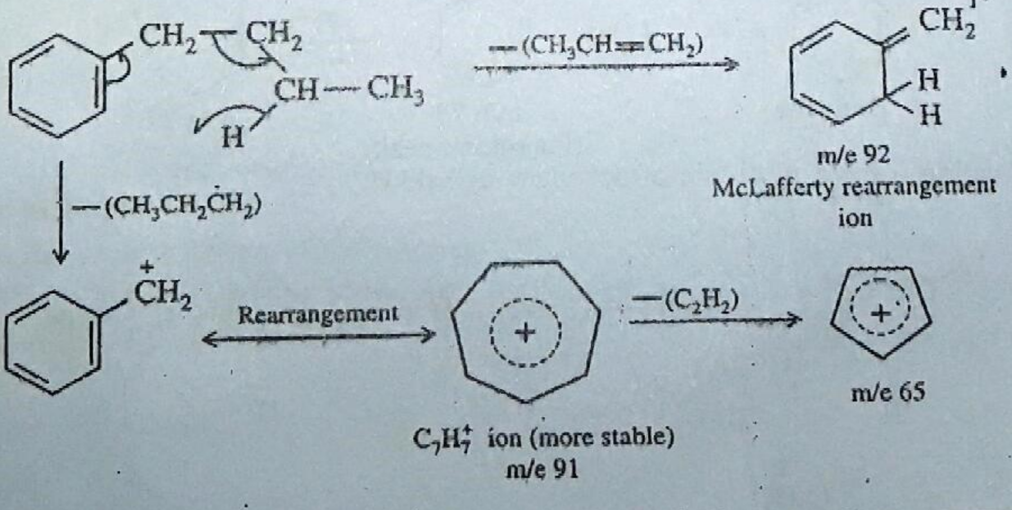


Fig. 7.15. Mass spectrum of n-butyl benzene.

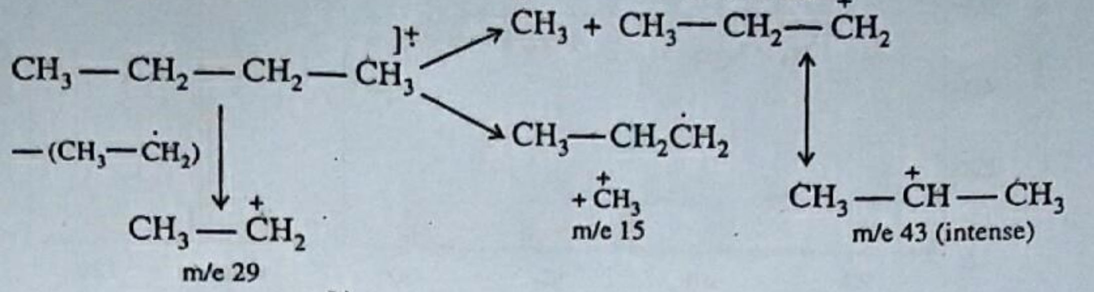
The various fragmentation modes of n-butyl benezene.



Examples for Practice

1. **Fragmentation of *n*-Butane.** The various fragmentation modes of *n*-butane giving parent ion and daughter ion peaks are:

$$\underset{n\text{-butane}}{CH_3-CH_2-CH_2-CH_3} + e \longrightarrow \underset{M^{+}\ (m/e\ 58)}{[CH_3-CH_2-CH_2-\dot{C}H_3]^{+}} + 2e$$

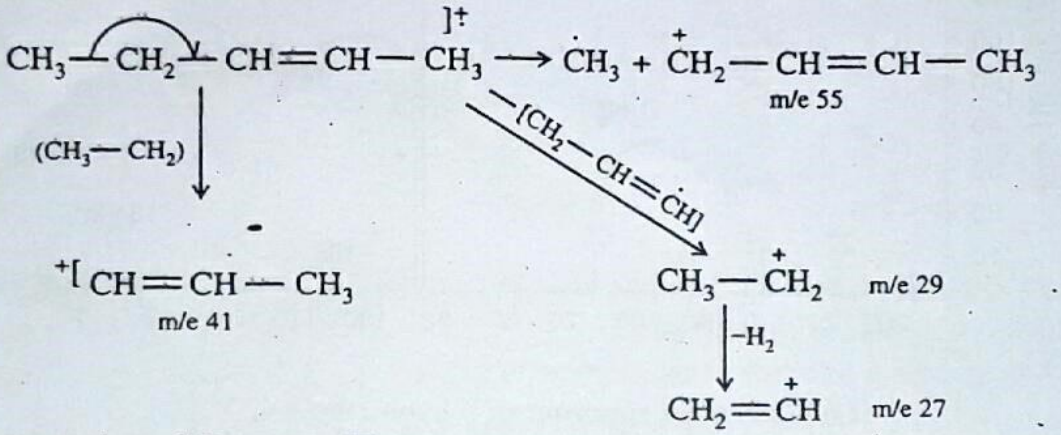


$$[CH_3-CH_2-CH_2]^{+} \longrightarrow H_2 + \underset{m/e\ 41}{CH_2=CH-\overset{+}{C}H_2}$$

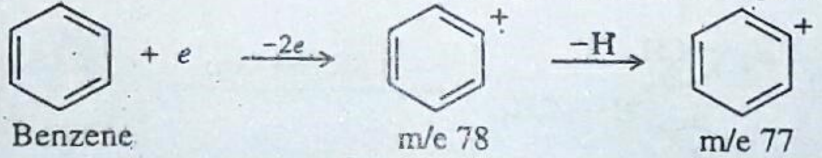
$$\text{Also} \quad \underset{m/e\ 29}{CH_3-\overset{+}{C}H_2} \longrightarrow H_2 + \underset{m/e\ 27}{CH_2=\overset{+}{C}H}$$

2. **Fragmentation of 2-Pentene.** The mass spectrum of 2-Pentene shows m/e peaks at 70, 55, 41, 39, 29, 27. The formation of these signals is explained below:

$$\underset{\text{2-Pentene}}{CH_3-CH_2-CH=CH-CH_3} \xrightarrow{+e} \underset{M^{+}\ (m/e\ 70)}{[CH_3-CH_2-CH=CH-CH_3]^{+}} + 2e$$

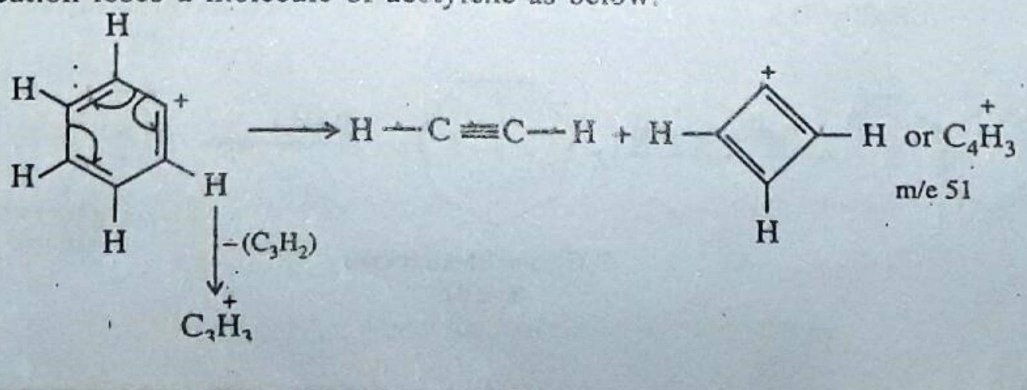


Fragmentation of Benzene. The parent peak in case of benzene is formed at m/e 78. other important peaks appear at 77, 51 and 37. The fragmentation mode is explained below:



(Parent ion peak)

Phenyl cation loses a molecule of acetylene as below:



7.13 Alcohols

Some important features of the mass spectra of alcohols are:

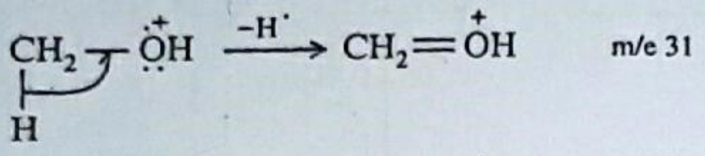
(*a*) The molecular ion peak of primary and secondary alcohol is usually of low abundance. It is not detected in tertiary alcohols.

(*b*) The parent ion peak is formed by the removal of one electron from the lone pairs on the oxygen atom of primary and secondary alcohols.

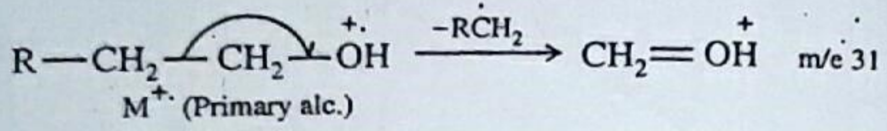
(*c*) The number of fragmentation modes in alcohols depend upon the fact whether it is primary, secondary or tertiary alcohol.

(*d*) The fragmentation of carbon-carbon bond adjacent to oxygen atom (α-cleavage) is the preferred fragmentation mode.

(*e*) The signal at m/e 31 appears in large abundance in the mass spectrum of methanol and other aliphatic primary alcohols. This signal corresponds to the formation of oxonium ion ($CH_2{=}\overset{+}{O}H$) and is formed by the cleavage of carbon-hydrogen bond in methanol.



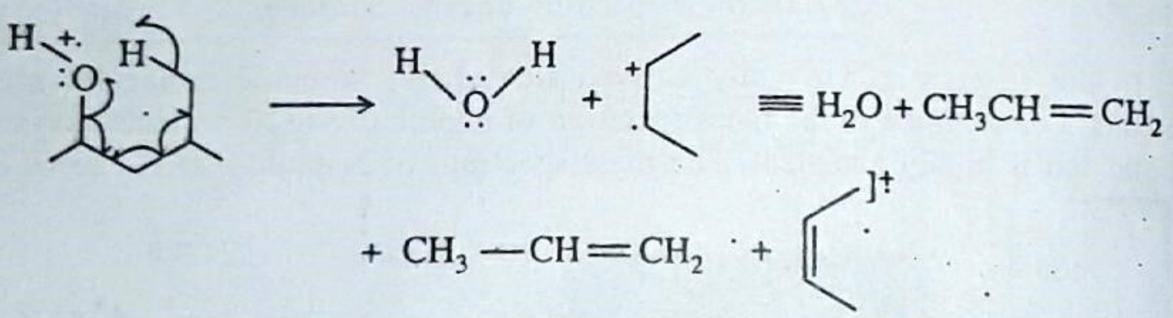
$$\underset{H}{CH_2}-\overset{+\cdot}{\ddot{O}}H \xrightarrow{-H^\cdot} CH_2{=}\overset{+}{O}H \quad \text{m/e 31}$$



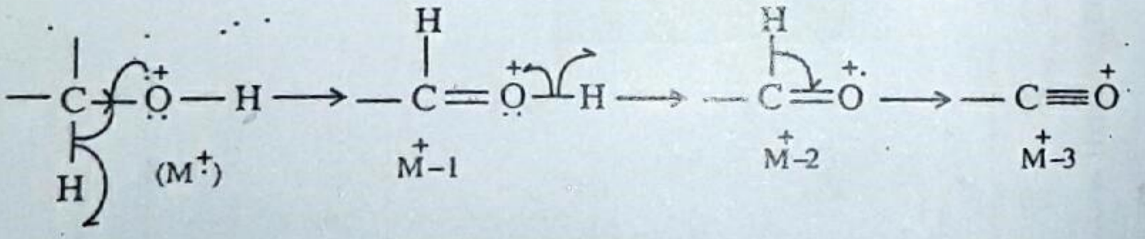
$$\underset{M^{+\cdot}\text{ (Primary alc.)}}{R-CH_2-CH_2-\overset{+\cdot}{O}H} \xrightarrow{-R\dot{C}H_2} CH_2{=}\overset{+}{O}H \quad \text{m/e 31}$$

(*f*) Primary alcohols show $M^+ - 18$ peaks, corresponding to the loss of water.

(*g*) A primary alcohol having a chain of four or more carbon atoms shows a peak which corresponds to $M^+ - (18 - C_nH_{2n})$. It can be shown mechanistically as follows:



(*h*) Long chain members may show peaks corresponding to successive loss of H-radicals at M—1, M—2, and M—3. It can be represented as shown.



(*i*) The $CH_2{=}\overset{+}{O}H$ is the most significant peak in the spectra of primary alcohols.

(*j*) Secondary alcohols cleave to give prominent peaks due to $R{-}CH{=}\overset{+}{O}H$ at m/e 45, 59, 73 ... Tertiary alcohols fragment to give prominent peaks due to $RR'C{=}OH$ at m/e 59, 73, 87 ...

(*k*) In addition to the α-cleavage, primary alcohols also undergo β-, γ-, δ- cleavage to form peaks at m/e 45, 59, 73 ...

EXAMPLES. Consider the mass spectrum of 1-Butanol. It is shown below.

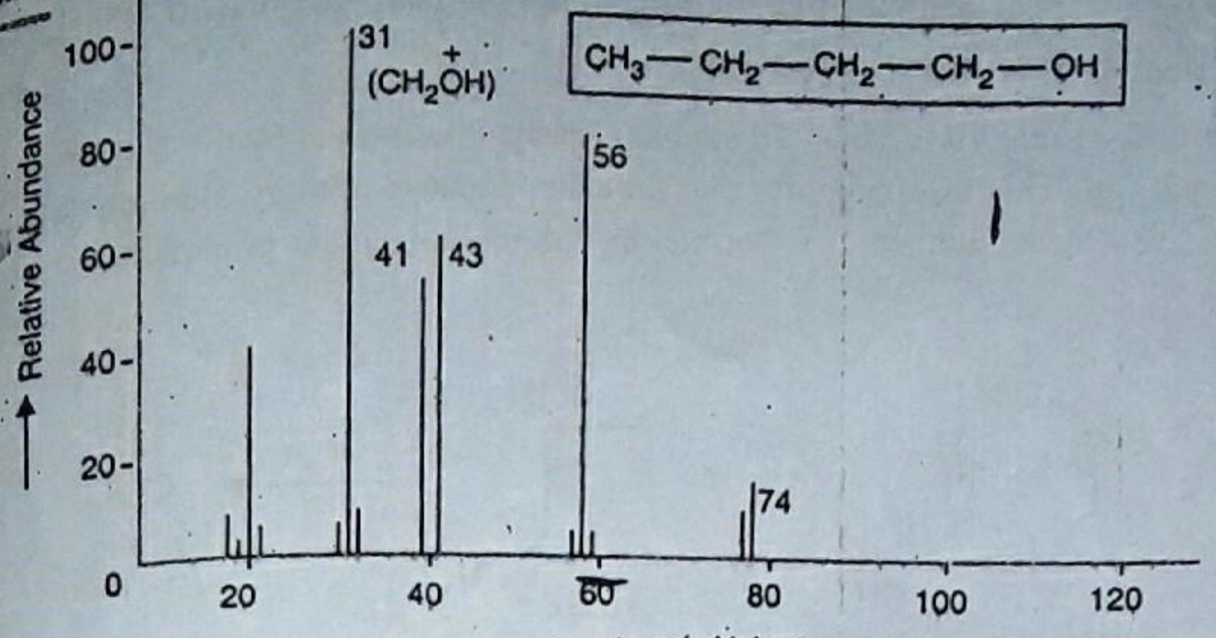
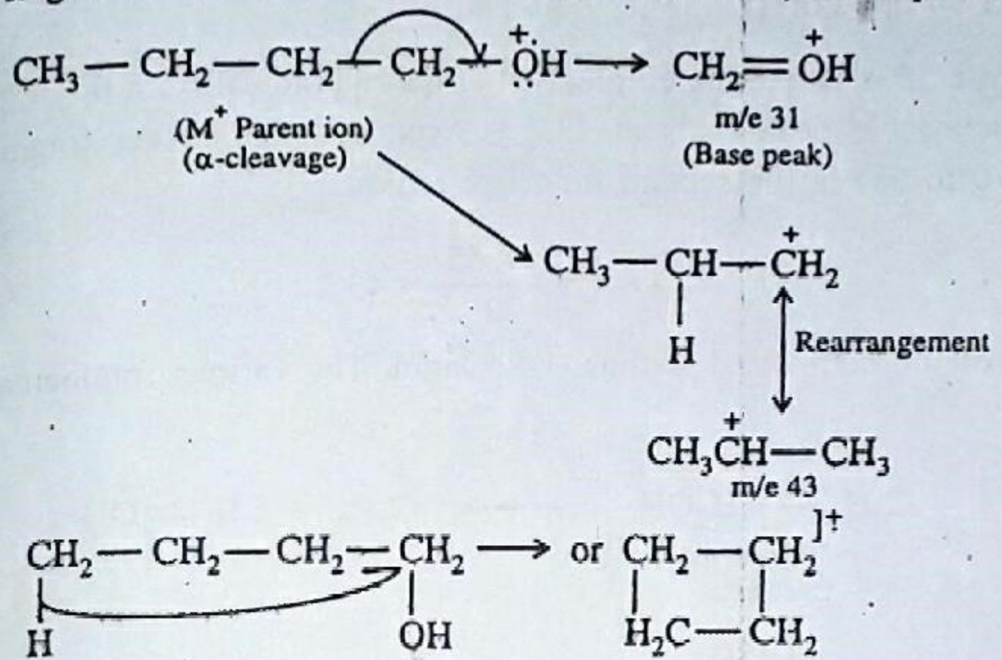


Fig. 7.16. Mass spectrum of 1-Butanol.

The various fragmentation modes of 1-butanol (shown above) are explained below:



EXERCISE. Draw the mass spectrum of 1-Hexanol and mention the relative abundance of each signal.

EXAMPLE. Consider the mass spectrum of 2-Butanol (secondary alcohol). It is shown below.

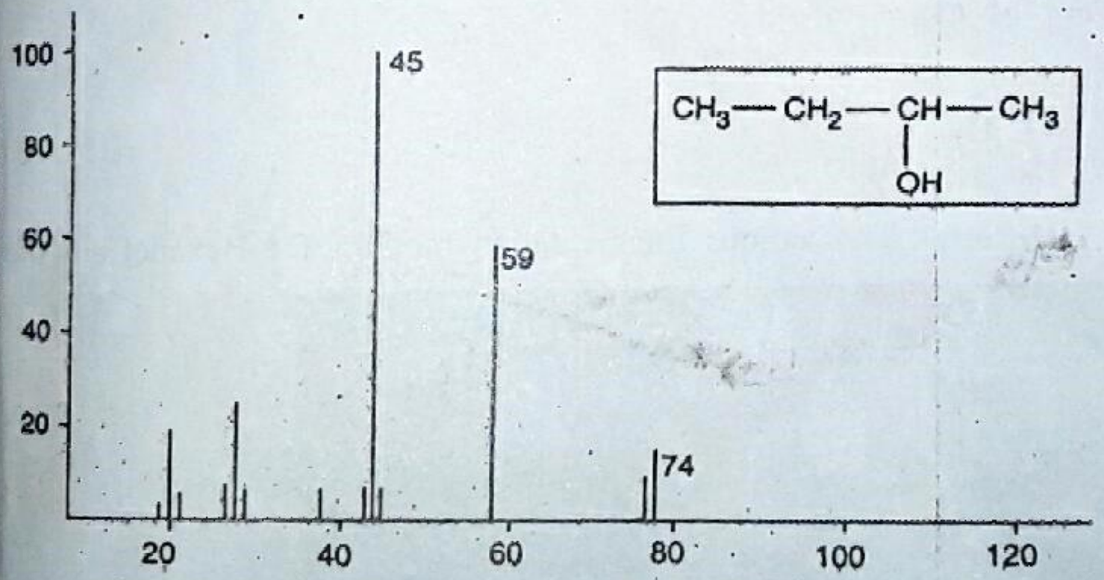
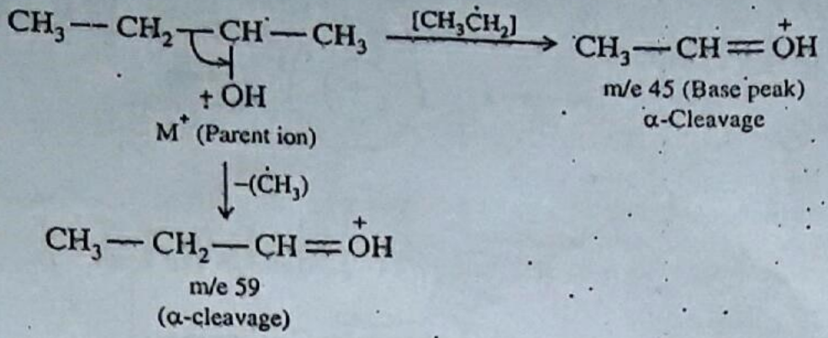


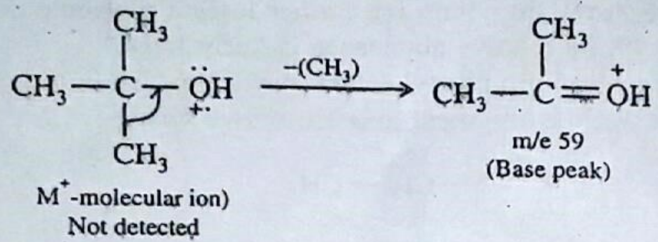
Fig. 7.17. Mass spectrum of 2-Butanol.

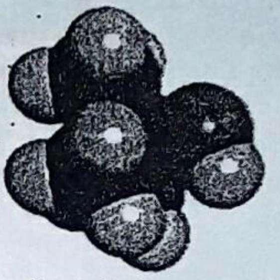
The various fragmentations shown in the figure can be explained as follows:



Exercise. Draw the mass spectrum of 2-methyl butanol-1 and also mention the relative abundance of the various fragment ions.

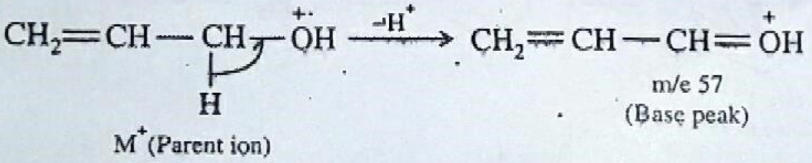
In case of tertiary alcohol, the molecular ion peak is not formed. The signal due to α-cleavage is the most significant and is the base peak. Consider the mass spectrum of tertiary butyl alcohol (2-methyl, 2-propanol).



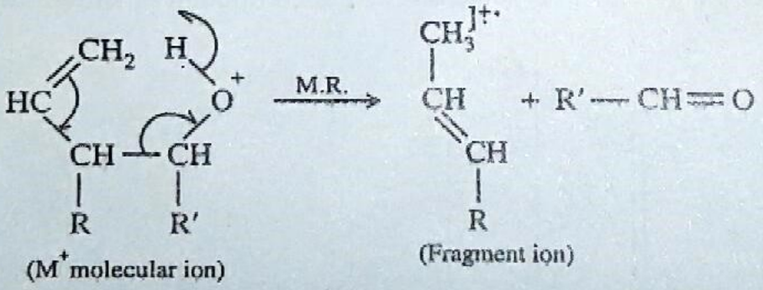


In case of cyclic alcohols, the fragmentation patterns are quite complicated. In case of cyclohexanol, molecular ion peak appears at m/e 100. It loses a hydrogen radical to form $M^+ - 1$ peak at m/e 99. This, in turn loses a molecule of water to form a signal at $M^+ - H - H_2O$ at m/e 81.

In allyl alcohol, ($\overset{+}{M} - H$) ion is formed due to its high stability.



The McLafferty rearrangement ion peak has also been reported in these compounds.



Aromatic alcohols

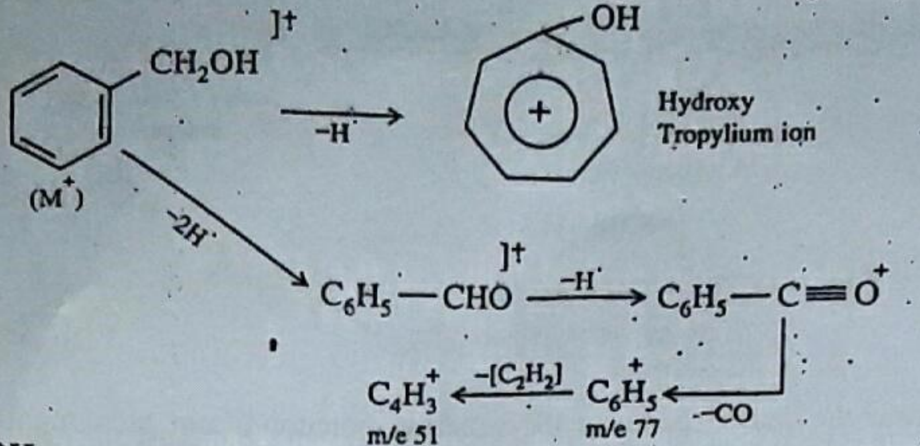
Some important features of the mass spectra of aromatic alcohols are:

(*a*) The relative abundance of the parent ion ($\overset{+}{M}$) of aromatic alcohols is fairly large.

(*b*) Some of the fragment modes of benzyl alcohol are loss of one, two or three hydrogen atoms.

(*c*) The fragment ion, ($M^+ - H$) further eliminates CHO radical.

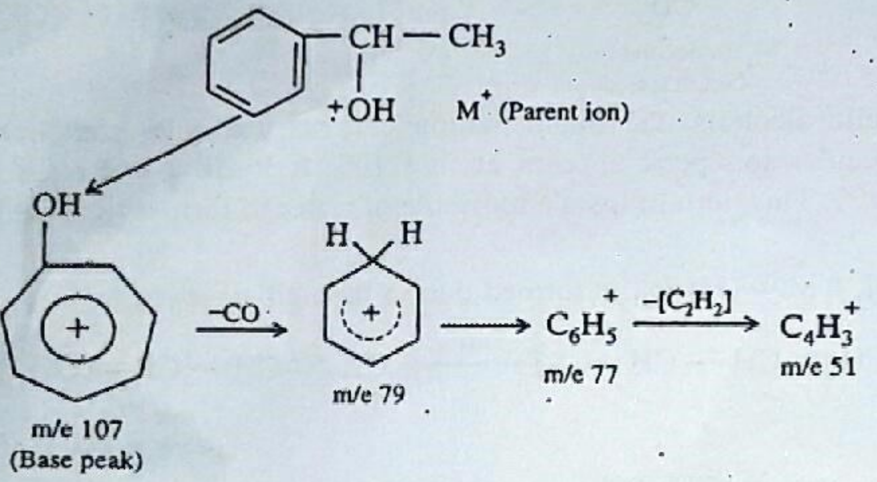
(*d*) (M$^+$ —H) fragment of benzyl alcohol also rearranges to form hydroxy tropylium ion.



(*e*) The —OH group in the benzylic positions fragments in a way which favour charge retention on the aryl group.

EXAMPLE. Consider the mass spectrum of 1-Phenyl ethanol. The base peak corresponds to the elimination of methyl radical. The peak at m/e 107 is the base peak and is represented by hydroxy tropylium ion. Hydroxy tropylium ion further loses a molecule of carbon monoxide to give fragment ion at m/e 79. Its relative abundance is fairly large.

Further it loses hydrogen to form phenyl cation (m/e 77) which in turn eliminates a molecule of acetylene as usual. The various fragment ions are shown below :



EXAMPLE. Deduce the structure of the compound with molecular formula, $C_5H_{12}O$. There is a metastable peak at (m^*) 43.3. The spectrum of the compound is shown below:

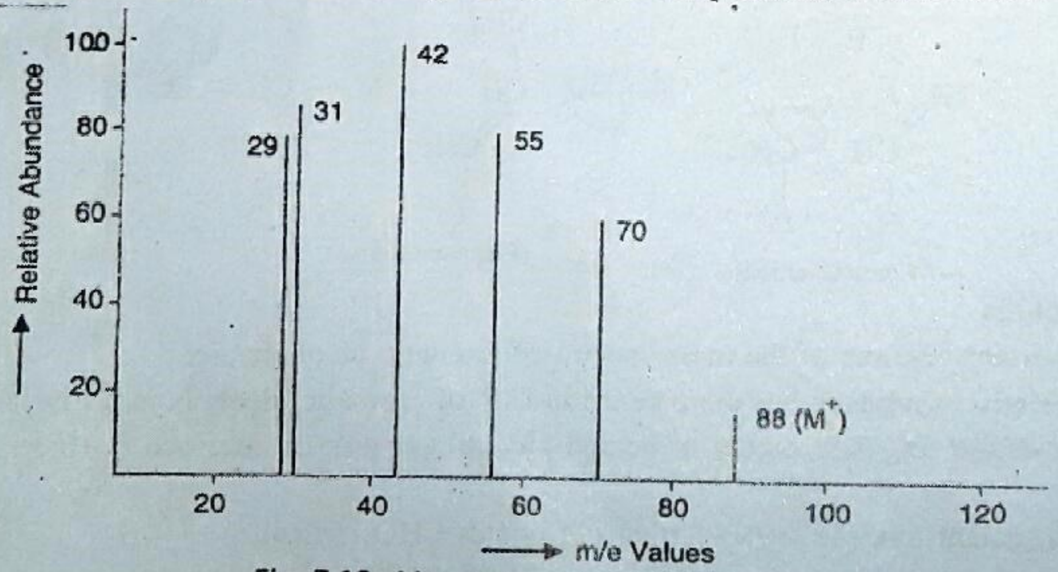
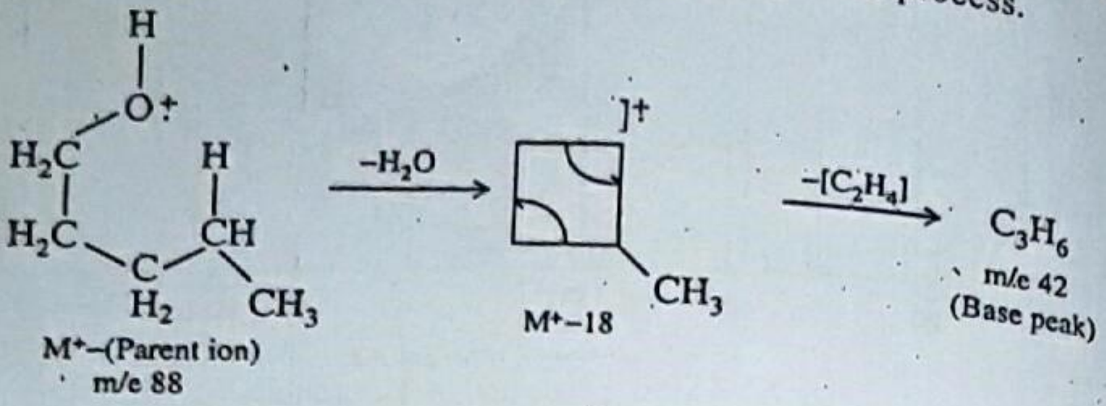


Fig. 7.18. Mass spectrum of 1-Pentanol.

SOLUTION. The appearance of a significant peak at m/e 31 reveals that the compound m be primary alcohol. It is due to $CH_2{=}\dot{O}H$ ion.

Another peak at m/e 70 is M^{+}— 18 signal. Clearly, it is formed by the loss of water molecu from the parent ion. This also supports that the component is primary alcohol. The base peak m/e 42 is of even mass number. It is formed by the rearrangement process.

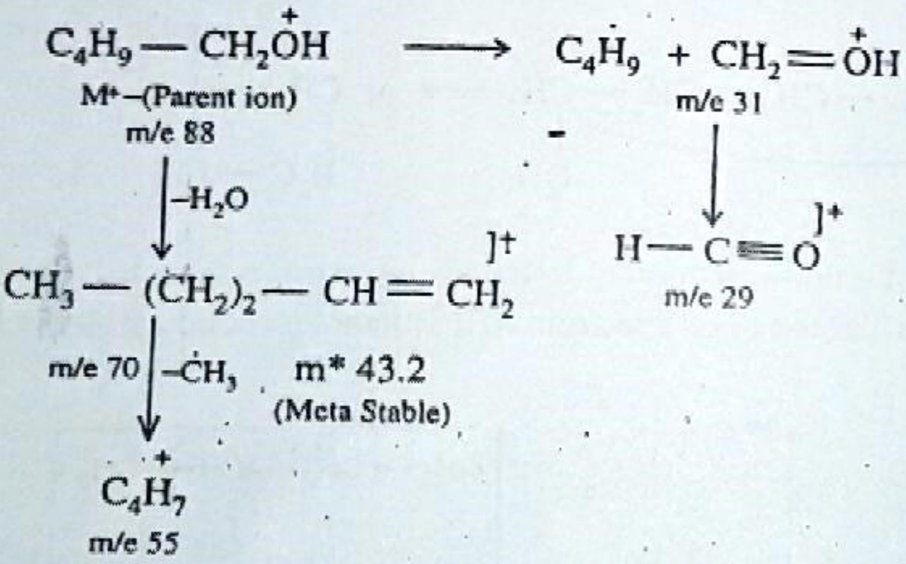


We know that a primary alcohol also loses a molecule of ethylene after the elimination water molecule. (M^{+}—18—C_2H_4).

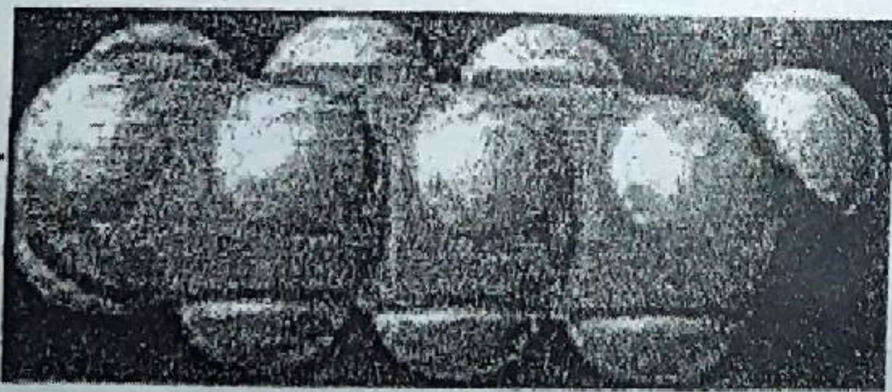
The signal at m/e 55 is due to the elimination of methyl radical from the fragment ion forme at m/e 70. The metastable peak (m^*) at 43.2 is explained due to the fragmentation reactio $\overset{+}{m_1} \rightarrow \overset{+}{m_2}$ (*i.e.*, 70 to 55) in the second field free region.

$$m^* = \frac{m_2^2}{m_1} = \frac{55 \times 55}{70} = 43.2$$

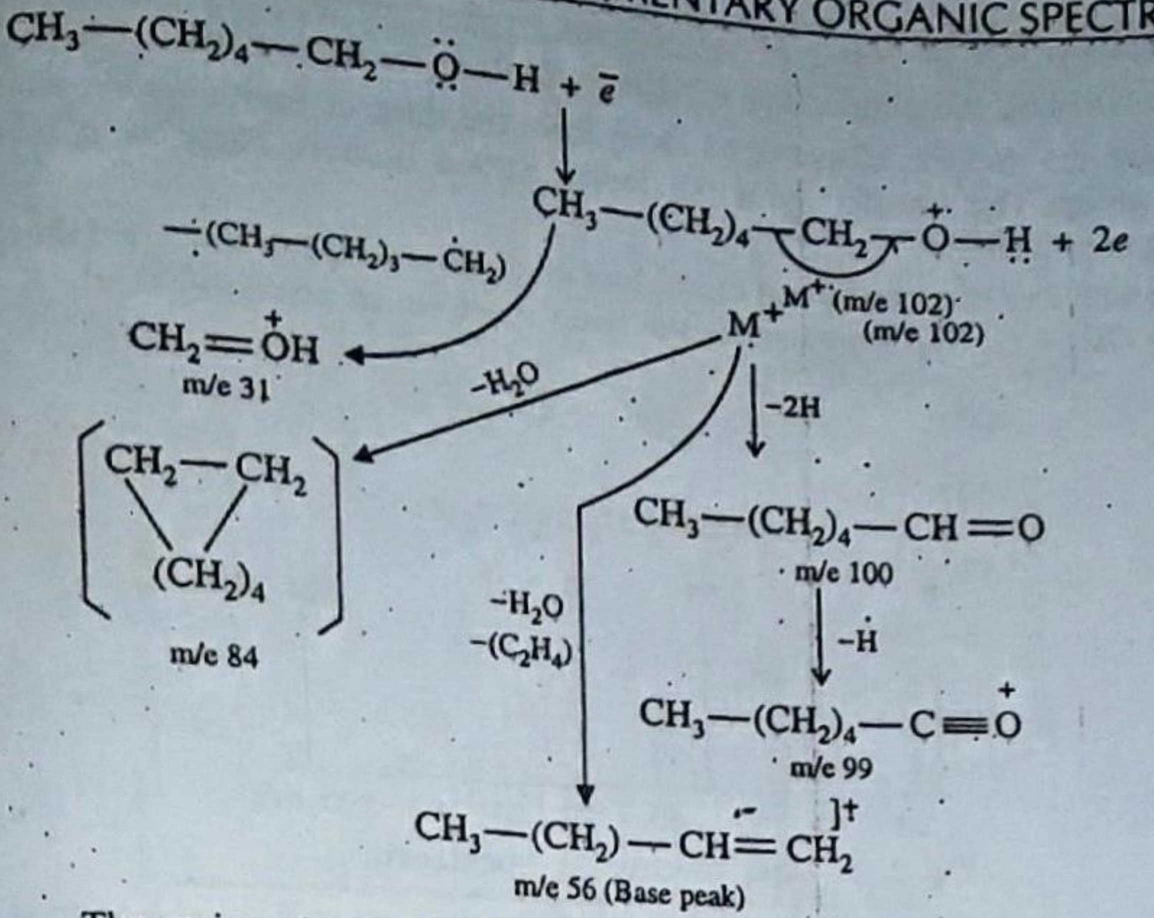
The structure of the compound is thus, 1-Pentanol. The various fragmentation patterns ar shown below:



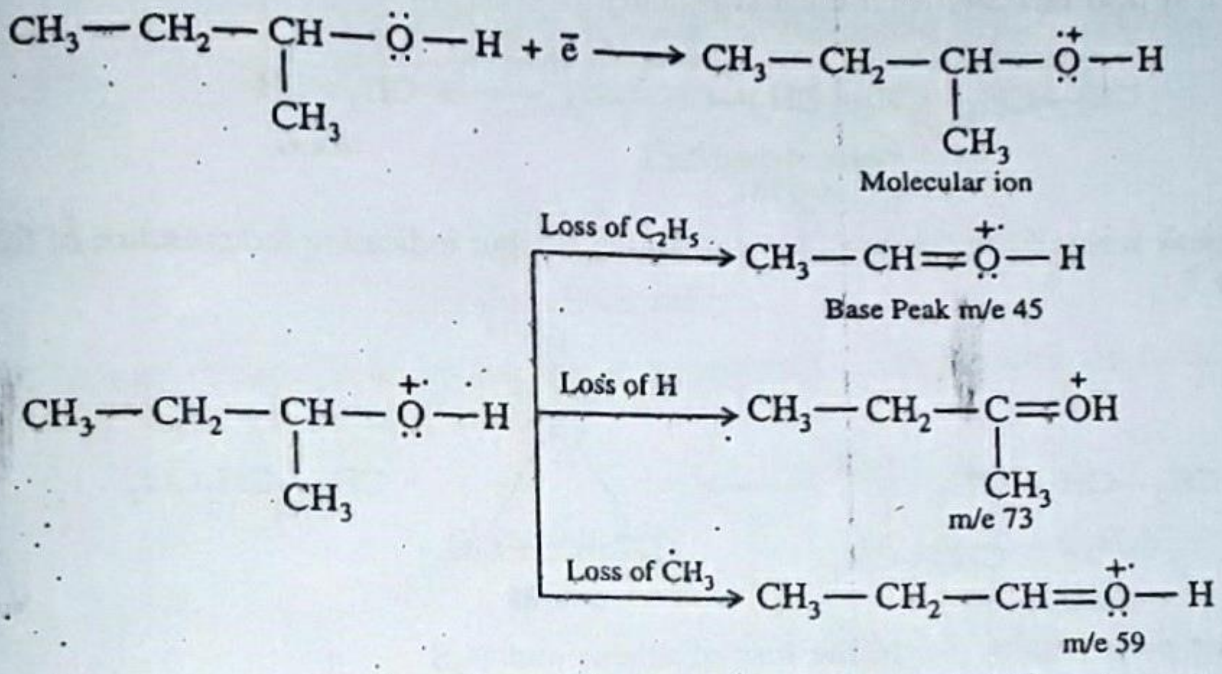
Fragmentation of 1-Hexanol. The various fragmentation modes of 1-Hexanol are show below:



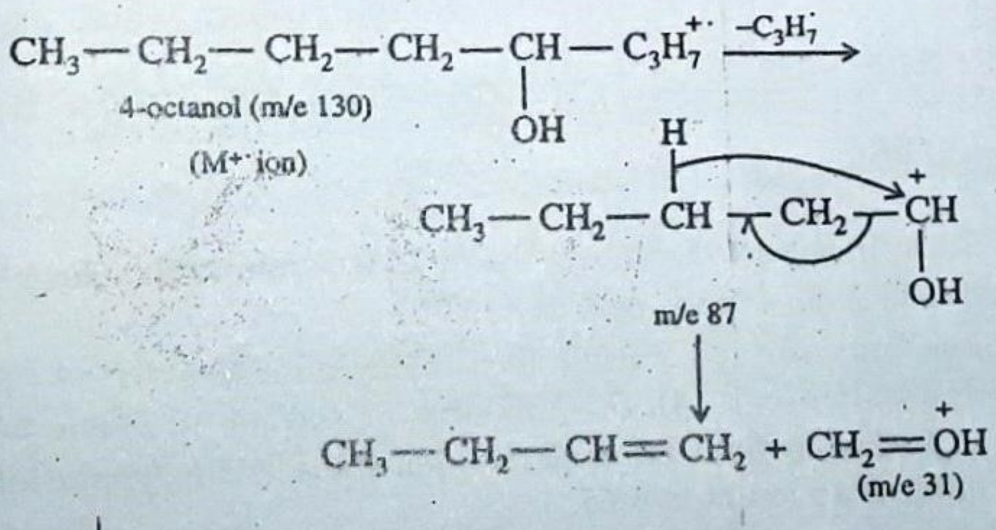
1-Hexanol



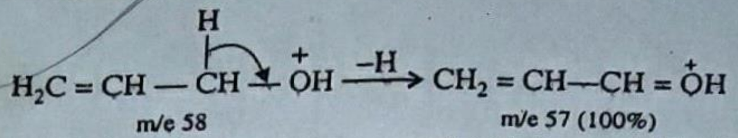
- The various fragmentation patterns of sec-butyl alcohol are shown below:



The various fragmentation ions formed in the case of 4-octanol (M^{+}. m/e 130) are shown below:



Unsaturated Alcohols. In unsaturated alcohols, the loss of hydrogen radical from the hydroxyl group is most likely and the resulting ion-possesses high stability. Thus, in allyl alcohol, a peak at m/e 57 is formed in 100% abundance.



$$\underset{m/e\ 58}{H_2C=CH-\overset{H}{CH}-\overset{+}{O}H} \xrightarrow{-H} \underset{m/e\ 57\ (100\%)}{CH_2=CH-CH=\overset{+}{O}H}$$

Alicyclic alcohols. Consider the mass spectrum of cyclohexanol. The base peak in this case is formed at m/e 57. The molecular ion peak is of low abundance. Loss of water molecule produces an ion radical at m/e 82 is fair abundance. The mass spectrum of cyclohexanol is shown in figure.

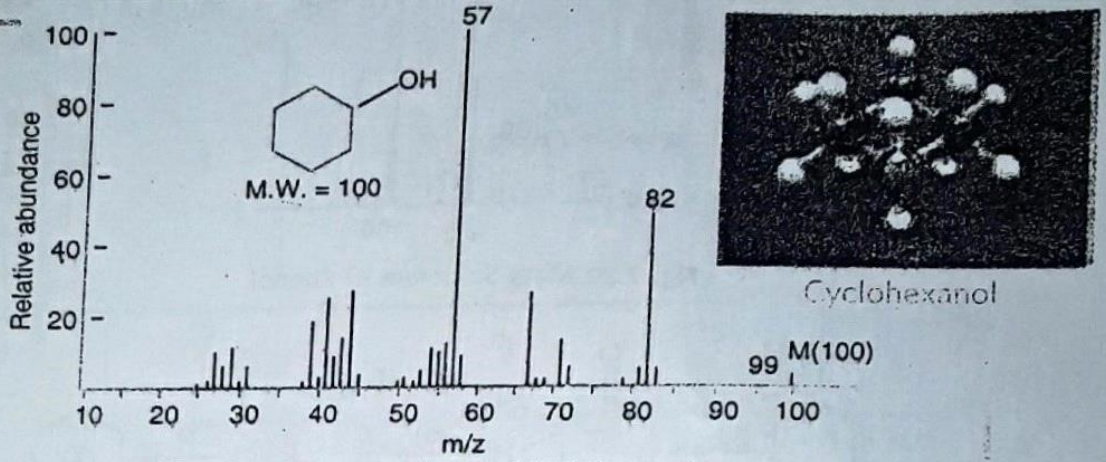
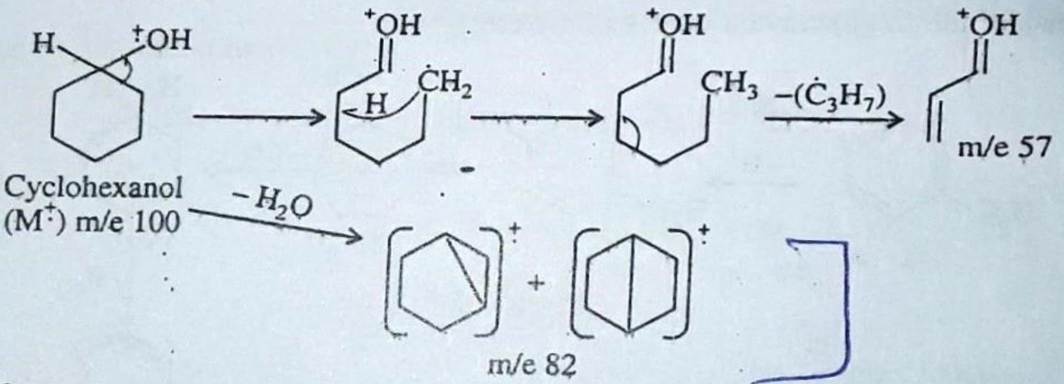


Fig. 7.19. Mass spectrum of Cyclohexanol.

The various fragmentation modes are shown below :



7.14 Phenols

Some important features of the mass spectrum of phenols are:

(*a*) The molecular ion peak (M+.) is intense.

(*b*) The peak due to the loss of hydrogen radical, $M^{+\cdot}$—H is small.

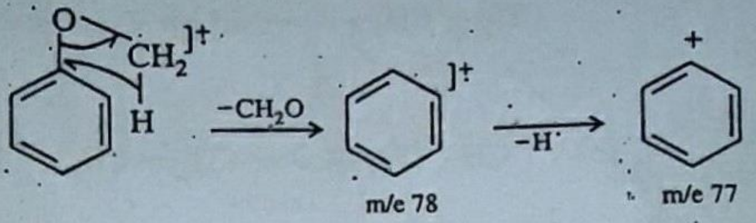
(*c*) The fragment ion due to the loss of carbon monoxide is most significant. M–29 is less intense than M–28.

(*d*) Cresols form very intense (M–H) peak due to the formation of hydroxy tropylium ion.

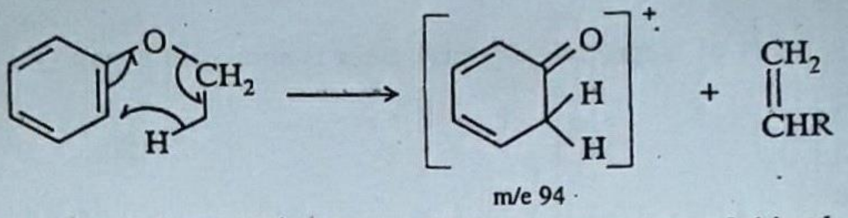
(*e*) In catechol ($\overset{+}{M}$ – 18) peak is intense while $\overset{+\cdot}{M}$—28 and $\overset{+}{M}$—29 ions are formed in abundance in resorcinol and quinol.

The mass spectrum of phenol is shown in figure 7.20.

(*b*)



Also in general.



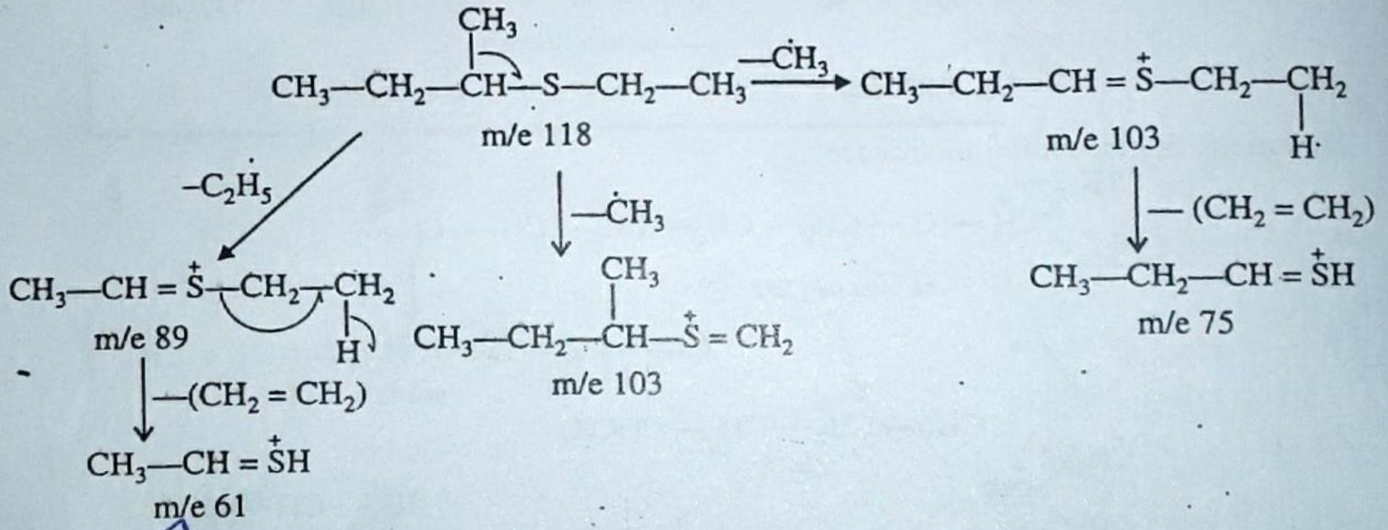
(*iii*) **Thioethers :** Some important features of the mass spectra of thioethers are :

(*a*) The molecular ion peaks of thio-ethers are more intense than aliphatic ethers.

(*b*) α-cleavage of C–S bond with positive charge on sulphur is the favoured mode of fermentation. The smallest alkyl chain is lost compared to the usual behaviour in which bigger chain is lost.

(*c*) β-cleavage of the bond form $RCH=\overset{+}{S}H$ ions giving rise to peaks at m/e 46, 61, 75, 89.

Consider the fragmentation pattern in the mass spectrum of sec-butyl ethyl ether.



7.17 Aliphatic Aldehydes and Ketones

(*a*) Aliphatic Carbonyl Compounds

Some important features of the mass spectra of aliphatic aldehydes and ketones are:

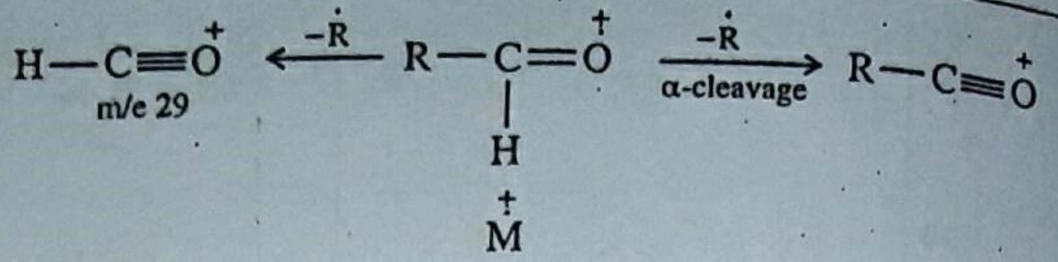
(*a*) The intensity of the molecular ion peak decreases as the alkyl chain length increases.

(*b*) The major fragmentation processes are α- and β-cleavage. In α-cleavage, the bigger group on either side of the carbonyl group (ketone) is preferably lost.

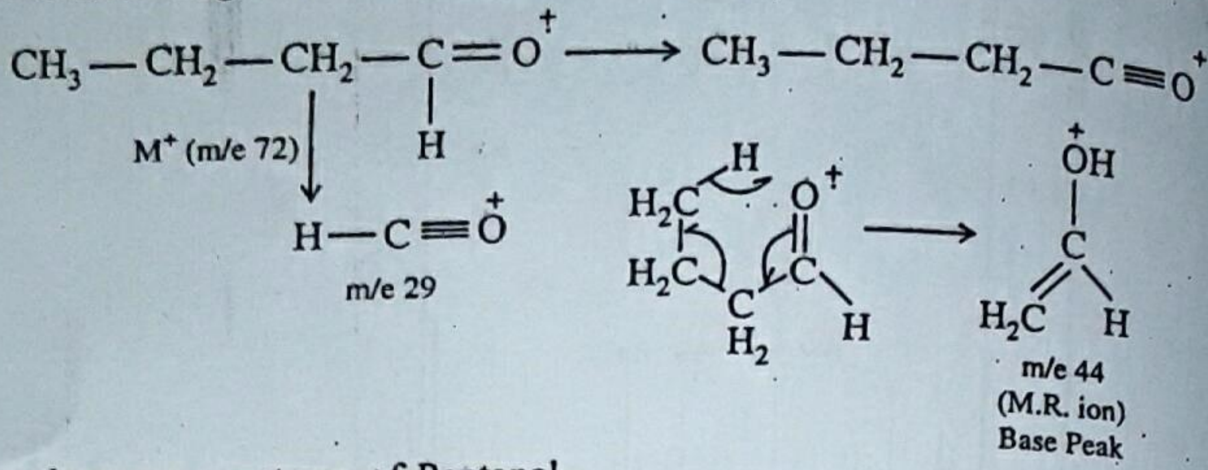
(*c*) In aldehydes and ketones containing γ-hydrogen atom, McLafferty rearrangement ion is most significant. In an aldehyde, which is not α-substituted, a peak due to this is formed at m/e 44. It may be base peak.

(*d*) The McLafferty rearrangement ion in methyl ketones which are not α-substituted appears at m/e 58 and is quite abundant.

(*e*) In lower aldehydes, α-cleavage is prominent with retention of charge on oxygen.



(*f*) In aldehydes, methyl or alkyl radical is preferably lost compared to hydrogen radica Consider the various fragmentation modes of butanal.



Consider the mass spectrum of Pentanal.

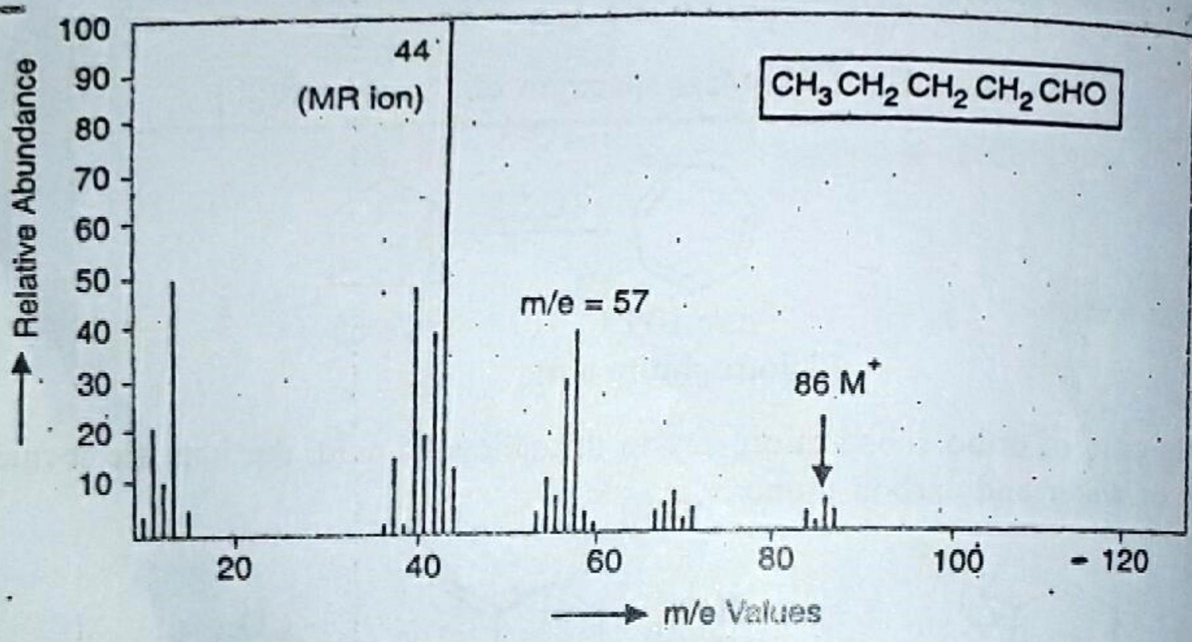
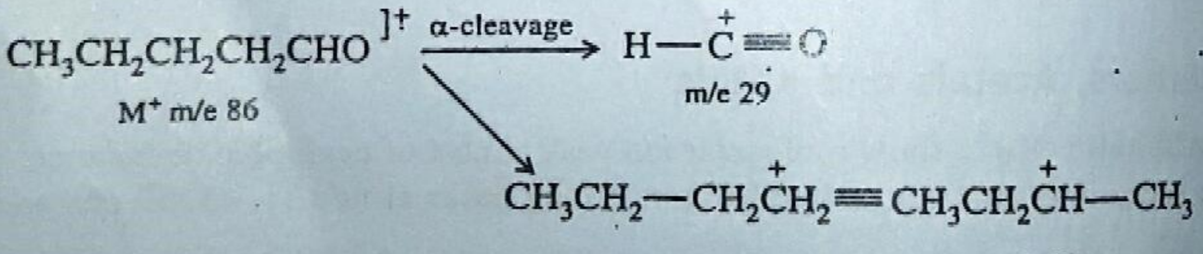
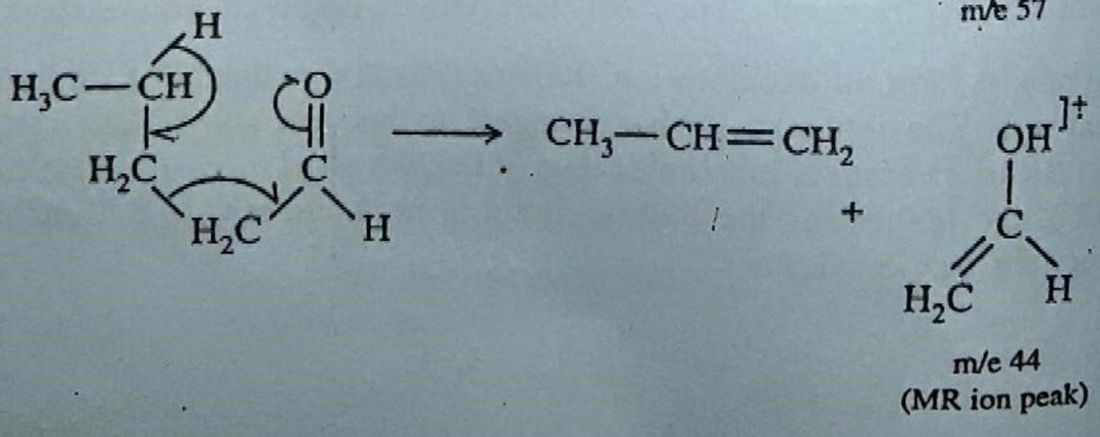


Fig. 7.24. Mass spectrum of Pentanal.

The various fragmentation modes of pentanal are :





Consider the mass spectrum of 3-pentanone.

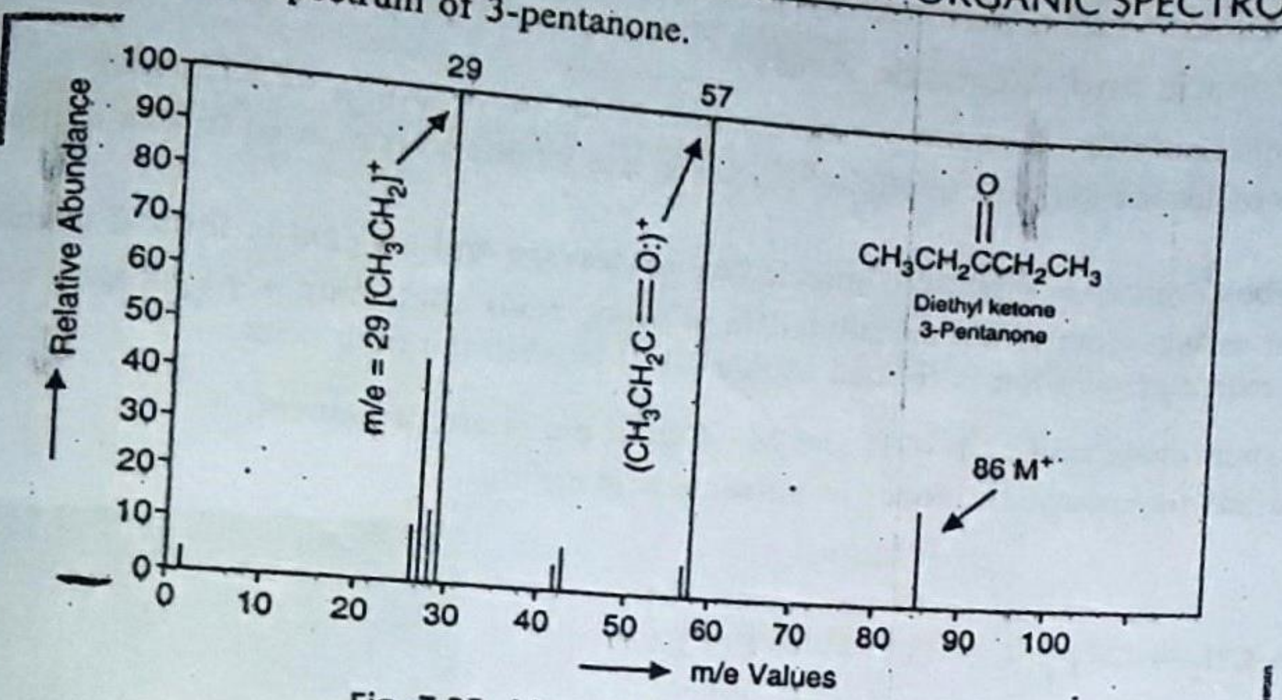
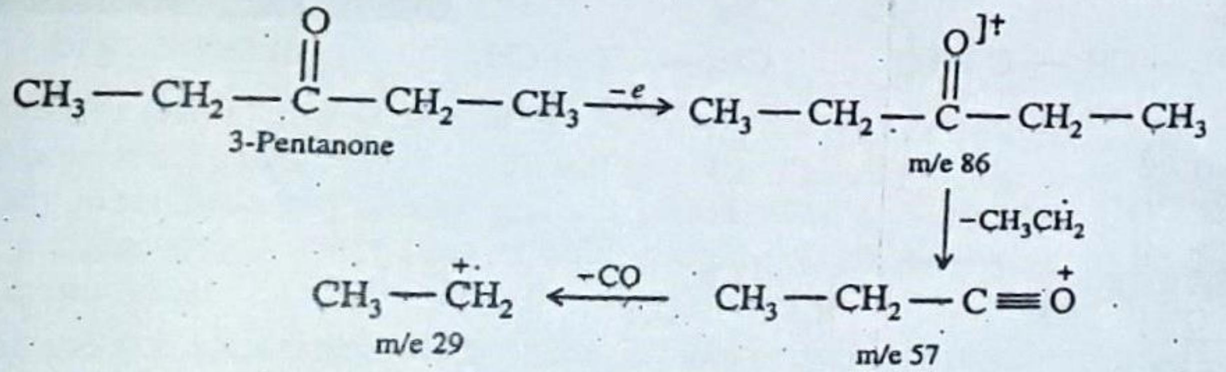


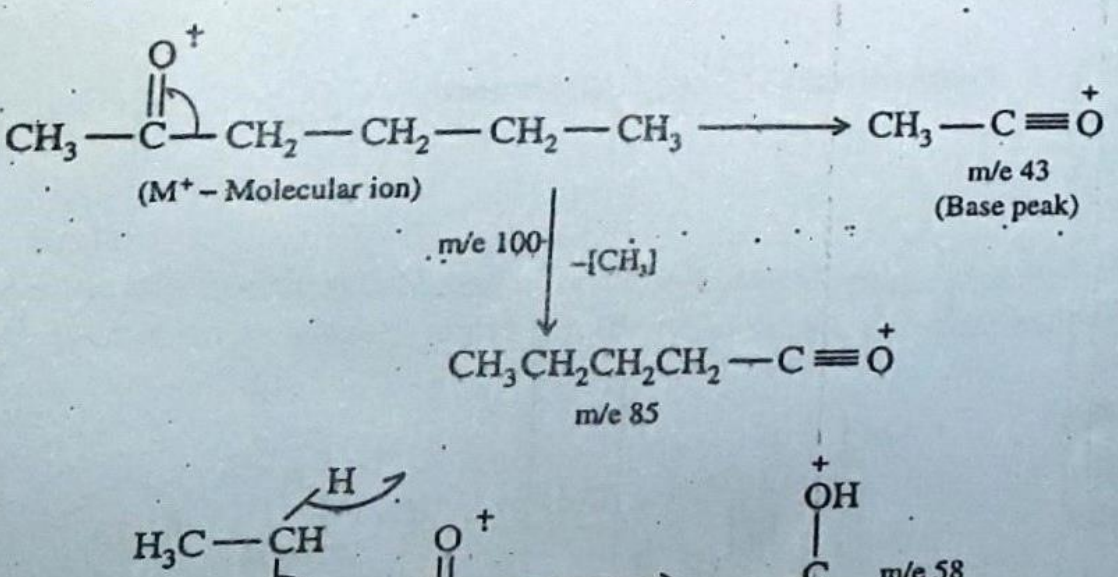
Fig. 7.25. Mass spectrum of 3-pentanone.

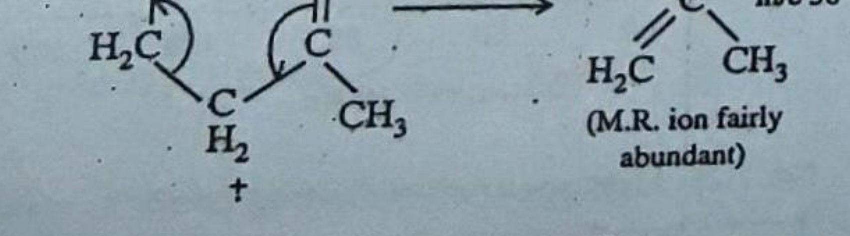
The various fragmentation modes in the spectrum of 3-pentanone are shown below :



In 3-Pentanone there is no γ-hydrogen atom and thus, no McLafferty rearrangement ion peak formed.

Consider the various fragmentation modes of 2-hexanone.





From the fragment ions draw the mass spectrum of 3-hexanone.

(b) Aromatic aldehydes and ketones

In these compounds, parent ion peak is intense. $\overset{+\cdot}{M}-1$, $\overset{+\cdot}{M}-28$ due to the elimination of CO in benzaldehyde are formed. Peak at m/e 77 due to $C_6H_5^+$ followed by the one at m/e 51 due to $C_4H_3^+$ also result. Consider benzaldehyde.

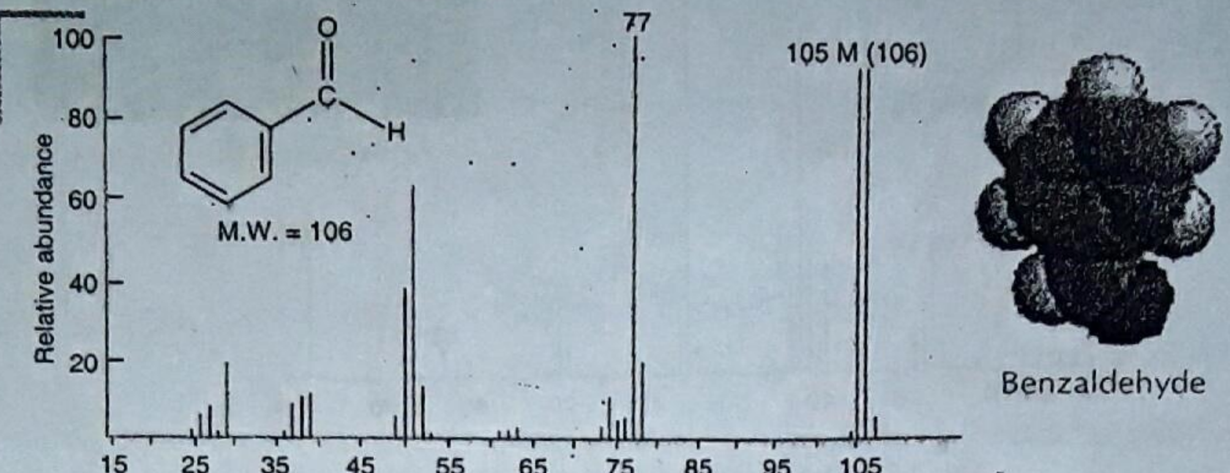
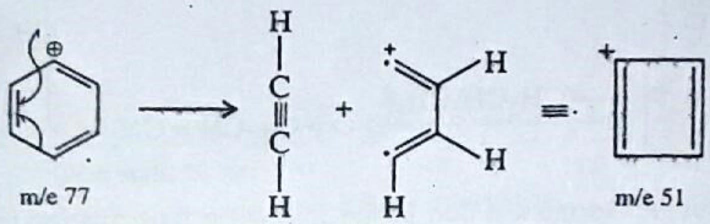


Fig. 7.26 Mass spectrum of Benzaldehyde.

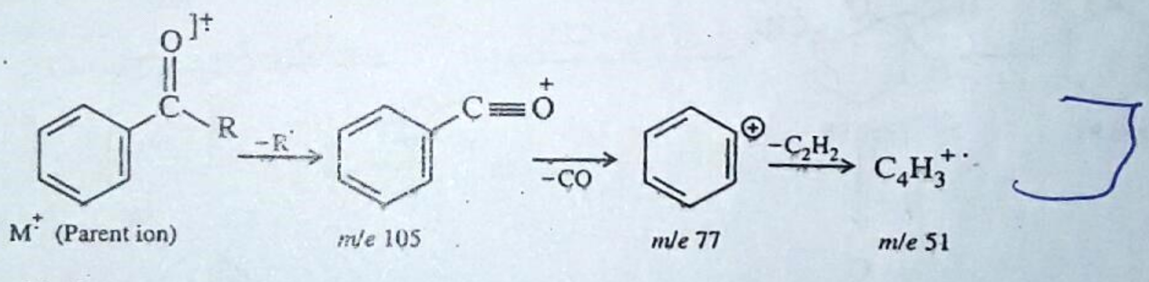
$$\underset{(M^{+\cdot}-1)}{C_6H_5-C\equiv\overset{+}{O}} \xleftarrow{-(\dot{H})} \underset{(M^{+\cdot})}{C_6H_5CH\overset{+}{O}} \xrightarrow{-(CO)} \underset{m/e\ 78}{C_6H_6^{+\cdot}} \xrightarrow{-(\dot{H})}$$

$$\underset{m/e\ 77}{C_6H_5^+} \xrightarrow{-(C_2H_2)} \underset{m/e\ 51}{C_4H_3^+}$$



In ketones, the loss of larger group is preferred by an α-cleavage.

Consider the fragmentation of alkyl phenyl ketone:



7.18 Cyclic ketones

Some important features of the cyclic ketones are :

(a) The molecular ion peak of cyclic ketones is quite intense.

(b) A base peak in cyclopentanone or Cyclohexanone is formed by α-cleavage followed by hydrogen transfer rearrangement. A peak due to $CH_2=CH-C\equiv\overset{+}{O}$ is formed at m/e 55.

(*c*) Peaks are formed by the loss of ethylene, carbon monoxide molecules in fair abundance in case of cyclohexanone.

The mass spectrum of cyclohexanone is shown below :

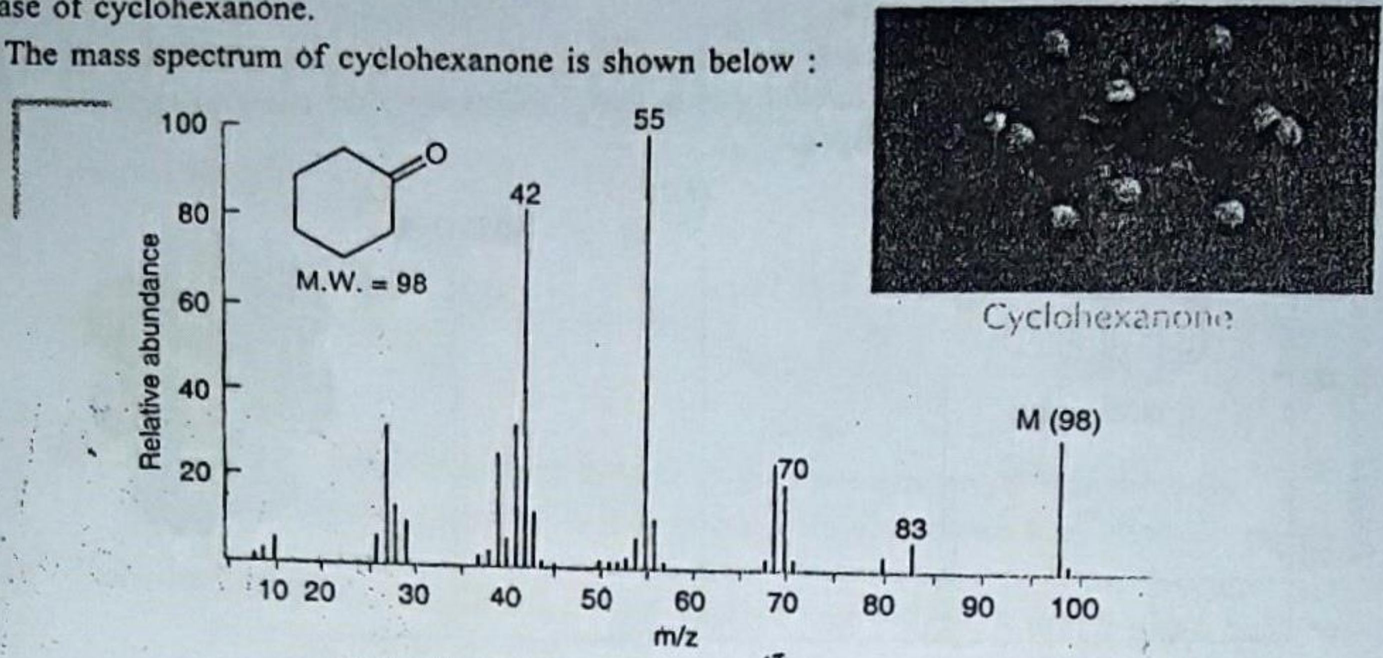
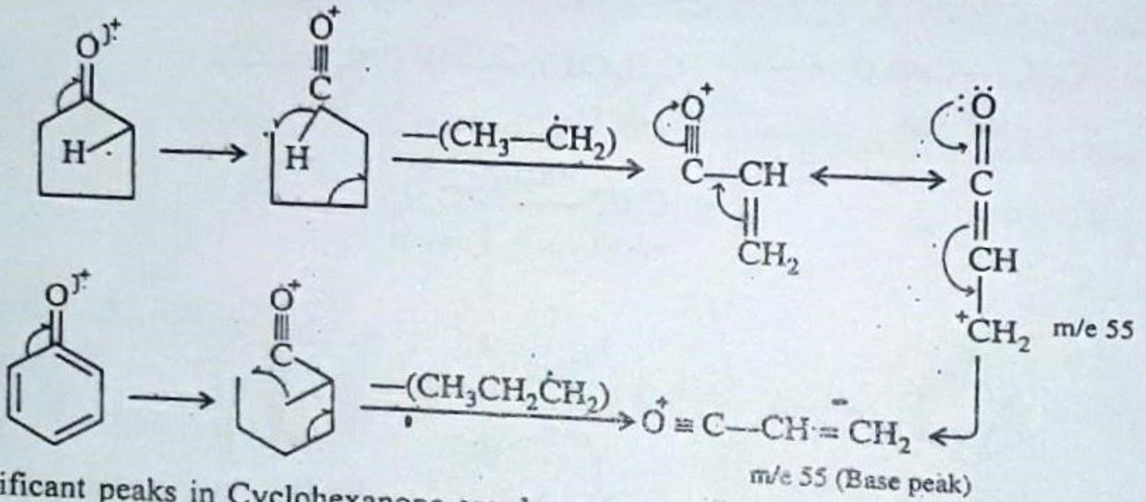
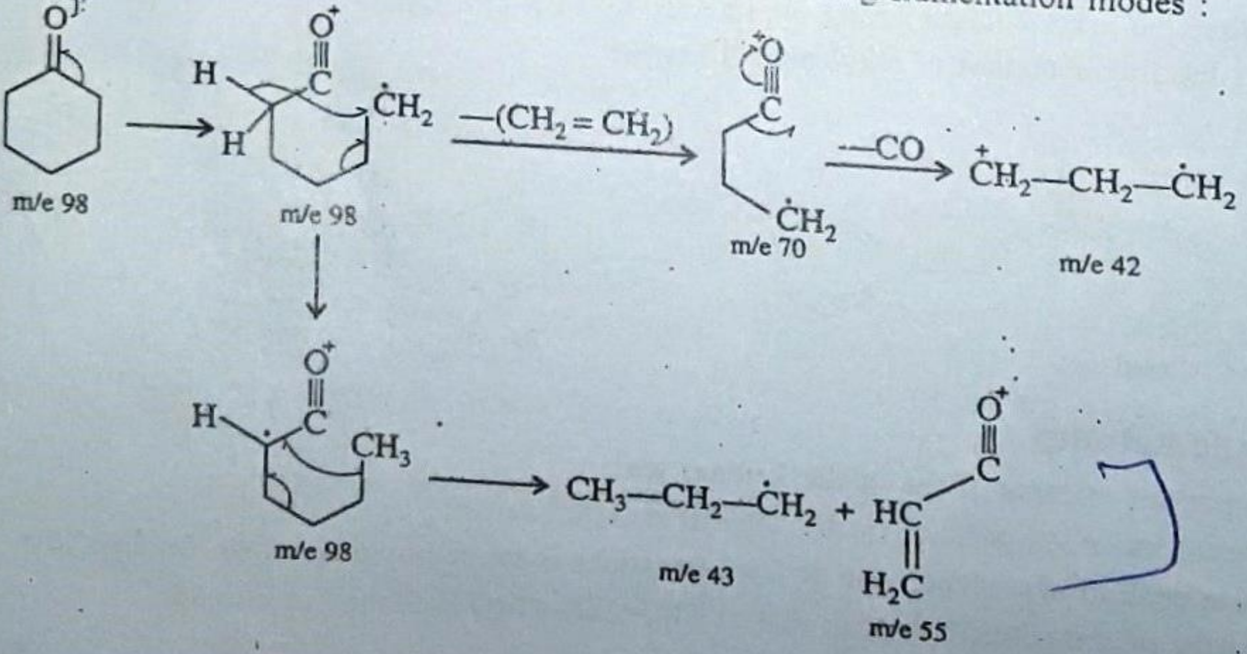


Fig. 7.27. Mass spectrum of Cyclohexanone.

The fragmentation pattern in Cyclopentanone and Cyclohexanone are shown.



Significant peaks in Cyclohexanone are due to the following framentation modes :



7.13 Aliphatic and Aromatic Acids

(A) Aliphatic Acids : Some important features of the mass spectra of acids are:

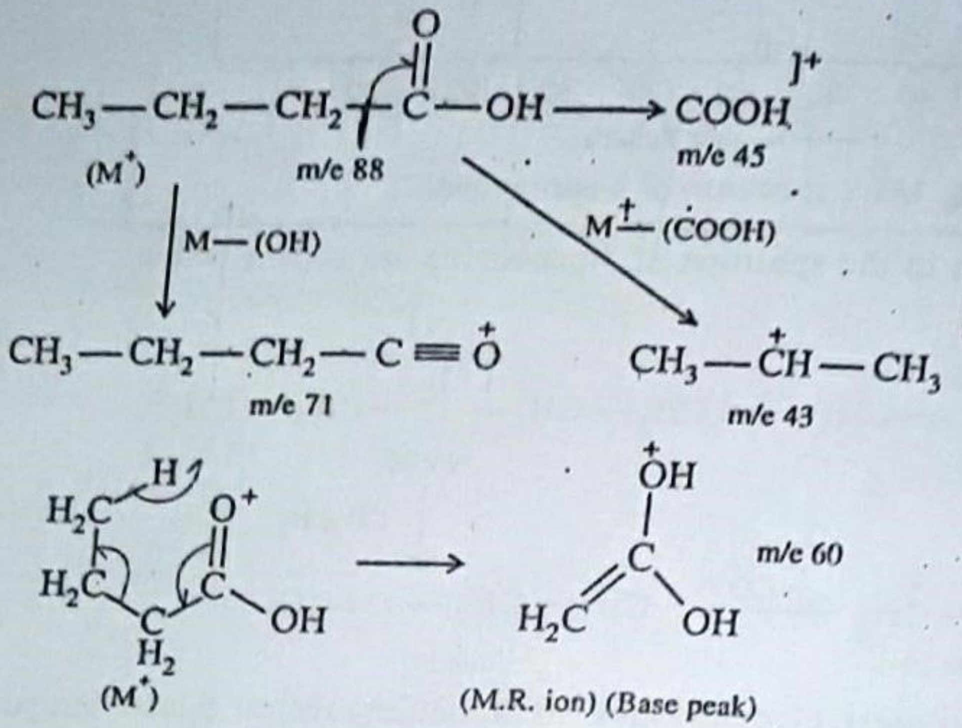
(*a*) The molecular ion peak in aliphatic acids is less intense as compared to that of acids.

(*b*) Carboxyl group is directly eliminated by α-cleavage and a signal is formed at

(*c*) If α-carbon atom is not substituted in aliphatic acids containing a γ-hydrogen McLafferty rearrangement ion is formed at m/e 60. It is often the base peak.

(*d*) In short chain acids, $\overset{+}{M}$—OH and $\overset{+}{M}$—COOH peaks are prominent.

The various fragmentation modes in butanoic acid are :



Butanoic acid

Consider the mass spectrum of Pentanoic acid.

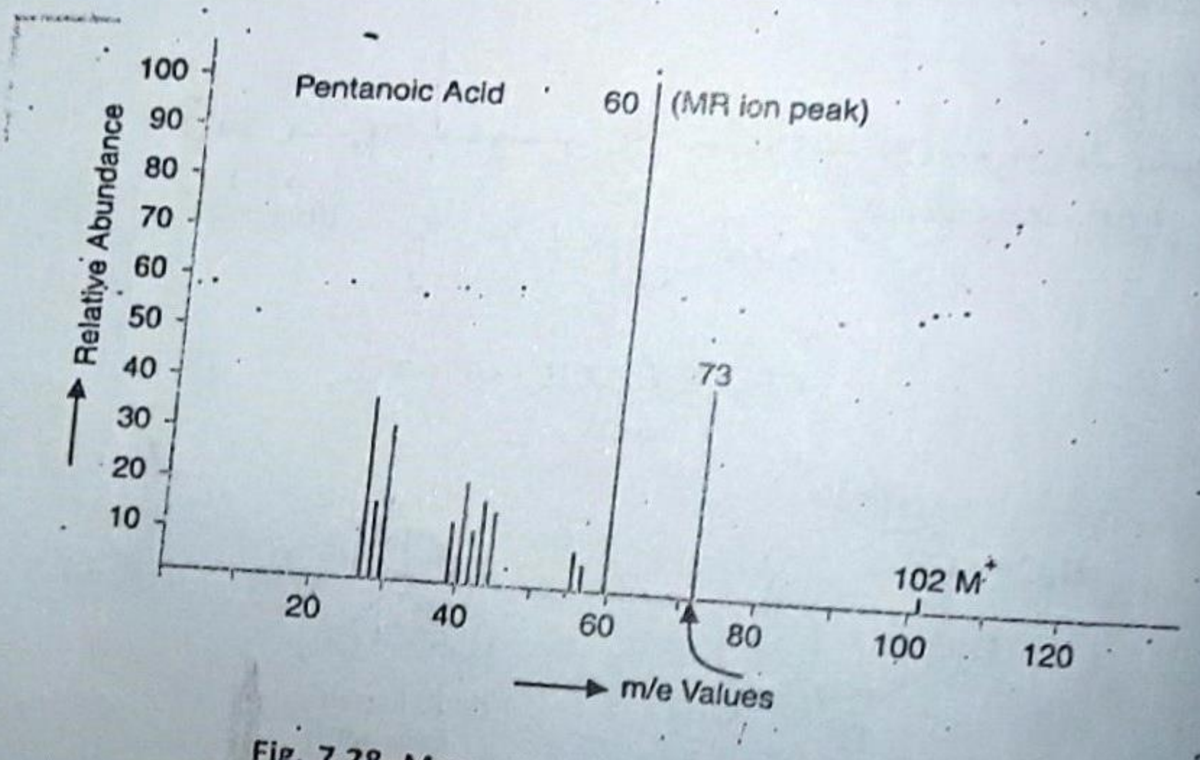
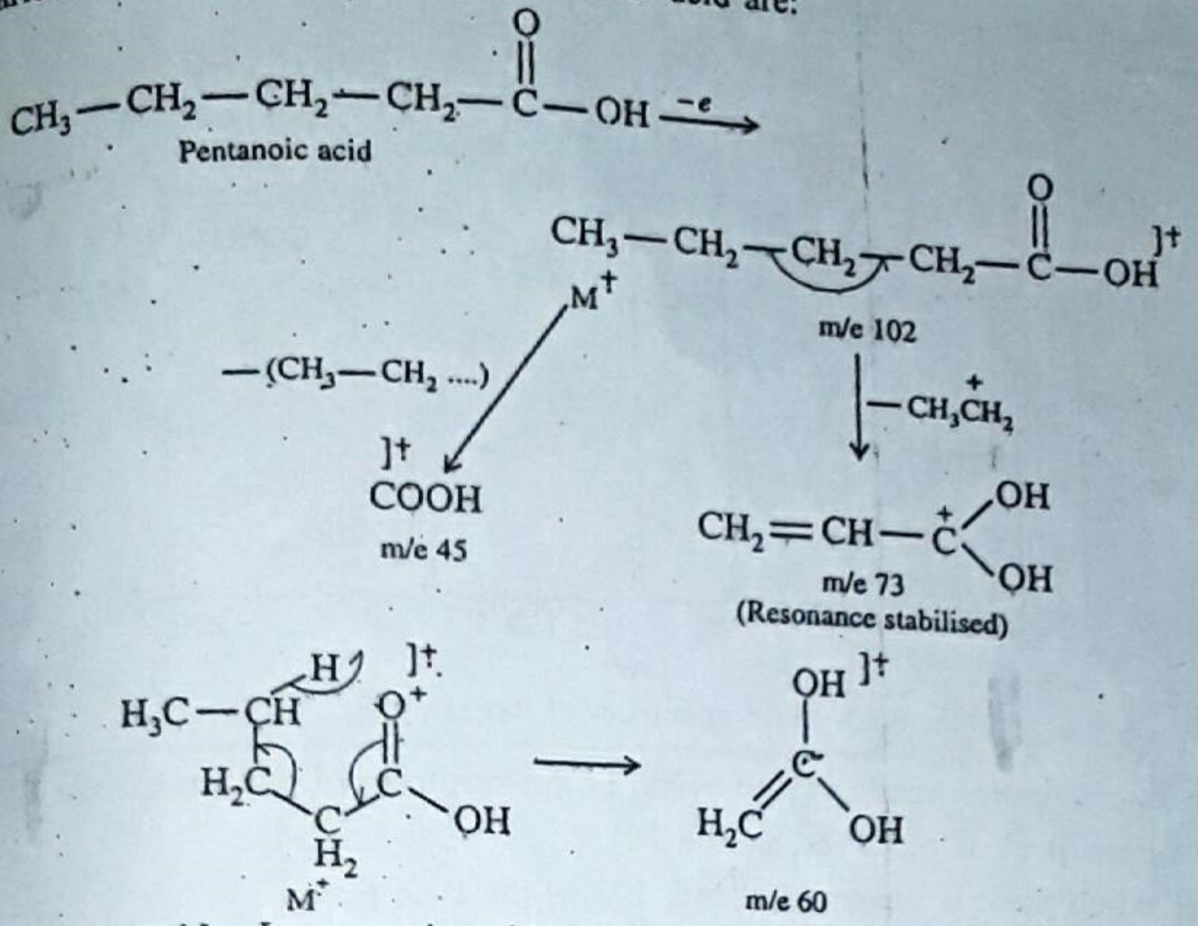
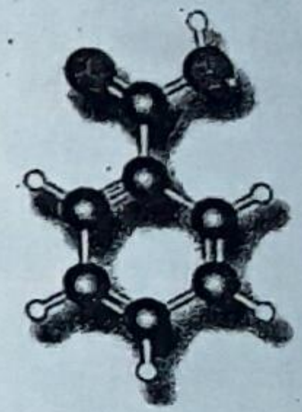


Fig. 7.28. Mass spectrum of Pentanoic acid.

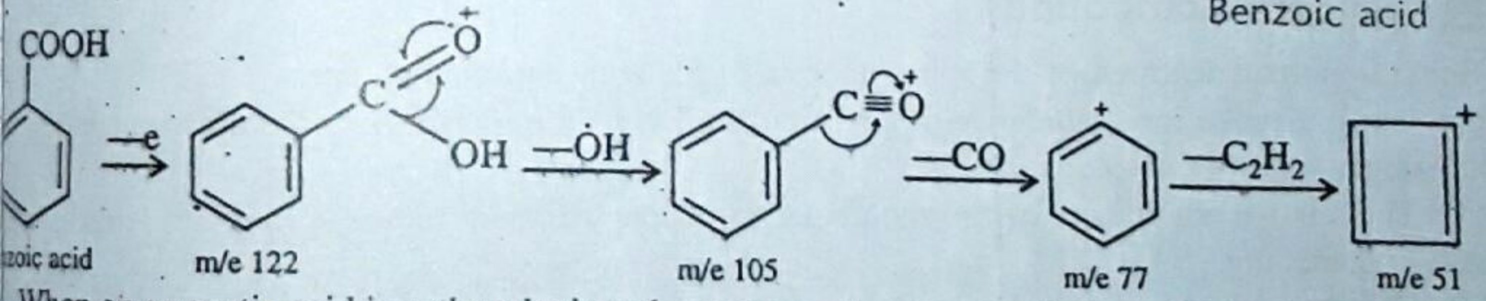
The various fragmentation modes of pentanoic acid are:



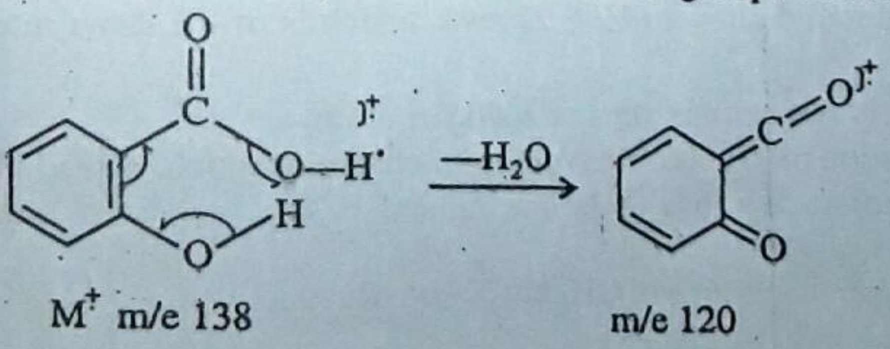
(B) **Aromatic acids.** In aromatic acids, the parent ion peak is intense. me other prominent peaks are M — 17 and M —45. If an alkyl group is sent or any other hydrogen bearing group is present ortho to —COOH up, then a signal due to M–18 (loss of water molecule) is also observed. is called **ortho effect.**


Benzoic acid

Consider the various fragmentation modes in benzoic acid. In benzoic id, (M^+ – OH) peak is quite prominent. It is followed by another peak due the loss of CO molecule. It appears at m/e 77. This in turn loses a molecule acetylene.



When an aromatic acid is orthosubstituted, a water molecule gets eliminated from the molecular provided hydrogen atom is suitably located in the ortho group. Consider saticyclic acid.



Esters

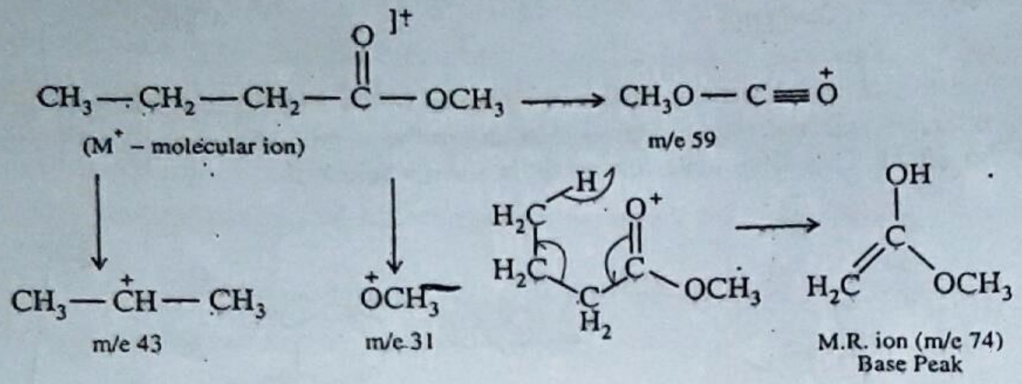
Some important features of the mass spectrum of esters are:

(*a*) The molecular 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/e 59) are observed.

(*d*) The methyl esters not substituted at the α-carbon atom show McLafferty rearrangement ion at m/e 74. Methyl substitution at a carbon atom shifts the position of McLafferty rearrangement peak at m/e 88. The various fragmentation modes of methyl butanoate are shown below:



(*e*) The molecular ion peak is comparatively more intense. Benzyl acetate and alkyl acetate eliminate neutral ketene molecule to form a base peak.

The mass spectrum of 1-propyl ethanoate is shown.

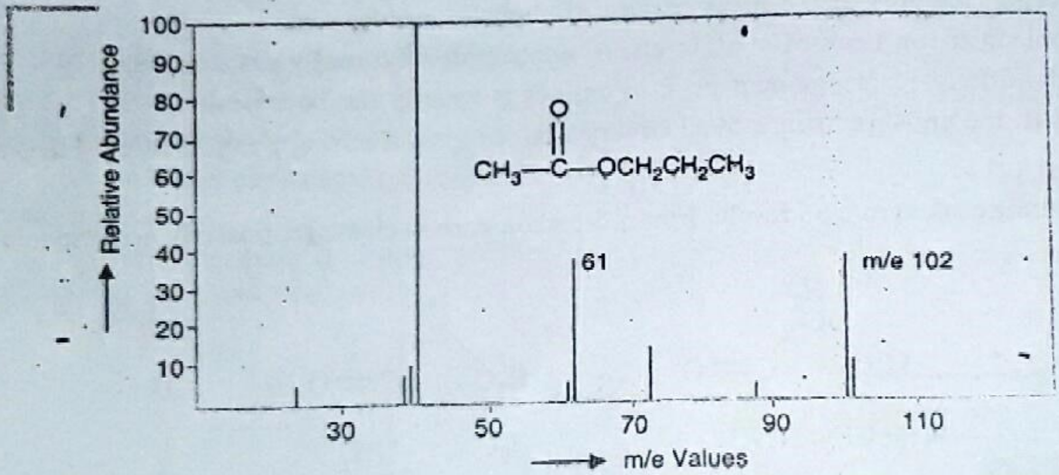
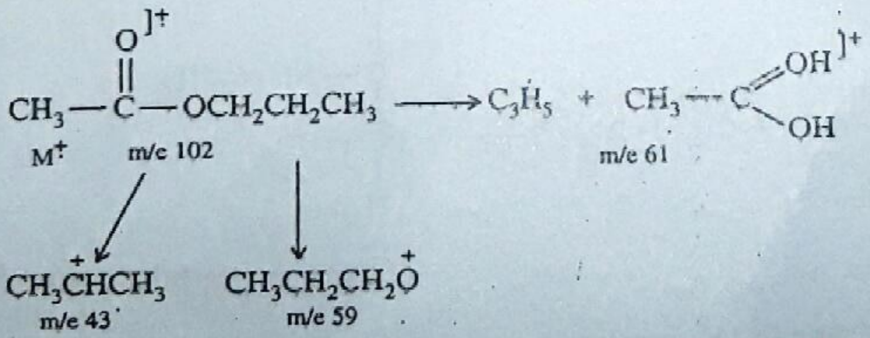
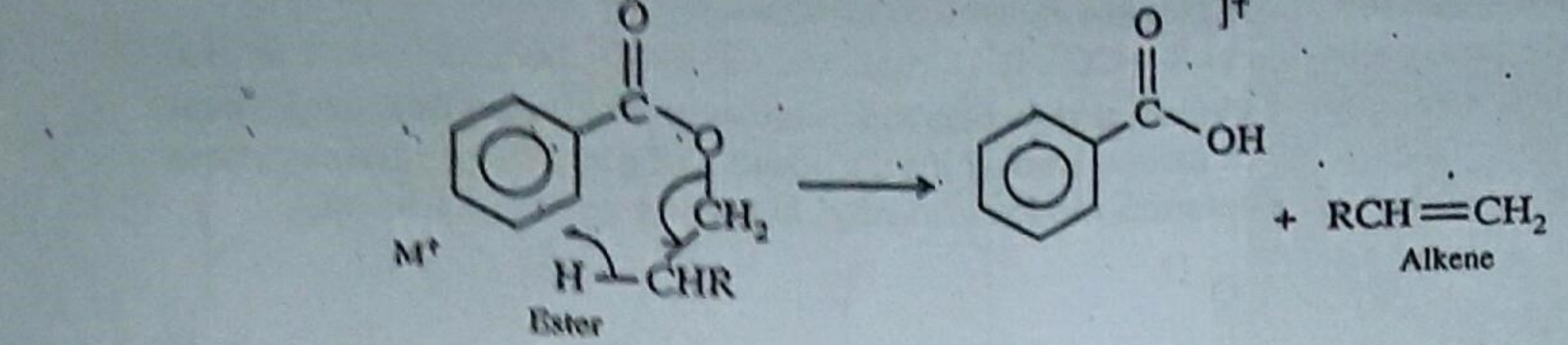


Fig. 7.29. Mass spectrum of n-Propyl ethanoate.

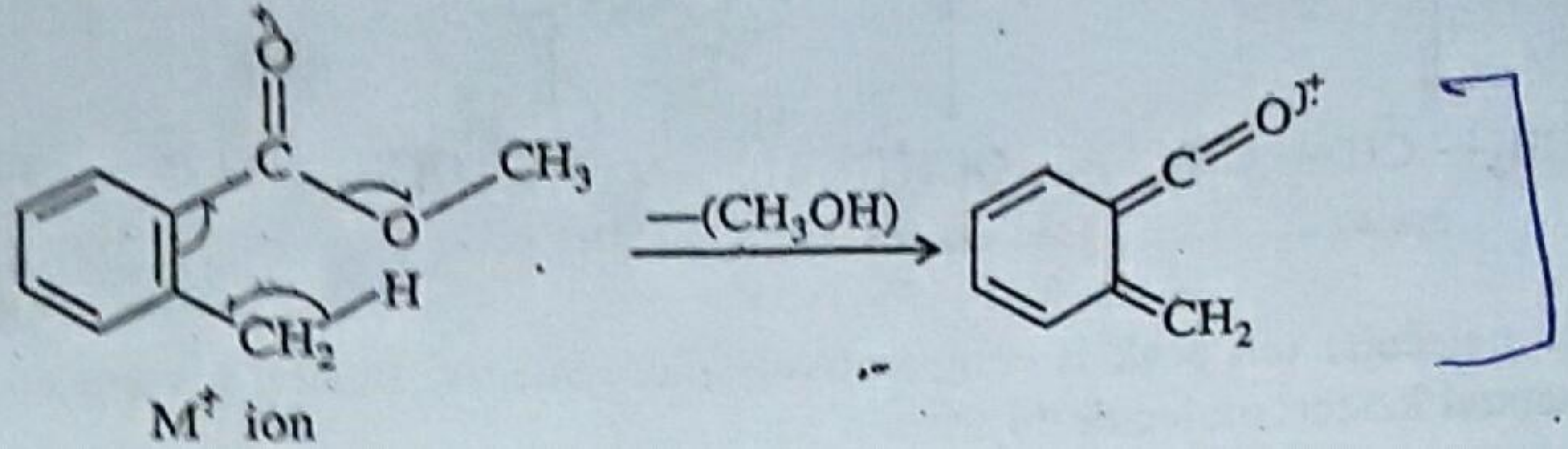
It can be distinguished from methyl butanoate by a peak at 61. It is due to McLafferty rearrangement ion.



In case of esters where alkyl group is ethyl or higher, alkene is usually lost.



In aromatic esters in which ortho position is occupied by an alkyl group, the hydrogen atom of alkyl group interacts with the ester function resulting in the elimination of an alcohol molecule. It is called ortho effect. This fragmentation mode is shown below :



Consider the mass spectrum of benzamide.

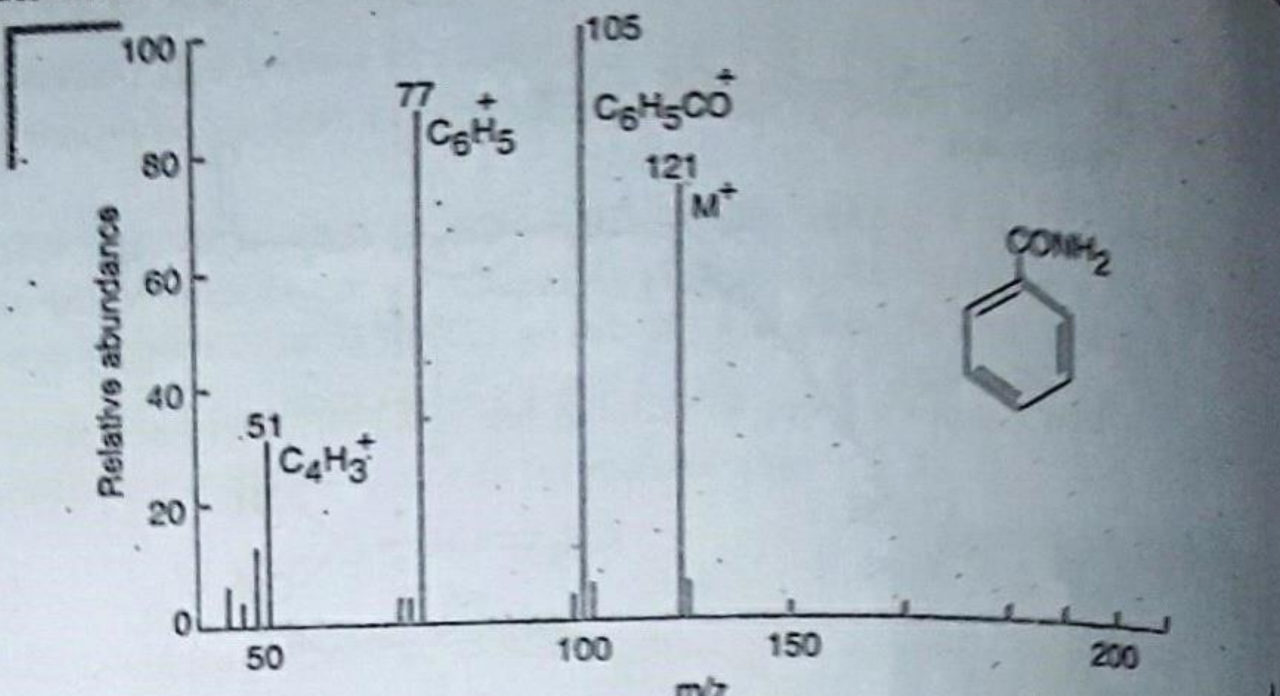


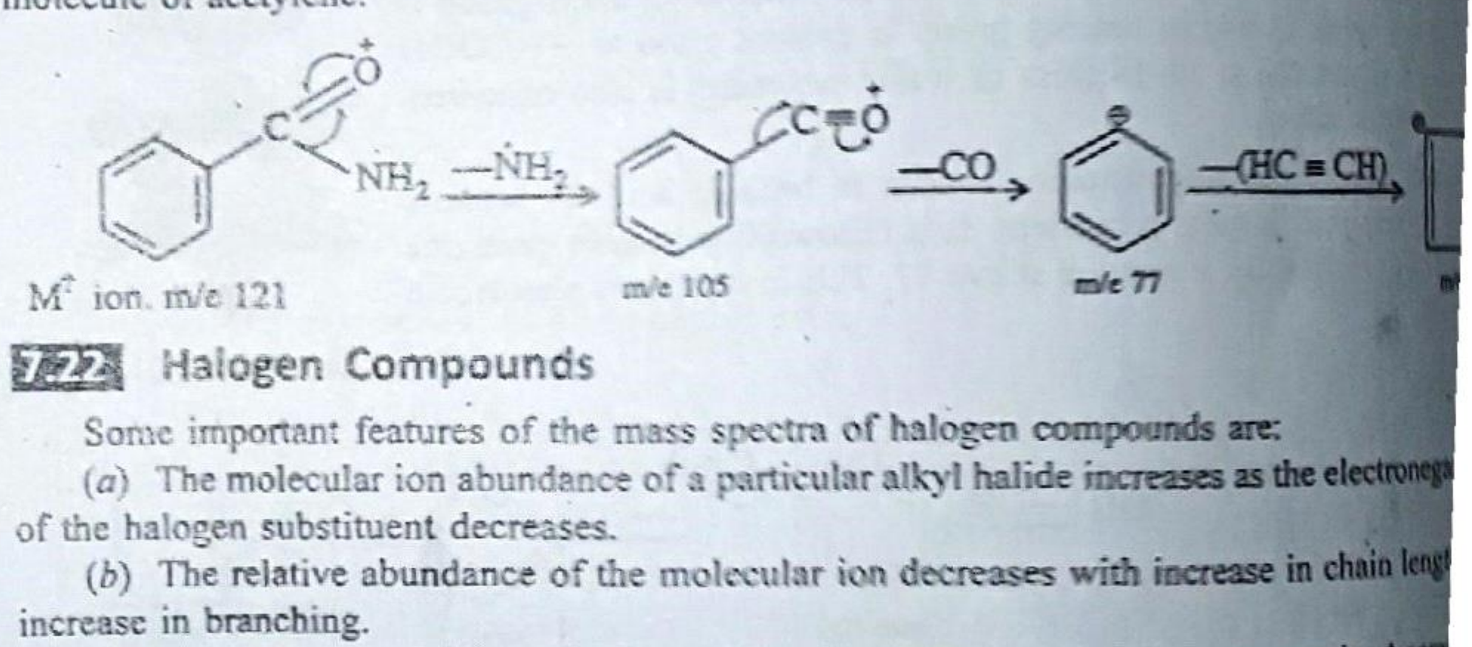
Fig. 7.30. Mass spectrum of Benzamide.

The various fragmentation modes as observed in the spectrum of benzamide are :

(*i*) Molecular ion peak is observed at m/e 121.

(*ii*) Benzoyl cation peak is observed at m/e 105 as the base peak.

(*iii*) Further loss of CO forms another peak at m/e 77 due to $C_6H_5^+$ ion which in turn lose molecule of acetylene.



7.22 Halogen Compounds

Some important features of the mass spectra of halogen compounds are:

(*a*) The molecular ion abundance of a particular alkyl halide increases as the electroneg of the halogen substituent decreases.

(*b*) The relative abundance of the molecular ion decreases with increase in chain leng increase in branching.

(*c*) Compounds containing chlorine and bromine show characteristic isotope peaks. A com containing one chlorine atom shows M + 2 peak which is one third in intensity of parent

(*d*) A monobromo compound shows (M + 2) peak which is of the same intensity con to the parent peak.

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

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

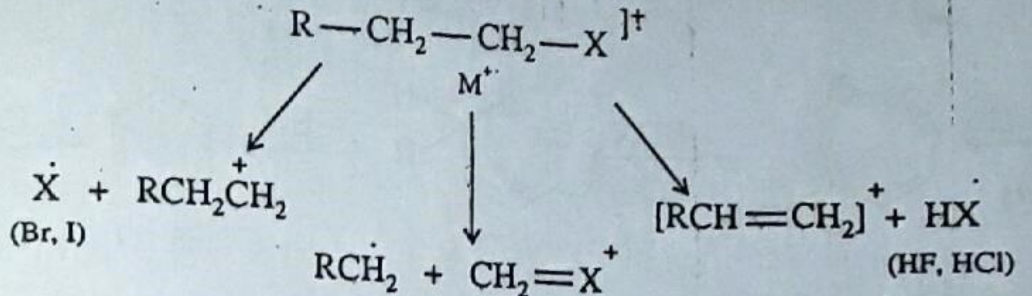
$$R-CH_2-\overset{+\cdot}{X} \longrightarrow CH_2=\overset{+}{X} + \dot{R}$$

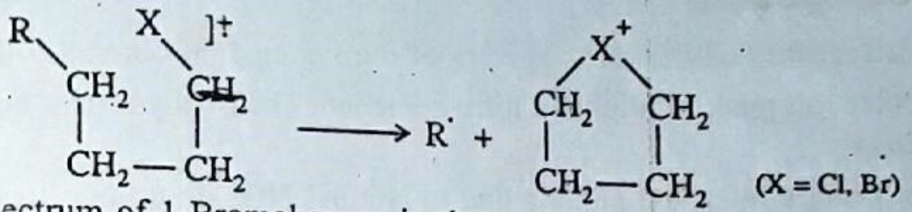
$$\underset{(M^{+})}{R-CH_2-\overset{+\cdot}{X}} \longrightarrow R\overset{+}{C}H_2 + X \text{ (Preferable mode)}$$

EXAMPLE. *In the mass spectrum of ethyl chloride, we observe (i) 64 (M^+), 66([Intensity ratio 1 : 3] (ii) 29 (Base peak) (The loss of Cl radical is the preferable mo*

EXAMPLE. *In the mass spectrum of ethyl bromide, CH_3CH_2Br, the peaks at m/e 108, 110 and m/e 79 and 81 are formed in equal intensity. The peak at m/e 29 due to the loss of Br radical is the base peak (100% abundance).*

Consider the fragmentation modes of *n*-alkyl halide.





The mass spectrum of 1-Bromohexane is shown below:

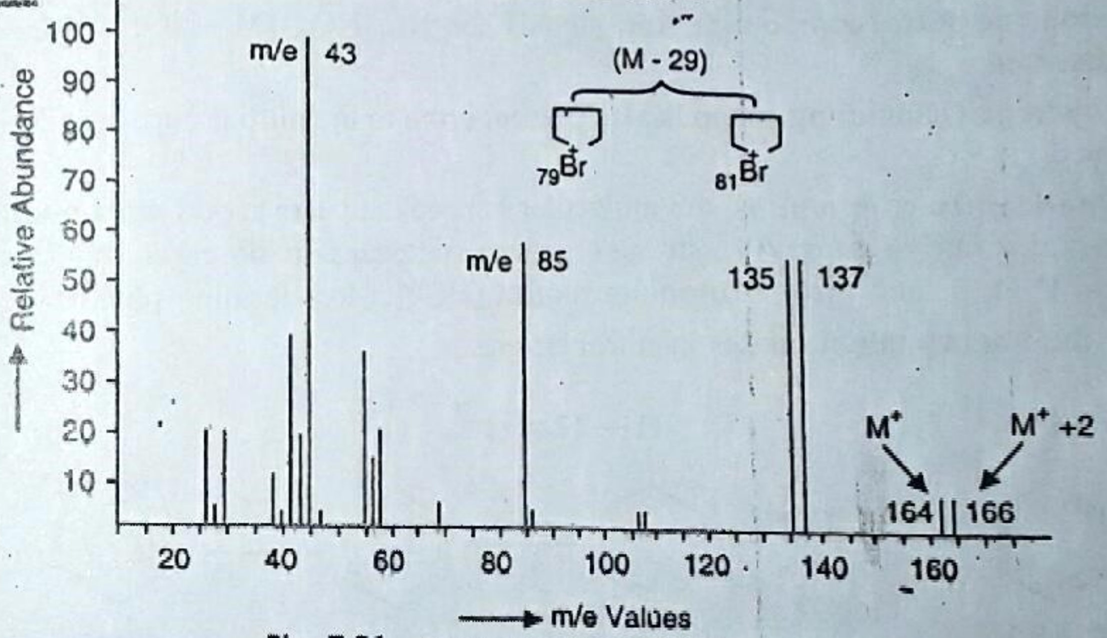
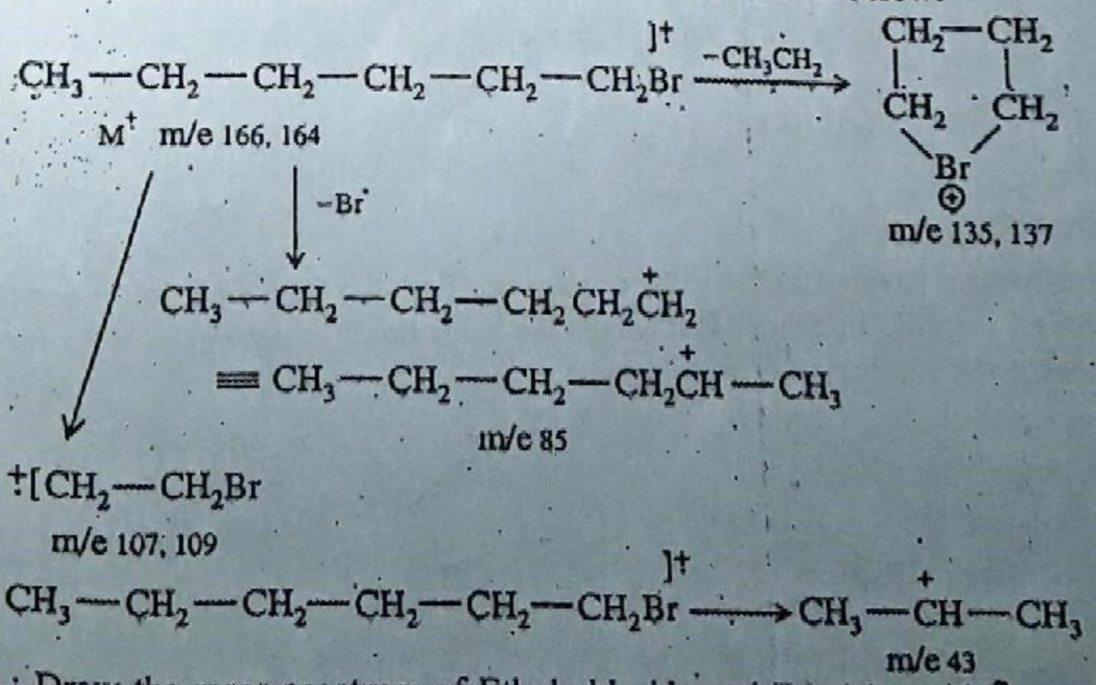


Fig. 7.31. Mass spectrum of 1-Bromohexane.

The various fragmentation modes of 1-Bromohexane are shown below:



Exercise : Draw the mass spectrum of Ethyl chloride and Ethyl bromide.