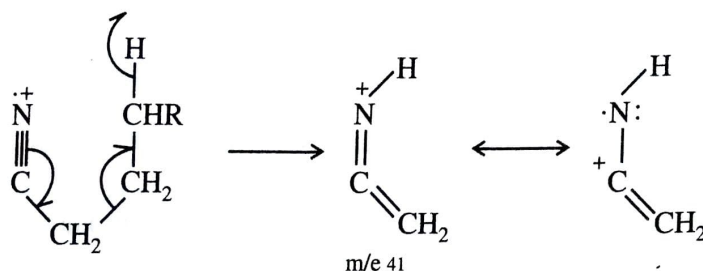


### 7.25 Aliphatic Nitriles

Some important features of the mass spectra of aliphatic nitriles are:

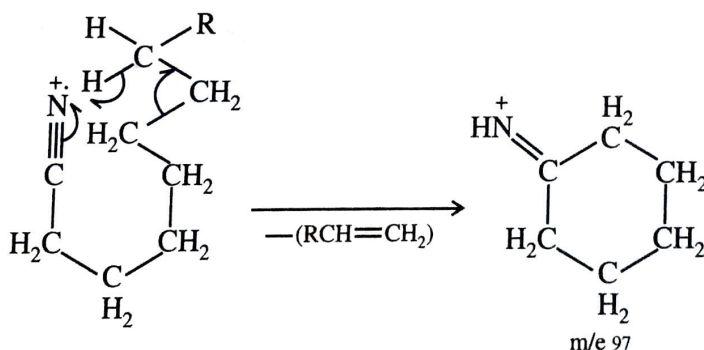
(i) The molecular ion peak of aliphatic nitriles is weak or may be absent.



(ii) A weak but diagonistically useful  $(M-1)$  peak is formed by the loss a  $\alpha$ -hydrogen atom to form a stable ion.

(iii) The base peak of straight chain nitriles between  $C_4$  and  $C_9$  is  $m/e 41$ . This peak is due to the ion resulting from hydrogen rearrangement in a six membered transition state.

(iv) A peak at  $m/e 97$  is characteristic and intense in straight chain nitriles  $C_8$  and higher. The following mechanism has been suggested.

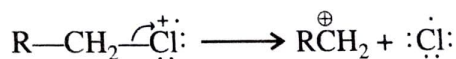


### 7.26 Important Features in Mass Spectroscopy

1. Mass spectrophotometer gives a record of the relative abundance of ions according to the  $m/e$  ratio.
2. Molecular ion peak is not generally visible in case of alcohols.
3. A peak corresponding to the ion of maximum abundance is called the base peak.
4. The molecular ion or the parent ion peak may or may not be the base peak. Usually, it is not. The molecular ion has usually the highest  $m/e$  value in the spectrum and its  $m/e$  value is equal to the molecular mass of the compound.  $M + 1$  and  $M + 2$  peaks also appear in very low abundance and are called isotope peaks.
5. The molecular ion is usually not much stable and tends to fragment. The fragmentation of molecular ion produce daughter ions of definite  $m/e$  value which help in structure determination.

6. In McLafferty rearrangement, an alkane molecule is lost in a cyclic rearrangement with  $\gamma$ -hydrogen.
7. The intensity of  $M + 1$  peak is valuable to know the number of carbon as well as nitrogen atoms. In case nitrogen is absent, the number of carbon atoms can be calculated by dividing the relative intensity of  $M + 1$  peak by 1.1.
8. In a typical case, if  $M + 2$  peak of the parent ion looks larger than the  $M + 1$  peak, the compound may contain Sulphur, Chlorine or bromine atom.
9. If a compound contains chlorine atom, then pair of peaks are obtained at two mass units apart in the intensity ratio 1 : 3. But in case, bromine atom is present, then pair of peaks at two mass unit apart are of equal intensity.
10. The most intense peak in the mass spectrum is called the **base peak**. Its relative intensity or abundance is taken as 100 and the intensities of other peaks, including the parent peak are expressed as percentage of parent peak.
11. Mass to charge ratio ( $m/z$ ) is a dimensionless ratio of the mass number of the given particle to the number ( $z$ ) of the charge carried by the particle. Usually the particle is singly charged and the ratio is often expressed as  $m/e$ . Doubly charged particle are insignificant in the mass spectra of organic compounds. But the peak corresponding to stable doubly charged ions may be sometimes useful.
12. The relative abundance (RA) of the given ion tells its intensity relative to the base peak which is the most intense peak in the spectrum.
13. Fragmentation of the molecular ion occur by the cleavage of bonds in two ways *i.e.*, heterolytic or homolytic.

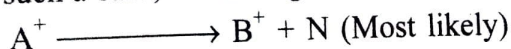
Heterolytic cleavage is designated by the arrow ( $\curvearrowright$ ) to denote the transfer of a pair of electrons in the direction of the charged site as shown below:



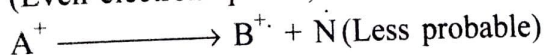
Hemolytic cleavage is designated by the fishhook arrow ( $\frown$ ) to denote the transfer of the single electron as shown below.



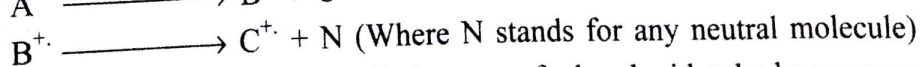
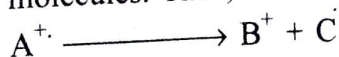
14. Metastable ions are generally broader than the normal peaks and also these are of low abundance. Moreover, these ions do not necessarily occur at the integral  $m/e$  values.
15. According to **Even electron rule**, an even electron species will not normally break into two odd electron species because the total energy of this product mixture would be too high. In such a case, an ion degrades to another ion and a neutral molecule. For example.



(Even electron species)

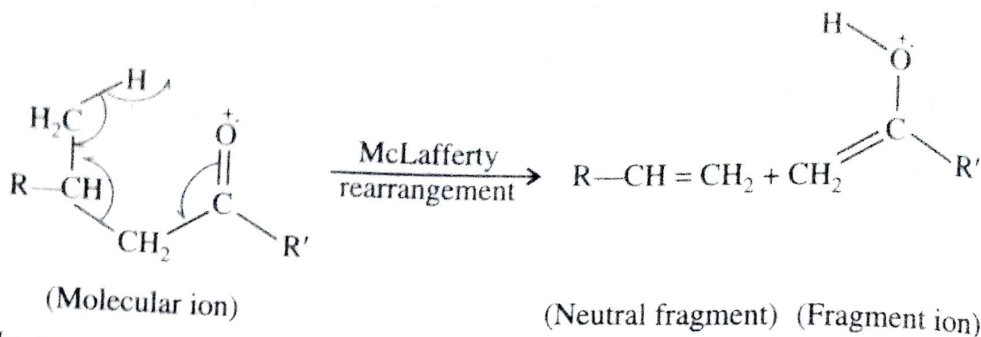


But the radical ions (odd electron species) fragment by the loss of radicals or even electron molecules. Thus,

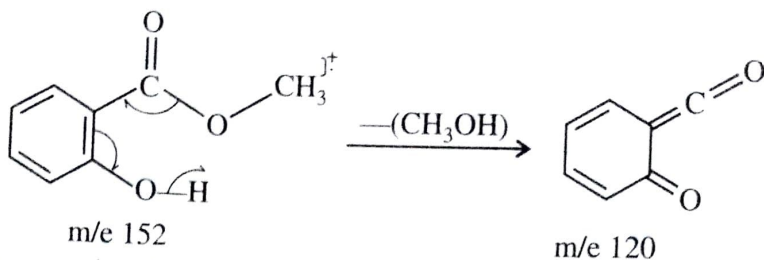


16. McLafferty rearrangement involves  $\beta$ -cleavage of a bond with  $\gamma$ -hydrogen rearrangement to form a cation radical and a neutral molecule. This rearrangement is meant for compounds, containing  $\gamma$ -hydrogen with respect to a multiple bond.

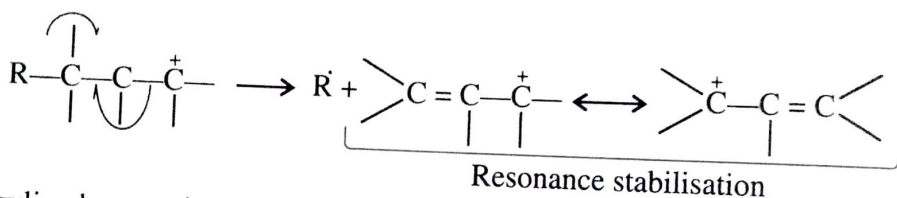




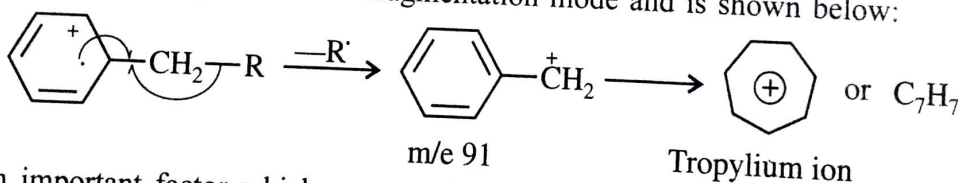
In case, ester, acid etc are orthosubstituted, then a loss of alcohol or water takes place through a six membered transition state. It is an ortho effect. Consider the following fragmentation mode.



17. Allylic cleavage involves a cleavage of carbon-carbon bond, beta to double bond. This type of cleavage is more likely because of the resonance stabilisation of allyl cation. This type of fragmentation mode can be explained as the basis of homolytic fission induced by a radical site.



18. Benzylic cleavage involves the cleavage of carbon-carbon bond beta to aromatic ring. It is an energetically favourable fragmentation mode and is shown below:



19. An important factor which governs the mass spectral pathway is the stability of ions, radicals or neutral molecules formed as a result of fragmentation of molecular ion. The most prominent peaks in the mass spectrum should correspond to the most stable fragment ions. The relative abundance of an ion depends upon its (i) stability (ii) rate of formation and (iii) rate of further decomposition.

20. McLafferty rearrangement peak in case of unsubstituted aldehydes appears at  $m/e$  44, that for ketone at  $m/e$  58, for acids at  $m/e$  60 and for methylesters at  $m/e$  74.

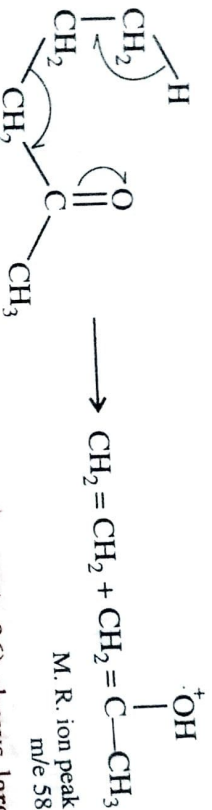
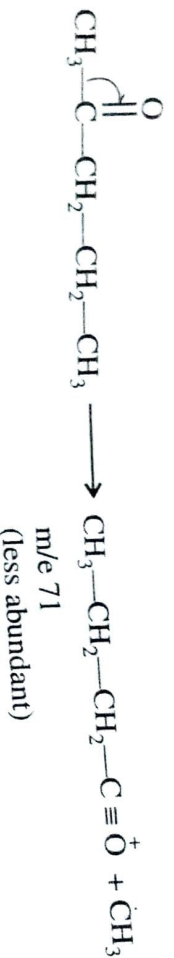
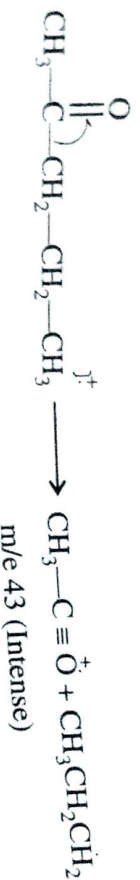
21. According to nitrogen rule when a molecule or ion contains an odd number of nitrogen atoms, it will have an odd mass number. When the molecule is devoid of nitrogen or contains an even number of nitrogen atoms, then the mass number of the molecule will be even. In other words, a species with zero or even number of nitrogen atoms, odd electron ions will have an even mass number and vice-versa.

22. In case of primary alcohols, a prominent peak with high relative abundance is also due to  $(M-H_2O)$  ion.

**727 Simple Problems on Mass Spectroscopy**

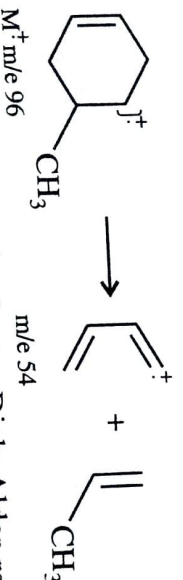
1. Predict the structure of the compound whose peaks in the mass spectrum have  $m/e$  values 86, 71, 58, 43 (100%)

**SOLUTION.** The peak at  $m/e$  86 appears to be the molecular ion peak. Thus, the molecular mass of the compound is 86. The peak at  $m/e$  58 is the McLafferty rearrangement peak for ketones which contain a  $\gamma$ -Hydrogen atom. Thus, the probable structure is Pentan-2-one. The various fragmentation mode, are shown below:



2. A hydrocarbon with molecular mass  $\text{C}_7\text{H}_{12}$  ( $M^+$  at  $m/e$  96) shows large peaks at  $m/e$  54 and due to  $M-15$ . What structure can be assigned to the compound?

**SOLUTION.** Compared to saturated hydrocarbon ( $\text{C}_7\text{H}_{16}$ ), the given compound ( $\text{C}_7\text{H}_{12}$ ) is deficient of four hydrogen atoms. A large ( $M-15$ ) peak points to the presence of branched methyl group. As the compound is hydrocarbon, the peak at  $m/e$  54 is due to  $\text{C}_4\text{H}_6$  which is nothing but butadiene. The parent hydrocarbon appears to be cyclic alkene with a branched methyl group. The most likely structure of the compound is 4-methyl cyclohexene. The fragmentation mode is shown below:



The elimination of butadiene is the result of retro-Diels Alder reaction.

3. What is the most characteristic feature of the mass spectra of compounds containing one bromine atom.

**SOLUTION.** A compound which contains one bromine atom exhibits a pair of peaks of almost equal intensity and the peaks are 2 mass units apart. It is due to equal abundance of  $^{79}\text{Br}$  and  $^{81}\text{Br}$  isotopes.

4. Predict the structure of the organic compound which exhibit  $m/e$  peaks at 15, 43, 57, 91, 105 and 148 in its mass spectrum.

**SOLUTION.** The peak at  $m/e$  148 appears to be the molecular ion peak. Thus, the molecular mass of the compound is 148.

The peak at  $m/e$  15 is due to methyl group and that at  $m/e$  43 may be due to  $\text{CH}_3\text{CO}$ -group.

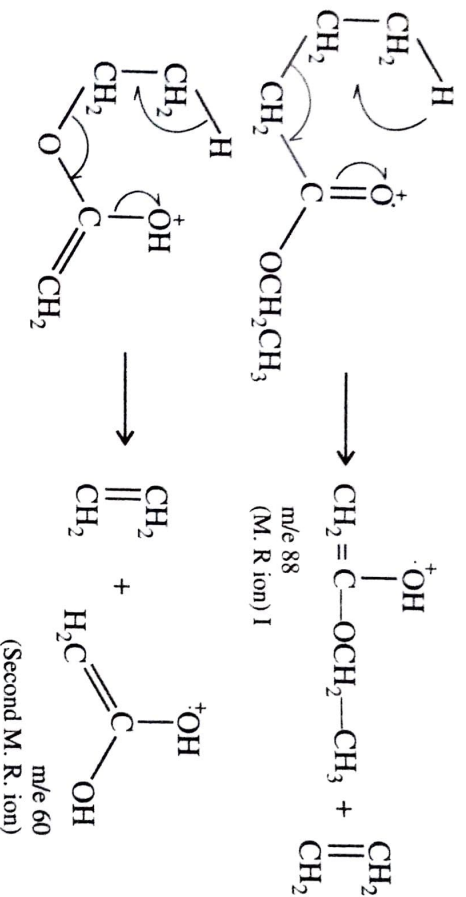


A prominent peak at  $m/e$  91 is clearly due to benzyl group ( $C_6H_5CH_2^+$ ) which rearranges to most stable tropylium cation. Adding  $CH_2$  to benzyl unit, a peak at  $m/e$  105 should be due to  $C_6H_5CH_2CH_2^+$ . Combining all these units, the most likely structure of the organic compound is :



5. Ethyl butanoate shows two characteristic peaks in its mass spectrum due to odd electron ions at  $m/e$  88 and 60 and an abundant ion at  $m/e$  71. Explain the fragmentation.

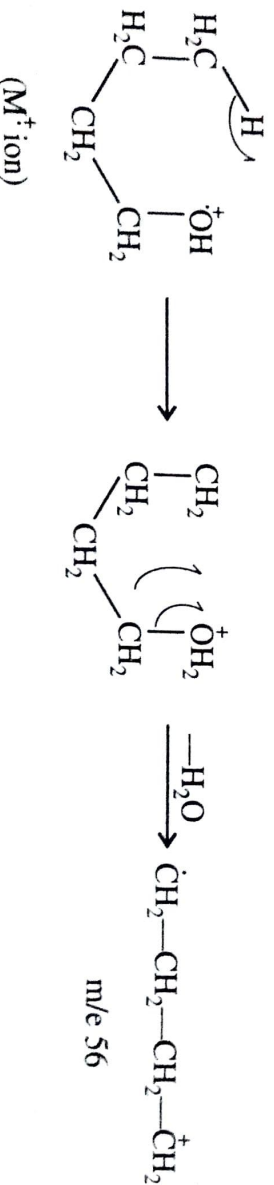
**SOLUTION.** It is known that methyl ester which is not  $\alpha$ -substituted exhibits McLafferty's rearrangement peak at  $m/e$  74. Since a peak is formed at  $m/e$  88, the ester can be ethyl butanoate or methylbutanoate with methyl group at  $\alpha$ -position. Thus,  $m/e$  88 is the result of McLafferty rearrangement.



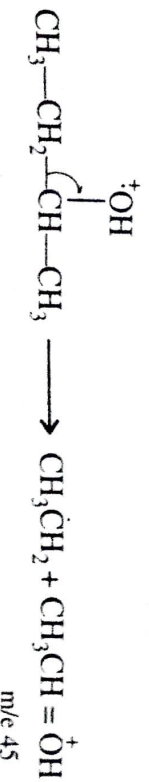
6. How will you distinguish between the isomeric alcohols with molecular formula  $C_4H_{10}O$  by mass spectroscopy?

**SOLUTION.** The Isomeric alcohol, of molecular formula  $C_4H_{10}O$  are primary, secondary and tertiary alcohols.

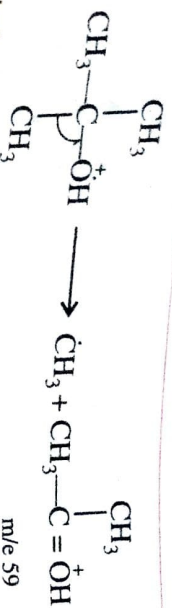
(a) In primary alcohol,  $CH_3-CH_2CH_2CH_2OH$ , the base peak results by the loss of water molecule and it appears at  $m/e$  56 as below:



(b) In secondary alcohol,  $CH_3CH(OH)CH_2CH_3$ , a base peak is formed at  $m/e$  45 by the loss of ethyl radical.

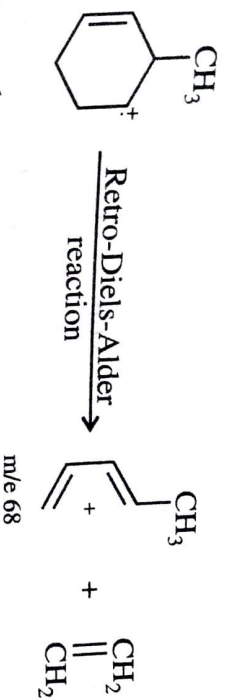


(c) In tertiary alcohol,  $(CH_3)_3C-OH$ , the base peak is formed at  $m/e$  59 by the loss of methyl radical.



7. How can you distinguish between 3-methyl and 4-methyl cyclohexene on the basis of mass spectroscopy?

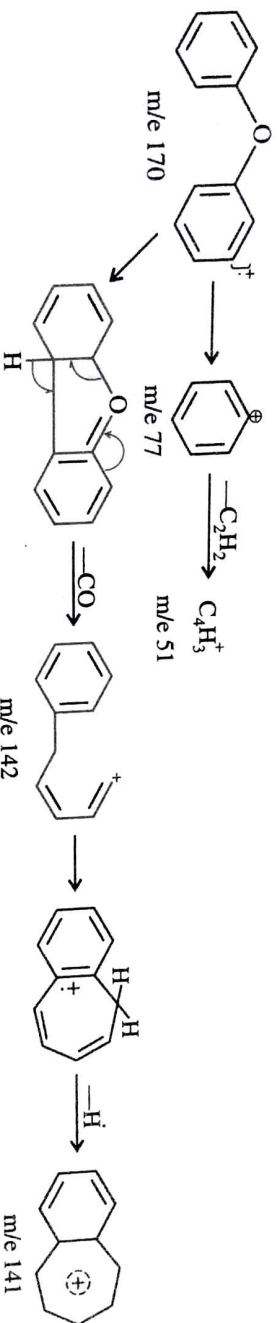
**SOLUTION.** It is known that in cyclic alkenes, a retro-Diels-Alder reaction gives, a charged diene fragment and neutral ethylene molecules. Clearly, the  $m/e$  value of diene gives a useful information about the position of the double bond. 3-Methyl cyclohexene gives a diene fragment as shown below:



4-Methyl cyclohexene does not form a diene fragment.

8. Describe the various fragmentation mode, of diphenyl ether.

**SOLUTION.** In diphenyl ether, the peak due to the ion formed by the loss of carbon monoxide is quite prominent. The various fragmentation modes are shown:



### 7.27 Short Questions with Answer

1. Define mass spectroscopy.

**Ans.** In mass spectroscopy, the vapours of the substance are bombarded with energetic electrons. The molecular ion and fragment ions are formed which are separated according to their  $m/e$  ratio. Mass spectrum of a substance is a plot between  $m/e$  values of the ions versus relative abundance.

2. What do you mean by the base peak ?

**Ans.** The most intense or the abundant peak in the mass spectrum of the compound is called the base peak.

3. Name some compounds in which the molecular ion peak is not often visible.

**Ans.** In case of alcohols, especially, tertiary alcohols and also in case of highly branched compounds, the molecular ion peak or the parent peak is not often visible.

4. What do you know about  $M^+$  and  $M^{+\cdot}$  ion ?

**Ans.**  $M^+$  is called the parent ion radical when the neutral gaseous molecule of the substance loses an electron.



All the organic compounds are even electron species.  $M^+$  ion is a cation which is trivalent carbon less one electron pair bond.



5. How a molecular ion is a powerful tool for structure determination ?

**Ans.** The molecular ion of an organic compound is no longer stable and thus tends to fragment. The various fragment ions formed are studied in the form of their  $m/e$  values against their relative abundances which provide an excellent tool for structural determination of the compound.

6. Do all the bonds in a molecular ion undergo fission ?

**Ans.** No. All the bonds in a molecular ion do not undergo fission. Some bonds break rapidly while others do not. The reason is that 70 eV energy may not be sufficient to break all the bonds.

7. At what pressure, the vapours of the given sample are introduced in the mass spectrometer? Explain.

**Ans.** The vapours of the substance under examination are introduced at low pressure ( $10^{-5} - 10^{-6}$  mm) in the spectrometer. The reason is that it is necessary to minimise the collisions between ions and the un-ionised molecules. Such collisions produce new ions which are difficult to interpret in the spectrum.

8. What is the most characteristic feature of compounds containing one bromine atom? Do fluorine and iodine containing compounds show the same feature in their mass spectra ? Give reasons.

**Ans.** The compound containing one bromine atom gives a pair of peaks of equal intensity separated by two mass units. The reason is that the isotopes  $^{79}\text{Br}$  and  $^{81}\text{Br}$  occur in equal abundance (ratio 1:1). Fluorine and iodine do not have isotopes and thus  $M + 2$  peak is not observed when fluorine or iodine atom is present in the compound.

9. What do you understand by Nitrogen rule ?

**Ans.** According to this rule, a molecule of even numbered molecular mass must contain no nitrogen atom or an even number of nitrogen atoms. An odd numbered molecular mass requires an odd number of nitrogen atoms.

10. Describe the importance of metastable peaks.

**Ans.** The metastable peaks in the mass spectrum greatly contribute in structure elucidation. From the position of the parent ion and the daughter ion, the position of the metastable ion is calculated and confirmed in the spectrum under examination. Metastable peaks are broadened and less intense. The most likely reason for this is that some of the excitation energy leading to bond capture may be converted into additional kinetic energy.

11. Predict the relative abundance of the parent ion in case of (i) Propane and (ii) *n*-Pentane.

**Ans.** The relative abundance of propane is more than that of *n*-Pentanes. The abundance of the molecular ion peak can be increased with respect to the abundance of fragment ions by running the spectrum at low ionisation potential, *i.e.*, by bombarding low energy electrons.

12. What is McLafferty rearrangement ?

**Ans.** The loss of an alkene fragment by a cyclic rearrangement of a carbonyl compound with  $\gamma$ -hydrogen is termed as McLafferty rearrangement.

13. What is typical in the mass spectrum of a compound containing (i) one bromine atom (ii) one chlorine atom?

**Ans.** In the mass spectrum of such a compound, pairs of peaks are formed for the molecular ion and the fragment ions at two units apart with a relative abundance equal to 1:1. Similarly, peaks are seen for a compound containing one Cl-atom but with a relative abundance of 3:1.







18. Predict about the most intense peaks which appear in case of straight chain and branched chain alkanes.

Ans. The most intense peaks for the straight chain and branched chain alkanes appear at  $m/e$  43 and  $m/e$  57 due to  $C_3H_7^+$  and  $C_4H_9^+$  ions. The relative abundance of parent ion peak decreases with the increase in the chain length. In case of branched chain, the parent ion peak is not observed.

19. What do you say about the molecular ion peak in the mass spectrum of alcohols ? Which peak is of largest abundance in primary alcohols ?

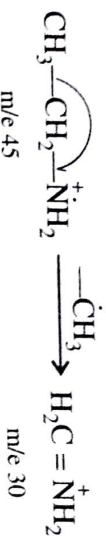
Ans. The molecular ion peak of primary and secondary alcohol is usually of low abundance and it is undetectable in tertiary alcohols. In primary alcohols, the signal at  $m/e$  31 appears in large abundance. This signal corresponds to the formation of oxonium ion ( $CH_2=OH^+$ ).

20. How will you characterise a primary amine by means of a mass spectrum ?

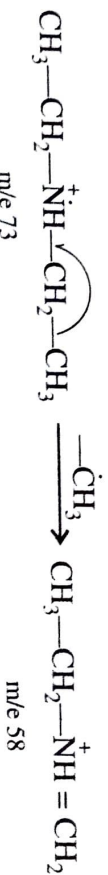
Ans. The molecular ion peak is formed at the odd number and also for the primary amine, the base peak appears at  $m/e$  30 due to  $CH_2=NH_2^+$ . It results from the molecular ion by  $\alpha$ -cleavage.

21. How would you distinguish between Ethylamine, diethylamine and triethylamine on the basis of mass spectroscopy ?

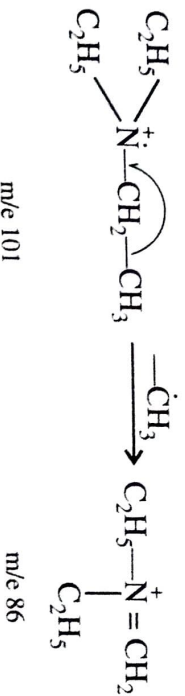
Ans. (i) In the case of ethylamine, the base peak is formed at  $m/e$  30.



(ii) In the mass spectrum of diethylamine, the intense peak at  $m/e$  58 is formed. It is due to the loss of methyl radical.



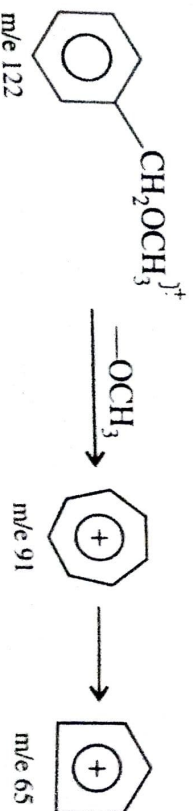
(iii) In case of triethylamine, the most intense peak is formed at  $m/e$  86 by the loss of methyl radical.



It may be noted that in each case, further fragmentation of this initially formed fragment ion produces a peak at  $m/e$  30.

22. Give the typical fragmentation pattern in benzyl methyl ether.

Ans. Benzyl methyl ether fragments by the loss of methoxy radical to give benzyl cation which rearranges to more stable tropylium cation. Thus the peak due to this is the base peak. It further fragments to give a peak at  $m/e$  65 due to  $C_5H_5^+$ .



23. In the mass spectrum of toluene, strong peaks are formed at  $m/e$  91 and  $m/e$  65. Also a broad peak appears at 46.4. Justify the origin of these signals.

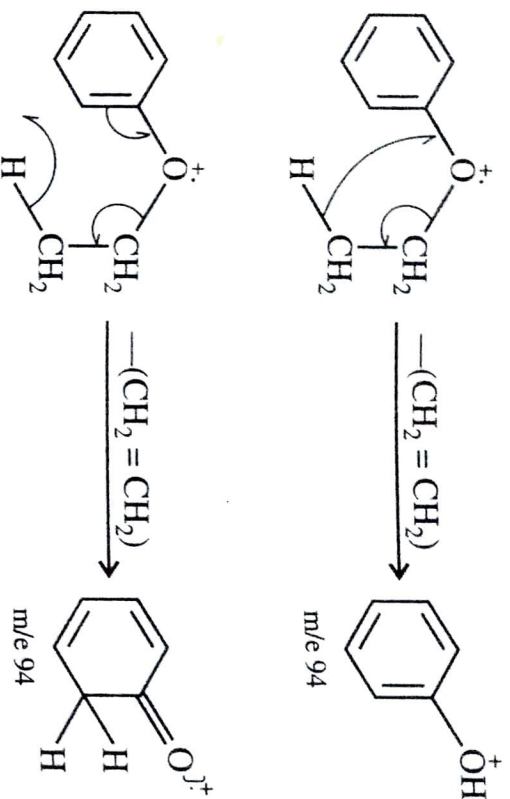




$m/e$  45. The  $\alpha$ -cleavage results in the formation of base peak at  $m/e$  30. The parent ion loses a hydrogen radical to give the signal at  $m/e$  44.

**27. How do you explain that  $m/e$  94 ion is formed in the mass spectrum of phenetol ?**

**Ans.** The peak of  $m/e$  94 is formed as a result of McLafferty rearrangement which can be shown below.



#### FURTHER READING

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by the use of mass spectrometry and the use of capillary GC/MS for metabolic profiling has led to the discovery of many specific enzymatic deficiencies over the past 25 years.

### 5.9.5 Geological applications

Many natural processes lead to small changes in the isotopic composition of elements from what are regarded as "normal". Since living organisms cease to take up  $^{14}\text{C}$  when they die, a determination of  $^{14}\text{C}$  content in a fossil reveals the date of death to within 1%. The  $^{34}\text{S}$  isotope is important in determining the origin of fossil fuels and the H/D ratio of water is latitude dependent so that pure tropical fruit juice may be distinguished from concentrations that have been diluted locally.

### Sample Problems

**Q. 1.** Do all the bonds in a molecular ion undergo fission?

*Sol.* All the bonds in the molecular ion do not undergo fragmentation. Some bonds do not break while other do so rapidly. This may be due to the insufficient energy being available at 70 eV, even if all the electron's impact energy was transferred to the  $\text{M}^+$  ion.

**Q. 2.** What happens when the energy of the ionising electrons is increased beyond 70 eV? Do more bonds undergo fragmentation?

*Sol.* If the energy of the electron beam is increased, no significant changes occur in the mass spectrum. Eventually, the second ionization energy is reached and  $\text{M}^{2+}$  ions are formed.

**Q. 3.** Since the Quasi-Equilibrium Theory predicts that the redistribution of smaller amounts of energy would occur more rapidly, the weak bond or bonds will fragment, reducing the overall energy and there will be insufficient vibrational energy left for any stronger bond to be broken. It is only the fragment ions which are prominent in the mass spectrum and characteristic of the structure. In many compounds, molecular ion peaks are either very weak or completely absent from the spectrum. Explain how to overcome this limitation.

*Sol.* The presence of weak molecular ions for many molecules or their complete absence means that unambiguous molecular weight information may be difficult to obtain under high energy (70 eV) electron ionization. This problem may be solved by lowering the electron energy and thus the internal energy distribution of the molecular ions, but this is the expense of absolute ion intensity. The preferred alternative is to use a soft ionization technique such as chemical ionization.

**Q. 4.** At what pressure, the sample vapour are introduced inside the mass spectrometer? Explain. *Sol.* Sample vapour are introduced at low pressure ( $10^{-5}$  –  $10^{-6}$  torr) in the spectrometer because it is necessary to minimize the number of collisions between ions and non-ionized molecules. These



collisions lead to reactions that yield new ions containing parts of collision partners and consequently cause some difficulty in spectral interpretation.

After ionization and fragmentation, what is the function of mass spectrometer to provide a mass spectrum?

The spectrometer sorts out all the cations (including the radical cation) according to their  $m/z$  values and records these values (decreasing from right to left) as line signals along the abscissa of the chart. At the same time the instrument records their relative abundances as signal heights plotted as intensities along the ordinate. The radicals are not detected.

What is the most characteristic feature of the mass spectra of compounds containing one bromine atom? Do fluorine and iodine containing compounds display the same feature in their mass spectra? Give reasons.

A compound containing one bromine atom exhibits a pair of peaks roughly of equal intensity, separated by two mass units, in the molecular ion region of the mass spectrum. This is due to the equal abundance of  $^{79}\text{Br}$  and  $^{81}\text{Br}$  isotopes. Fluorine and iodine are isotopically pure, hence no such  $M + 2$  peaks are observed in the spectra of compounds containing these elements.

Electron impact mass spectrometers are used in some cases, to produce negative ions. What alterations would have to be made to the source components and electrical connections for negative ion mass spectrometry?

The polarity of the electrical connection between the ion repeller and the first accelerating plate would have to be reversed. This would allow the negatively charged repeller to cause the negatively charged ions to move out of the ion source.

What is the condition for rapid energy distribution about the ionized molecule?

The ions have life times of  $10^{-5}$ – $10^{-6}$  s in the mass spectrometer source, while a molecular vibration of  $10^{10}$ – $10^{12}$  Hz takes  $10^{-10}$ – $10^{-12}$  s. This is true for about a million vibrations to take place before the molecular ion fragments. This initial excess energy is distributed rapidly around the various bonds of the molecular ion and consequently any of the bonds might break. This distribution of the initial input of the energy to the molecular ion is called Quasi-Equilibrium Theory (QET).

Suggest the structure of a compound with molecular formula  $\text{C}_{10}\text{H}_{12}\text{O}$ , whose mass spectrum shows peaks at  $m/z$  15, 43, 57, 91, 105 and 148.

- Sol.*
- The appearance of a peak at  $m/z$  15 suggests a methyl group.
  - Since the mass of the carbonyl group is 28, the peak at  $m/z$  43 ( $15 + 28 = 43$ ) indicates the presence of an acetyl group ( $\text{CH}_3\text{CO}$ ) in the compound.
  - The maximum  $m/z$  value at 148 shows its molecular weight.
  - The elimination of the acetyl group from the molecular gives  $m/z$  105 which is an observed peak in the spectrum.
  - The peak at  $m/z$  91 (150–14) suggests a  $\text{CH}_2$  group attached to  $\text{CH}_3\text{CO}$ . This shows the presence of the unit  $\text{CH}_3\text{COCH}_2$  (molecular weight = 57) leaving  $148-57 = 91$  to be explained.
  - The peak pertaining to  $m/z$  91 is likely to be  $\text{C}_7\text{H}_7$ , whose precursor is the stable benzyl cation  $\text{C}_6\text{H}_5-\overset{+}{\text{C}}\text{H}_2$ . Hence the suggested structure is  $\text{C}_6\text{H}_5-\text{CH}_2\text{CH}_2\text{COCH}_3$ .

(v) The peak at  $m/z$  91 (150–14) suggests a  $\text{CH}_2$  group attached to  $\text{CH}_3\text{CO}$ . This shows the presence of the unit  $\text{CH}_3\text{COCH}_2$  (molecular weight = 57) leaving  $148-57 = 91$  to be explained.

(vi) The peak pertaining to  $m/z$  91 is likely to be  $\text{C}_7\text{H}_7$ , whose precursor is the stable benzyl cation  $\text{C}_6\text{H}_5-\overset{+}{\text{C}}\text{H}_2$ . Hence the suggested structure is  $\text{C}_6\text{H}_5-\text{CH}_2\text{CH}_2\text{COCH}_3$ .

How will you distinguish among three isomeric butanols on the basis of mass spectrometry: 1-Butanol, 2-Butanol and 2-Methyl-2-propanol.

The three isomeric butanols are distinguished as described below:



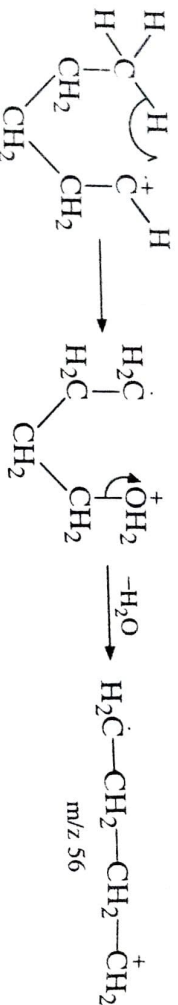
- 1-Butanol  
(Primary alcohol)
- 2-Butanol  
(Secondary alcohol)
- 2-Methyl-2-propanol  
(Tertiary alcohol)

Q. 10.

*Sol.*

The most general cleavage involves fission of C-COH bond, when the largest alkyl group is lost most readily. Hence the mass value for the base peak easily distinguishes the isomeric butanols.

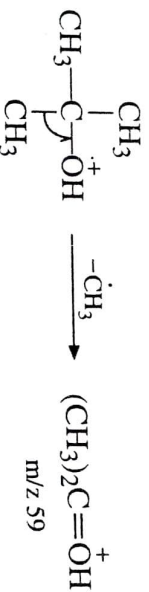
(i) In 1-butanol, the base peak, formed by the loss of water molecule, occurs at  $m/z$  56.



(ii) In 2-butanol, the base peak ( $m/z$  45) corresponds to cation formed by the loss of ethyl radical.



(iii) In 2-methyl-2-propanol (t-butyl alcohol), the base peak, formed by the loss of  $\text{CH}_3$ , occurs at  $m/z$  59.



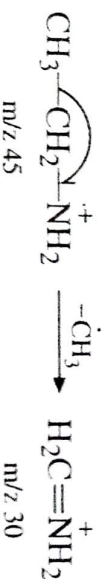
**Q. 11.** Describe some unusual aspects of amines which help in identifying them.

*Sol.* Amines present some unusual aspects which help in identifying them. They are as follows:

- An odd integral molecular weight of the compound indicates the presence of nitrogen.
- They have a high tendency to capture protons and the normally low ( $M + 1$ ) peak will increase in intensity if the pressure in the ion source is increased.
- If the amine is present in the form of salt, it does not usually volatilize in the mass spectrometer but decompose to give the free amine and the acid. If the acid component is HCl or HBr, then strong peaks at  $m/z$  36 and 38 (for HCl) and  $m/z$  80 and 82 (for HBr) will be obtained. These peaks are of importance because organic chloro and bromo compounds do not give these peaks in such abundance.

**Q. 12.** How would you distinguish among ethylamine, diethylamine and triethylamine on the basis of their mass spectral studies.

*Sol.* In the case of ethylamine, the most intense peak in the spectrum occurs at  $m/z$  30. This peak arises from  $\beta$ -cleavage

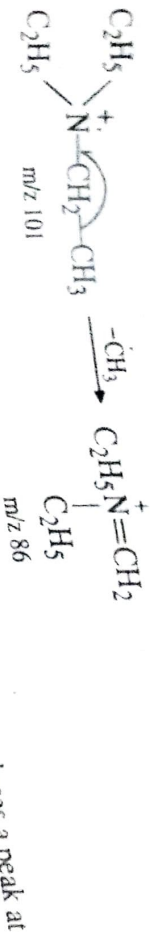


In the mass spectrum of diethylamine, the intense peak at  $m/z$  58 is due to the loss of methyl radical.



In triethylamine, the loss of methyl radical produces the most intense peak at  $m/z$  86.



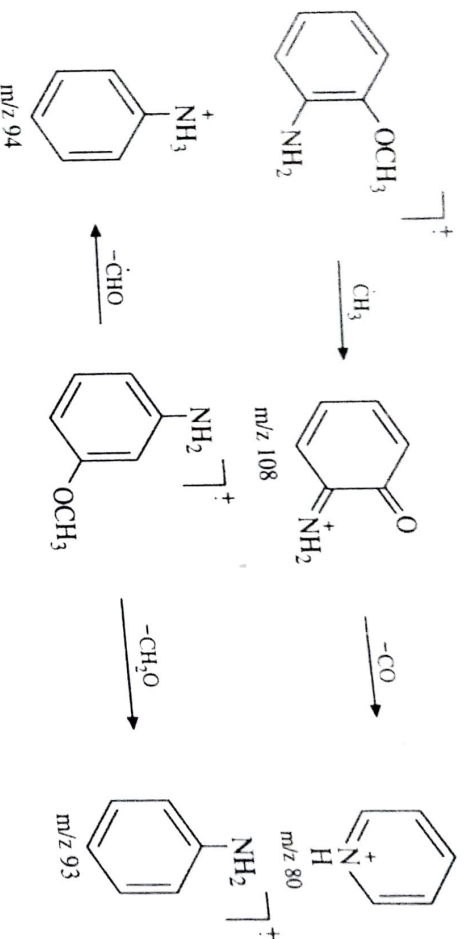


In each case, however, further fragmentation of this initially formed fragment ion produces a peak at  $m/z$  30

Q. 13. How would you distinguish between o- and m-anisidines on the basis of mass spectral studies. The (M-CH<sub>3</sub>) ion is a significant peak in the spectrum of o-anisidine whereas the loss of both CHO and CH<sub>2</sub>O occurs in m-anisidine.

Alkylamines exhibit the base peak at  $m/z$  106. Name the ion which is responsible for it and explain

Q. 14.



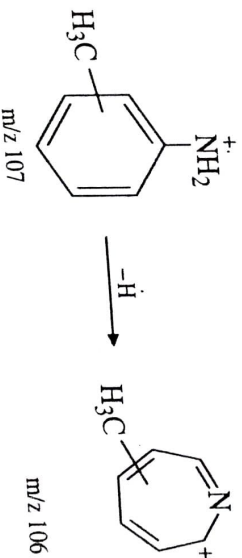
its formation.

The three isomeric alkyl anilines lose H to give  $m/z$  106 as the base peak and then lose HCN to give

$m/z$  79. The most likely explanation for this is the formation of azatropylium ion.

Q. 15.

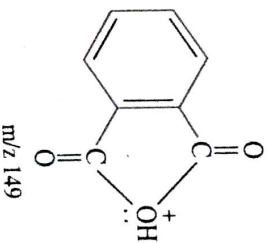
Write the formula of the compound which is responsible for the appearance of a strong characteristic



peak at  $m/z$  149 in the mass spectra of all esters of phthalic acid. Describe the mechanism of its formation starting from diethylphthalate.

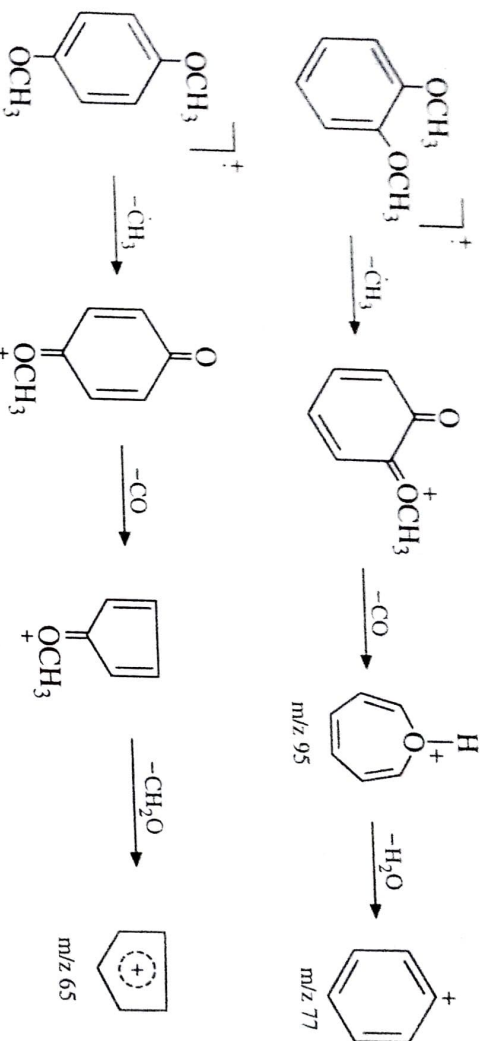
Sol.

The characteristic peak at  $m/z$  149 in all esters of phthalic acid is due to the formation of the following compound:

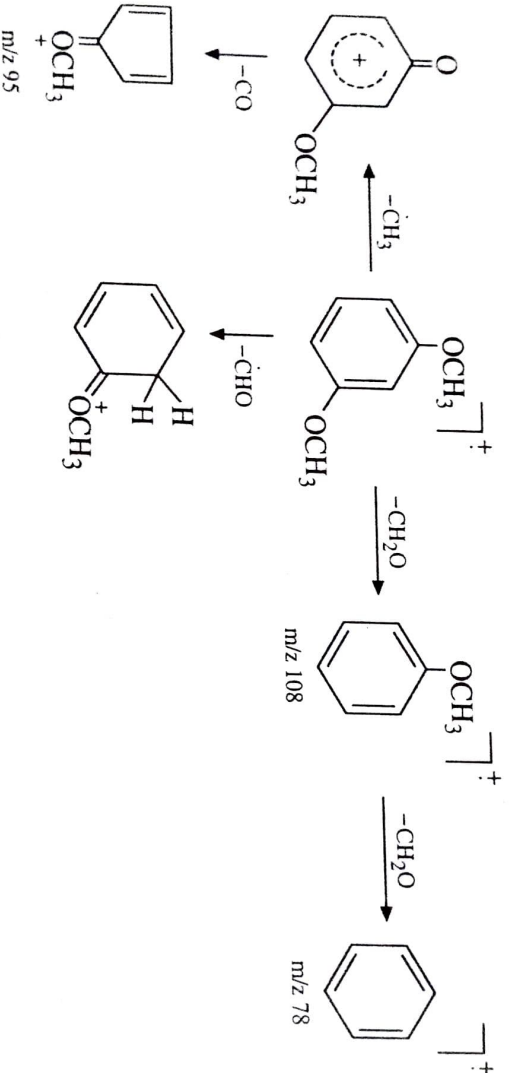


**Q. 16.**

How would you distinguish among *o*-, *m*-, *p*-dimethoxybenzenes on the basis of mass spectrometry. The *o*- and *p*-dimethoxybenzenes exhibit very little loss of formaldehyde. The ( $M-\text{CH}_3$ ) ion is abundant. This ion further eliminates a molecule of carbon monoxide.

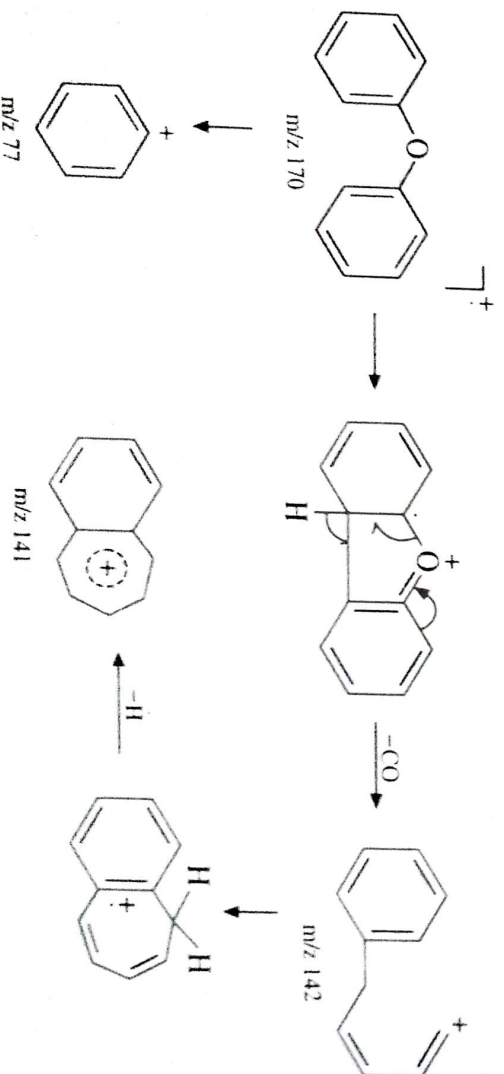


*m*-Dimethoxybenzene, however, shows loss of one and two molecules of formaldehyde and a minor loss of methyl radical, followed by the elimination of CO and a loss of CHO mass units, as described in the following scheme.



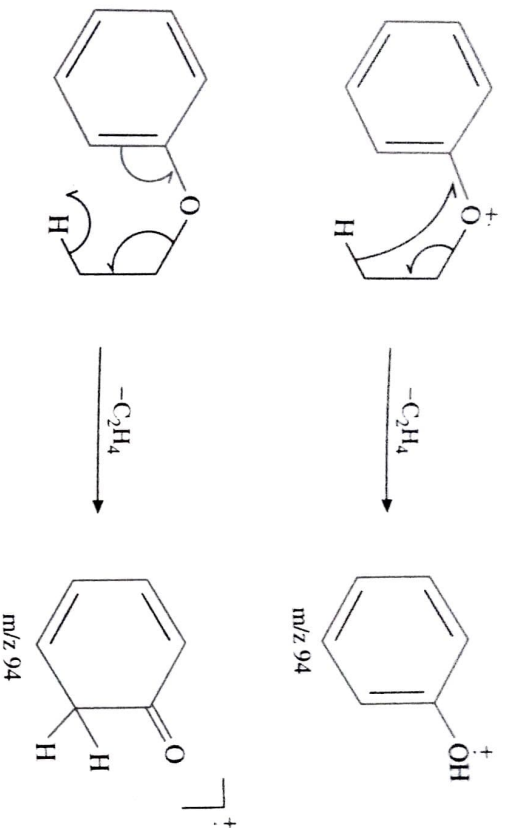
**Q. 17.**

**Sol.** Predict the fragmentation pattern of diphenyl ether. An interesting rearrangement process which operates in diphenyl ether is the loss of carbonmonoxide from the molecular ion.





Q. 18. How will you explain the formation of an ion at  $m/z$  94 in the mass spectrum of phenetole? A four or six centered McLafferty rearrangement can explain the formation of  $m/z$  94 ion, as described below:

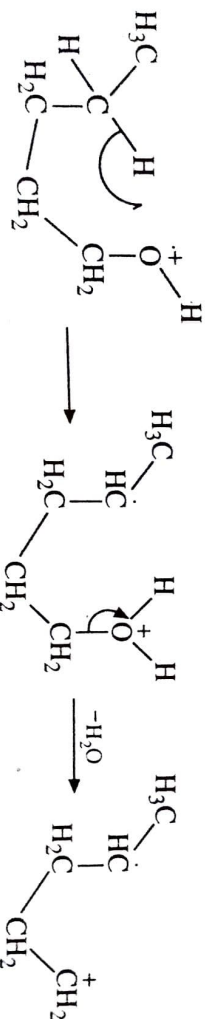


Q. 19. How will you account for the appearance of prominent peaks at  $m/z$  31, 42 and 70 in the mass spectrum of n-pentanol.

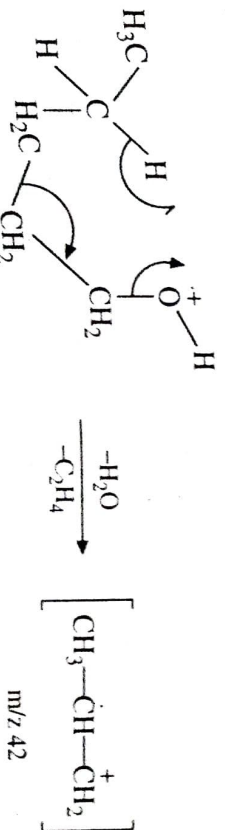
Sol. (i) The appearance of a prominent peak at  $m/z$  31 is due to the formation of  $CH_2 = \overset{+}{O}H$  as shown below:



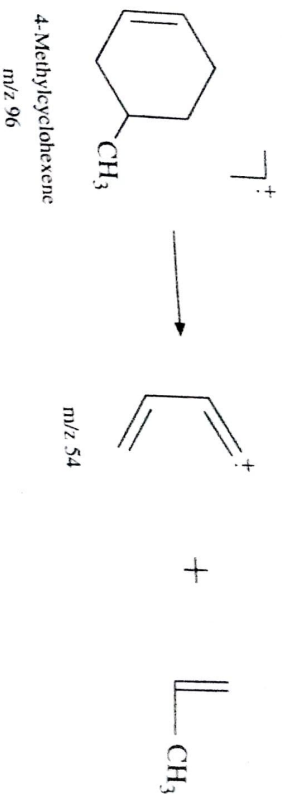
(ii) Another prominent peak at  $m/z$  70 in the mass spectrum of n-pentanol is due to the loss of water molecule. This elimination by electron impact has been rationalised as follows:



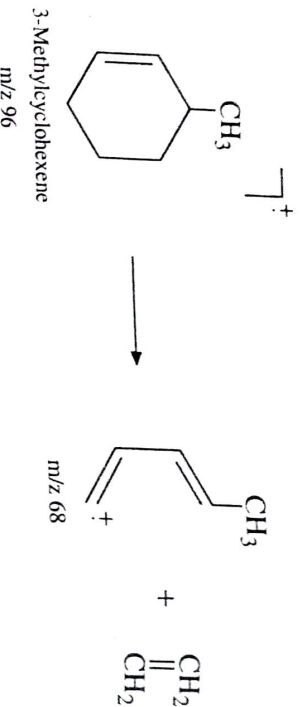
(iii) Elimination of water together with the elimination of ethylene from n-pentanol accounts for the presence of a peak at M-ethylene (28) + water (18) =  $M-46 = m/z$  42



Q. 20. How will you distinguish between 3-methyl and 4-methylcyclohexene on the basis of mass spectrometry? Sol. A retro-Diels-Alder reaction of 4-methylcyclohexene will eliminate butadiene fragment at  $m/z$  54



whereas a retro-Diels-Alder reaction of 3-methylcyclohexene gives a diene fragment at m/z 68 as depicted below:



2. 21.

How would you identify the presence of F or I by using mass spectrometric method?

High resolution mass spectrometry can be used to identify the presence of F or I because both F and I are mass deficient. The relative atomic mass of fluorine is 18.998495 and that of iodine is 126.904470. This means that the compounds containing F or I will usually have precise atomic masses, relative to  $^{12}\text{C}=12.0000$ , which are less than the nominal mass and hence can be identified. It is for this reason that polyfluoro compounds such as polyfluorokerosene (PEK),  $\text{CF}_3(\text{CF}_2)_n\text{CF}_3$  are used as calibrants in high resolution work. The ions from these polymeric mixtures turn up in regular series such as  $\text{CF}_3^+$ ,  $\text{CF}_3\text{CF}_2^+$ ,  $\text{CF}_3\text{CF}_2\text{CF}_2^+$  with m/z 69, 119 and 169 respectively. They are significantly mass deficient:

Ion	Accurate mass ( $^{12}\text{C} = 12.0000$ )
$\text{CF}_3^+$	68.99549
$\text{CF}_3\text{CF}_2^+$	118.99248
$\text{CF}_3(\text{CF}_2)_2^+$	168.98947

This deficiency takes them well out of the range of accurate masses expected for most organic compounds, i.e., their accurate atomic weights are less than a whole number, unlike the common elements, H and N which are mass proficient.

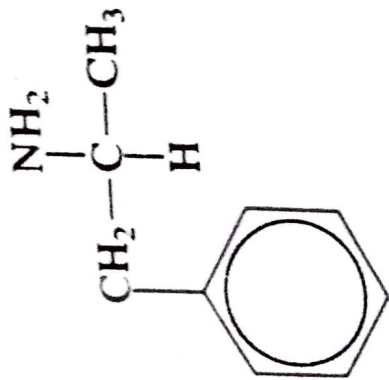
Predict the molecular formula of an organic compound which gives the following peaks in the isotopic clusters of its mass spectrum.

m/z	94	95	96	97
(Relative abundance)	(100)	(6.1)	(96)	(1.1)

The most intense peak is at m/z 94 and is the molecular ion peak. So the isotopic clusters of the compounds is given by:

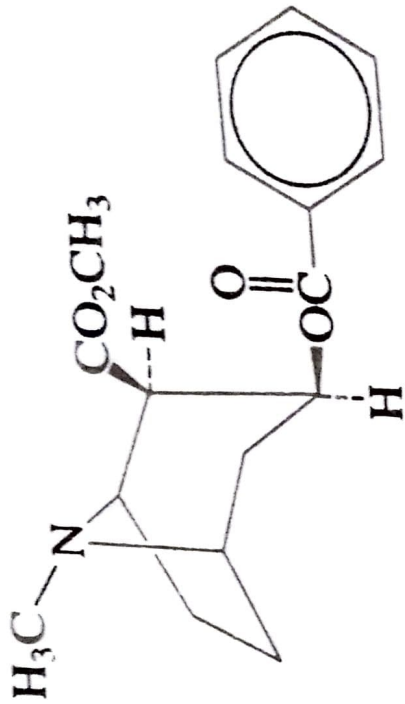
M	94	100
M + 1	95	6.1
M + 2	96	96
M + 3	97	1.1





**Amphetamine**

(Antidepressant, central nervous system stimulant.)



**Cocaine**

**Scheme 6.52**

## EXERCISES AND PROBLEMS

1. Attempt to assign structures to three compounds from their mass spectra (Fig. 6.35, I-III). Only the IR spectrum of II shows strong C=O band around  $1680\text{ cm}^{-1}$ .
2. A hydrocarbon with a molecular formula  $C_7H_{12}$  ( $M^{+}$  at  $m/z = 96$ ) shows large peaks due to (M-15) and at  $m/z = 54$ . What structure can be assigned to this compound.
3. How can one do distinction between 3-methyl and 4-methyl-cyclohexene on the basis of mass spectroscopy.

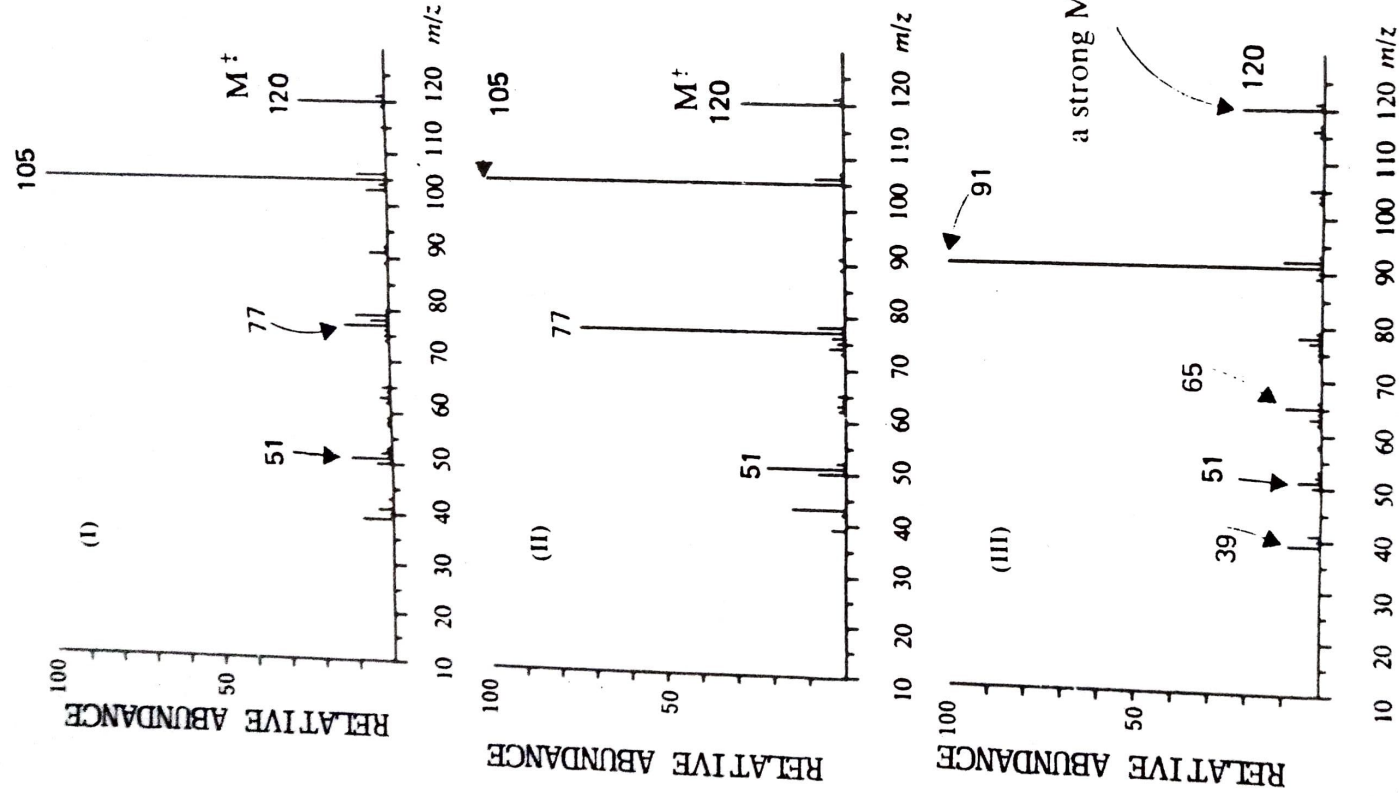


Fig. 6.35

- The mass spectrum of 1-hexanol gives a base peak at  $m/z = 56$ . How can one account for this?
- A compound with the molecular formula  $C_9H_{10}O_2$  (Molecular weight = 150.0681) has the following structure (*O*-methyl toluate). How mass spectral fragmentation confirms this?



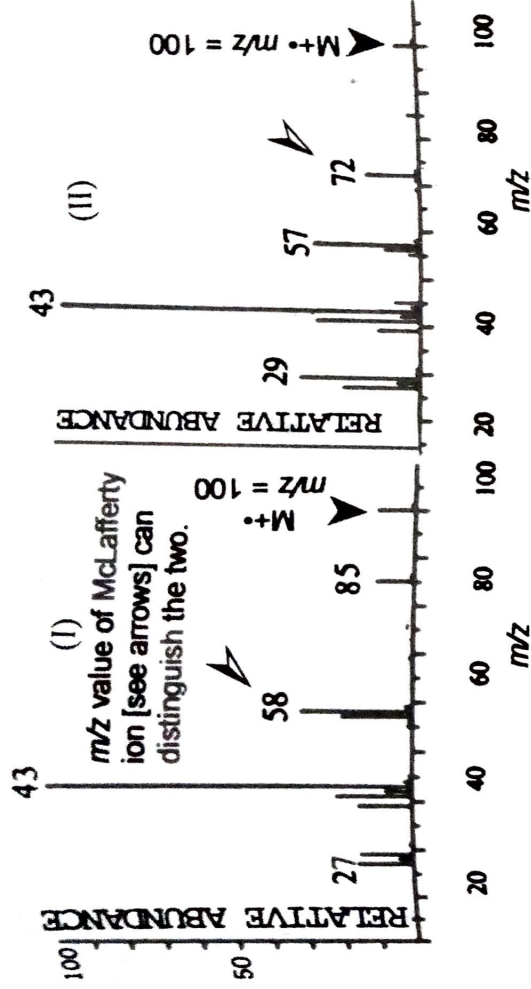
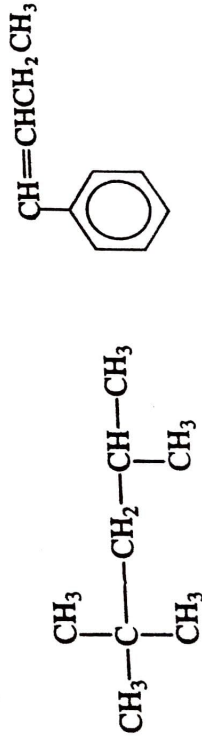


Fig. 6.36

- The mass spectra (Fig. 6.36, I and II) are of the isomeric ketones, 3- and 4-methyl-2-pentanone. How can you do a distinction between the two? (Hint account for the peaks marked with arrows).
- Predict the fragmentation in the following compounds from their molecular ions.
  - Benzyl acetate
  - 2-Ethylphenol
  - 1-Phenylethanol.
- How can you use the information of *ortho* effect to explain the formation of the ion  $m/z = 149$  in the esters of phthalic acid.
- Ethyl butanoate in its mass spectrum show two characteristic peaks due to odd-electron ions at  $m/z = 88$  and  $60$  and an abundant ion at  $m/z = 71$ . Explain the fragmentation.
- If in a tertiary amine  $R^1-CH_2NR^2R^3$ ,  $R^1 > R^2 > R^3$  and if  $R^2 = CH_3$  and  $R^3 = C_2H_5$ , explain the formation of an ion  $m/z = 44$  on its fragmentation.
- By examining the structures of the following alkane and a cinnamyl compound, how one is guided to the predominant fragmentation of their molecular ions?



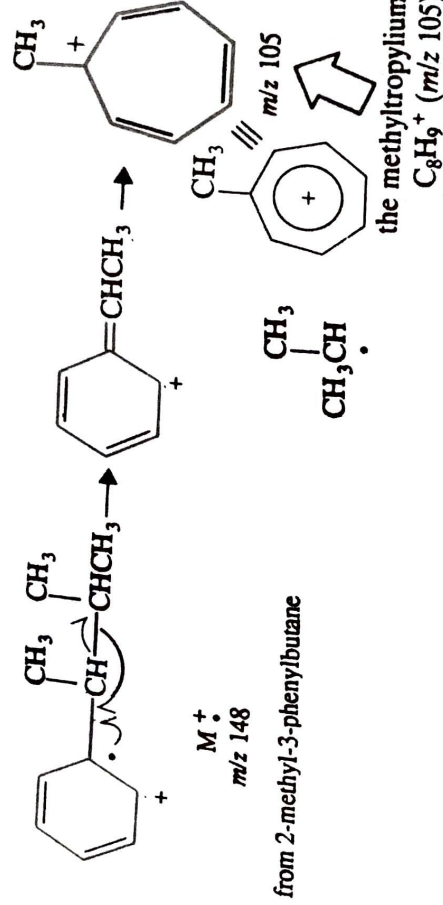
- Loss of  $H_2O$  from an alkyl alcohol shows the presence of a hydrogen on a  $\gamma$ - or  $\delta$ -carbon atom. This process is also common to thiols which eject  $H_2S$ . Amines however, do not eliminate  $NH_3$ , why?



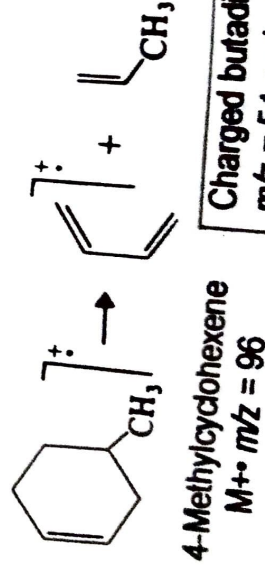
13. Comment on the typical fragmentation of benzyl methyl ether. How alkyl benzyl amines fragment?

## ANSWERS TO THE PROBLEMS

1. Spectrum (II) is of acetophenone. An organic compound with a phenyl moiety will give a prominent peak at  $m/z = 77$ ; those having benzyl moiety at  $m/z = 91$  and either  $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2$ -,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)$ - or  $\text{C}_6\text{H}_5\text{CO}$ - at  $m/z = 105$ . The mass spectrum (III) thus represents *n*-propylbenzene ( $\text{C}_6\text{H}_5\text{CH}_2\text{-CH}_2\text{-CH}_3$ ). The molecular ion of 2-methyl-3-phenylbutane fragments as shown to give a base peak at  $m/z$  105. This can also be true of isopropyl benzene, thus (I) is isopropylbenzene.

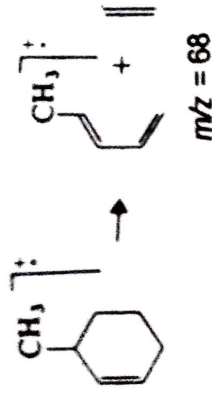


2. The index of hydrogen deficiency in this compound is two (an alkane with seven carbon atoms would be  $\text{C}_7\text{H}_{16}$ , the difference  $\text{C}_7\text{H}_{16} - \text{C}_7\text{H}_{12}$  is four hydrogen atoms, thus the index of hydrogen deficiency is two). The large ( $M-15$ ) points to the presence of a branched methyl group. The peak at  $m/z = 54$  is due to  $\text{C}_4\text{H}_6$ , i.e., butadiene. A retro-Diels-Alder reaction will eliminate charged butadiene fragment  $m/z = 54$  from a cyclic alkene and the presence of a cycloalkene is in keeping with the index of hydrogen deficiency. The compound is 4-methylcyclohexene.



3. In cyclic alkenes a retro-Diels-Alder reaction gives a charged diene fragment and an unchanged ethylene fragment. The  $m/z$  of the charged diene fragment then gives useful information on the position of double bond. Thus unlike 4-methylcyclohexene 3-methylcyclohexene gives a charged diene fragment, with  $m/z = 68$ .





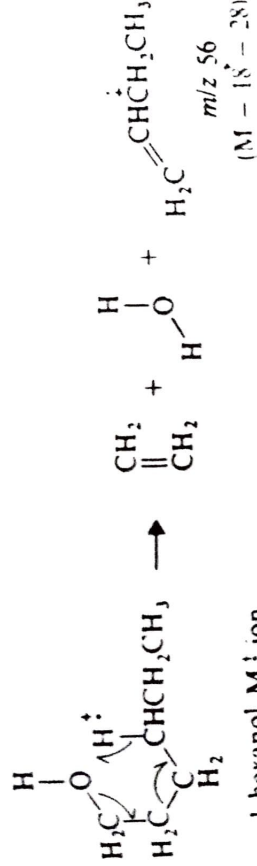
A charged butadiene system  $m/z = 68$  and ethylene.

$m/z = 68$

### 3-Methylcyclohexene

$M^{+\bullet}$   $m/z = 96$

4. This peak results from the elimination of water as well as ethylene (M-46) from the molecular ion of 1-hexanol via a six-centred mechanism in a concerted reaction.

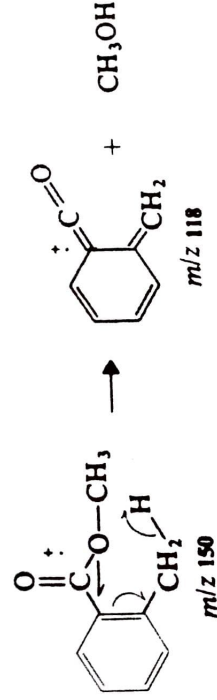


$m/z$  56

( $M - 18 - 28$ )

1-hexanol  $M^+$  ion

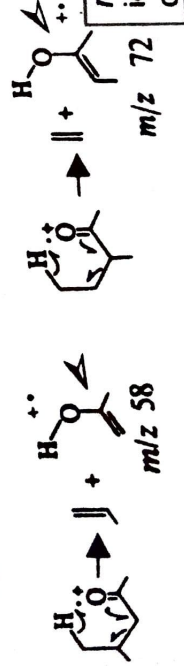
5. The compound has an alkyl aromatic system, thus strong peaks at  $m/z = 91$  and 65 will appear. Large peaks at  $m/z = 118$  and 119 will be due to loss of 32 and 31 amu. The  $m/z = 119$  is the loss of  $OCH_3$ , and the loss of  $CH_3OH$  to give  $m/z = 118$  can occur only if the compound is an *ortho* ester (*ortho* effect).



$m/z$  150

$m/z$  118

6. Both the ketones are methyl ketones as revealed by peak at  $m/z = 43$ . Spectrum (I), represents 4-methyl-2-pentanone while (II) is of 3-methyl-2-pentanone. Both the ketones have a  $\gamma$ -hydrogen and will undergo McLafferty rearrangement.



$m/z$  value of McLafferty ion [see arrows] can distinguish the two.

$m/z$  72

$m/z$  58

Loss of propylene ( $CH_3-CH=CH_2$  in (I)) will give an prominent peak at  $m/z = 58$ , while loss of ethylene ( $CH_2=CH_2$ ) in (II) will lead to a peak at  $m/z = 72$ . Since both are methyl ketones, the  $\alpha$ -cleavage (loss of larger alkyl group) in both leads to base peak at  $m/z = 43$ .







## SUMMARY

1. Mass spectrometer ionises molecules, sorts the ions according to their masses and gives a record of the abundance of ions of each mass: charge ratio ( $m/z$ ) (formerly  $m/e$ ).
2. Some compounds, e.g., alcohols may fail to give a visible molecular ion peak.
3. The ion (in mass spectrometry) with the same mass as the molecular weight of the original compound (*i.e.*, before the fragmentation) is called the molecular ion. The molecular ion has usually the highest  $m/z$  value in the spectrum, with the exception of a characteristic group of peaks at  $m/z$  values of  $M + 1$ ,  $M + 2$ , etc. (these are isotope peaks). Peaks in the mass spectrum are sharp and appear at integral mass values (the peaks due to doubly charged ions are exception). The peaks which are broad, spread over several mass units and are of low intensity are metastable peaks which give useful information about the mode of fragmentation.
4. The most intense peak in the spectrum is called the base peak.
5. The molecular ion  $M^{+}$  is not to be confused with a carbocation  $M^{+}$  containing a trivalent carbon less one electron pair bond.
6. The molecular ion (of an organic compound) is no longer as stable and will tend to fragment. It is this fragmentation, *i.e.*, breaking apart of the molecular ion that one studies and is a powerful structural tool. The molecular ion ( $M^{+}$ ) peak is often weak or nonexistent when the fragmentation is facile. This peak is small or nonexistent e.g., in the spectra of alcohols and amines since stable cations, oxonium or iminium ions are formed during their fragmentation.

In addition to EI method CI technique is promising to locate molecular ion peak. Field desorption (FD) method is used to record the mass spectra of non-volatile samples. The fast bombardment method FAB is used for polar molecules.

7. The exact mass, found by HRMS may be compared with tables to find the molecular formulas which are close to the experimental value.

8. There are two major types of fragmentations. In the first a neutral molecule (e.g.,  $H_2O$ ,  $C_2H_4$ ,  $CO$ ,  $HCl$ ,  $HCN$  and  $H_2S$ ) is eliminated. This loss of a neutral molecule gives a new fragment whose mass number has the same parity, *i.e.*, odd or evenness as the parent; the second fragmentation process involves a separation into the ion part and the radical part and this process changes that parity. Elimination of neutral fragments gives new radical cations which are termed odd electron fragments while those formed by the elimination of a free radical are termed even electron fragments. This rule may prove useful in deciding the mode of fragmentation.

9. The loss of an alkene fragment by a cyclic rearrangement of a carbonyl compound with  $\gamma$ -hydrogens is termed McLafferty rearrangement.

10. Some typical features may be helpful, *i.e.*, if the  $M + 2$  peak of the parent ion looks larger than the  $M + 1$  peak, the compound might contain S, Cl or Br. When there is a larger gap and a peak at 127, iodine may be present.

11. The intensity of the  $M + 1$  peak can be used to know the number of carbon as well as nitrogen atoms. In the absence of nitrogen, the maximum number of carbon atoms can be calculated by dividing the relative intensity of the  $M + 1$  peak by 1.1. Thus, e.g., a molecule with twelve carbon atoms will display a  $M + 1$  peak of 13.2 per cent. In case nitrogen is present its contribution to the  $M + 1$  peak will amount of  $0.4 \times$



- number of nitrogen atoms. This quantity must be subtracted from the measured relative intensity of the  $M + 1$  peak to know the number of carbon atoms.
- When in a compound Cl, Br, S or Si is present loss of a proton from the  $M + 2$  is likely to enhance the intensity of the  $M + 1$  peak. In the case of halogens, chlorine and bromine, there are two isotopes with substantial natural abundance which can lead to some rather distinctive patterns of peaks (spaced at intervals of two mass units) near the molecular ion peak. Thus the recognition of halogenated compounds from the characteristic patterns of these peaks can be done. Therefore, a compound which contains two chlorine or two bromine atoms or one chlorine and one bromine atom will display a distinct  $M + 4$  peak in addition of  $M + 2$  peak.
  - The number of nitrogen atoms present can be deduced with the help of nitrogen rule. When a molecule or ion contains an odd number of nitrogen atoms it will have an odd numerical value for the molecular weight. On the other hand, when the number of nitrogen atoms is even or zero, the molecular weight will be even numbered. The rule applies to the organic compounds containing C, H, O, N, S halogens, P, B, Si. In other words, in the case of species with either zero or an even number of nitrogens, odd electron ions will have an even mass number and even electron ions will have an odd mass number.

## FURTHER READINGS

1. McLafferty and F. Turecek, *Interpretation of Mass Spectra*, 4th ed., University Science Books, Mill Valley, CA, 1993.
2. D.H. Williams, and R.D. Bowen, *Mass Spectrometry. Principles and Applications*, 2nd ed., McGraw-Hill Book Co., London 1981.