

Fig. 3. Fragmentation of n-alkanes

The fragments that are probably to have been found in the mass spectra of n-alkanes are represented by the form described above.

Branched chain alkanes

Some important features of the mass spectra of branched chain alkanes are:

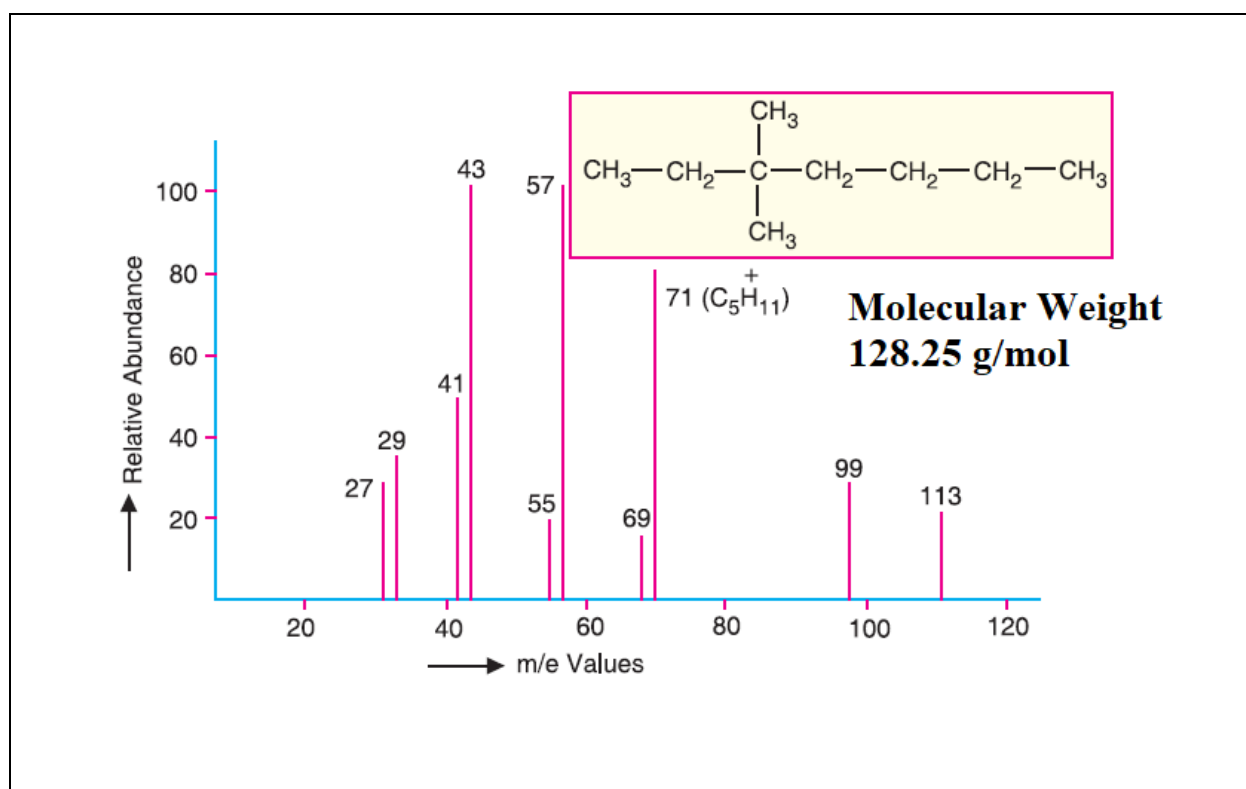
(1) Bond cleavage takes place preferably at the site of branching. Due to such cleavage, a more stable secondary or tertiary carbonium ion results.

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

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

(4) 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.

(5) 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.

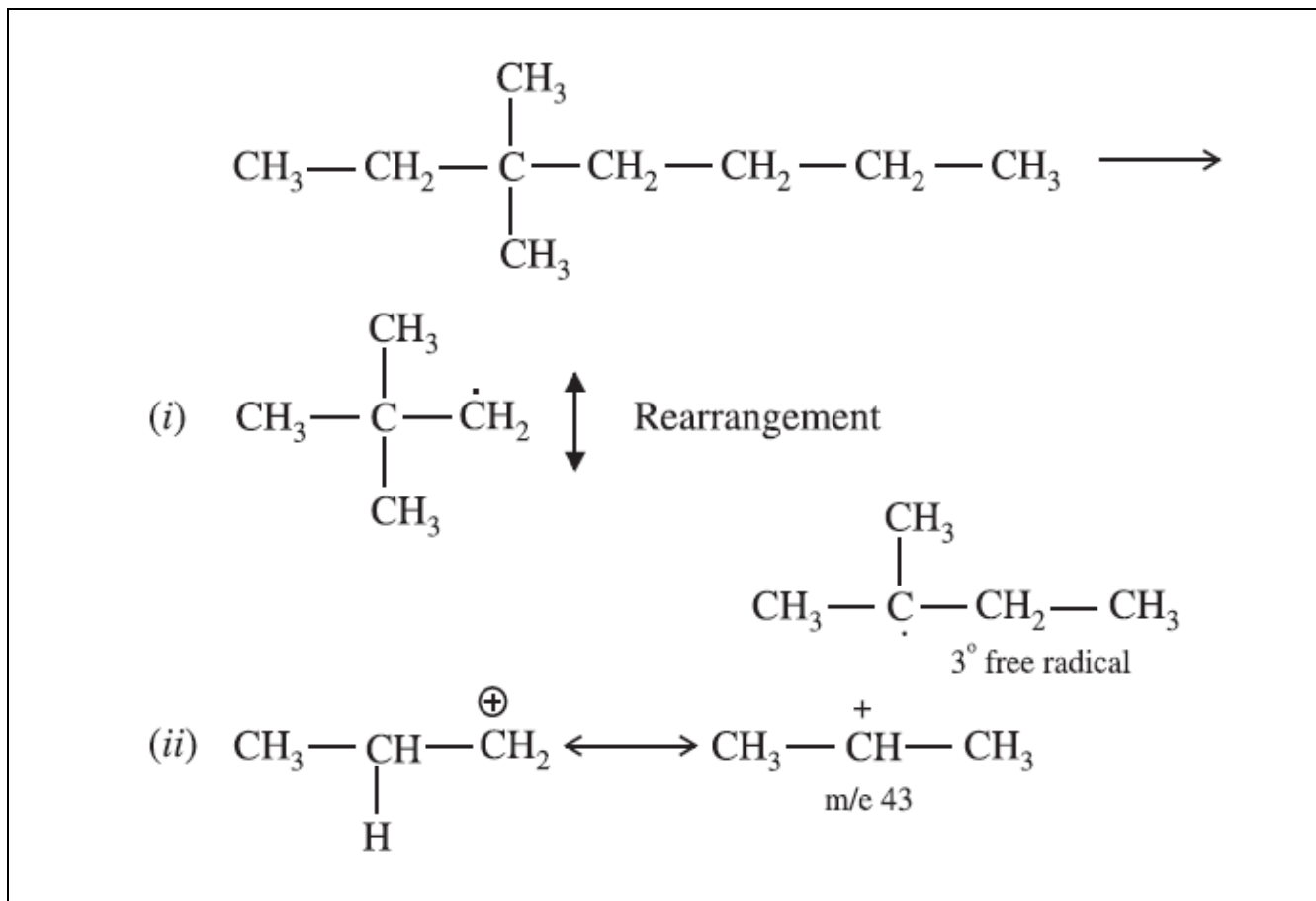


Explanation. 1- As expected, the loss of tertiary free radical forms a peak due to $C_4H_9^+$ ion at m/e 57.

2- Also the loss of n-butyl free radical results in the formation of tertiary carbonium ion at m/e 71 in much abundance.

3- The peak at m/e 71 is formed due to the loss of methyl radical in less abundance.

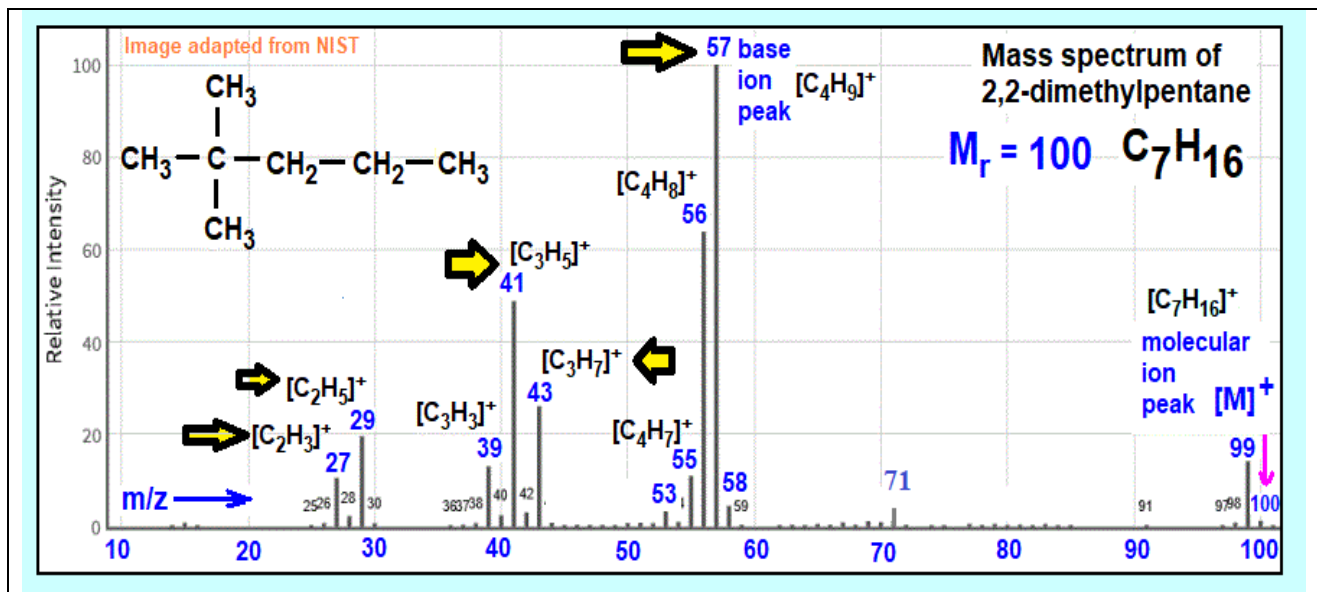
4- As expected, the branched chain compound does not form any molecular ion. The much abundant peak at m/e 43 ($C_3H_7^+$) is formed due to the loss of most stable free radical.

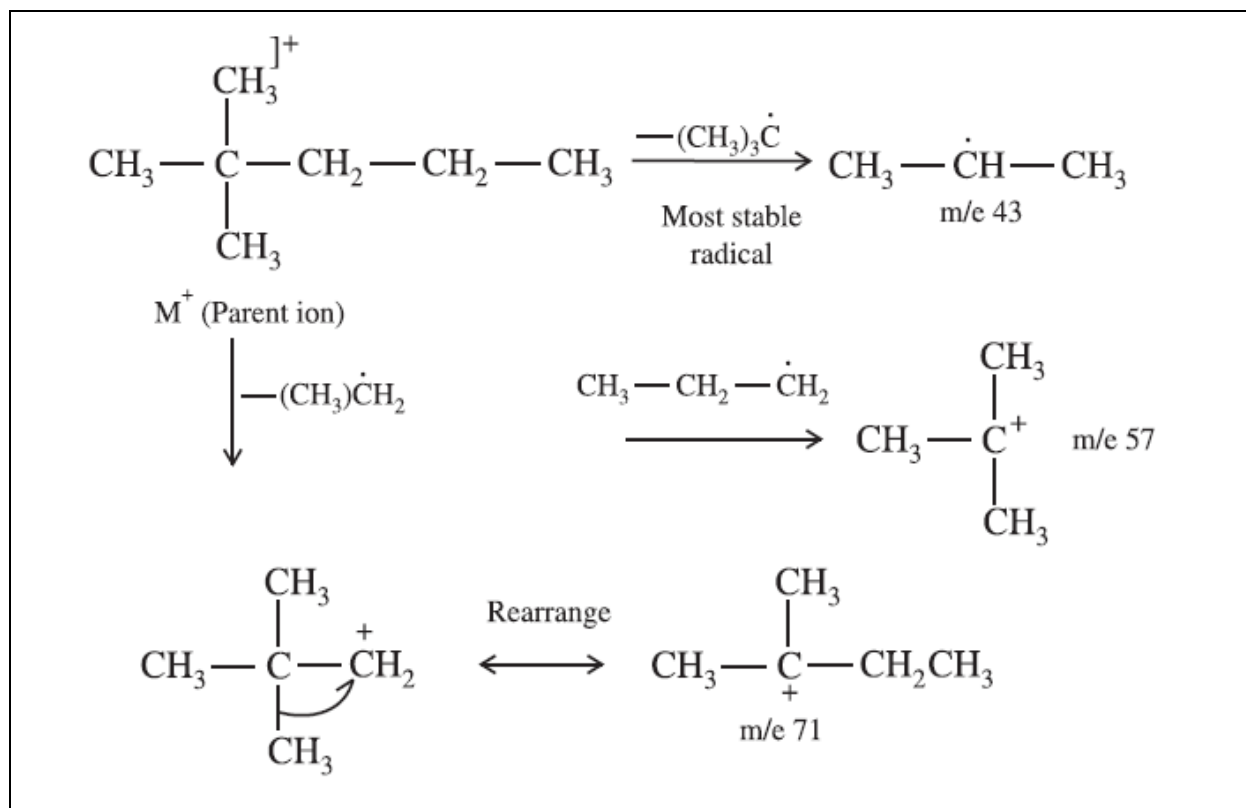


the mass spectrum of 2, 2 dimethyl pentane. Some important peaks of this spectrum can be predicted as follows:

- (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 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) { $H_2C=CH-$ (ethenyl or commonly known as vinyl). The parent alkene was $H_2C=CH_2$, ethene. }.





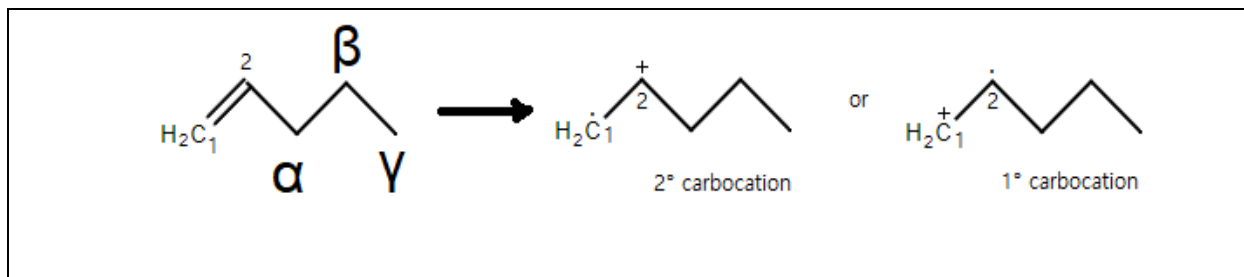
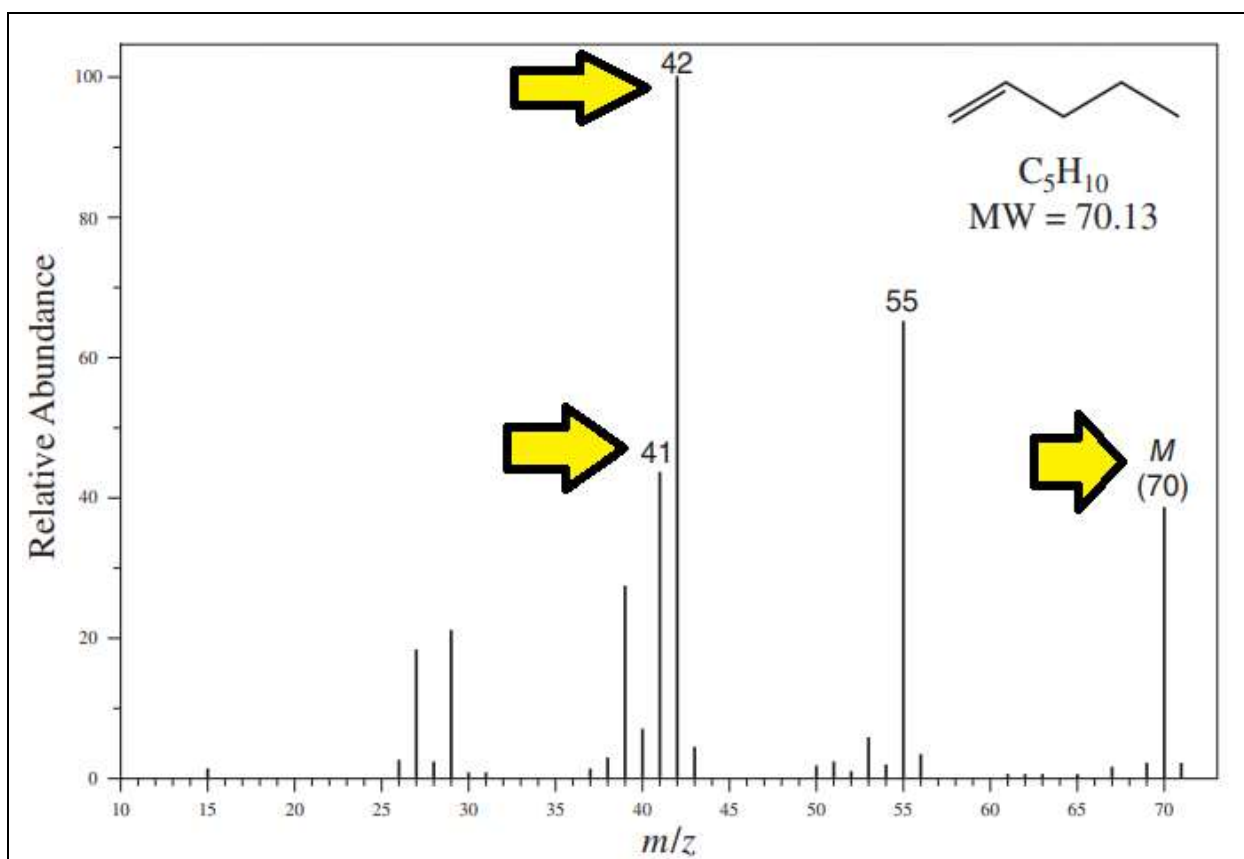
Alkenes (Olefins)

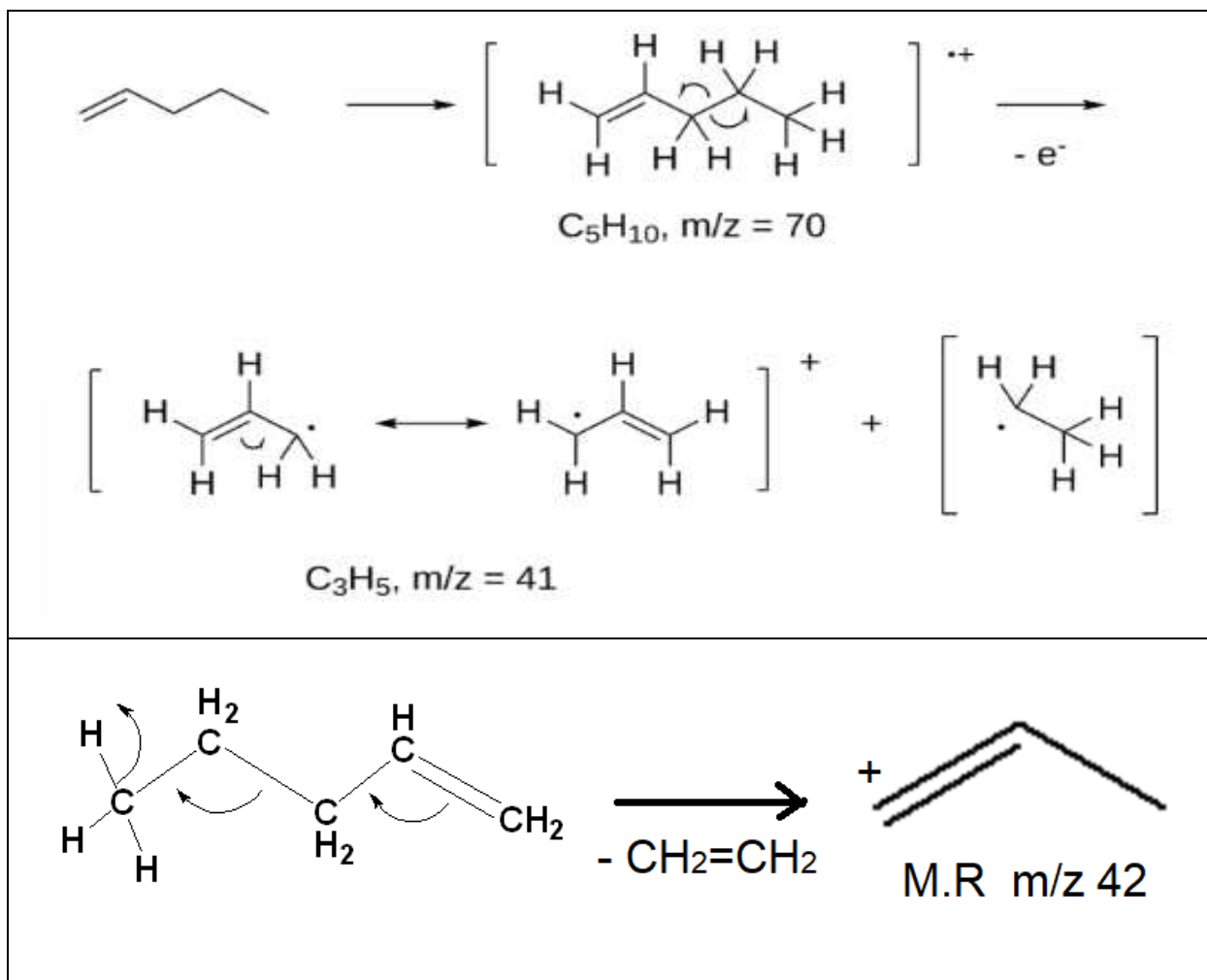
Some important features of the mass spectra of olefins are:

- (1) The molecular ion peak in the spectra of unsaturated compounds is more intense than the corresponding saturated analogues. The reason is the better resonance stabilisation of the charge on the cation formed by the removal of one of the π -electrons.
- (2) The relative abundance of the molecular ion peak decreases with increasing molecular mass.
- (3) A cyclic olefine also shows group of peaks which are 14 mass units apart.

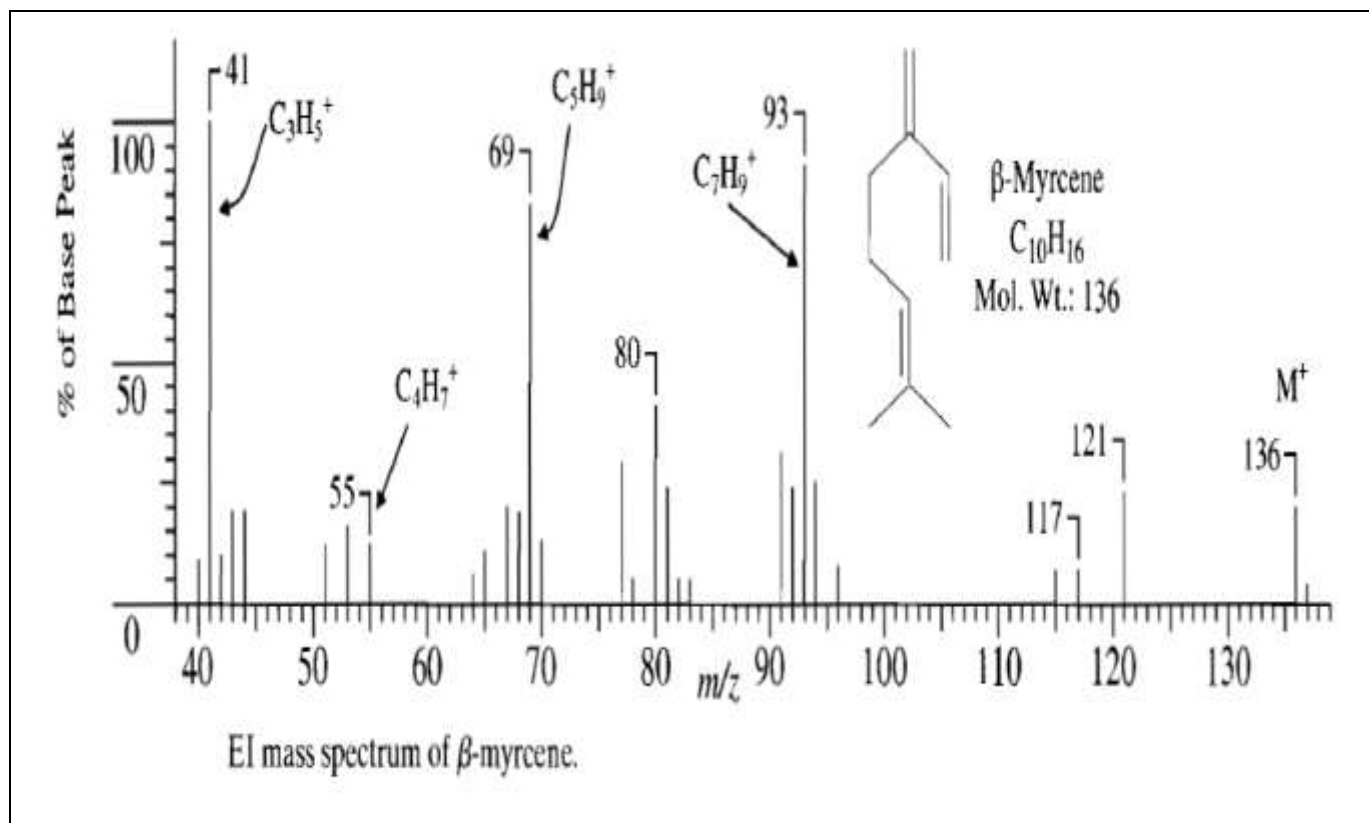
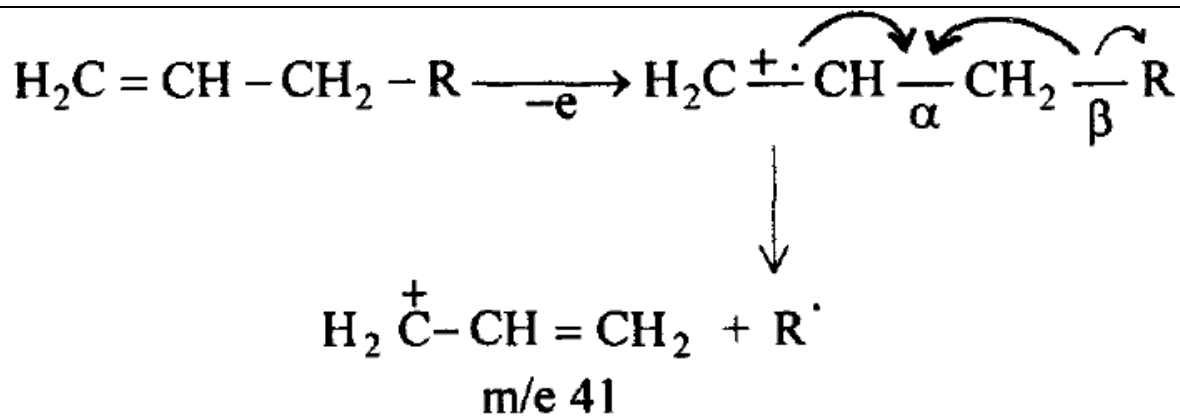
(4) The general mode of fragmentation induced by a double bond is the allylic cleavage.

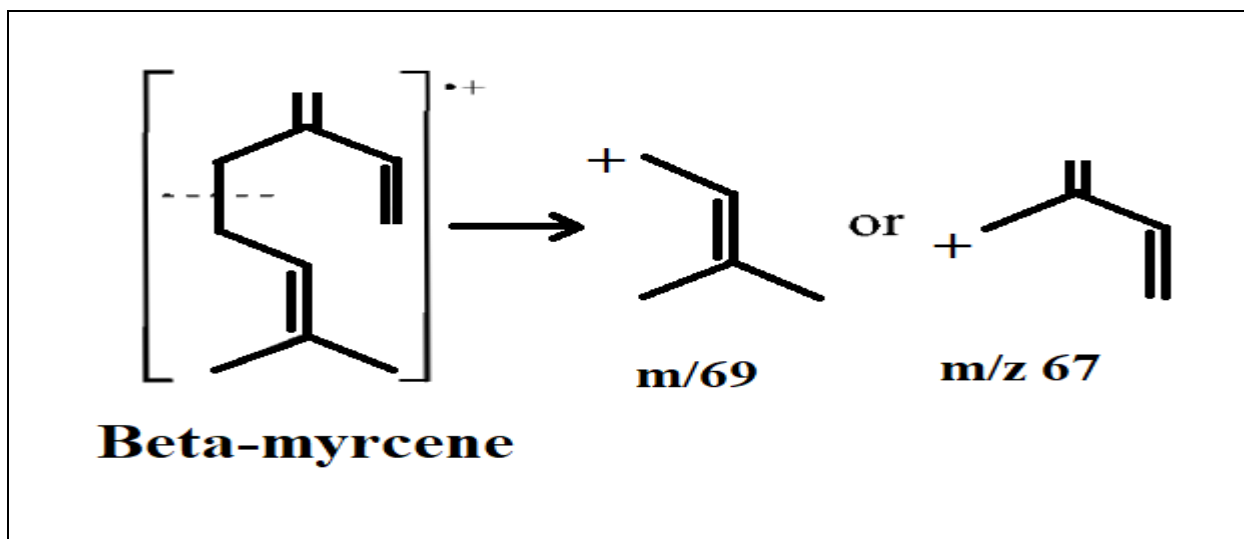
(5) The C_nH_{2n} ions (fragments) formed by McLafferty rearrangement are more intense. For example, Mc Lafferty rearrangement ion is formed at m/e 42 from 1-pentene due to the loss of ethylene molecule.





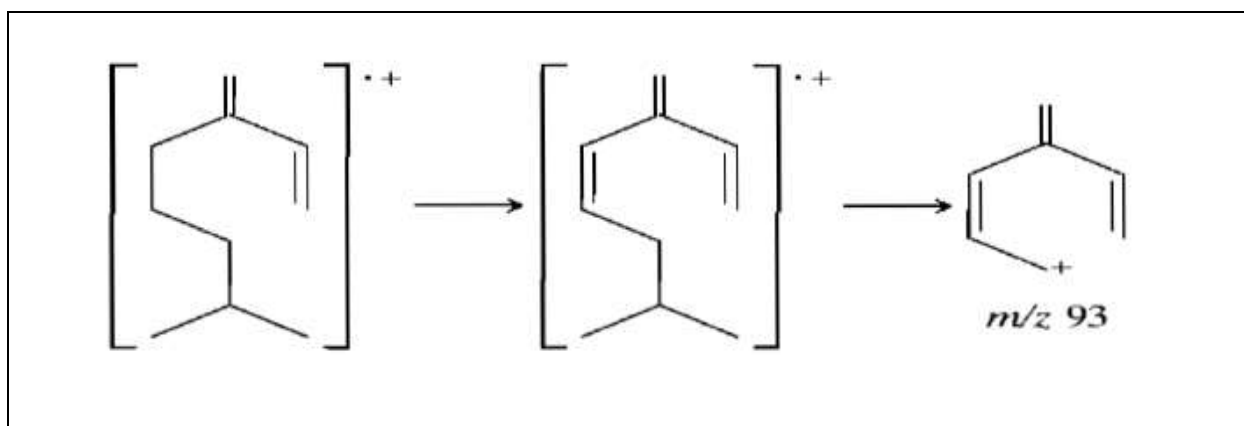
(6) The natural outcome of allylic cleavage is a series of fragments at masses 41,55,69, 83, with the general formula $\text{C}_n\text{H}^+_{2n-1}$ (allyl carbonium ions)

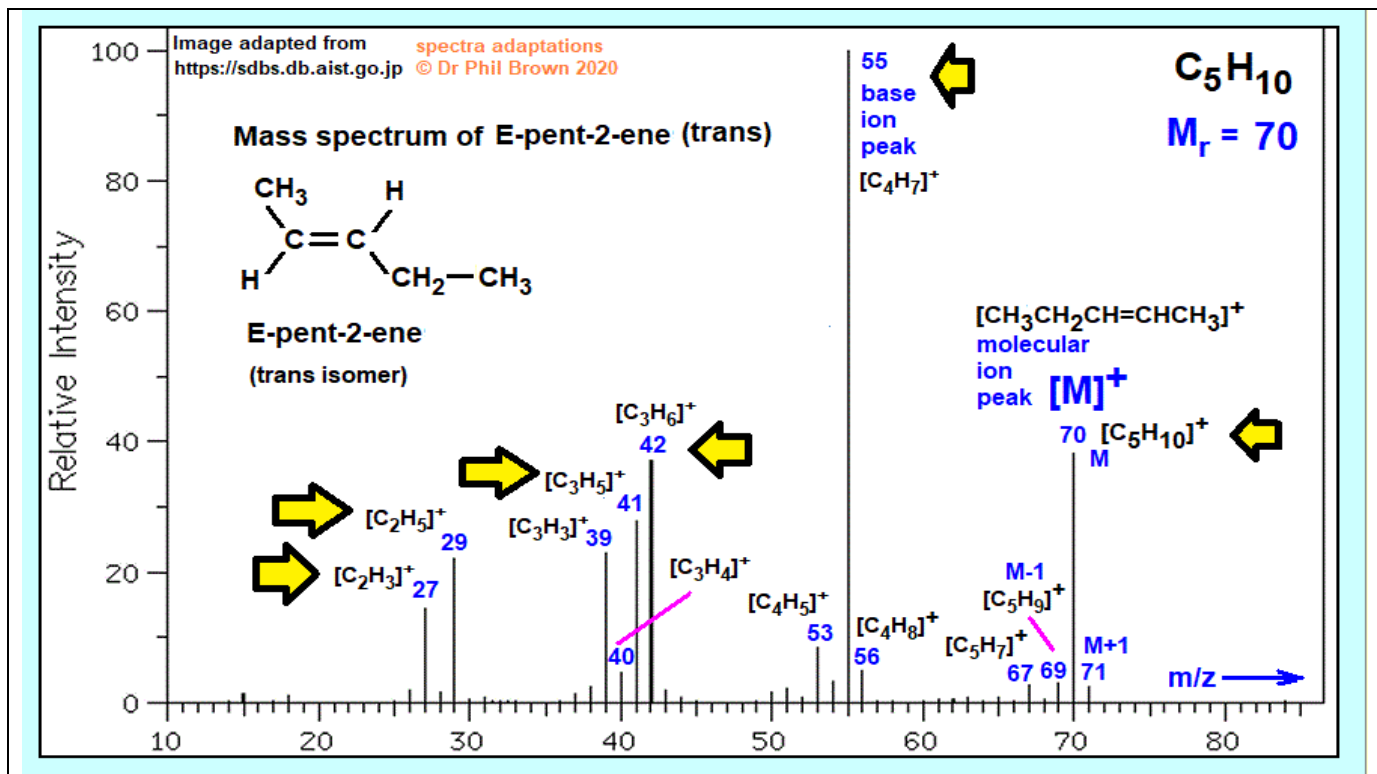




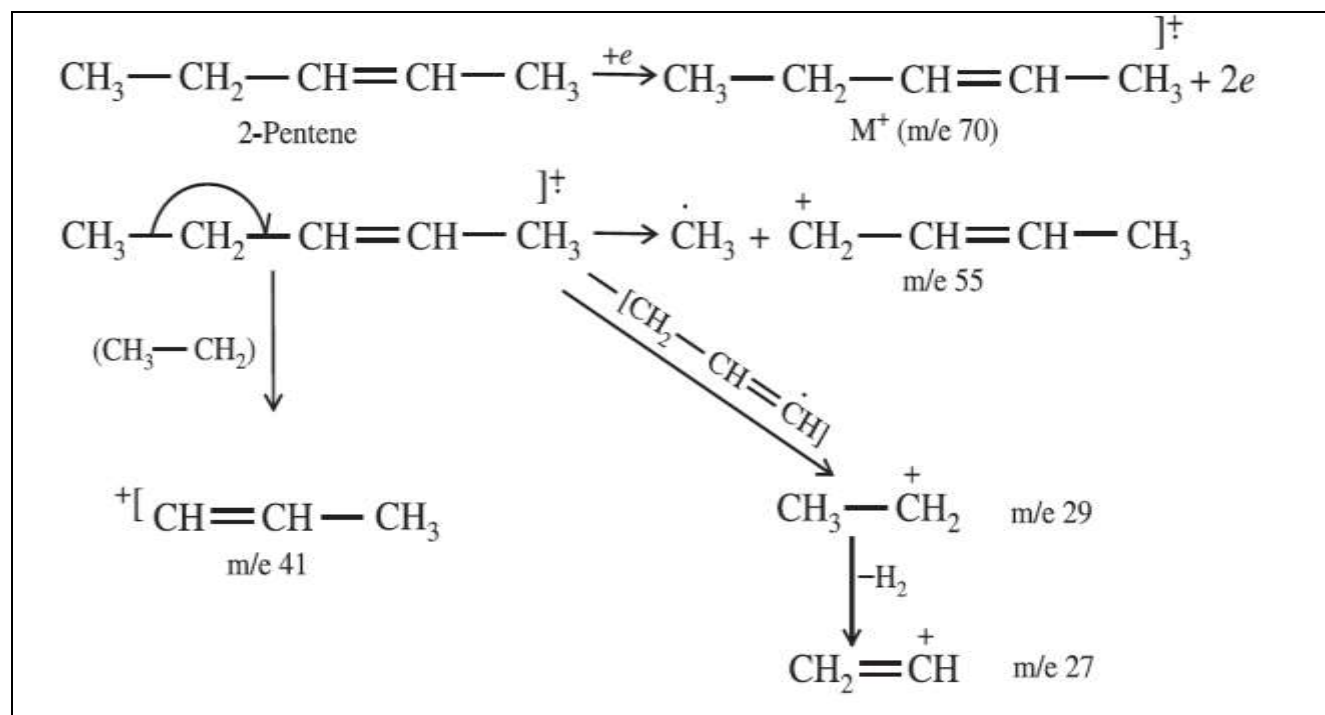
1- The peaks at m/z 67 and 69 are the fragments from cleavage of a bi-allylic bond.

2- The peak at m/z 93 is rationalized as a structure of formula $C_7H_9^+$, formed by double bond isomerization (resulting in increased conjugation), followed by allylic cleavage. The ion at m/z 93 has at least two important resonance forms that contribute to its stability.





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:



Aromatic Compounds

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

(1) 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.

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

(3) 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.

(4) If the aromatic ring is substituted by an alkyl group, a prominent peak is formed at m/e 91. benzyl ($C_6H_5C^+CH_2$) cation formed rearranges to tropylium cation ($C_7H_8^+$) m/z 92.

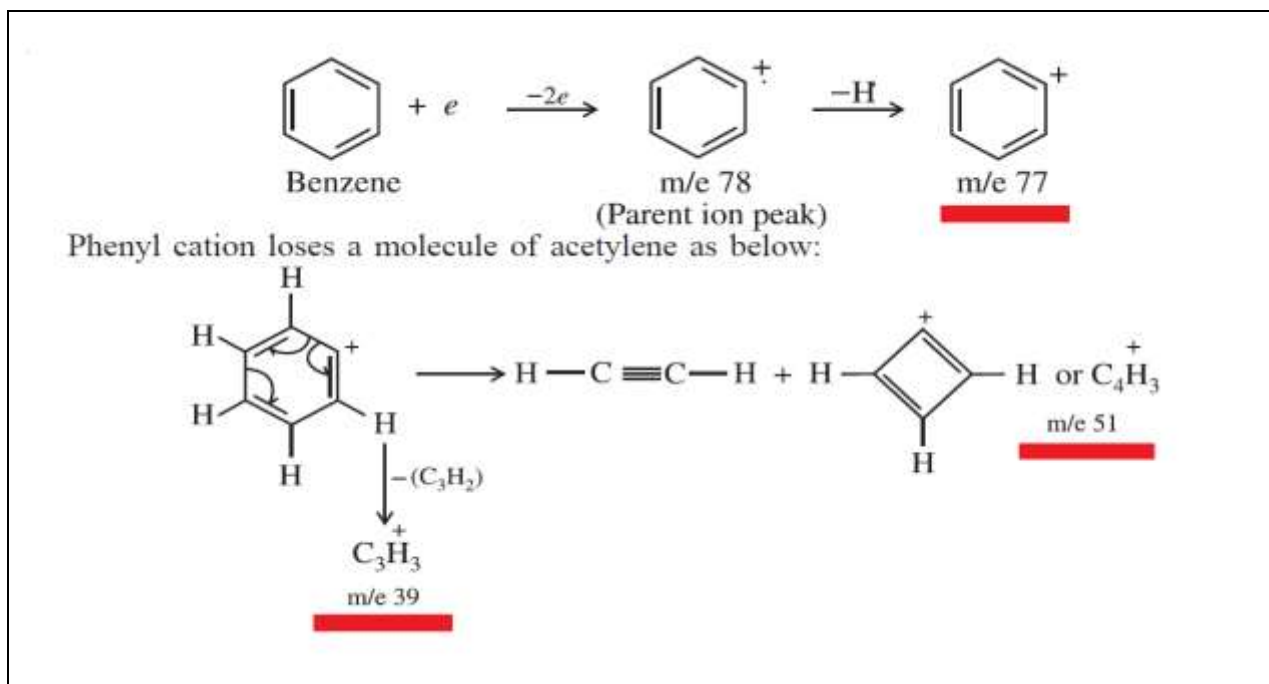
(5) A strong peak at $m/z = 92$ is observed in the case of many compounds containing a propyl or longer side chain. This peak is due to the $^+C_7H_8$ ion produced by the McLafferty rearrangement.

Fragmentation of Benzene :

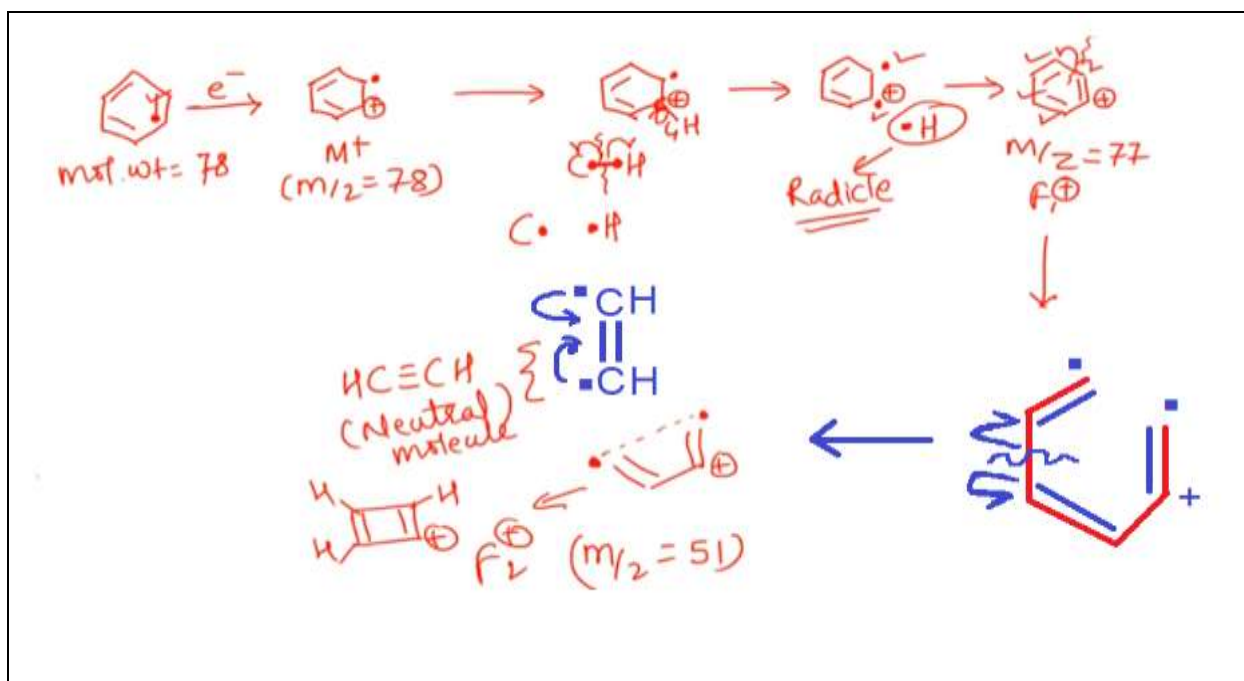
The parent peak in case of benzene is formed at m/e 78.

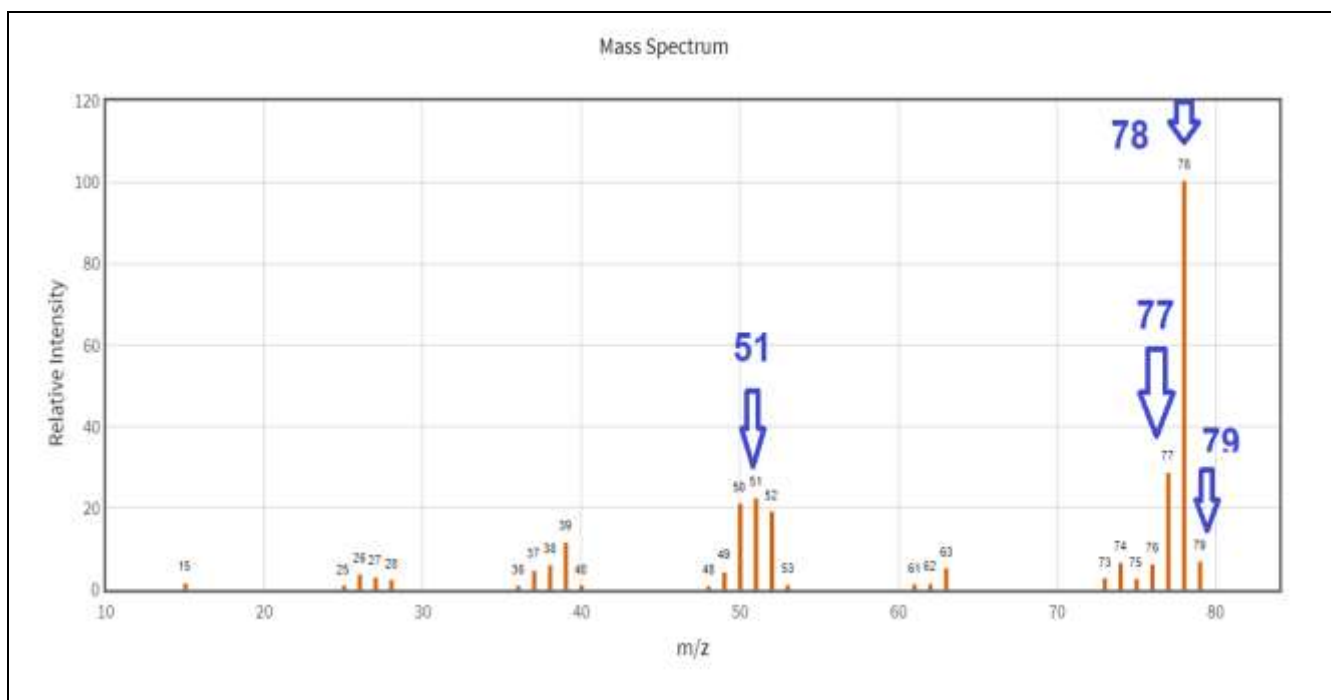
Other important peaks appear at 77, 51 and 37. The

fragmentation mode is explained below:

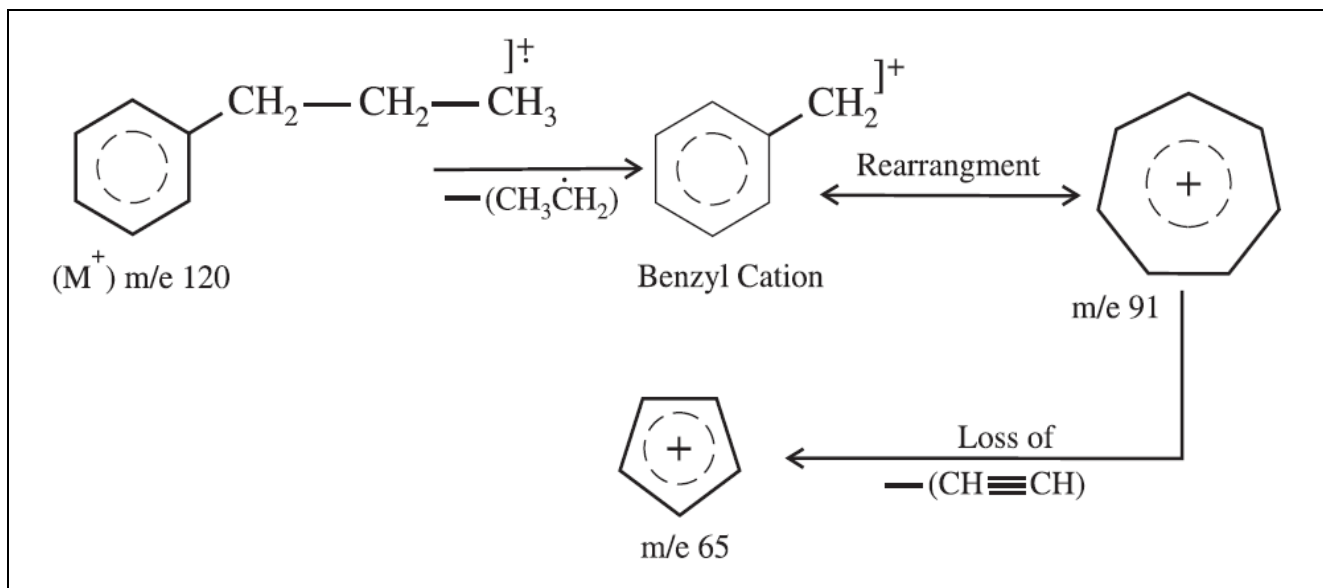


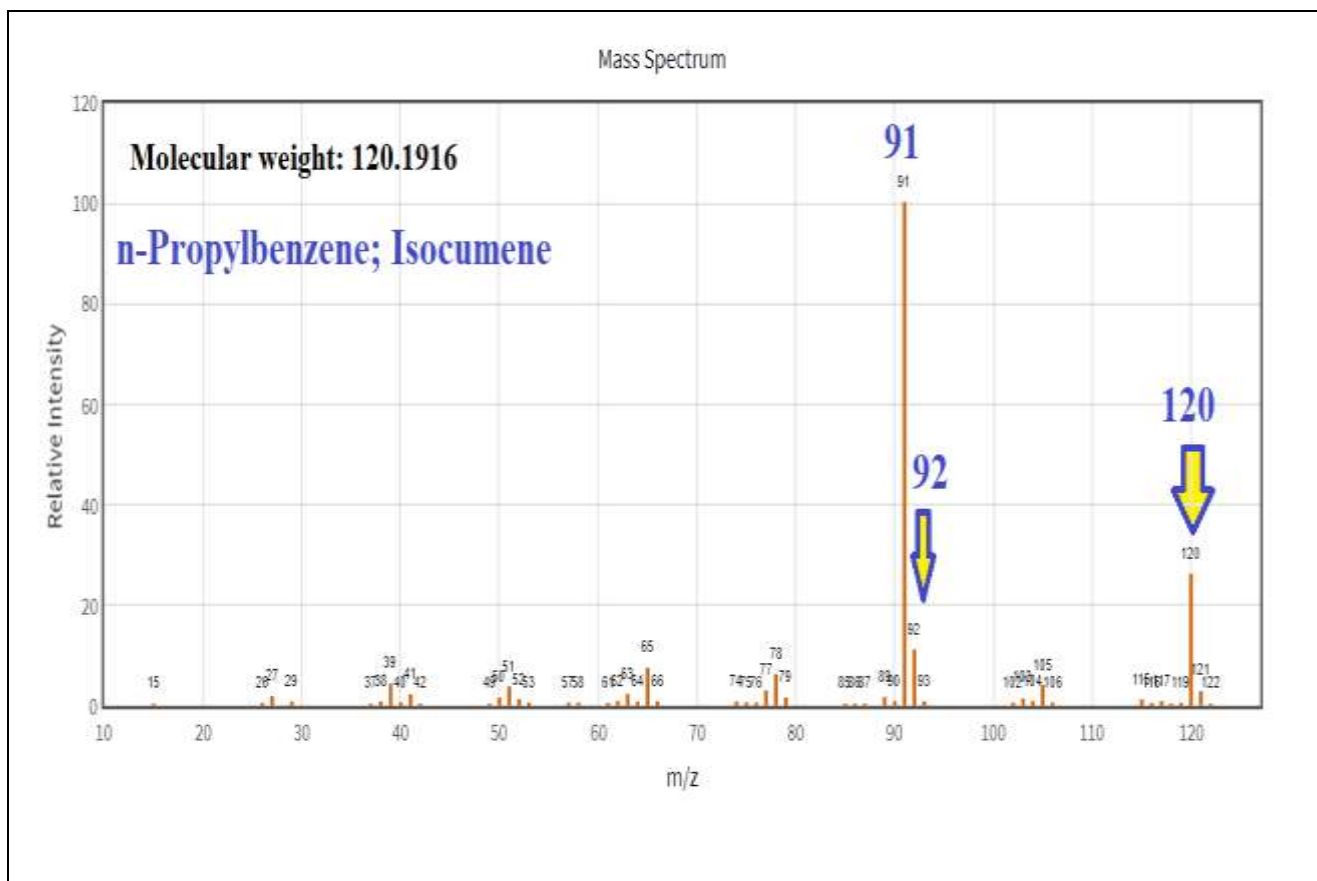
Further explanation of the process of fragmentation





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





Halogen Compounds

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

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

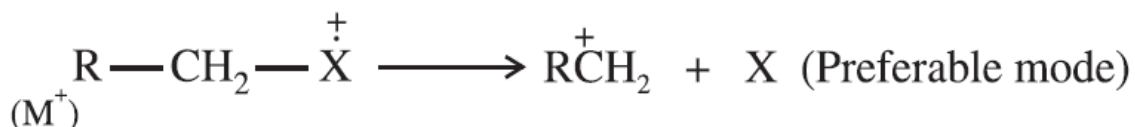
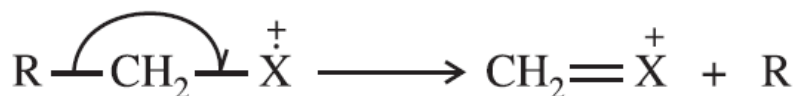
(2) The relative abundance of the molecular ion decreases with increase in chain length and increase in branching.

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

(4) A monobromo compound shows (M + 2) peak which is of the same intensity compared to the parent peak.

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

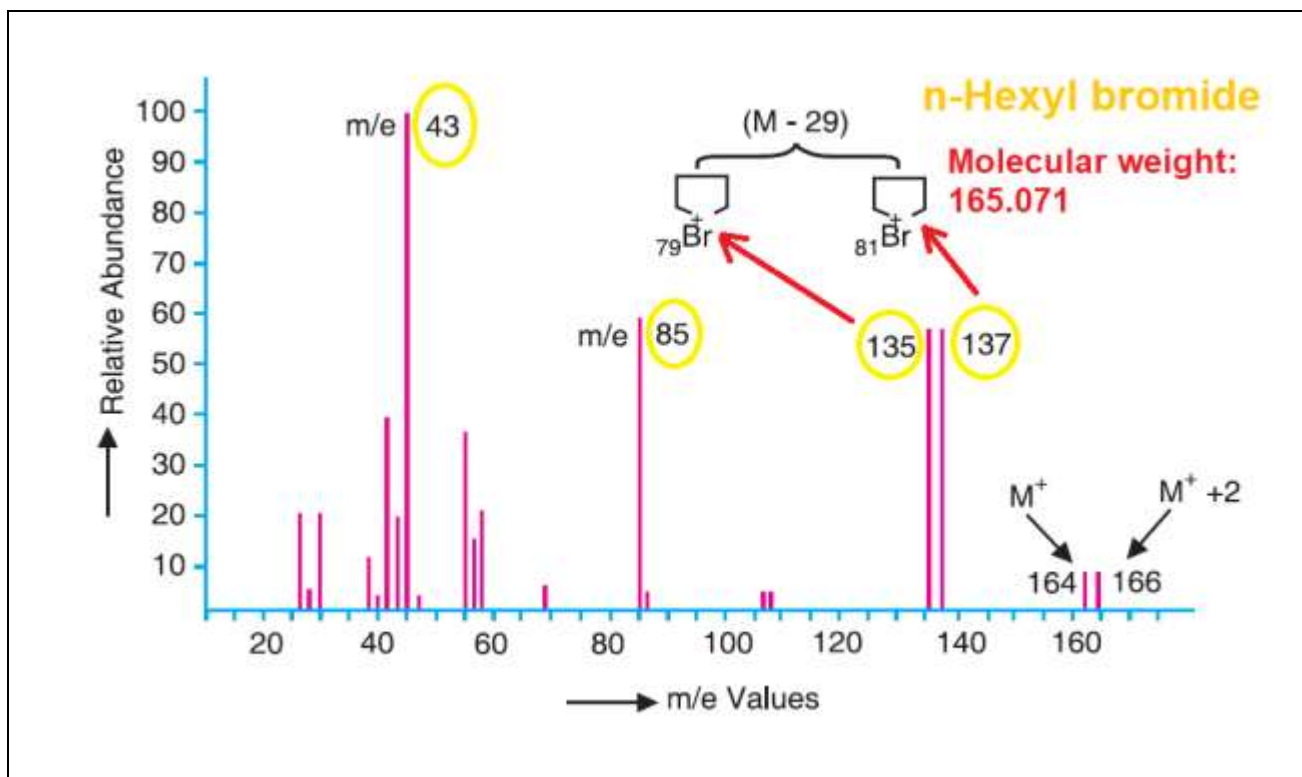
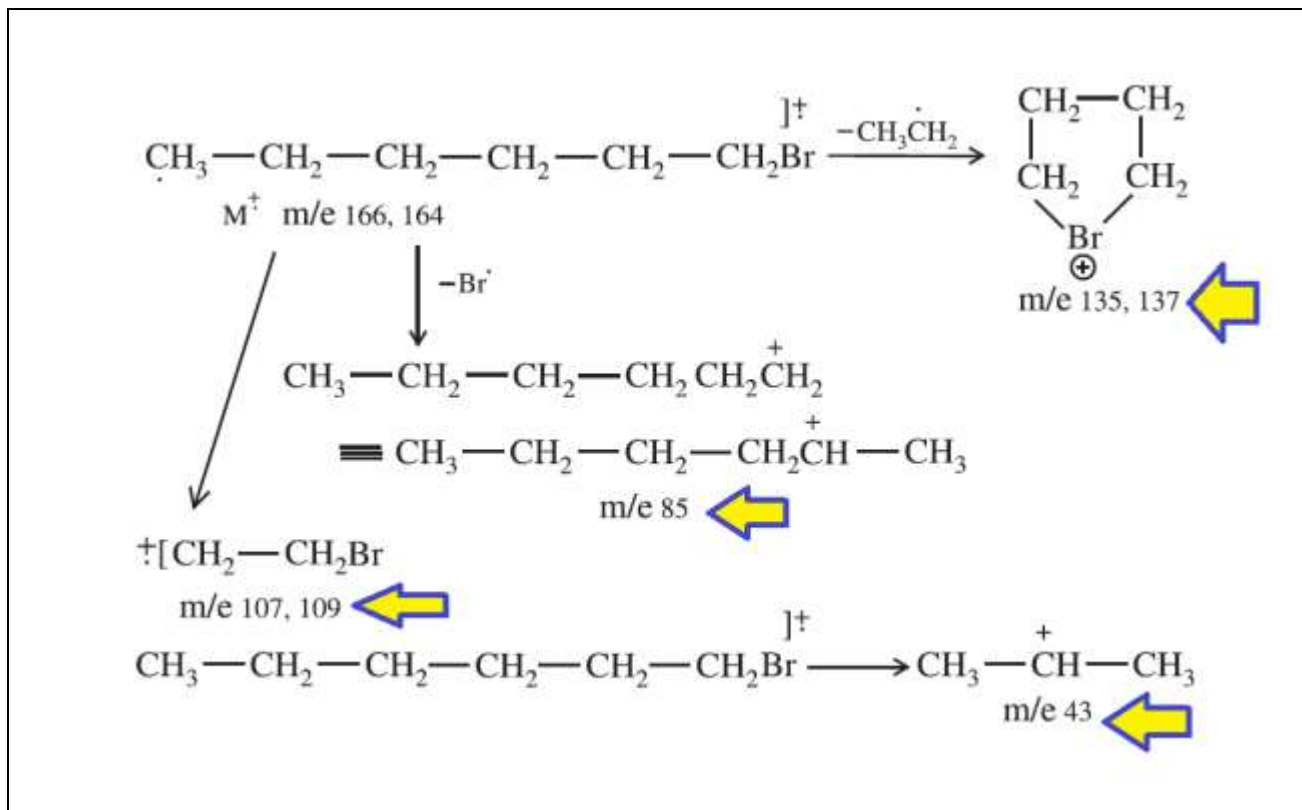
(6) Important fragmentation mode is α -cleavage with charge retention by the halogen containing fragment. Another mode leads to the loss of halide radical.



In the mass spectrum of ethyl chloride, we observe (1) 64 (M+), 66(M⁺+2) [Intensity ratio 1 : 3] (2) 29 (Base peak) (The loss of Cl radical is the preferable mode).

In the mass spectrum of ethyl bromide, CH₃CH₂Br, 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).

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



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

