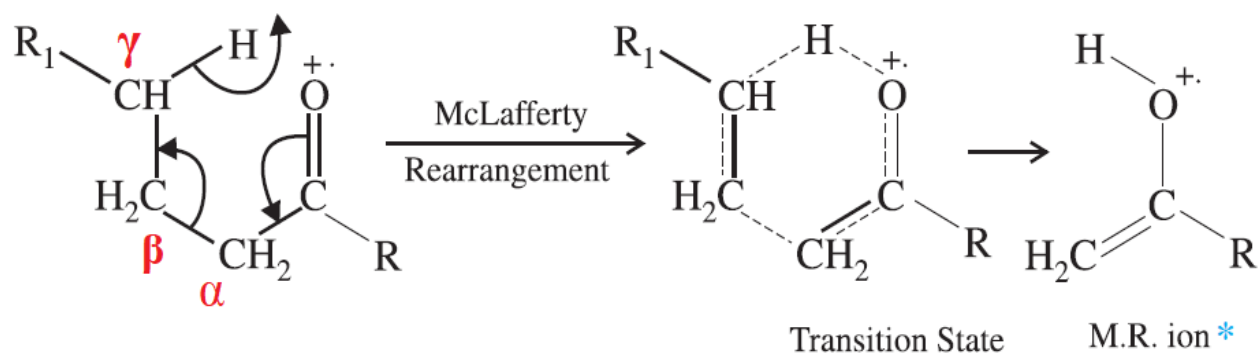
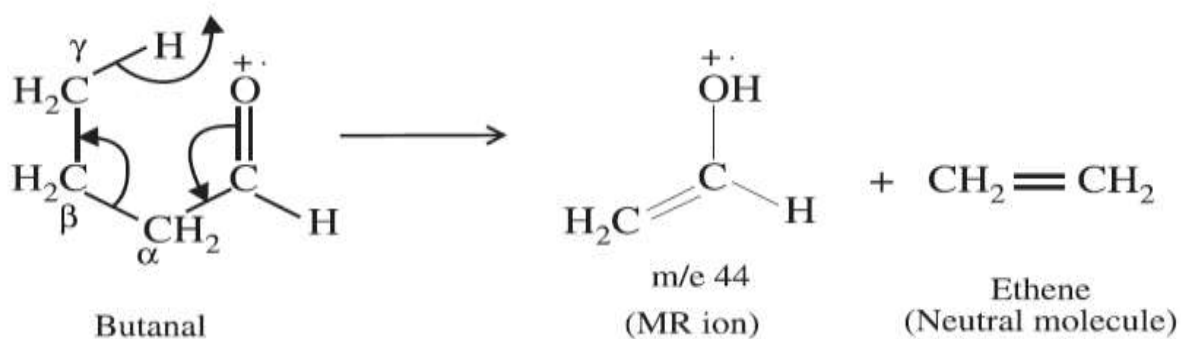


## McLafferty Rearrangement

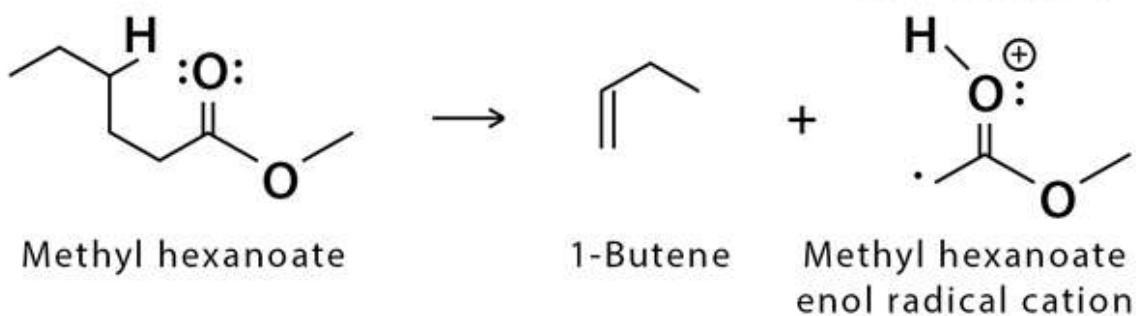
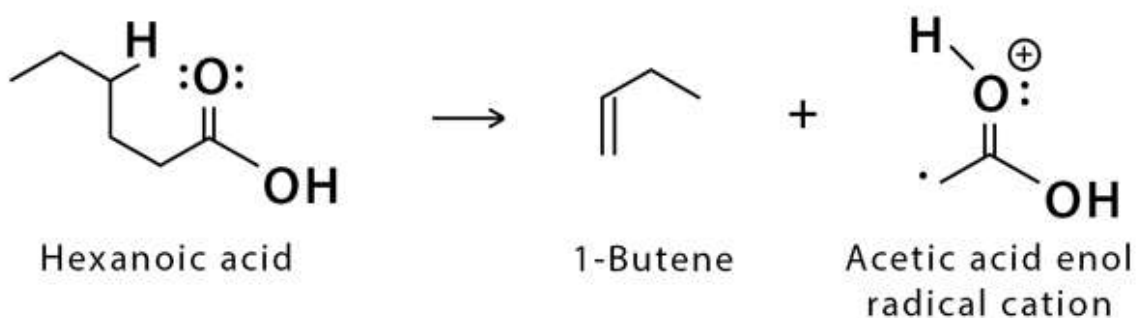
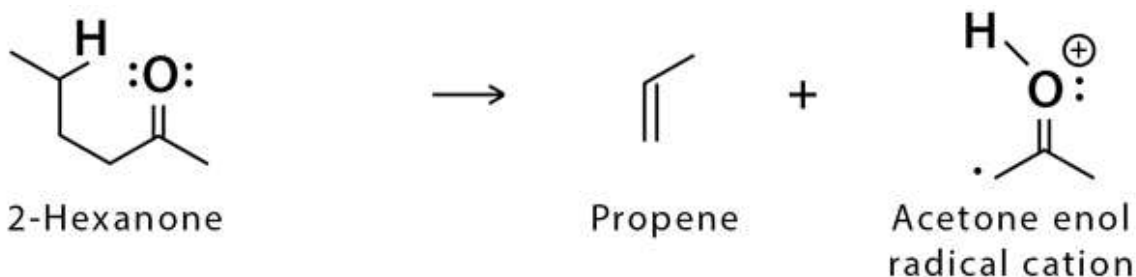
It involves the migration of  $\gamma$ -hydrogen atom followed by the cleavage of a  $\beta$ -bond. The rearrangement leads to the elimination of neutral molecules from aldehydes, ketones, amines, unsaturated compounds, substituted aromatic compounds

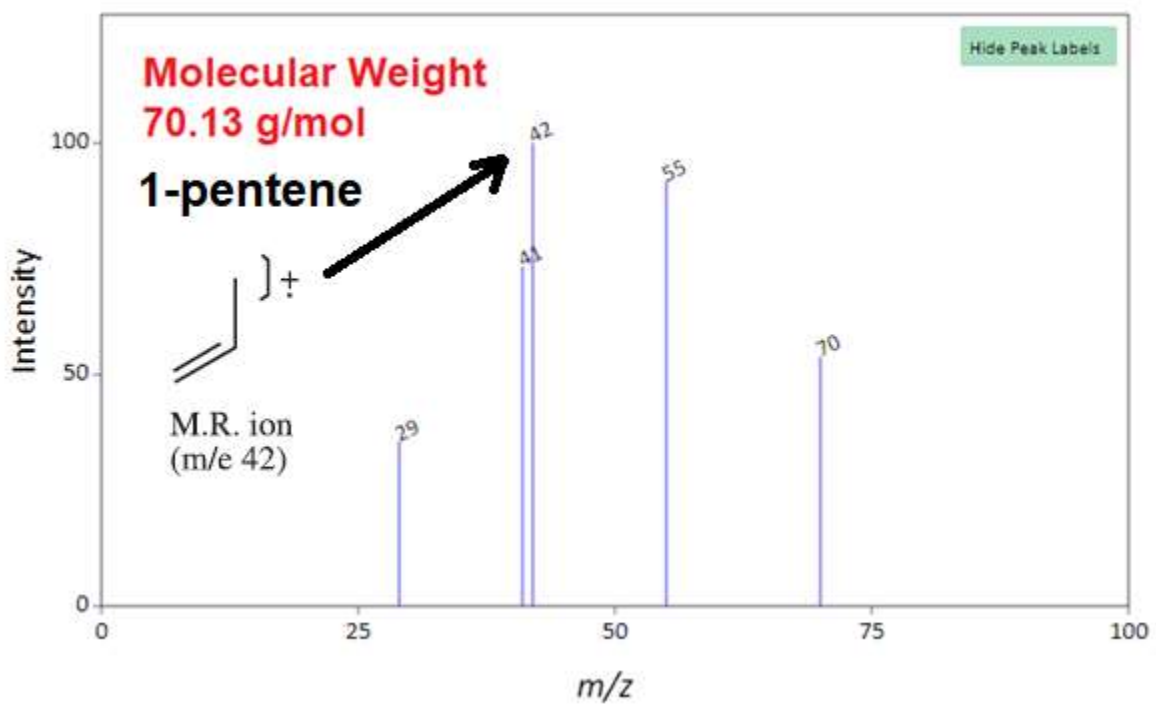
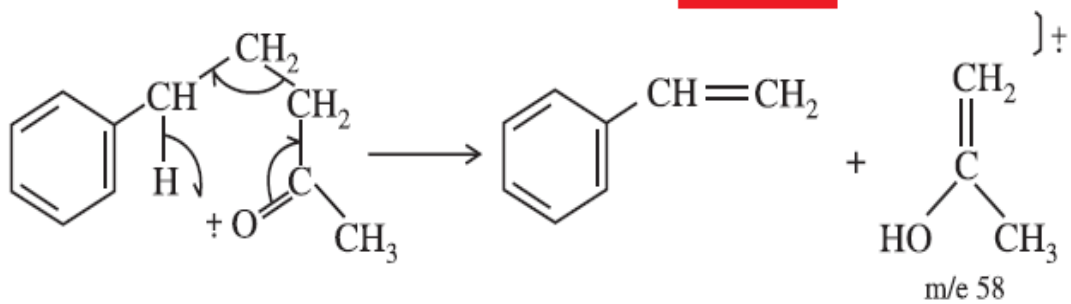
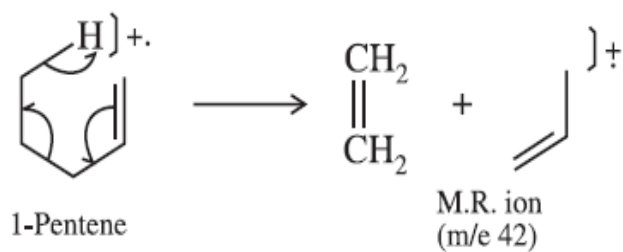


Butanal contains a  $\gamma$ -hydrogen atom. The McLafferty rearrangement ion formed in this case is shown below:

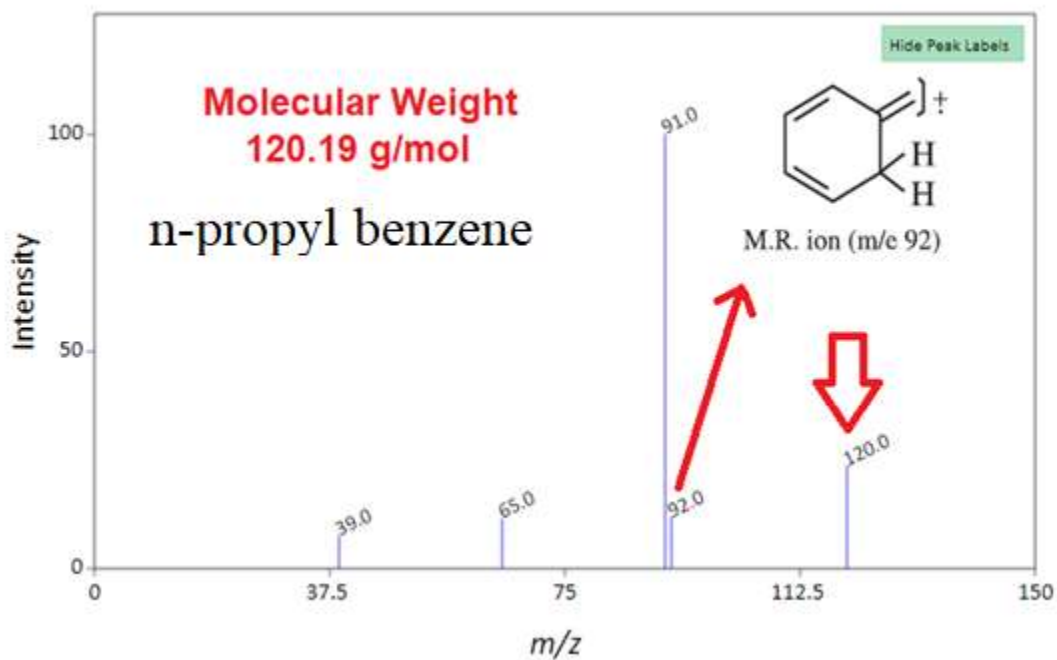
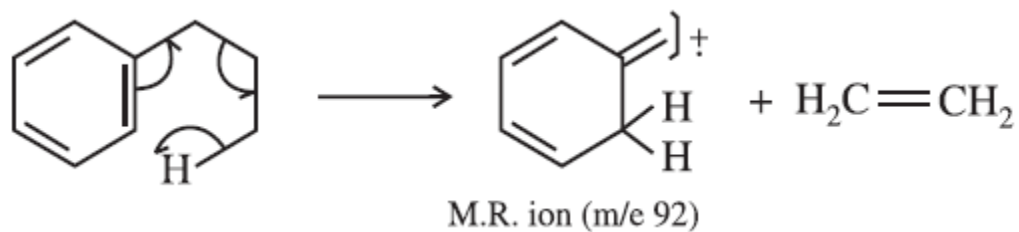


Similarly, a large number of organic compounds, viz. ketones, amines, alcohols, esters, acids which contain a  $\gamma$ -hydrogen atom forms a McLafferty rearrangement ion.





n-propyl benzene shows a McLafferty rearrangement ion peak in large abundance at m/e 92.

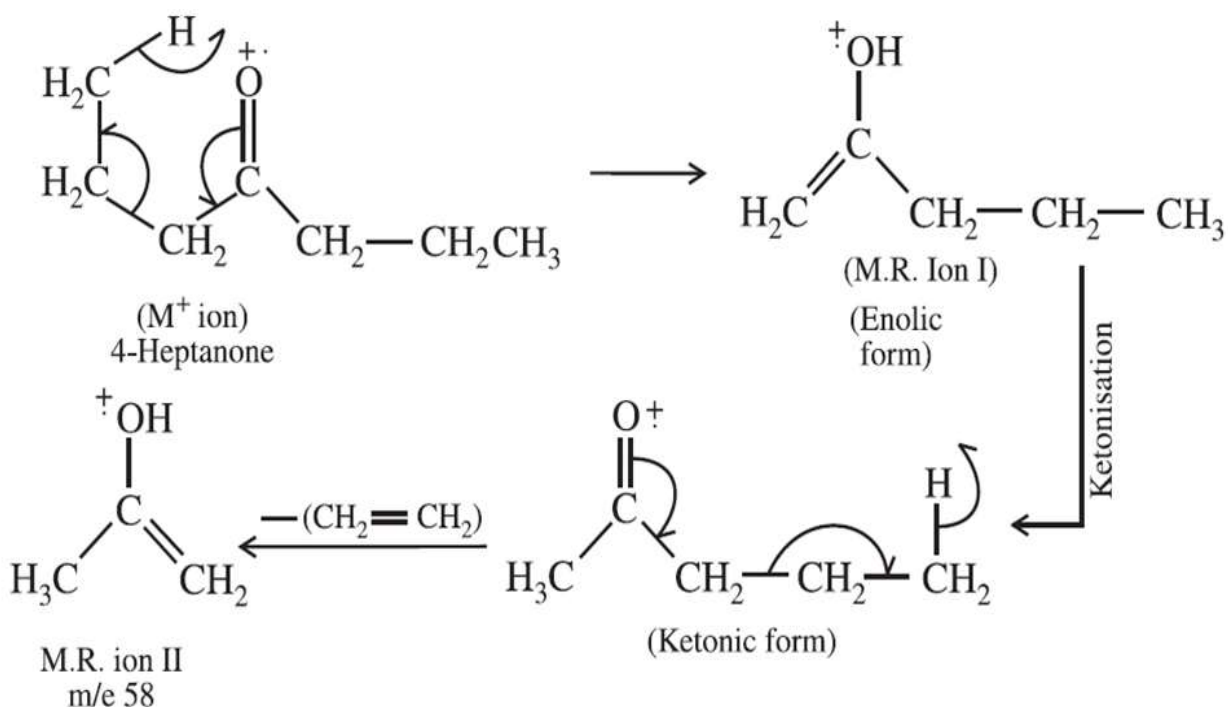


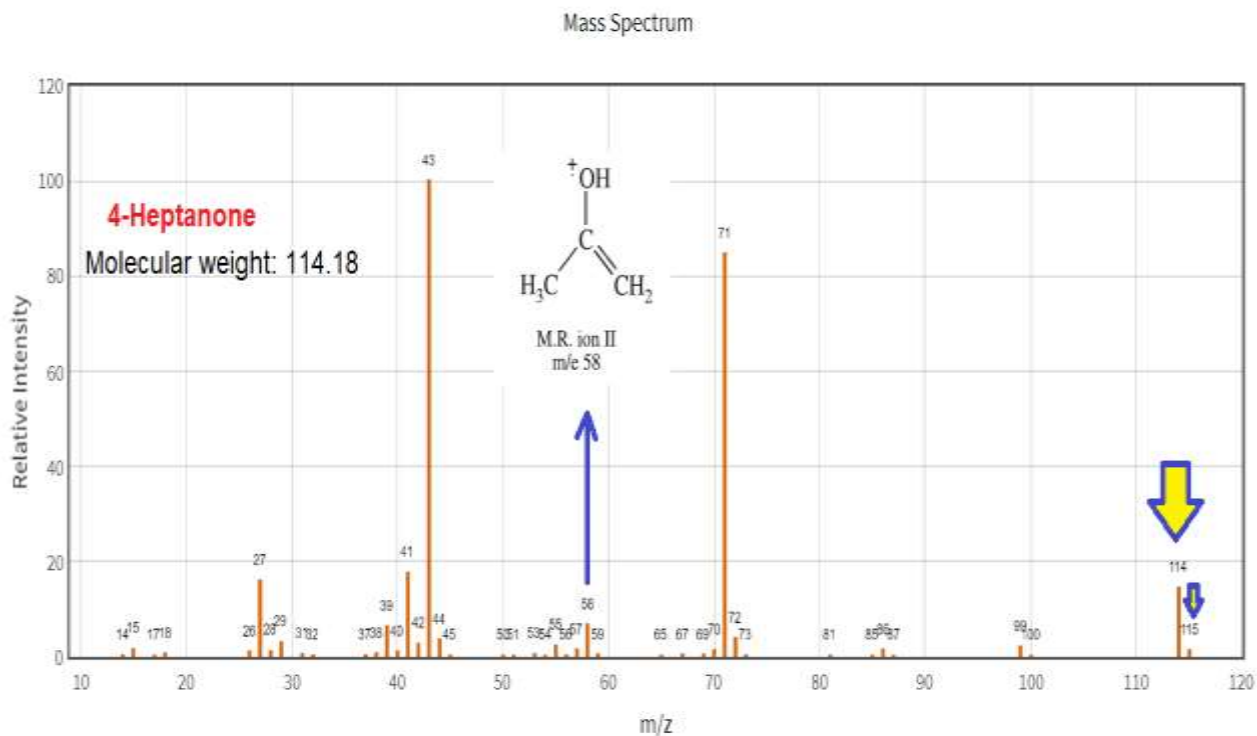
## Double McLafferty rearrangement

A double McLafferty rearrangement is also reported in certain ketones. The second hydrogen atom originates exclusively from the  $\gamma$ -position. A secondary hydrogen is preferred to a primary hydrogen atom in this process. The mechanism involves:

(i) Ketonisation of the intermediate enol ion by the hydrogen transfer.

(ii) Hydrogen transfer to enolic oxygen. Consider the McLafferty rearrangement in 4-Heptanone.





## Essential Properties of Hydrocarbon Mass Spectra

### 1- Alkanes (saturated hydrocarbons)::

- (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 ( $\text{CH}_2$ ). The most abundant peaks correspond to  $(\text{C}_n \text{H}_{2n+1})^+$  ion.

(iii) The most intense peaks are due to C3 and C4 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  $(C_nH_{2n})^+$  and  $(C_nH_{2n-1})^+$  ions in much less abundance.

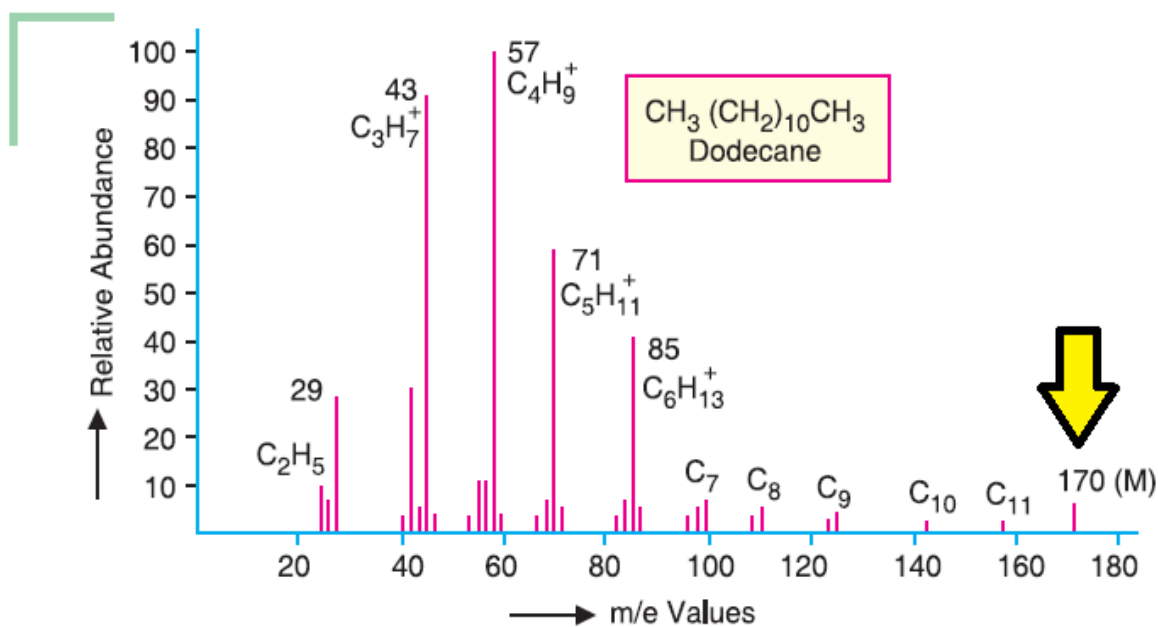


Fig. 7.7

It is very important to note that relative abundance of the ion (fragment ion) formed depends

upon the :

(i) stability of the ion formed

(ii) the stability of the radical which is lost.

The stability of the carbocation has the order  
allylic > tertiary > secondary > primary > methyl.

The stability of the free radical lost depends upon:

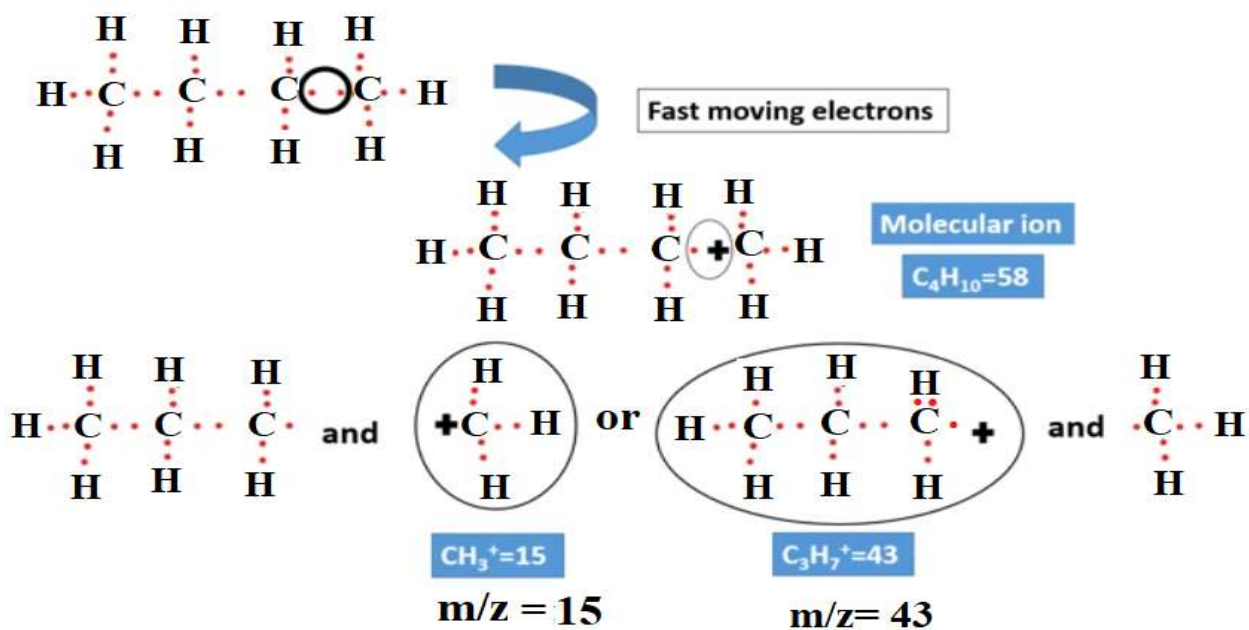
(i) The length of the straight chain since it allows greater dispersal of the odd electron. Greater the dispersal of odd electron, greater is the stability of the free radical. *n*-butyl free radical is more stable than *n*-propyl free radical. Greater the stability, easier the formation.

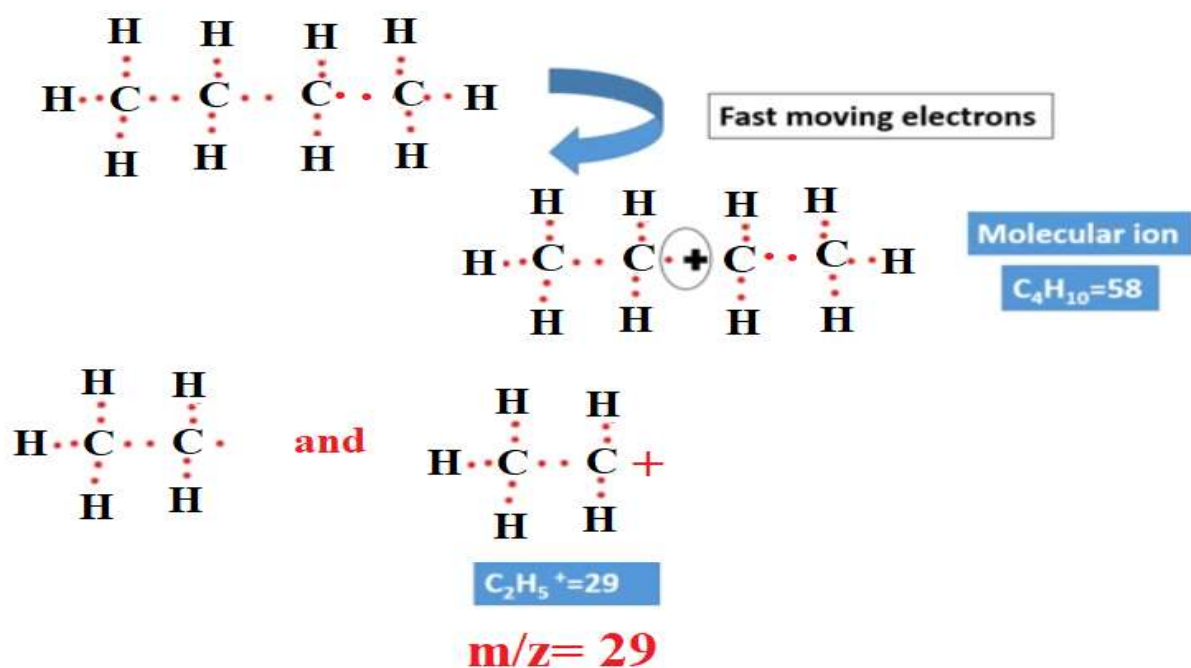
(ii) The nature of the free radical, whether primary, secondary or tertiary

the  $[M - CH_3]^+$  peak is characteristically very weak or missing.

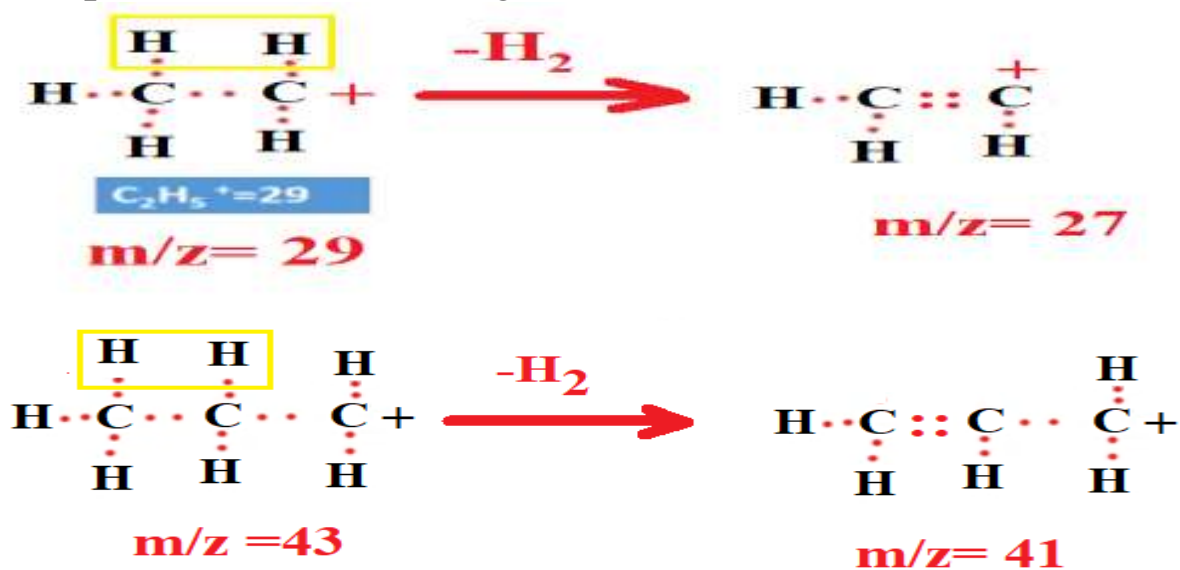


The spectrum of n-butane mass shows peaks at 15, 29 and 43

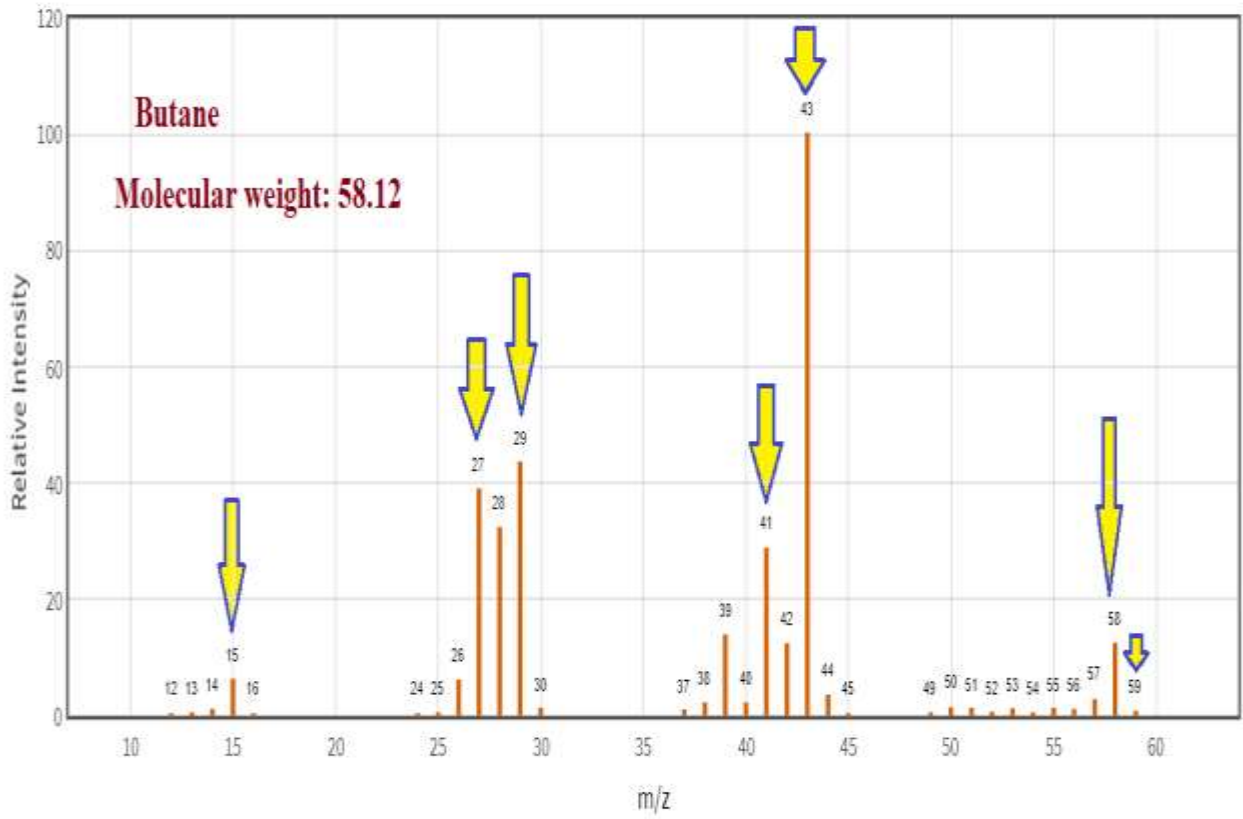


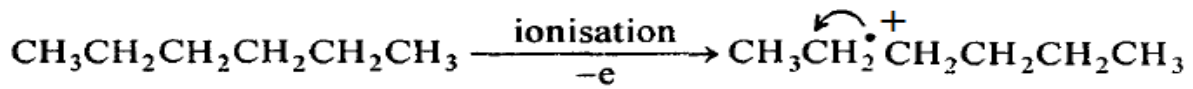


Additionally, a peaks at  $m/z$  27 and 41 are shown, which corresponds to the following ions:



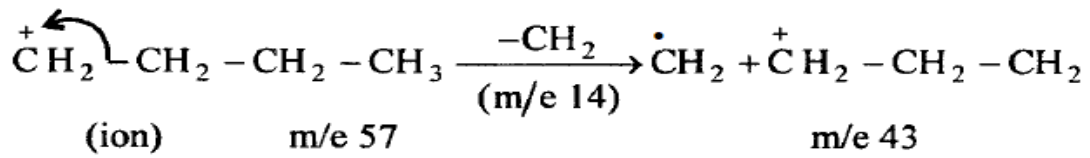
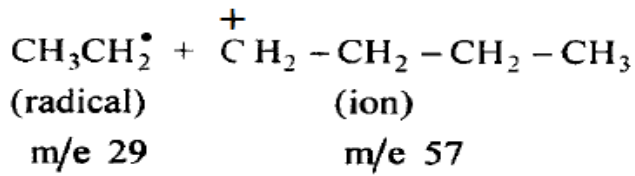
# Mass Spectrum



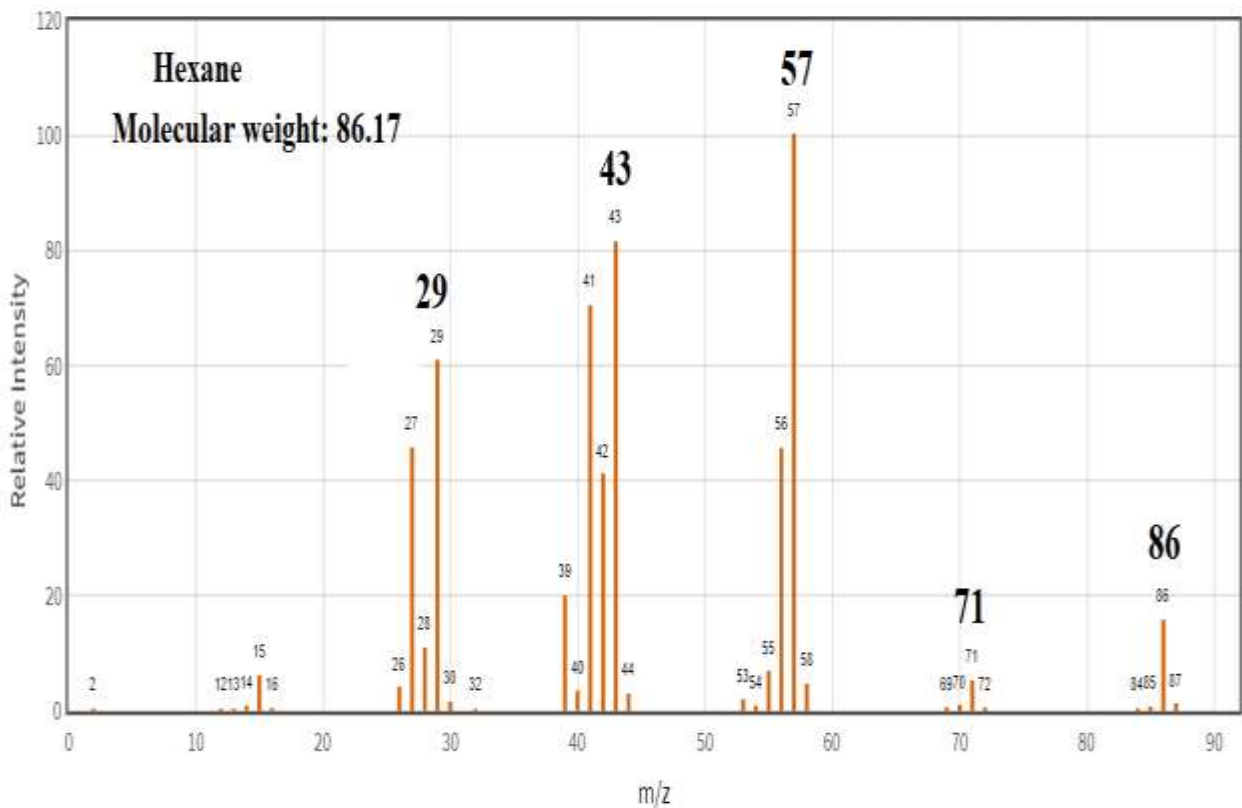


alkane

(Parent ion)



Mass Spectrum



Mass Spectrum

