

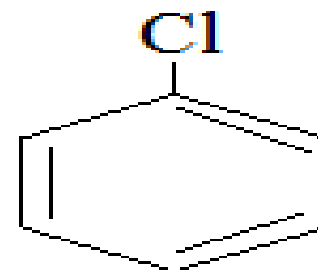
Isotopes

- Mass spectrometers are capable of separating and detecting individual ions even those that only differ by a single atomic mass unit.
- As a result molecules containing different isotopes can be distinguished.
- This is most apparent when atoms such as bromine or chlorine are present ($^{79}\text{Br} : ^{81}\text{Br}$, intensity 1:1 and $^{35}\text{Cl} : ^{37}\text{Cl}$, intensity 3:1) where peaks at "M" and "M+2" are obtained.
- molecular ion peak is diff. from a M+2 peak by 2 ➡ halogen.
- The intensity ratios in the isotope patterns are due to the natural abundance of the isotopes.
- "M+1" peaks are seen due the presence of ^{13}C in the sample.

Q. / A compound gives a mass spectrum with peaks at $m/z = 77$ (40%), 112 (100%), 114 (33%), and essentially no other peaks. Identify the compound.

First, your molecular ion peak is 112 and you have a M+2 peak at 114. Therefore, you have a halogen.

- Now, your molecular ion peak and M+2 peak are in a 3 to 1 ratio. This means chlorine.
- So, $112 - 35 = 77$ (C & H)
- C's $77/12 = 6$ carbons
- $6 \times 12 = 72$
- $77 - 72 = 5$
- $\text{C}_6\text{H}_5\text{Cl}$. DOUS $(2(6)+2-5-1)/2 = 4$

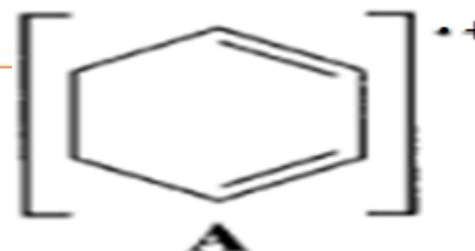


Fragmentation

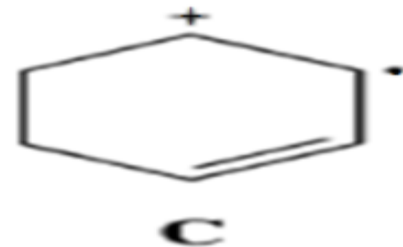
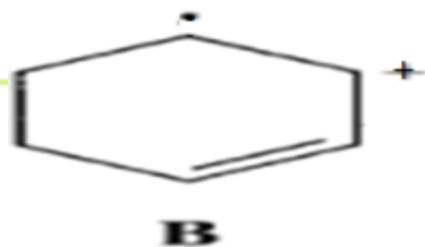
- The tendency is to represent the molecular ion with a delocalized charge.
- Localize the positive charge on either a π bond, or on a hetero atom.

i.e. Structures **A** and **B**, represent the molecular ion of cyclohexadiene.

Compound **A** is a delocalized structure; both the electron and the positive charge are delocalized over the π system. Since the electron removed to form the molecular ion is a π electron,



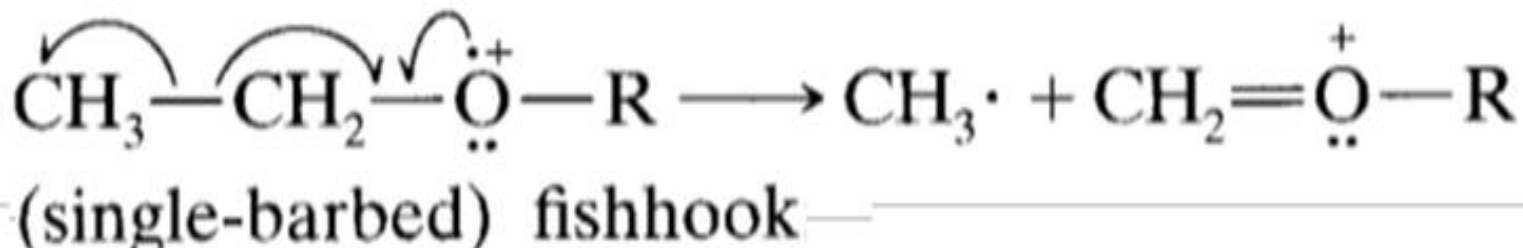
Structures such as **B** and **C** localize (the electron and the positive charge).



Fragmentation of the odd-electron molecular ion (radical-cation, $M^{\bullet+}$) may occur by :

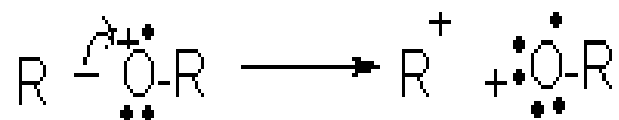
1. Homolytic cleavage :

In homolytic cleavage each electron “moves” independently as shown by a (single-barbed) fishhook; the fragments here are an even-electron cation and a free radical (odd electron).

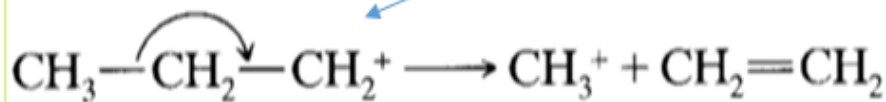
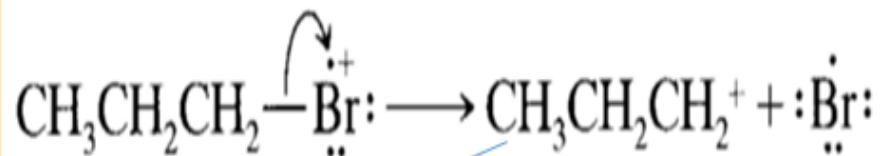


2. Heterolytic cleavage:

- Fragmentation by movement of two electrons:
- In this type of cleavage **both the electrons** of the bond are taken over by **one of the atoms**; the fragments are an **even electron cation** and a **radical** with the positive charge residing on the alkyl group.
- It is designated by a conventional arrow ($\curvearrowright$ or $\curvearrowleft$) to signify the **transfer of a pair of electrons** in the direction of the charged site.



final charge site is on the alkyl product.



the fragments are again an even-electron cation and a radical, but here the final charge site is on the alkyl product.

- Simultaneous or consecutive cleavage of several bonds may occur when energy benefits accrue from formation of :

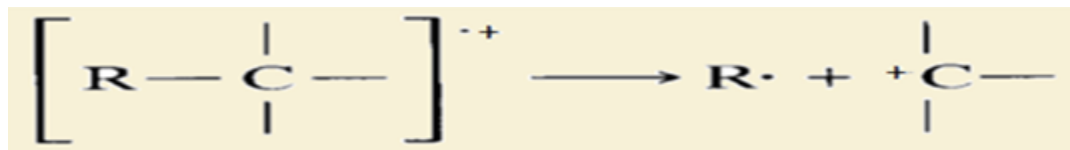
- a highly stabilized cation and/or a stable radical, or
- a neutral molecule, often through a well- defined low-energy pathway.

- The probability of cleavage of a particular bond is related to :

- the bond strength .
- the possibility of low energy transitions .
- the stability of the fragments .

A number of general rules for predicting prominent peaks in EI spectra can be written and rationalized by using standard concepts of physical organic chemistry.

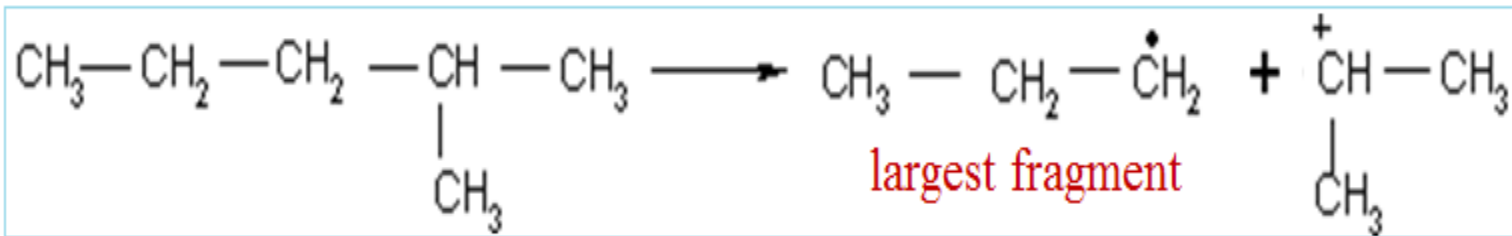
- 1.** The relative height of the molecular ion peak is greatest for the straight-chain compound and decreases as the degree of branching increases (rule 3).
- 2.** The relative height of the molecular ion peak usually decreases with increasing molecular weight in a homologous series. Fatty esters appear to be an exception.
- 3.** Cleavage is favored at alkyl-substituted carbon atoms: the more substituted, the more likely is cleavage.



Most Stable Benzylic > Allylic > Tertiary > Secondary >> Primary **Least Stable**

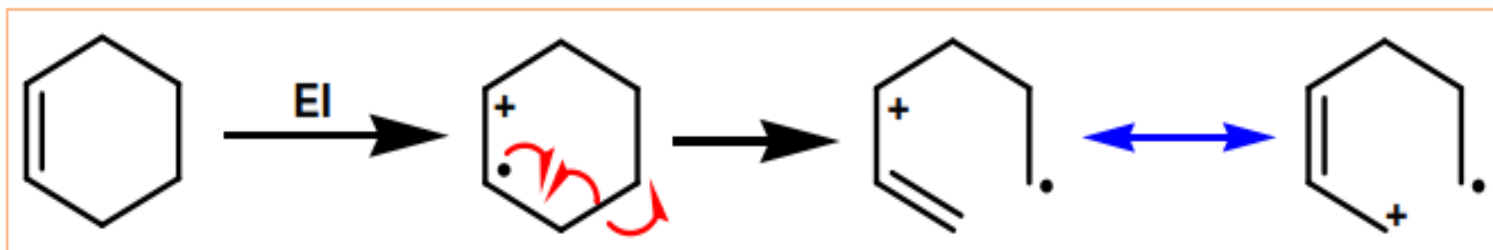
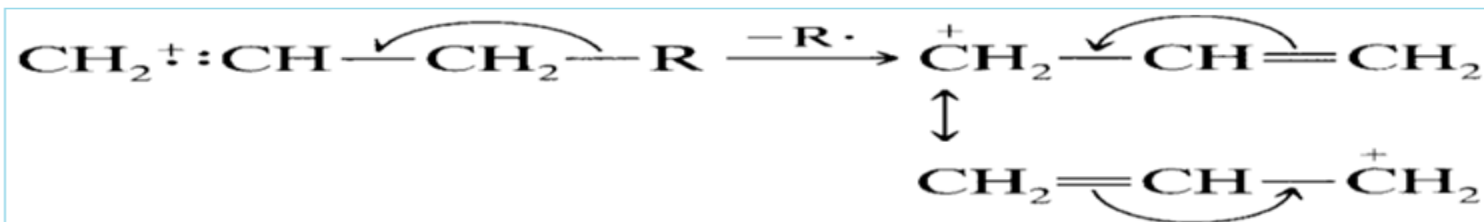
STEVENSONS RULE :

- ❖ When an ion fragments, the positive charge will remain on the fragment of lowest ionization potential .
- ❖ Generally the largest substituent at a branch is eliminated most readily as a radical, presumably because a long chain radical can achieve some stability by delocalization of the lone electron.
- ❖ Ex- cleavage of 1-methyl pentane



4. Double bonds, cyclic structures, and especially aromatic (or heteroaromatic) rings stabilize the molecular ion and thus increase the probability of its appearance.

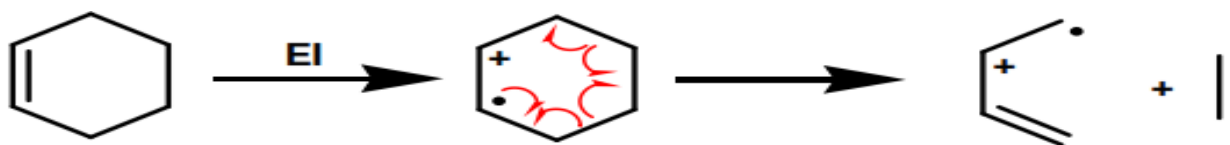
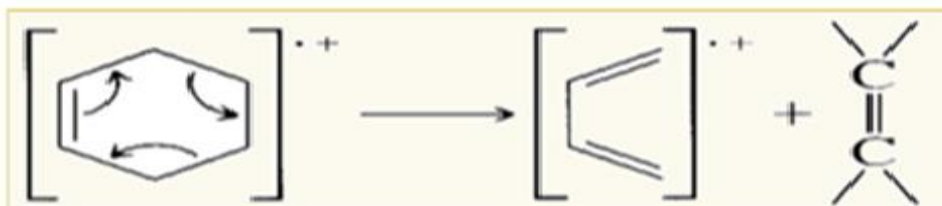
5. Double bonds favor allylic cleavage to give a resonance stabilized allylic carbocation, especially for cycloalkenes.



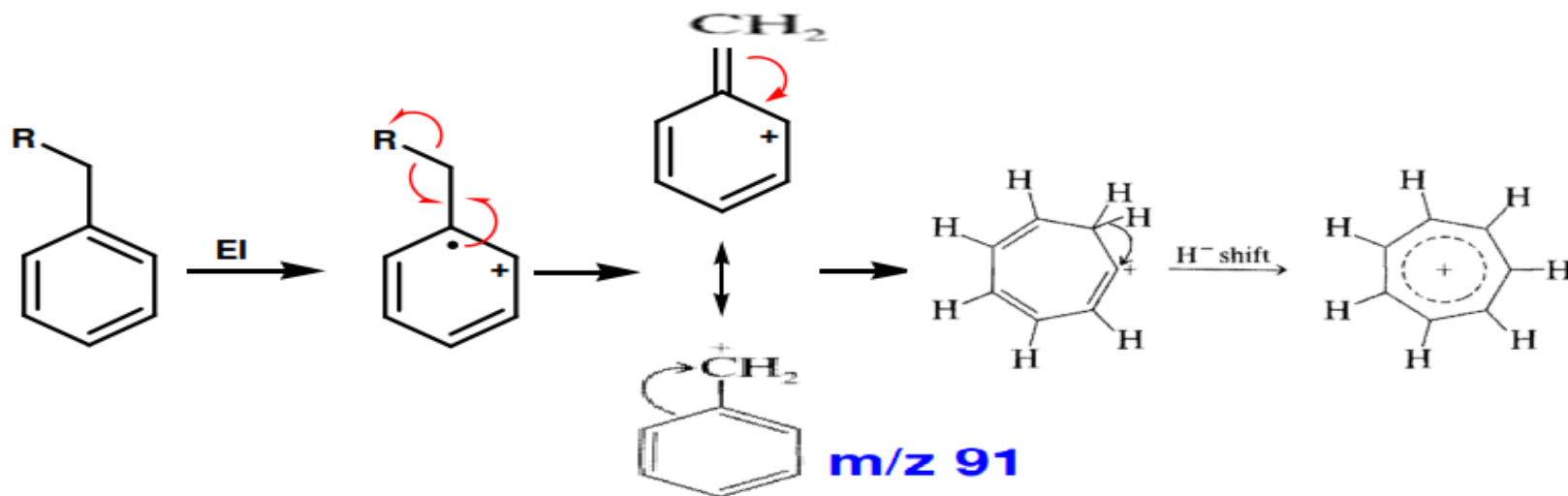
6. Saturated rings tend to lose alkyl side chains at the α bond. This is merely a special case of branching (rule 3). The positive charge tends to stay with the ring fragment.



Unsaturated rings can undergo a *retro*-Diels-Alder reaction:



7. In alkyl-substituted aromatic compounds, cleavage is at the bond β to the ring, giving the resonance-stabilized benzyl ion or, more likely, the tropylium ion:

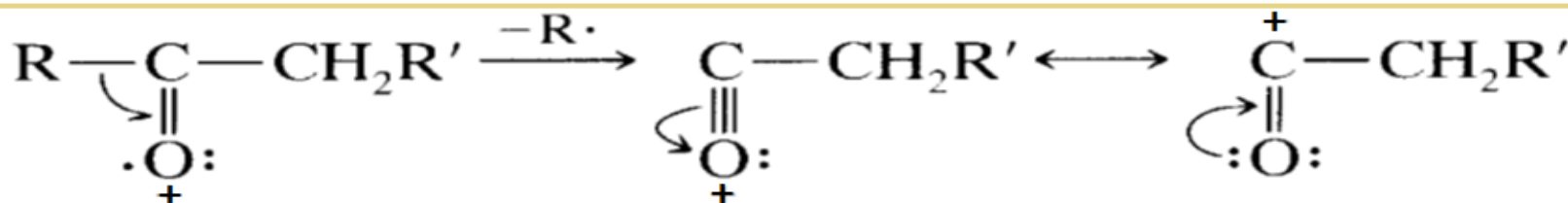
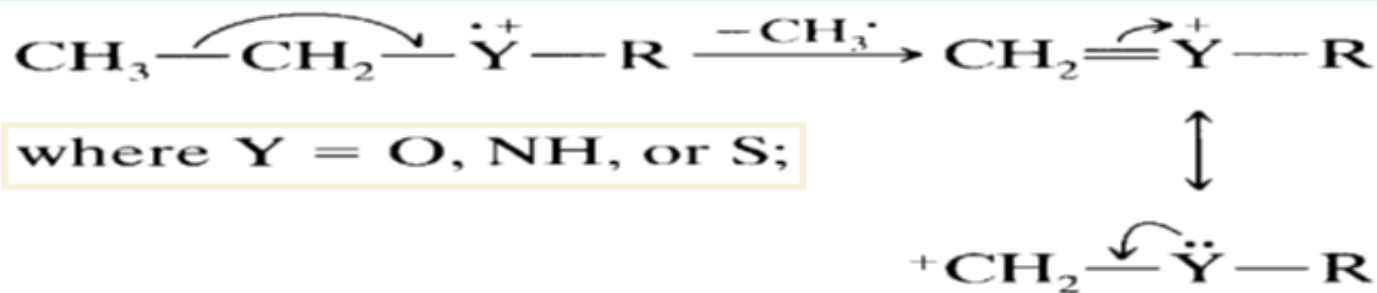


R = H

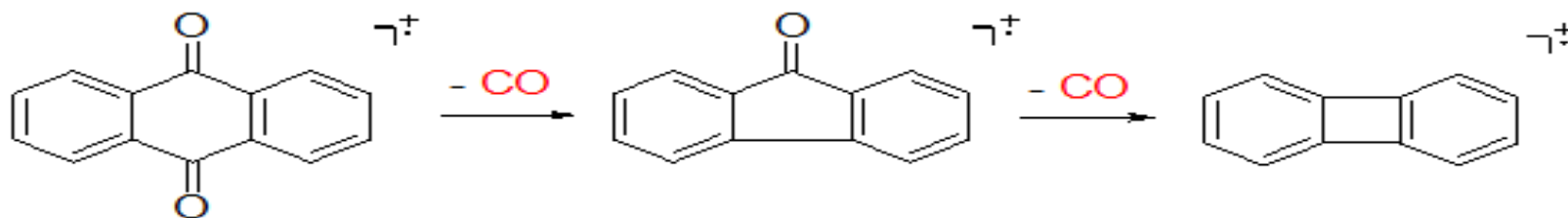
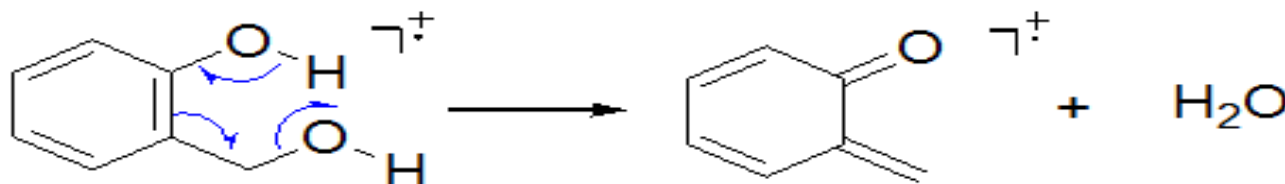
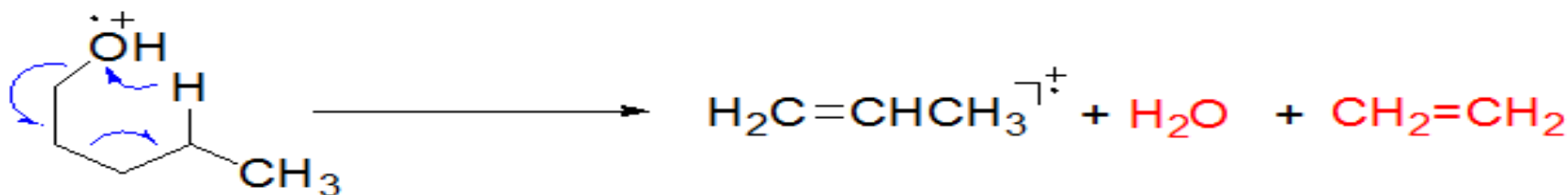
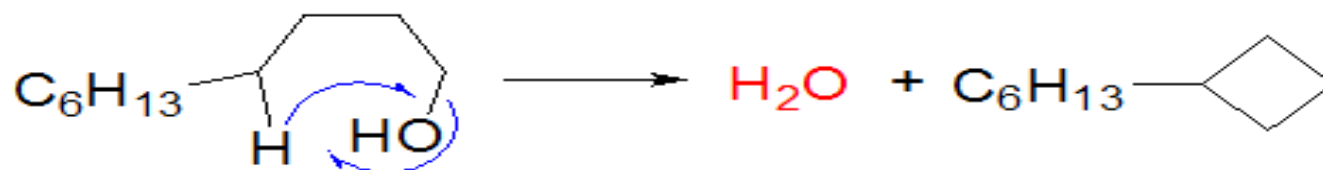
- the spectrum of toluene displays a strong molecular ion at $m/z = 92$.
- small $m + 1$ & $m + 2$ peaks
- a base peak at $m/z = 91$ (compound contains a benzyl unit)
- minor peaks $m/z = 65$ and below.

8.

The C—C bonds next to a heteroatom are cleaved, leaving the charge on the fragment containing the heteroatom whose non-bonding electrons provide resonance stabilization.



9. Cleavage is often associated with elimination of small, stable, neutral molecules, such as carbon monoxide, olefins, water, ammonia, hydrogen sulfide, hydrogen cyanide, mercaptans, ketene, or alcohols, often with rearrangement .



It should be kept in mind that the fragmentation rules above apply to EI mass spectrometry. Since other ionizing (CI, etc.) techniques often produce molecular ions with much lower energy or quasimolecular ions with very different fragmentation patterns, different rules govern the fragmentation of these molecular ions.

General modes of fragmentation:

Fragmentation of the molecular ion takes place in following modes:

◆ Simple cleavage

Homolytic cleavage

Heterotypic cleavage

Retro Diels-Alder reaction

◆

Scrambling

McLafferty rearrangement

Elimination

Rearrangements

Rearrangement ions are a result of intramolecular atomic rearrangement during fragmentation.

Rearrangements involving migration of hydrogen atoms in molecules that contain a heteroatom are especially common.

2.

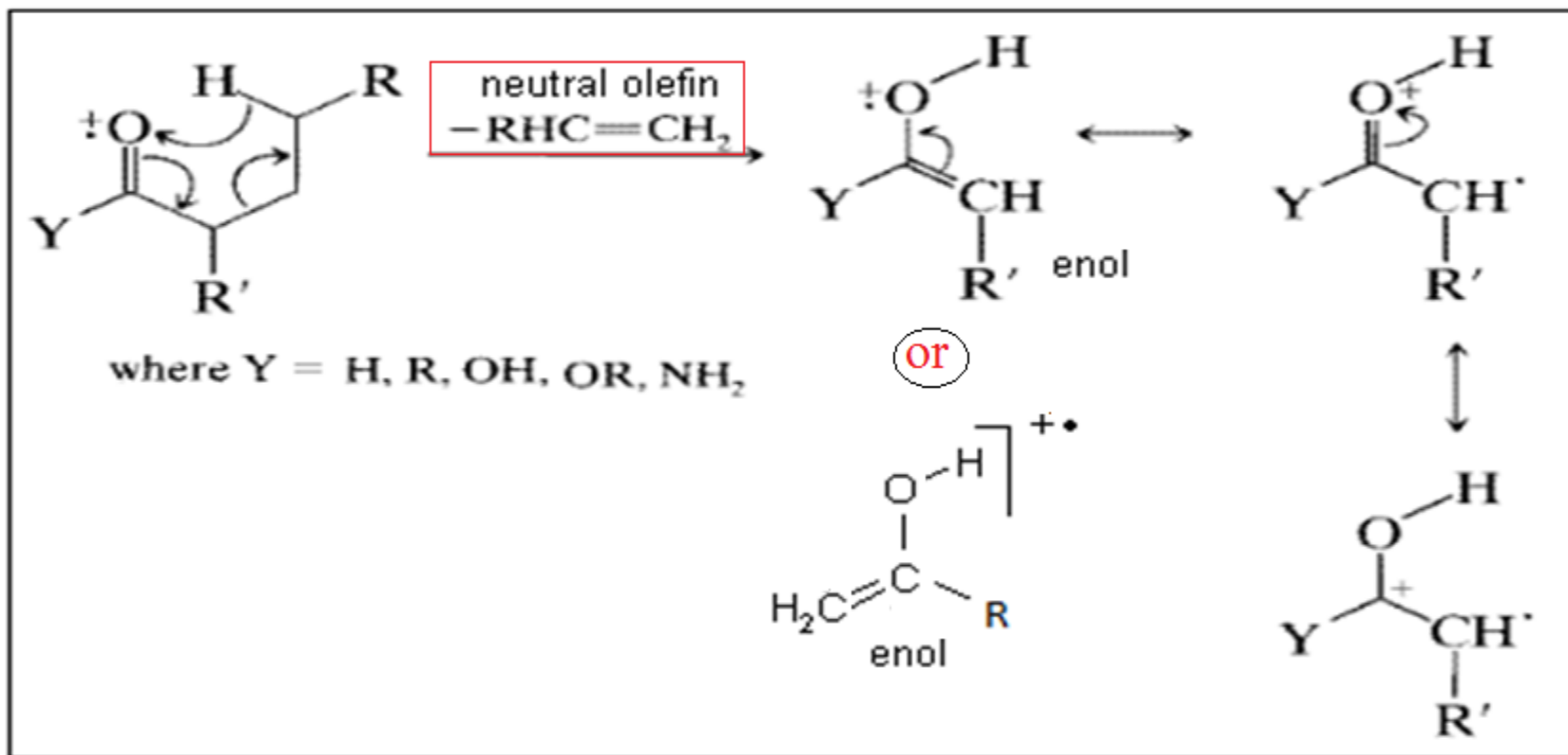
One important example is McLafferty rearrangement.

- ❖ Compounds containing hydrogen atom at position gamma to carbonyl group have been found to a relative intense peak.
- ❖ This is probably due to rearrangement and fragmentation is accompanied by the loss of neutral molecule.
- ❖ This rearrangement is known as McLafferty rearrangement.

- a) An appropriately located heteroatom e.g. O, N
- b) A pi electron system (usually a double bond) &
- c) An abstractable hydrogen atom gamma to the C = X system

The rearrangement results in the formation of charged enols and a neutral olefins.

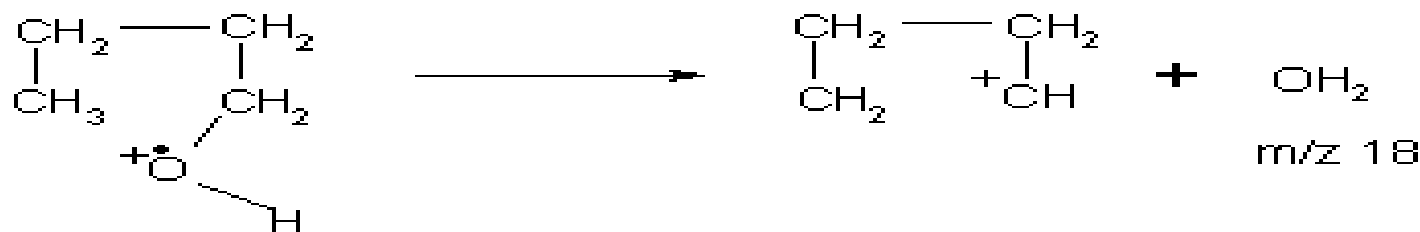
Radical cations localized on keto-type oxygen give β cleavage



Ketones, esters, carboxylic acids all give McLafferty products

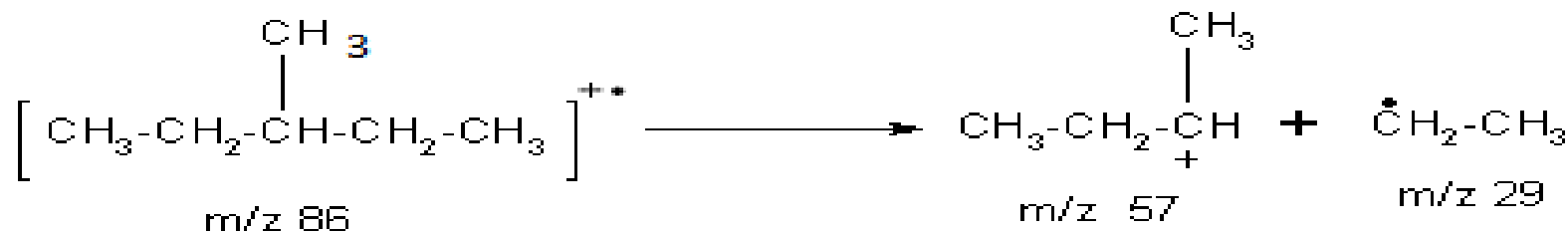
. Elimination: Fragmentation due to loss of small molecule:
 Loss of small stable molecules such as H_2O , CO_2 , CO , C_2H_4 from molecular ion during fragmentation.

Ex- An alcohol readily loses H_2O molecule and shows a peak 18 mass units less than the peak of molecular ion.



Fragmentation adjacent to the branching point:

In case of branched alkanes, bond fission takes place adjacent to the branching point. Hence this leads to the formation of more stable carbocation Ex: 3-methyl pentane



Derivatives

If a compound has low volatility or if the parent mass cannot be determined, it may be possible to prepare a suitable derivative.

The derivative selected should provide :

- enhanced volatility,
- a predictable mode of cleavage,
- a simplified fragmentation pattern,
- an increased stability of the molecular ion.

i.e. Compounds containing several polar groups may have very low volatility (e.g., sugars, peptides, and di-basic carboxylic acids).

- Acetylation of hydroxyl and amino groups -
- methylation of free acids are effective choices to increase volatility and give characteristic peaks.
- Reduction of ketones to hydrocarbons -
- Polypeptides have been reduced with LiAlH_4 to give volatile polyamino alcohols with predictable fragmentation patterns.

Saturated Hydrocarbons- Alkanes

Rules 1–3 apply quite generally; rearrangement peaks, though common, are not usually intense (random rearrangements), and numerous reference spectra are available.

A . Straight chain compounds: Following are the features of the mass spectra of Alkanes.

- The relative height of the parent peak decreases as the molecular mass increases in the homologous series.
- The Molecular ion peak (although weak) is normally present.
- The spectra generally consist of clusters of peaks separated by 14 mass units corresponding to differences of CH_2 groups.
- The largest peak in each cluster represents $\text{C}_n\text{H}_{2n+1}$ fragment. This is accompanied by C_nH_{2n} and $\text{C}_n\text{H}_{2n-1}$ fragment corresponding to the loss of **one** and **two** H atoms respectively.

The most abundant fragments are at C_3 and C_4 , and the fragment abundances decrease in a smooth curve down to $[M - C_2H_5]^+$; the $[M - CH_3]^+$ peak is characteristically very weak or missing.

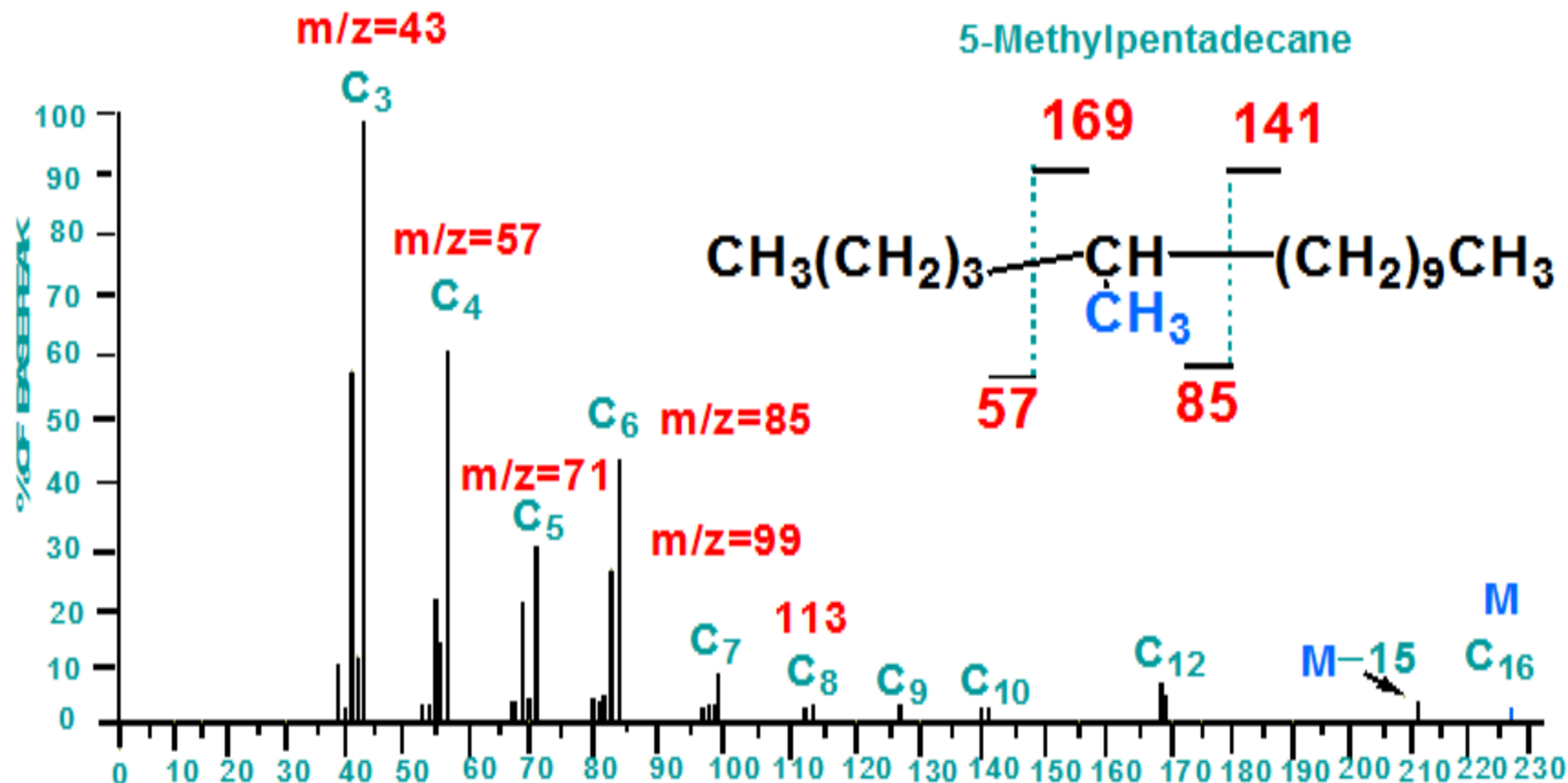
– Fragmentation often splits off simple alkyl groups:

- Loss of methyl $M^+ - 15$
- Loss of ethyl $M^+ - 29$
- Loss of propyl $M^+ - 43$
- Loss of butyl $M^+ - 57$

In longer chains – peaks at 43 and 57 are the most common

B. Branched Chain Hydrocarbons:

- Greater the branching in Alkanes less is the appearance of the molecular ion and if it appears, intensity will be low (M^+ peaks become weak).
- Bond cleavage takes place preferably at the site of branching. Due to such cleavage, more stable secondary or tertiary carbonium ions results. **Where the possibility of forming 2° & 3° carbocations is high, the molecule is susceptible to fragmentation.**
- Generally, largest substituent at a branch is eliminated readily as a radical. The radical achieves stability by the de-localization of lone electron.
- Greater number of fragments results from the branched chain compound compared to the straight compound. This is due to greater pathways available for cleavage.
- Peaks at 43 and 57 are the most common as these are the *iso*-propyl and *tert*-butyl cations

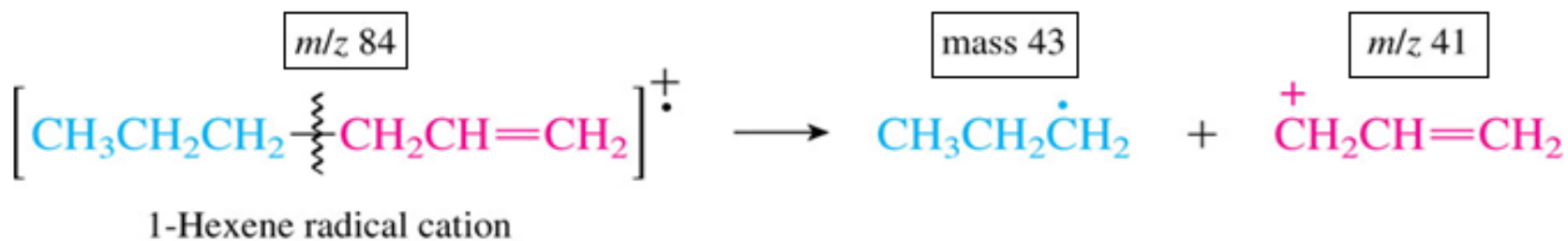
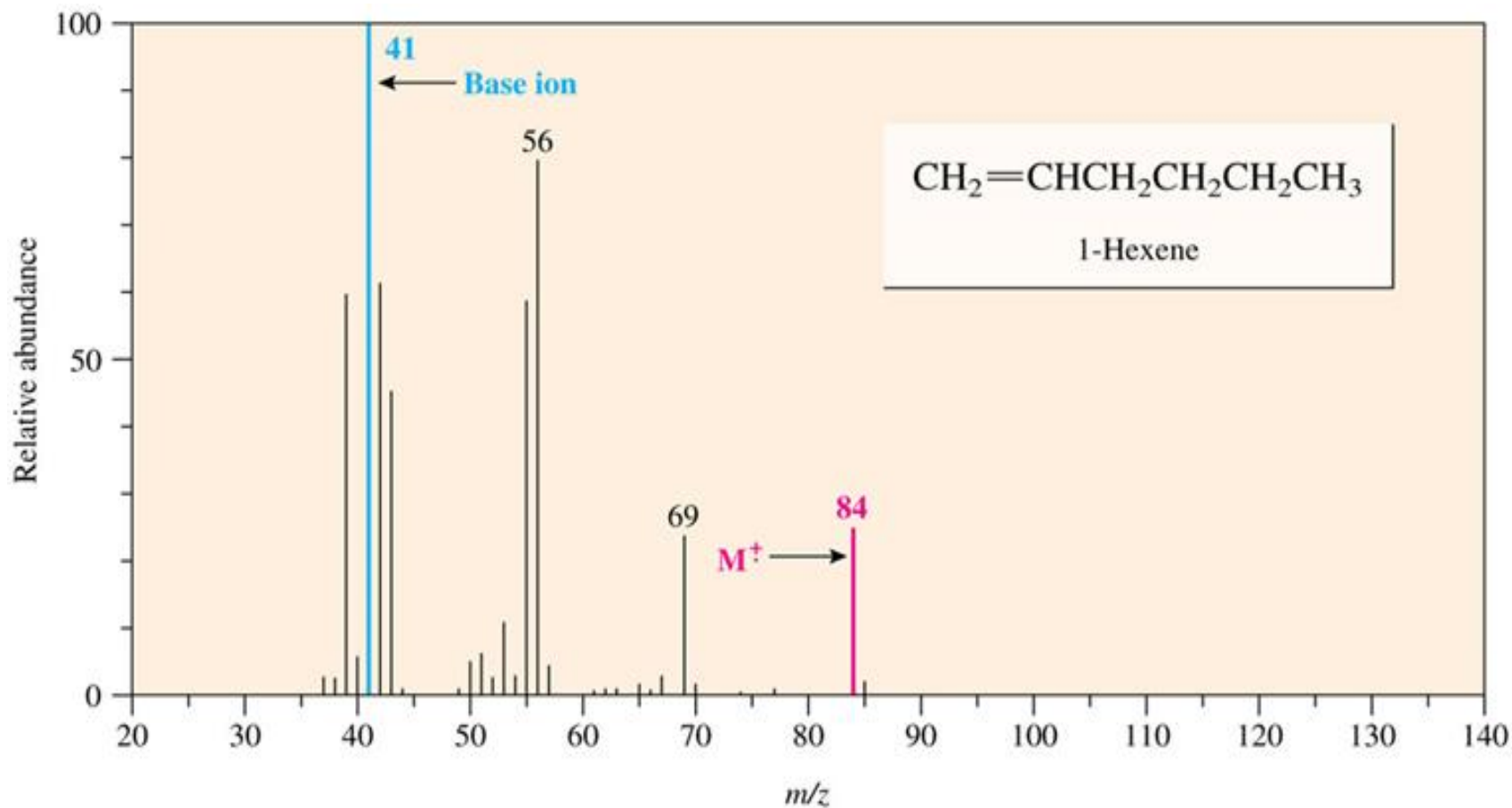


The peaks at m/z 169 and 85 represent cleavage on either side of the branch with charge retention on the substituted carbon atom.

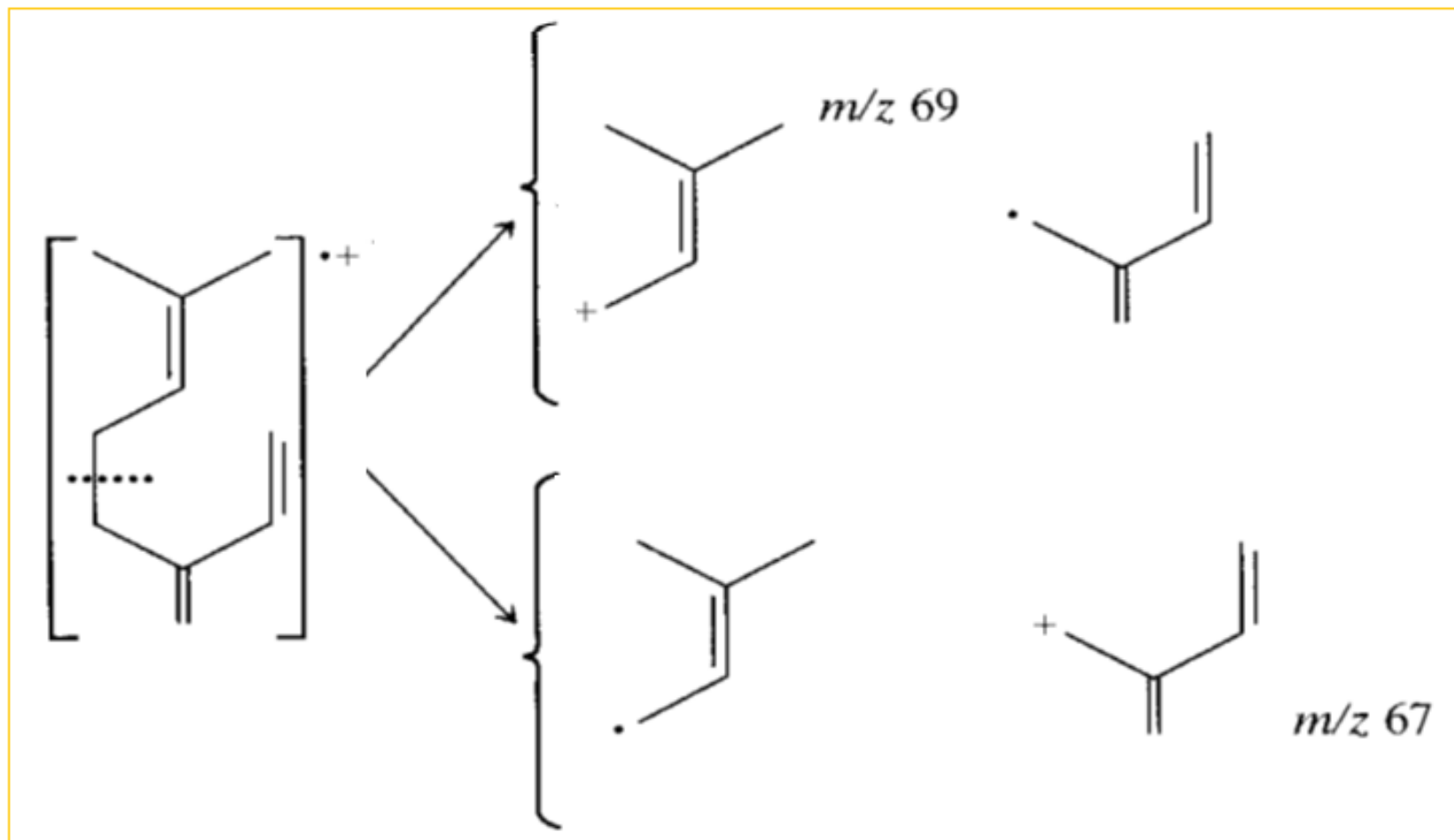
The presence of a distinct $M - 15$ peak also indicates a methyl branch.

Alkenes:

- The molecular ion of alkene containing one double bond tends to undergo allylic cleavage i.e. at the beta bond without the double bond and gives resonance structure.
- The molecular ion peak in the spectra of unsaturated compounds is more intense than the corresponding saturated analogues. The reason is the better resonance stabilization of the charge on the cation formed by the removal of one of the π -electrons.
- The relative abundance of the molecular ion peak decreases with increase in molecular mass.
- The cyclic olefine also shows group of peaks which are 14 mass units apart.
- The general mode of fragmentation is the allylic cleavage.
- The fragments formed by Mc Lafferty rearrangement are more intense.



In peak must involve rearrangement. The peaks at m/z 67 and 69 are the fragments from cleavage of a bi-allylic bond.



The peak at m/z 93 may be rationalized as a structure of formula $C_7H_9^+$ formed by isomerization (resulting in increased conjugation), followed by allylic cleavage.

