General Fragmentation Modes

The relative abundance of the fragment ion formed depends upon : (i) the stability of the ion

(*ii*) also the stability of the radical lost.

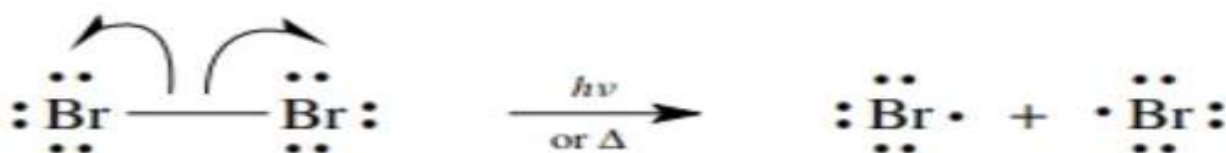The stability of the ion can be judged by stabilisation of the charge which depends upon :

(a) Resonance (b) Inductive effect, (c) Polarisability

The formation of a new bond is a powerful driving force for ion decompositions. The energy released during bond formation is available for the cleavage of some other bonds in the ion. Some important fragmentation modes are described below:

1. Simple cleavage. This process involves homolytic or heterolytic cleavage of a single covalent bond. The homolytic cleavage is initiated by a radical site.

(i) Homolytic cleavage. Odd electron ions have an unpaired electron which is capable of new bond formation. When a bond is formed, energy is released. The energy released by bond formation can help offset the

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energy required for the cleavage of some other bond in the ion. In the curved arrow formalism, the movement of single electrons is indicated by **half-headed arrows (fishhooks)**.
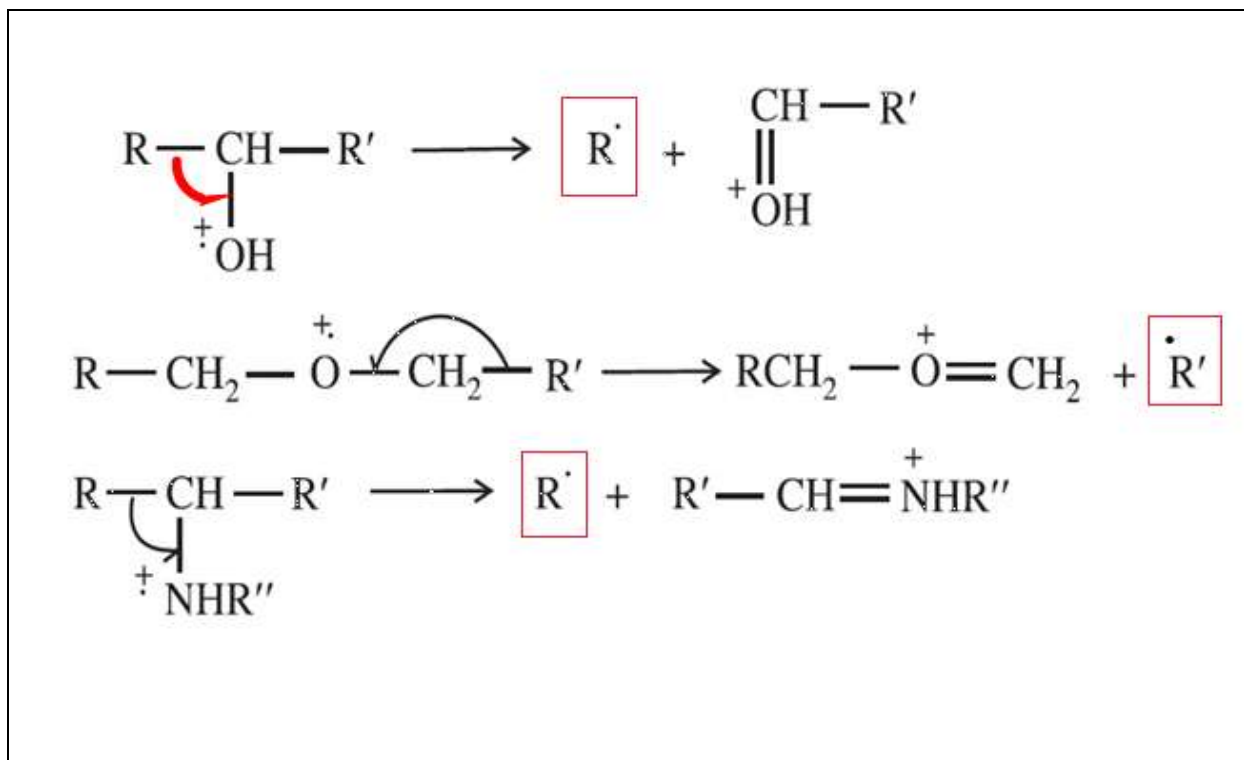
Homolytic cleavage
$$A{-}B \longrightarrow A^{\bullet} + B^{\bullet} \quad \text{free radicals}$$

$$:\!Br{-}Br\!: \xrightarrow[\text{or } \Delta]{hv} :\!Br^{\bullet} + {}^{\bullet}Br\!:$$

 Homolytic cleavage reactions are very common and **can be classed in the following types:**

(***a***) **Mode I.** This fragmentation mode operates in compounds in which a hetero atom is singly bonded to a carbon atom. Parent ion is formed by the removal of one electron from the heteroatom. A new bond is formed with the adjacent atom through the donation of the unpaired electron and the transfer of an electron from the adjacent bond.

$$R{-}\underset{\underset{X^{+\bullet}}{|}}{CH}{-}R' \longrightarrow R{\cdot} + R'{-}CH{=}X^{+}$$
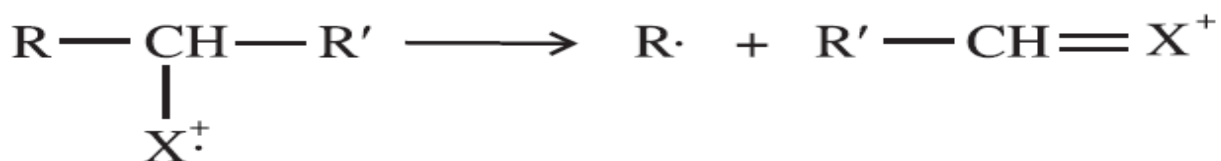
More abundant peaks are formed by the cleavage of carbon-carbon bond which is in the α position to the hetero atom in the mass spectra of <u>alcohols, amines, ethers</u>.

$$R\!-\!\!\overset{\displaystyle |}{\underset{\displaystyle \overset{+}{\cdot}OH}{CH}}\!\!-\!R' \longrightarrow \boxed{R^{\cdot}} \; + \; \underset{\displaystyle \overset{+}{\cdot}OH}{\overset{\displaystyle CH\!-\!R'}{\|}}$$

$$R\!-\!CH_2\!-\!\overset{+\cdot}{O}\!\frown\!CH_2\!-\!R' \longrightarrow RCH_2\!-\!\overset{+}{O}\!=\!CH_2 \; + \boxed{R^{\cdot}}$$

$$R\!-\!\!\overset{\displaystyle |}{\underset{\displaystyle \overset{+}{\cdot}NHR''}{CH}}\!\!-\!R' \longrightarrow \boxed{R^{\cdot}} \; + \; R'\!-\!CH\!=\!\overset{+}{N}HR''$$

(**b**) **Mode II.** When a hetero atom is attached to a carbon atom by a double bond, α-cleavage is the preferred fragmentation mode.

Acylium ion
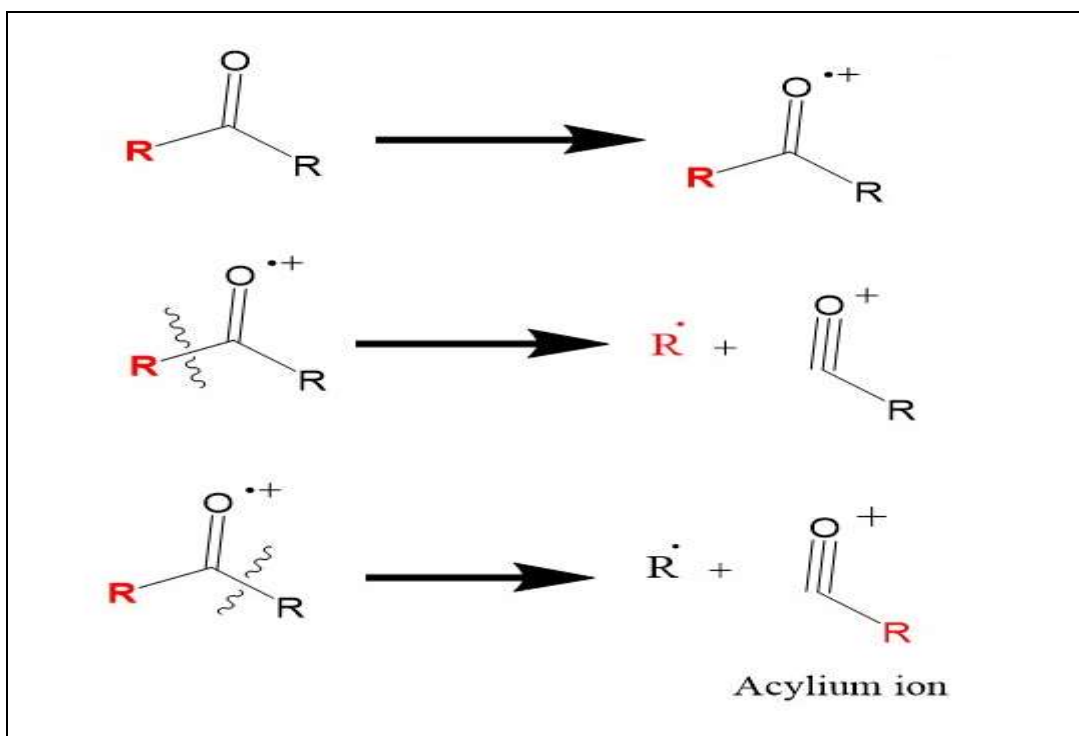
✱ Compounds containing -C≡N or C=S groups do not show this type of fragmentation.

✱In ketones, significant peaks are observed due to the cleavage of carbon-carbon bond which is alpha (α) to the carbonyl group.

✱Unsymmetrical ketones show two types of peaks since either alkyl group can be lost. The elimination of a bigger alkyl radical is preferred.

✱In the same way, the fragmentation mode in aldehydes, esters and amides leads to the cleavage of C—H, C—O and C—N bond respectively.

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*The presence of amino and hydroxyl groups which are electron donating in nature reduce the relative abundance of acylium $(R—C \equiv O)^+$ ion. The presence of electron withdrawing substituents such as nitro and cyano increase the relative abundance of the ion.

(*c*) **Mode III.** Benzylic cleavage is an energetically preferred fragmentation mode. It involves the cleavage of a carbon-carbon bond which is beta (β) to the aromatic ring.
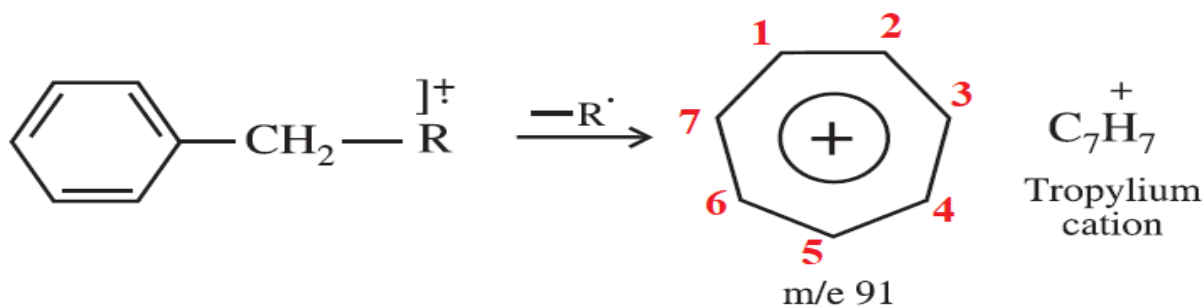
m/e 91

Considerable stabilization of the tropylium cation is provided by the aromatic-system. Thus, the mass spectrum of ethyl benzene **has a very intense** $(M^{·+}—CH_2)$ ion at m/e 91.
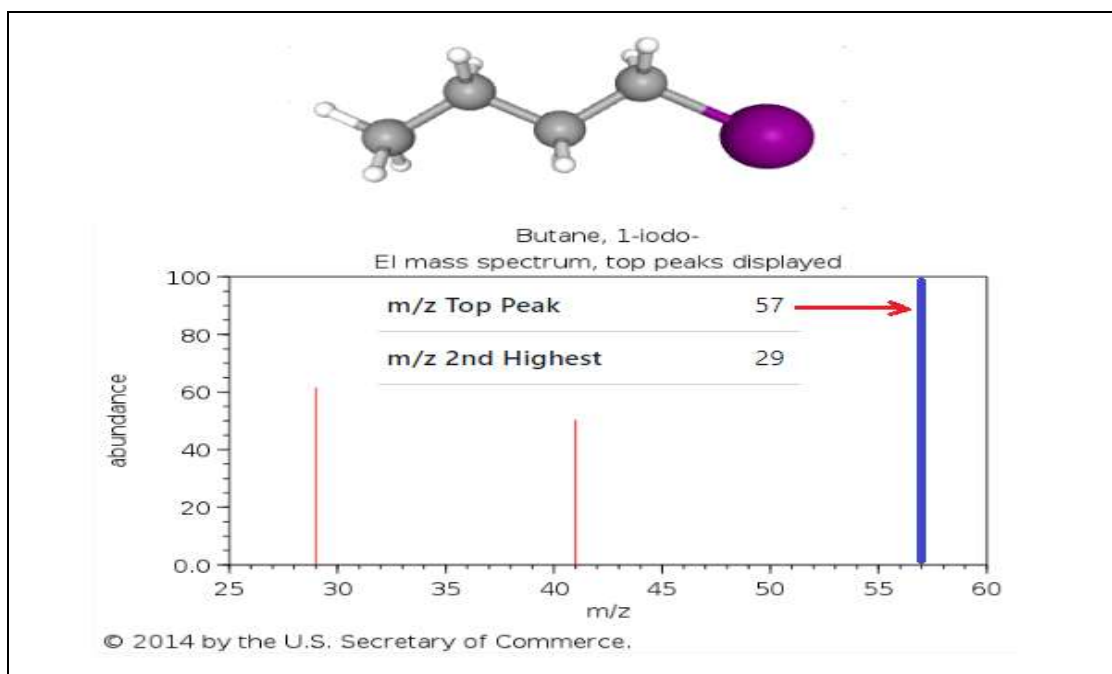
(ii) Heterolytic cleavage:

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When the atom in question is a positively charged carbon, the resulting species is called a **carbocation.** If it is negatively charged, it is called a **carbanion.**
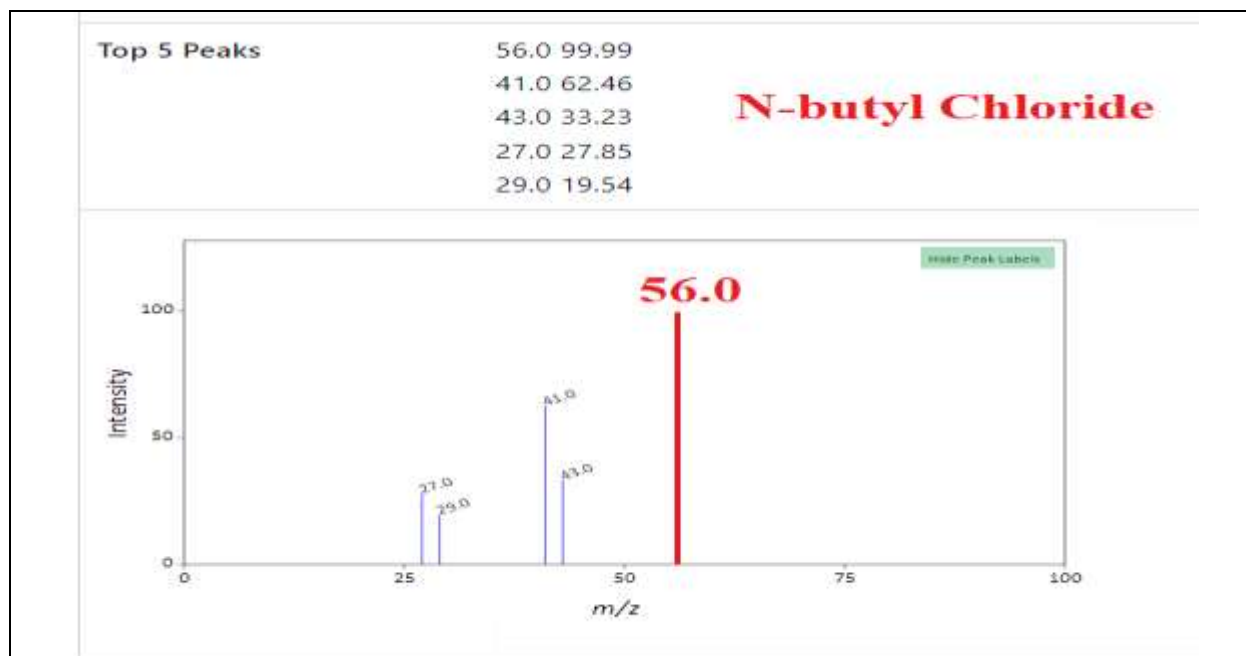
Heterolytic cleavage may be noted the cleavage of C—X (X = O, N, S, Cl) bond is more difficult than that of a C—C bond.
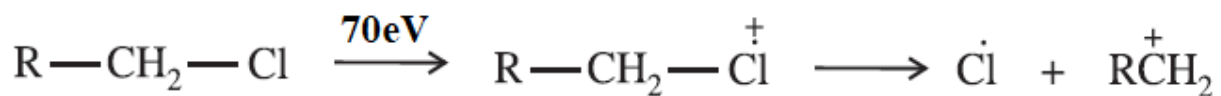
The result of this cleavage:

● The positive charge is carried by the carbon atom and not by the hetero atom.

● It can be shown in the fragmentation of alkyl halide. In the spectra of mono halogenated compounds, hydrocarbon ions are formed in more abundance.

● As the size of the halogen atom increases, the C—X bond becomes weak. Accordingly C—X bond in alkyl bromides and iodides are easily broken while alkyl chlorides are less susceptible to fragmentation.

● In n-butyl bromide and n-butyl iodide, simple cleavage leads to the loss of halogen atom. It forms a more abundant even electron ion at m/e 57.
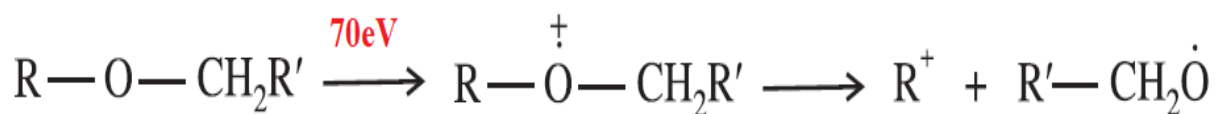
Butane, 1-iodo-
EI mass spectrum, top peaks displayed

m/z Top Peak   57

m/z 2nd Highest   29

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.●In n-butyl chloride, cleavage of C—Cl is difficult. Thus, elimination of HCl by a rearrangement process gives rise to a peak at m/e 56.
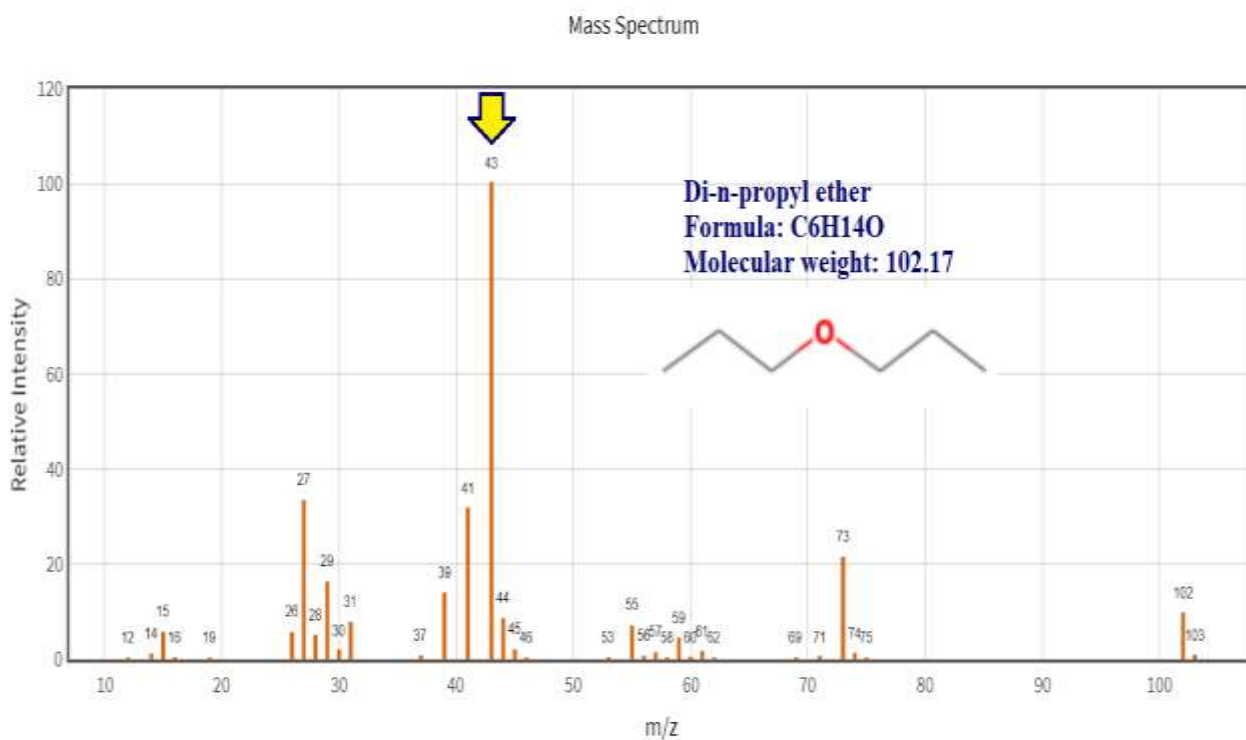

Top 5 Peaks   56.0 99.99
                     41.0 62.46   **N-butyl Chloride**
                     43.0 33.23
                     27.0 27.85
                     29.0 19.54

$$R\text{---}CH_2\text{---}Cl \xrightarrow{\text{70eV}} R\text{---}CH_2\text{---}\overset{+}{\underset{\cdot\cdot}{Cl}} \longrightarrow \overset{\cdot}{Cl} + R\overset{+}{C}H_2$$

● In ethers, the cleavage of C—O bond leads to the formation of an alkyl ion rather than an alkoxy ion.

$$R\text{---}O\text{---}CH_2R' \xrightarrow{\text{70eV}} R\text{---}\overset{+}{\underset{\cdot\cdot}{O}}\text{---}CH_2R' \longrightarrow R^+ + R'\text{---}CH_2\overset{\cdot}{O}$$

● In di-n-propyl ether, propyl ion appears as a base peak at m/e 43

Mass Spectrum

Di-n-propyl ether
Formula: C6H14O
Molecular weight: 102.17

2. Retro-Diel's-Alder reaction:: This reaction is an example of multicentred fragmentation which is characteristic of cyclic olefines. It 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 process is not accompanied by any hydrogen transfer rearrangement. The charge can be carried by any one of the fragments. The more highly substituted or more conjugated fragment which has a lower ionisation potential carries a charge. In simple system, the charge is carried by a diene.
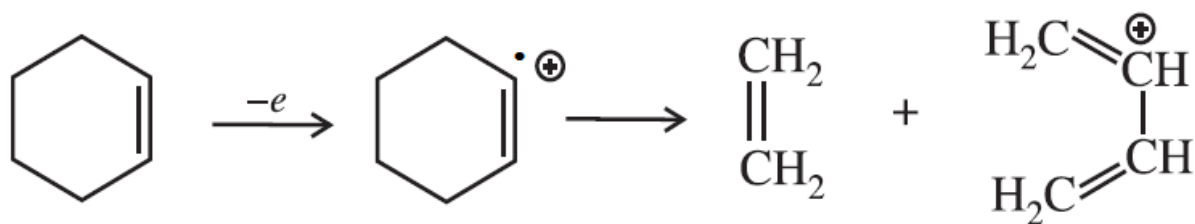
3. Hydrogen transfer rearrangements:: The simplest rearrangement involves the transfer of a hydrogen atom from one part of the molecule to another. These processes are very common in mass spectrometry.

4. McLafferty rearrangement ion::