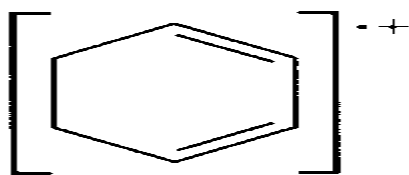


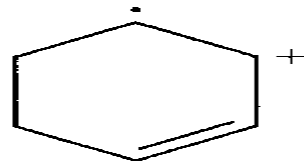
Fragmentation

Generally, the tendency is to represent the molecular ion with a delocalized charge. Djerassi's (1967) approach is to localize the positive charge on either a π bond (except in conjugated systems), or on a heteroatom. Whether or not this concept is totally rigorous, it

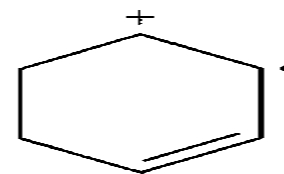
Structures **A** and **B**, for example, represent the molecular ion of cyclohexadiene. Compound **A** is a delocalized structure with one less electron than the original uncharged diene; both the electron and the positive charge are delocalized over the π system. Since the electron removed to form the molecular ion is a π electron, other structures, such as **B** or **C** (valence bond struc-



A

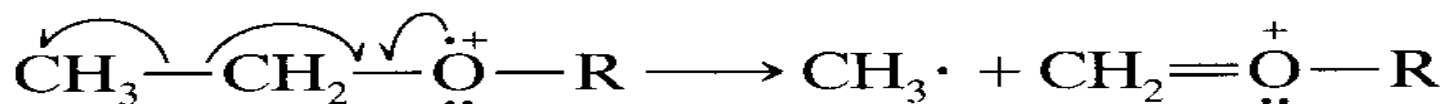


B

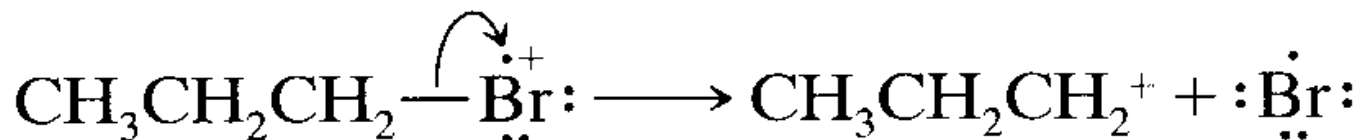


C

Fragmentation of the odd-electron molecular ion (radical-cation, $M^{\bullet+}$) may occur by homolytic or heterolytic cleavage of a single bond. 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).



In heterolytic cleavage, a pair of electrons “move” together toward the charged site as shown by the conventional curved arrow; the fragments are again an even-electron cation and a radical, but here the final charge site is on the alkyl product.



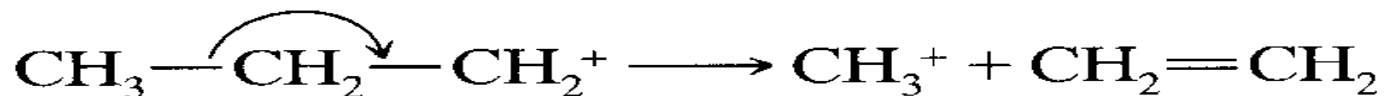
- Simultaneous or consecutive cleavage of several bonds may occur when energy benefits accrue from formation of :

- 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 .

ther fragmentation of an even-electron cation usually results in another even-electron cation and an even-electron neutral molecule or fragment.



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 (see 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.

Stevensons rule

3. Cleavage is favored at alkyl-substituted carbon atoms; the more substituted, the more likely is cleavage. This is a consequence of the increased stability of a tertiary carbocation over a secondary, which in turn is more stable than a primary.

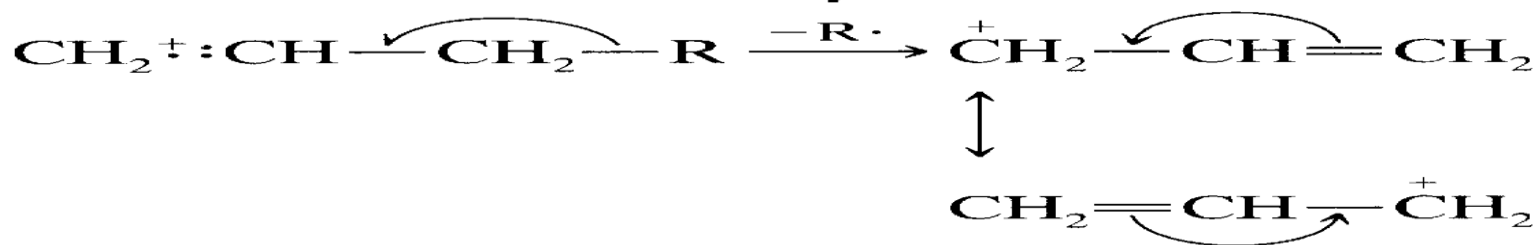


Cation stability order:

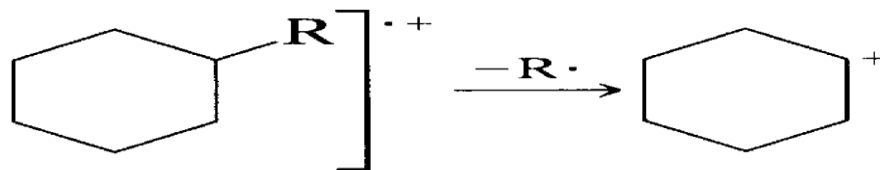


Generally, the largest substituent at a branch is eliminated most readily as a radical, presumably because a long-chain radical can achieve some stability by delocalization of the lone electron.

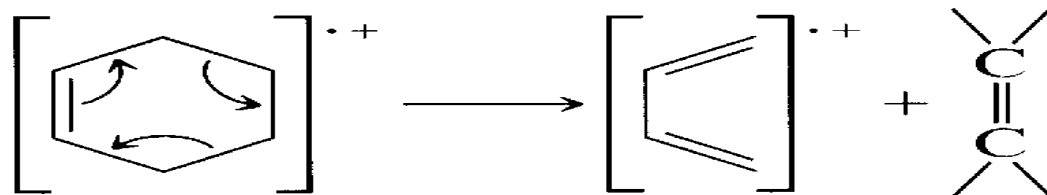
4. Double bonds, cyclic structures, and especially aromatic (or heteroaromatic) rings stabilize the molecular ion and thus increase the probability of its appearance.
5. Double bonds favor allylic cleavage and give the resonance-stabilized allylic carbocation. This rule



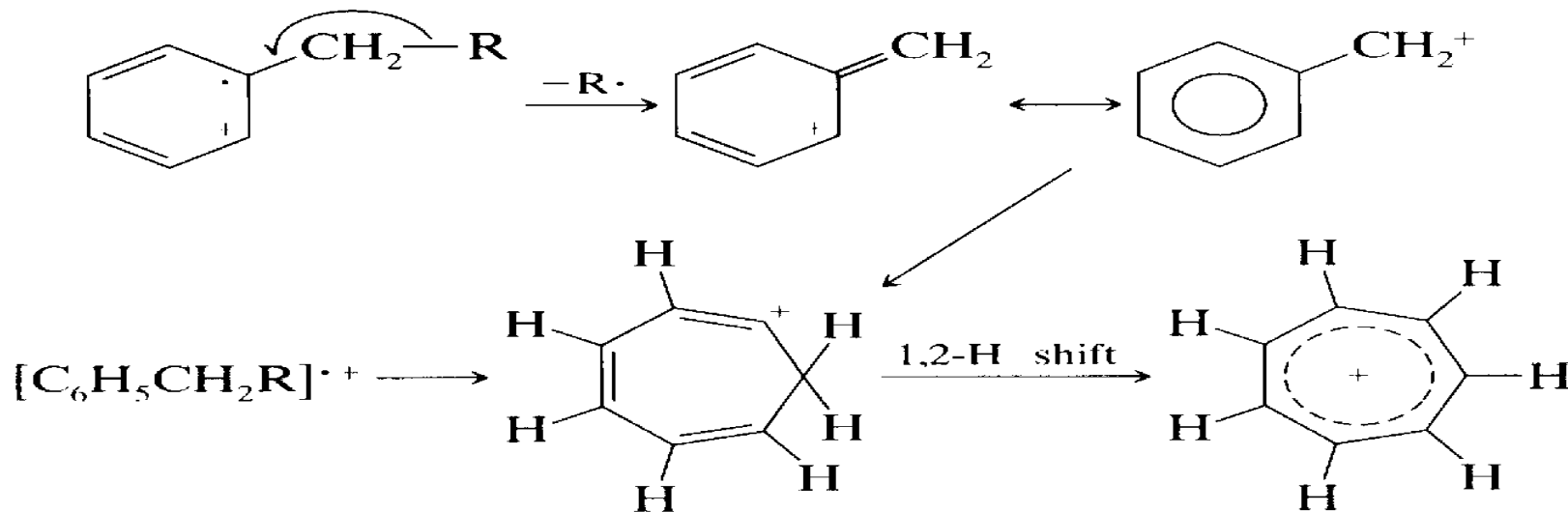
6. Saturated rings tend to lose alkyl side chains at the α bond. This is merely a special case of branching (rule 3). The positive charge tends to stay with the ring fragment.



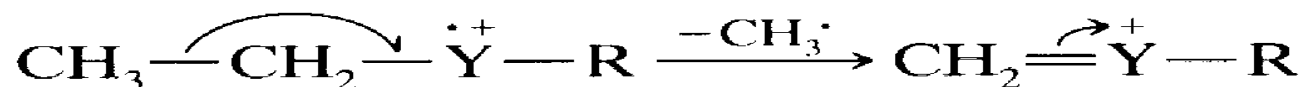
Unsaturated rings can undergo a *retro-Diels-Alder* reaction:



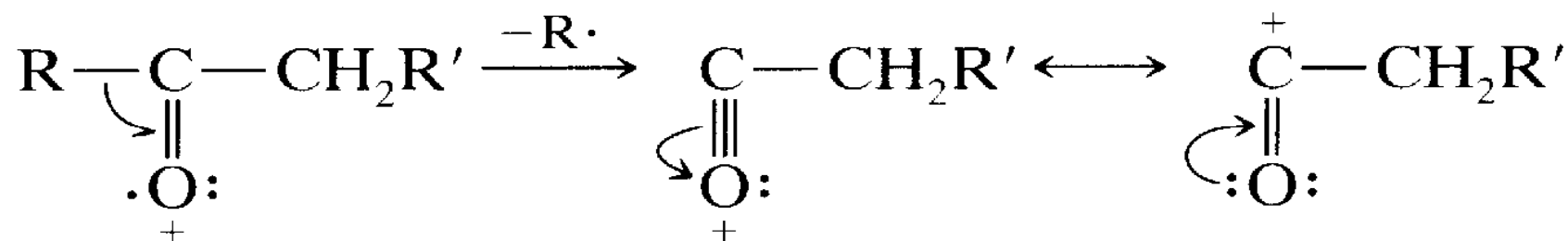
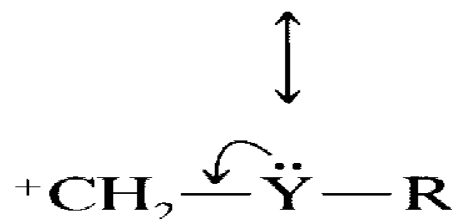
7. In alkyl-substituted aromatic compounds, cleavage is very probable at the bond β to the ring, giving the resonance-stabilized benzyl ion or, more likely, the tropylium ion:



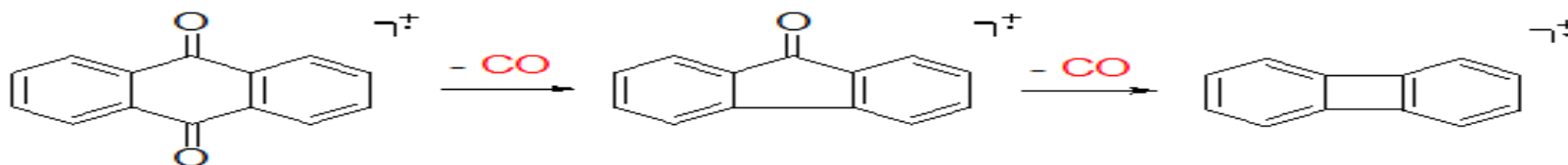
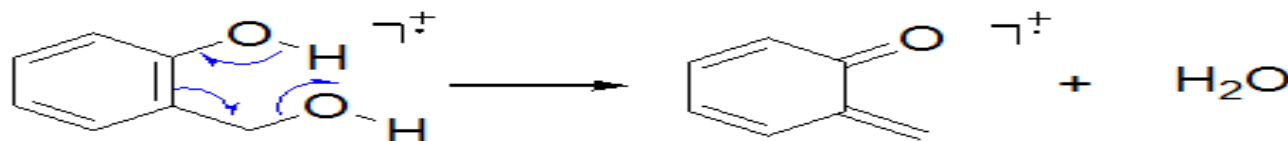
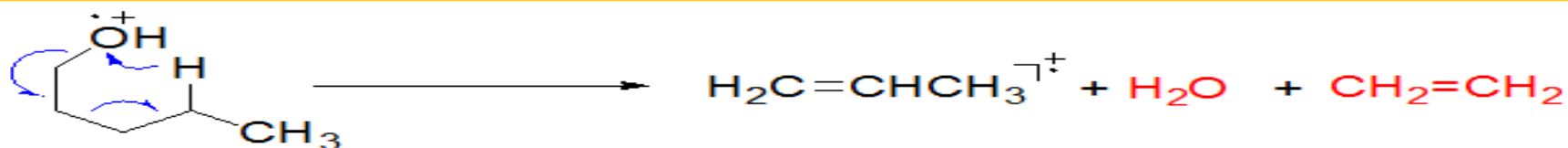
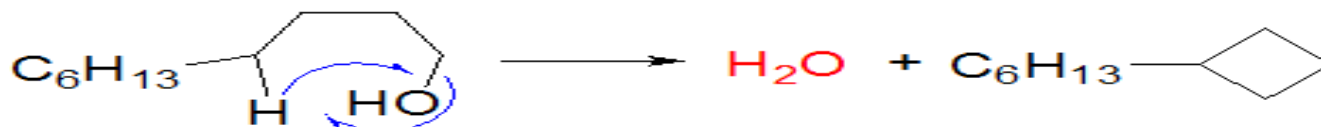
8. The C—C bonds next to a heteroatom are frequently cleaved, leaving the charge on the fragment containing the heteroatom whose nonbonding electrons provide resonance stabilization.



where Y = O, NH, or S;



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 (Section 2.8).

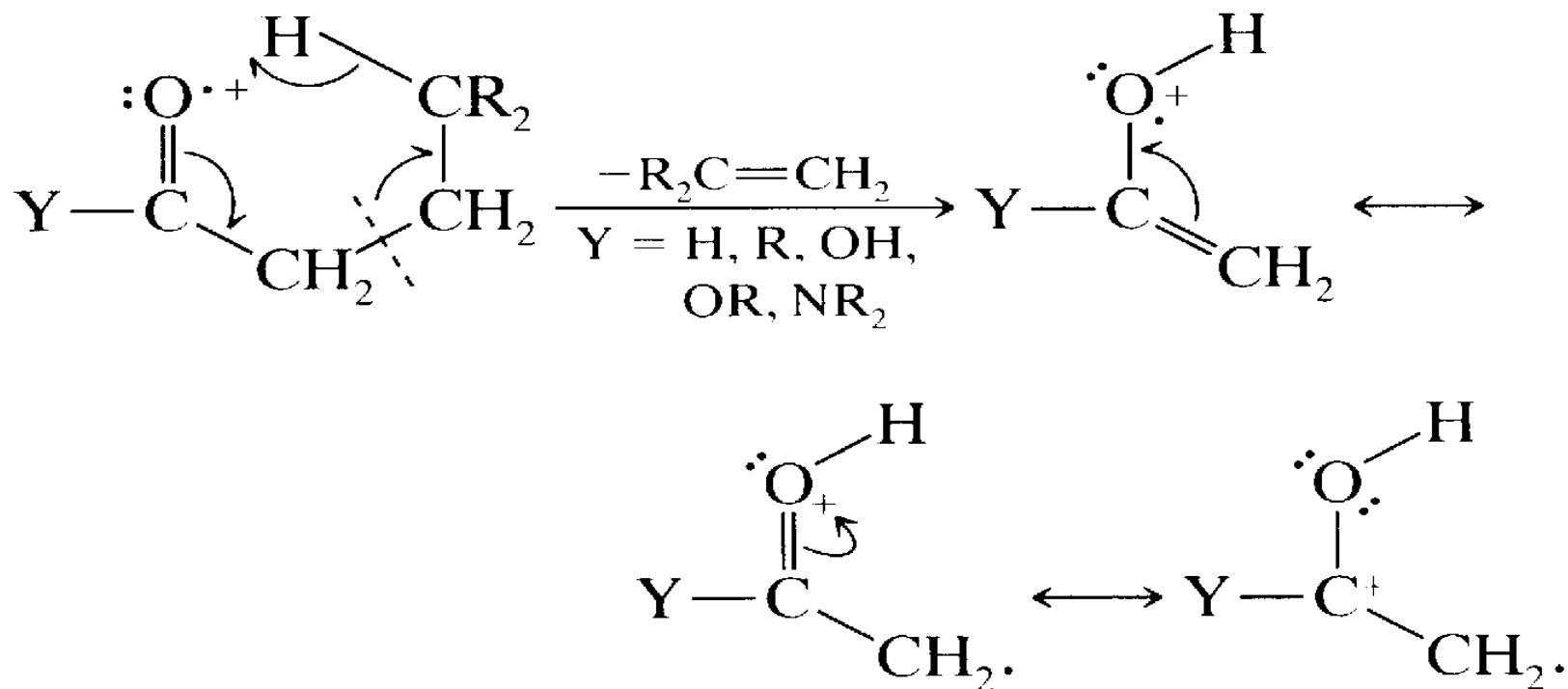


It should be kept in mind that the fragmentation rules above apply to EI mass spectrometry. Since other ionizing (CI, etc.) techniques often produce molecular ions with much lower energy or quasimolecular ions with very different fragmentation patterns, different rules govern the fragmentation of these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

Rearrangements

Rearrangement ions are fragments whose origin cannot be described by simple cleavage of bonds in the molecular ion but are a result of intramolecular atomic rearrangement during fragmentation. Rearrangements involving migration of hydrogen atoms in molecules that contain a heteroatom are especially common. One important example is the so-called McLafferty rearrangement.

To undergo a McLafferty rearrangement, a molecule must possess an appropriately located heteroatom (e.g., O), a π system (usually a double bond), and an abstractable hydrogen atom γ to the C=O system.



Such rearrangements often account for prominent characteristic peaks and are consequently very useful for our purpose. They can frequently be rationalized on the basis of low-energy transitions and increased stability of the products. Rearrangements resulting

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.

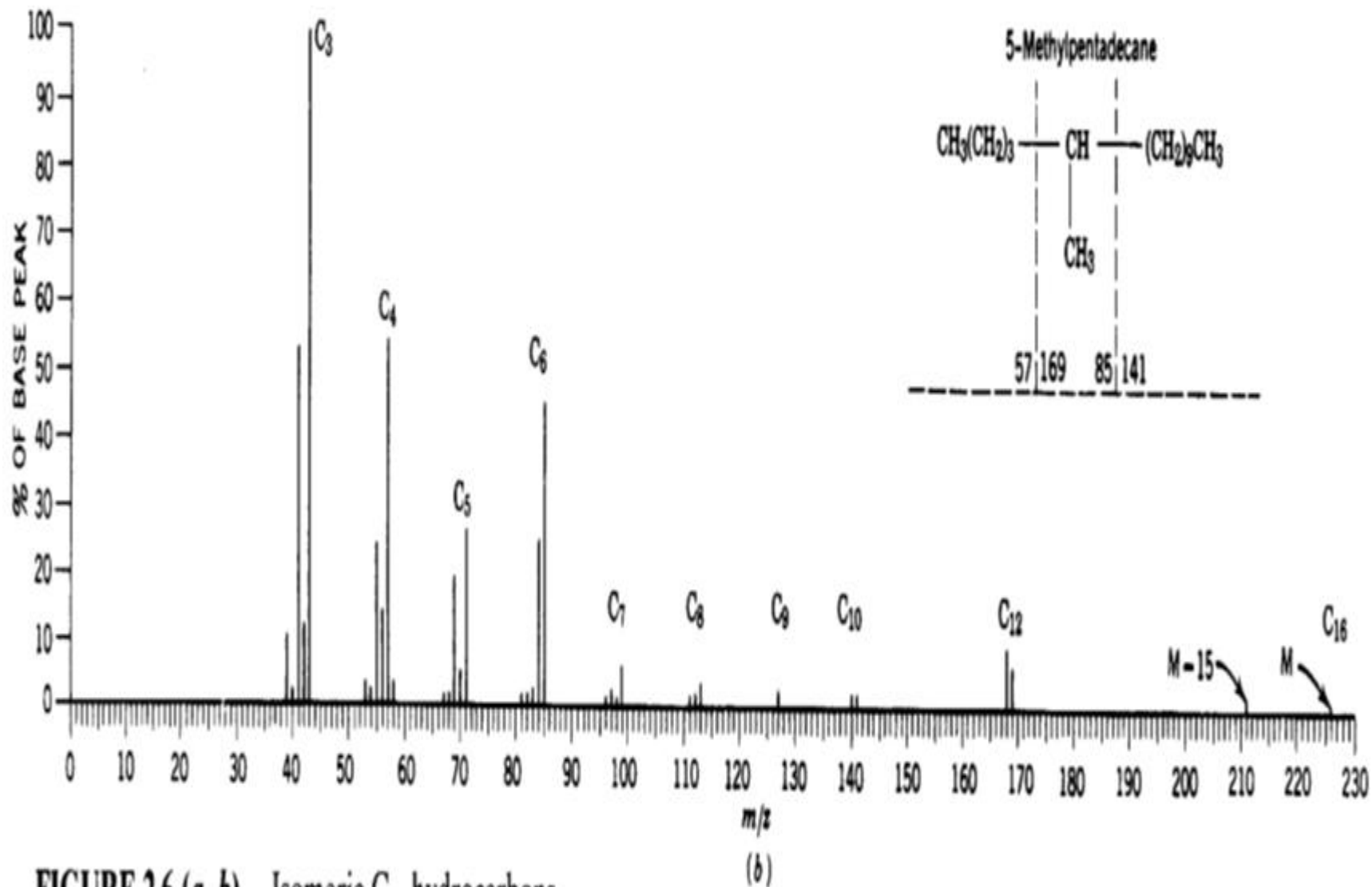
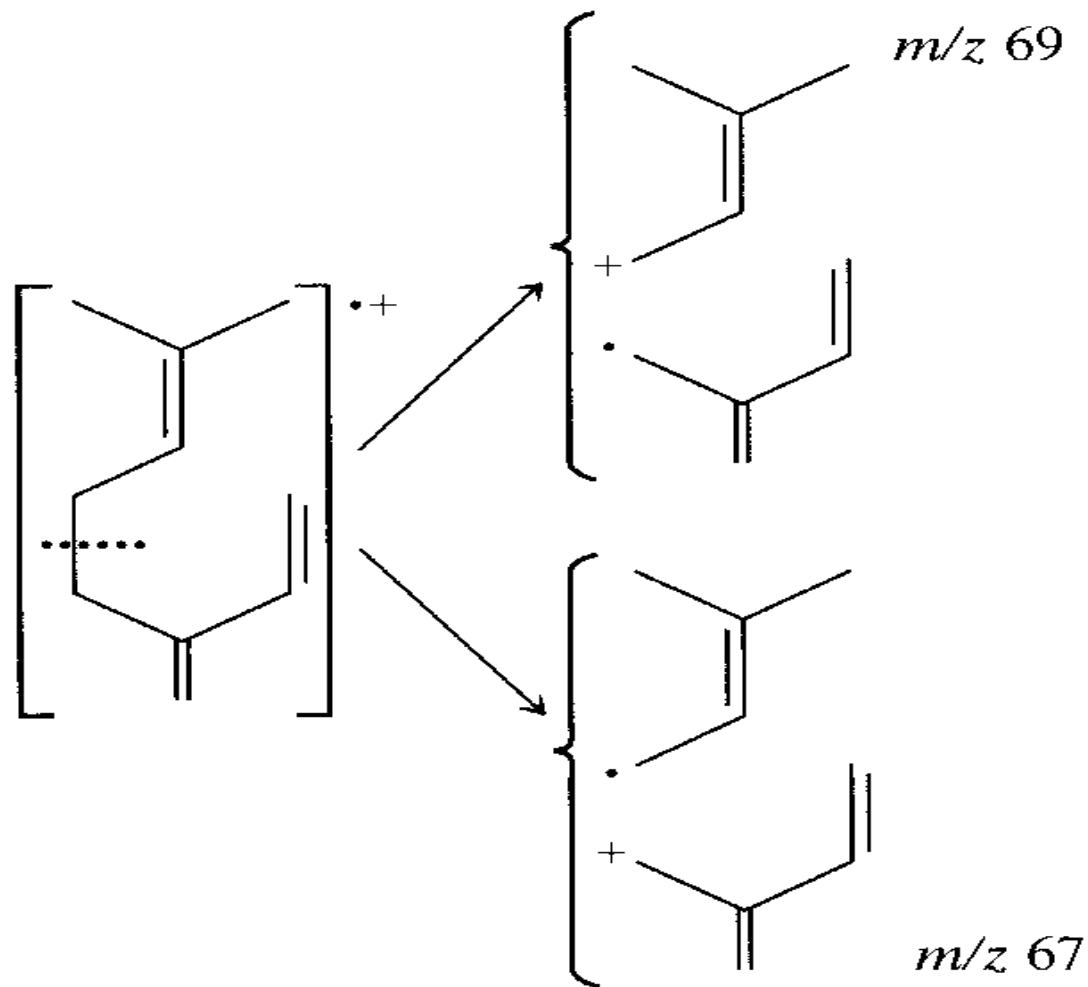


FIGURE 2.6 (a, b). Isomeric C_{16} hydrocarbons.

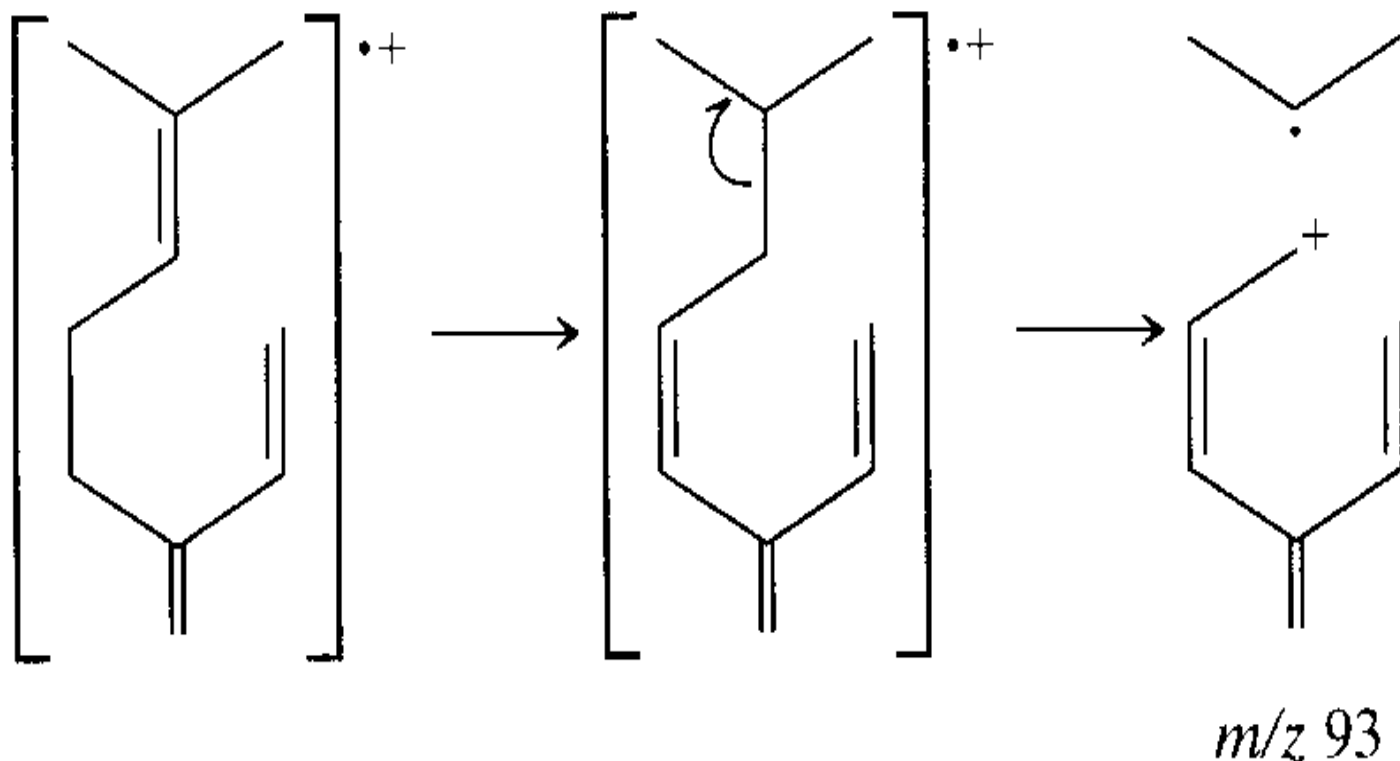
2.10.1.2 Alkenes (Olefins) The molecular ion peak of alkenes, especially polyalkenes, is usually distinct. Location of the double bond in acyclic alkenes is difficult because of its facile migration in the fragments. In

- 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.

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



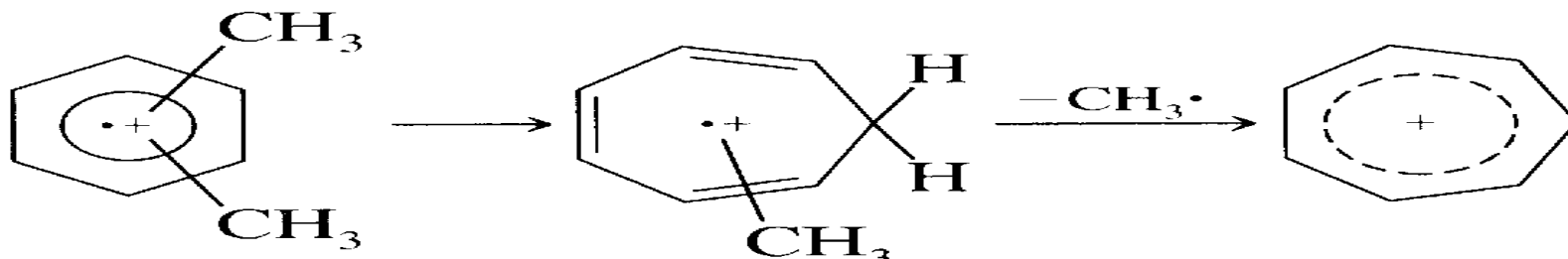
The peak at m/z 93 may be rationalized as a structure of formula $C_7H_9^+$ formed by isomerization (resulting in increased conjugation), followed by allylic cleavage.



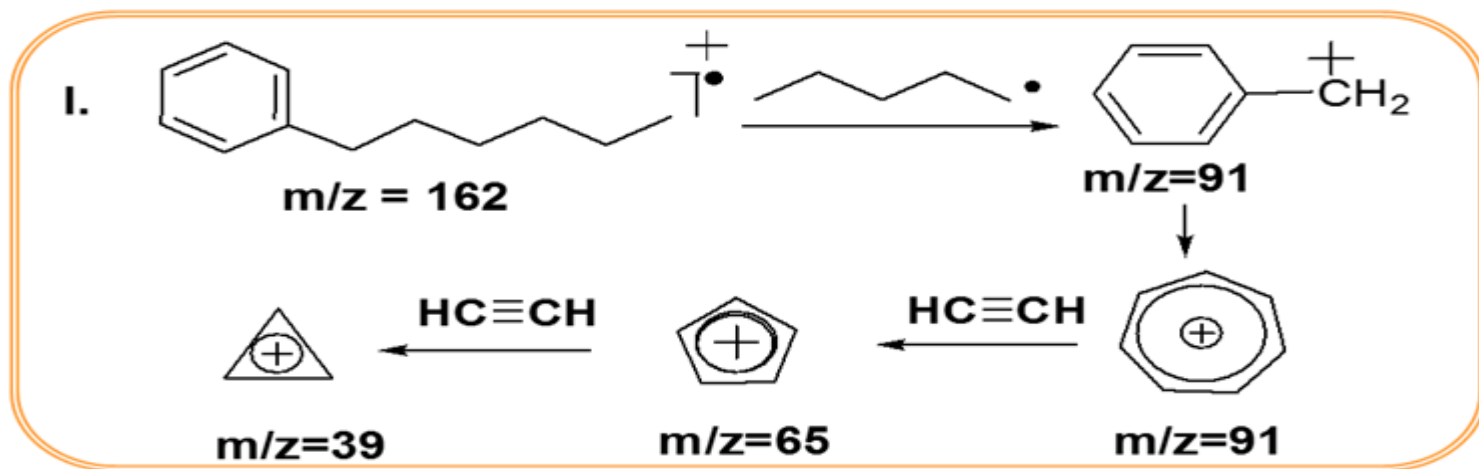
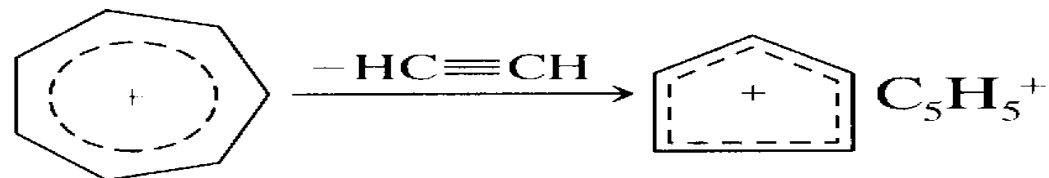
2.10.1.3 Aromatic and Alkyl Hydrocarbons An aromatic ring in a molecule stabilizes the molecular ion peak (rule 4, Section 2.7), which is usually sufficiently large that accurate intensity measurements can be made on the $M + 1$ and $M + 2$ peaks.

A prominent peak (often the base peak) at m/z 91 ($C_6H_5CH_2^+$) is indicative of an alkyl-substituted ben-

zene ring. Branching at the α carbon leads to masses higher than 91 by increments of 14, the largest substituent being eliminated most readily (rule 3, Section 2.7). A distinct and sometimes prominent $M - 1$ peak results from similar benzylic cleavage of a C—H bond.



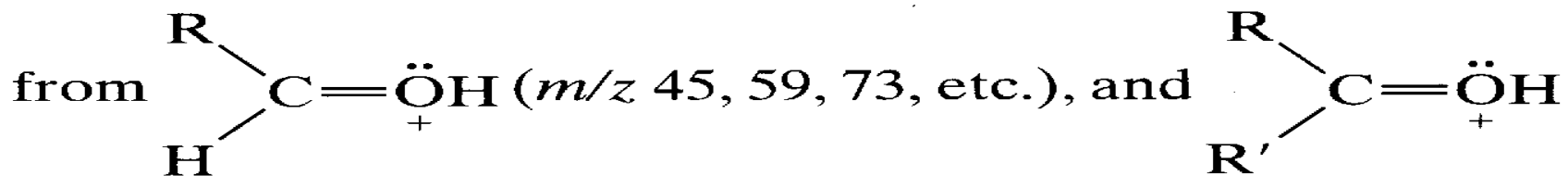
The frequently observed peak at m/z 65 results from elimination of a neutral acetylene molecule from the tropylium ion.



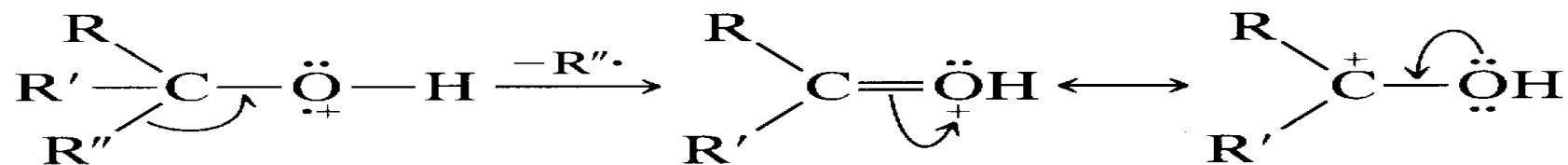
A characteristic cluster of ions resulting from an α cleavage and hydrogen migration in monoalkylbenzenes appears at m/z 77 (C_6H_5^+), 78 (C_6H_6^+), and 79 (C_6H_7^+).

2.10.2.1 Alcohols The molecular ion peak of a primary or secondary alcohol is quite small and for a tertiary alcohol is undetectable. The molecular ion of 1-

Cleavage of the C—C bond next to the oxygen atom is of general occurrence (rule 8, Section 2.7). Thus, primary alcohols show a prominent peak resulting from $\text{CH}_2=\ddot{\text{O}}\text{H}^+$ (m/z 31). Secondary and tertiary alcohols cleave analogously to give a prominent peak resulting



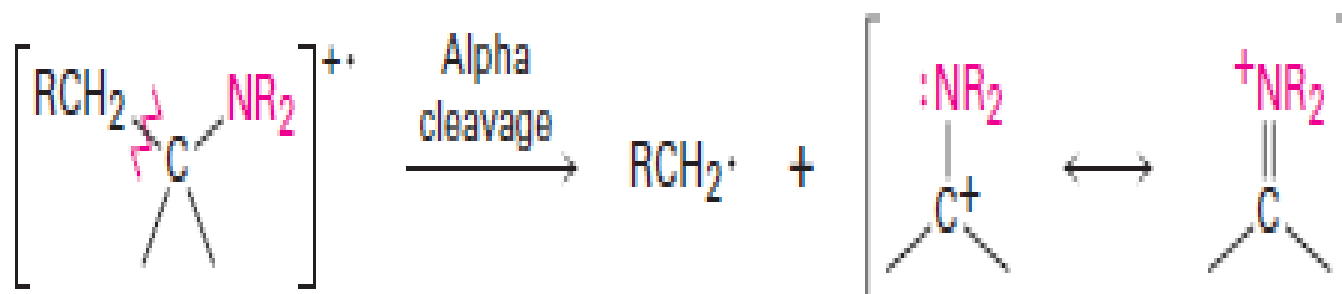
(m/z 59, 73, 87, etc.), respectively. The largest substituent is expelled most readily (rule 3).



where $\text{R}'' > \text{R}'$ or R . When R and/or $\text{R}' = \text{H}$, an $\text{M} - 1$ peak can usually be seen.

Amines

Aliphatic amines undergo a characteristic α cleavage in the mass spectrometer, similar to that observed for alcohols. A C–C bond nearest the nitrogen atom is broken, yielding an alkyl radical and a resonance-stabilized, nitrogen-containing cation.

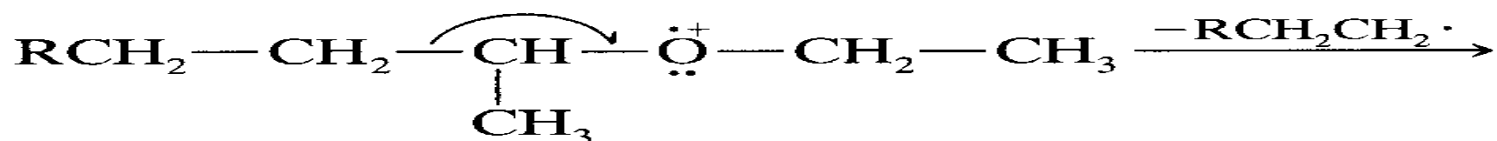


ether

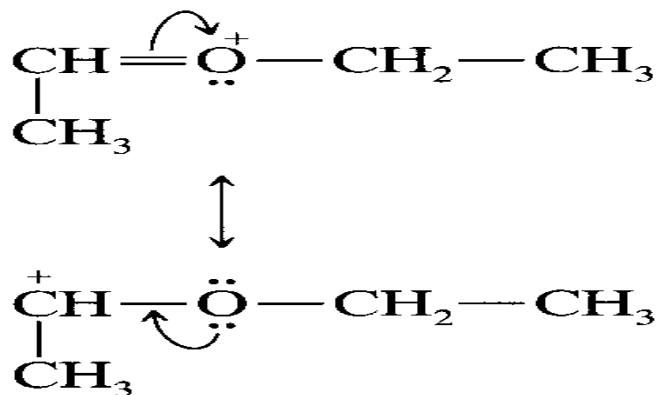
The presence of an oxygen atom can be deduced from strong peaks at m/z 31, 45, 59, 73, These peaks represent the RO^+ and ROCH_2^+ fragments.

Fragmentation occurs in two principal ways:

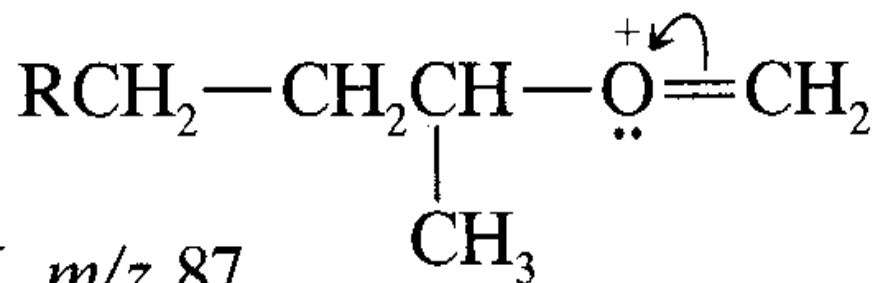
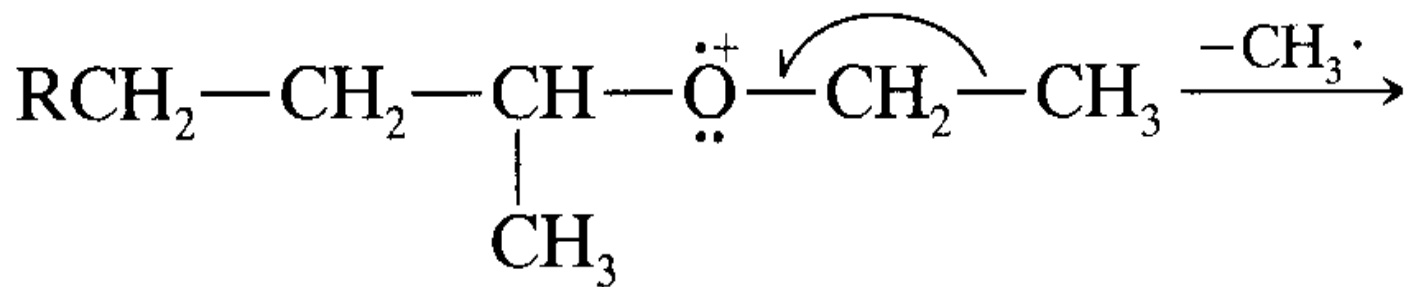
1. Cleavage of the C—C bond next to the oxygen atom (α , β bond, rule 8, Section 2.7)



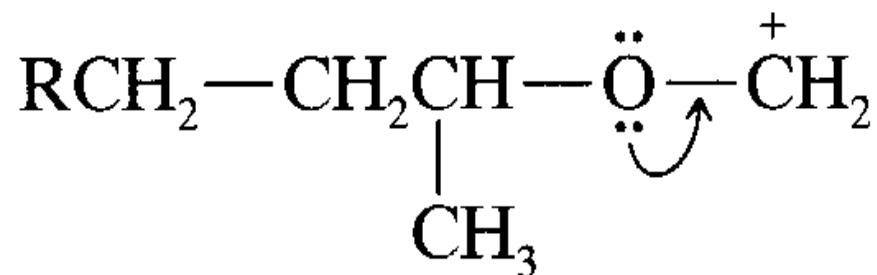
In Figure 2.11, $\text{R} = \text{H}$.



m/z 73



In Figure 2.11, R = H, m/z 87.



2. C—O bond cleavage with the charge remaining on the alkyl fragment.

