

Aromatic and Alkyl Hydrocarbons

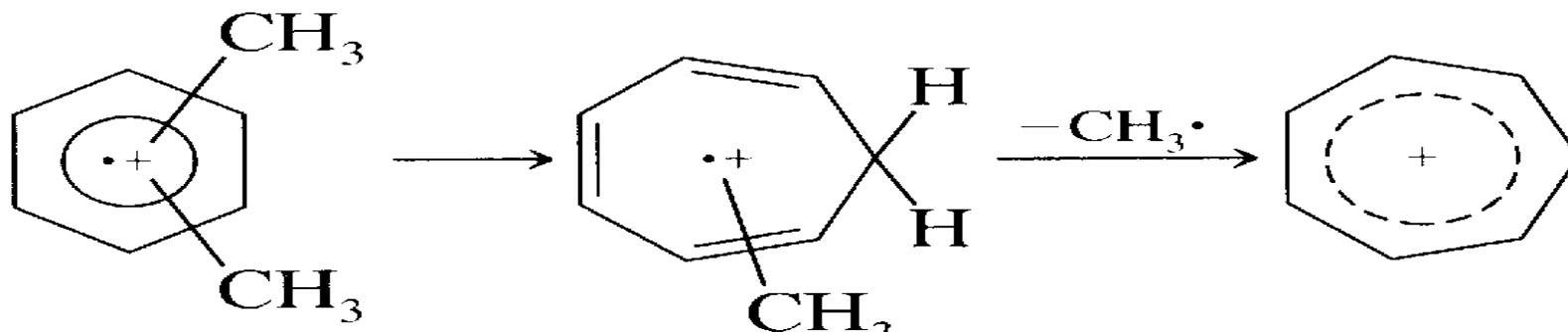
An aromatic ring in a molecule stabilizes the molecular ion peak (rule 4), which is usually sufficiently large that accurate intensity measurements can be made on the $M + 1$ and $M + 2$ peaks.

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

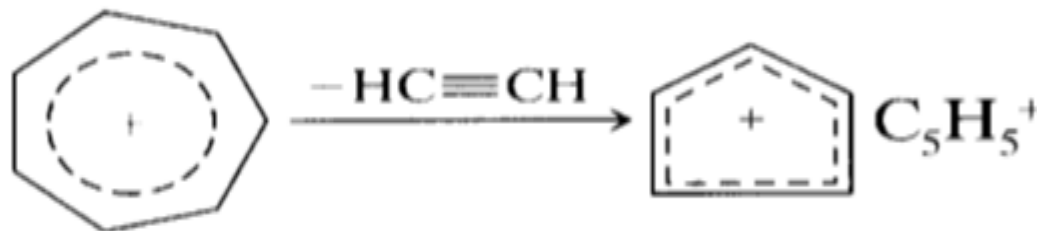
Branching at the α carbon leads to masses higher than 91 by increments of 14, the largest substituent being eliminated most readily (rule 3).

- It shows prominent mol ion peak, as compared to the alkanes and alkenes containing same number of C atoms. This is as a result of the stabilizing effect of the ring.

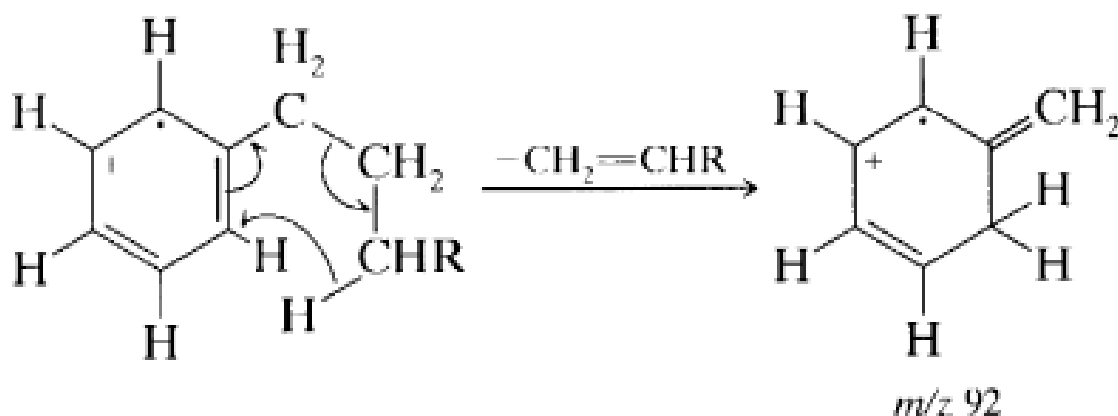
A distinct and sometimes prominent $M - 1$ peak results from similar benzylic cleavage of a C—H bond.



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

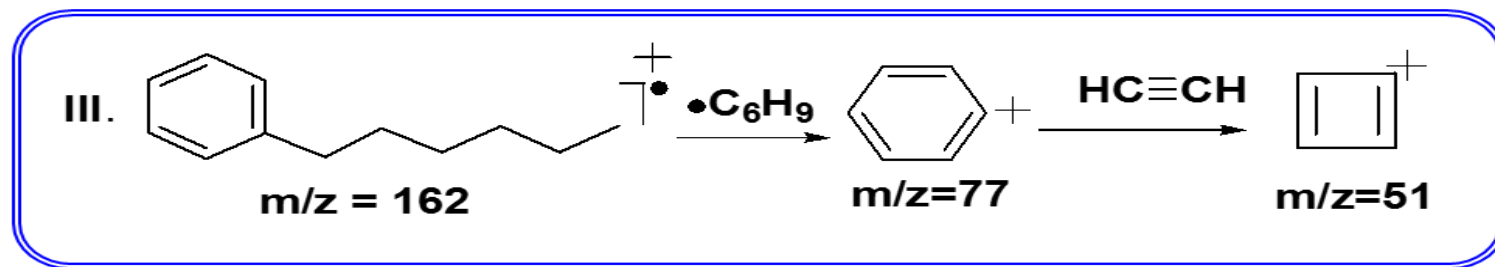
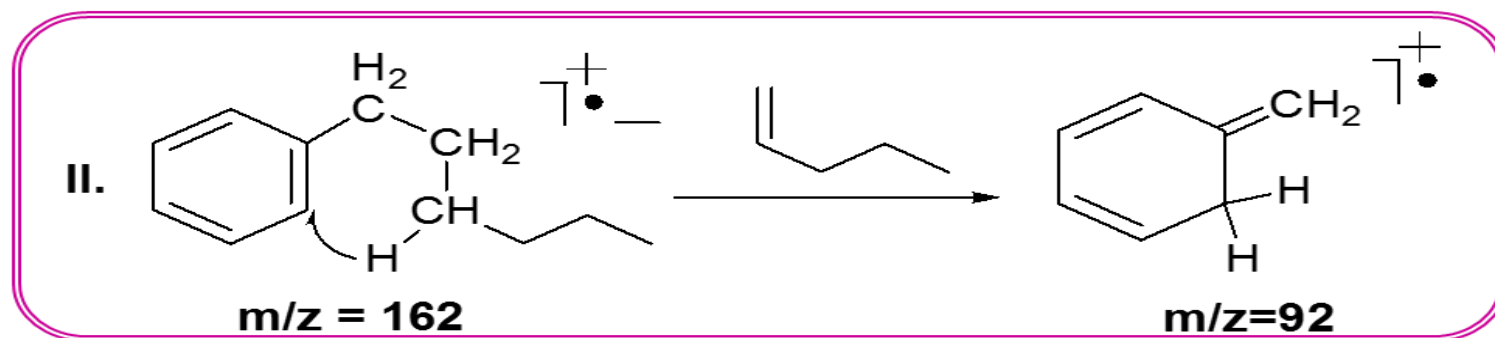
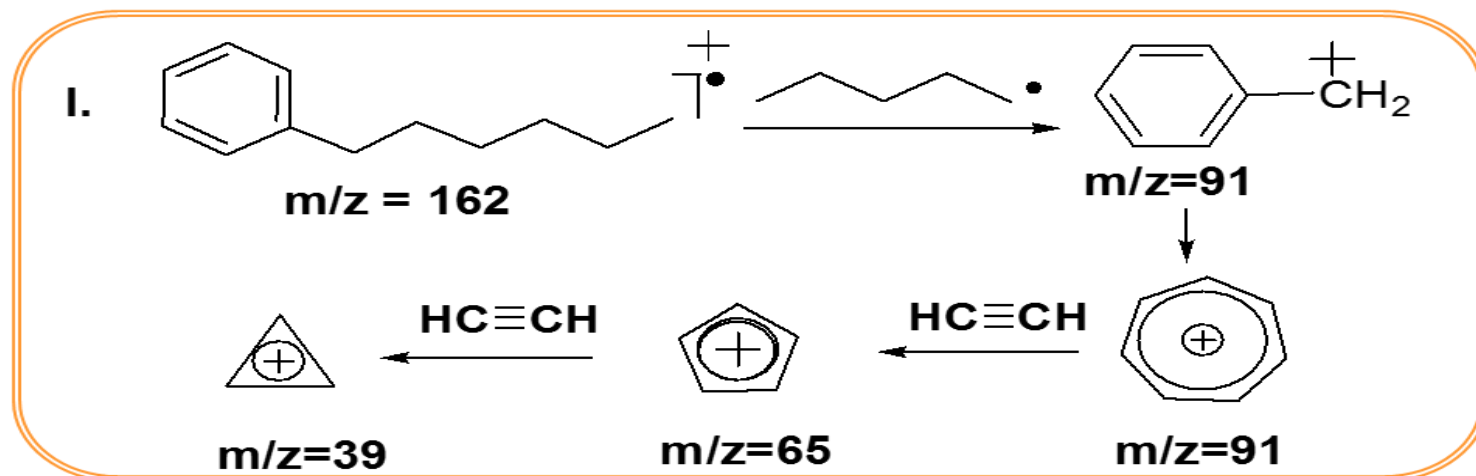


Hydrogen migration with elimination of a neutral alkene molecule accounts for the peak at m/z 92 observed when the alkyl group is longer than C_2 .

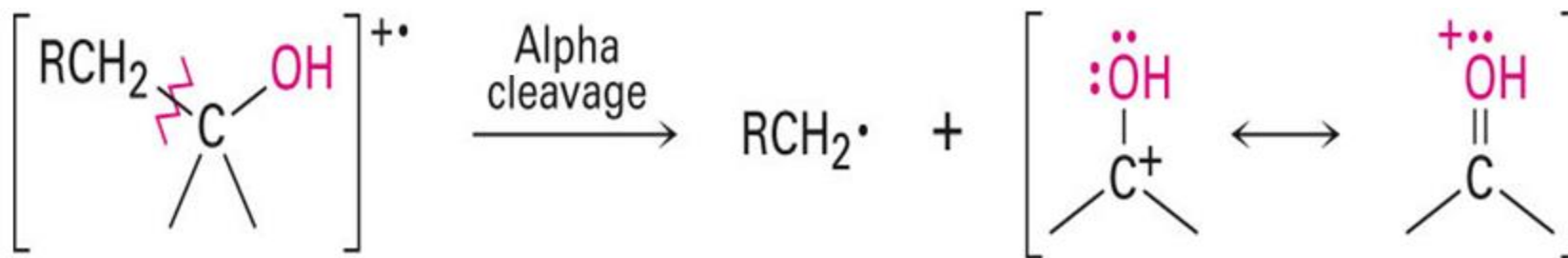


A characteristic cluster of ions resulting from an α cleavage and hydrogen migration in monoalkylbenzenes appears at m/z 77 ($C_6H_5^+$), 78 ($C_6H_6^+$), and 79 ($C_6H_7^+$).

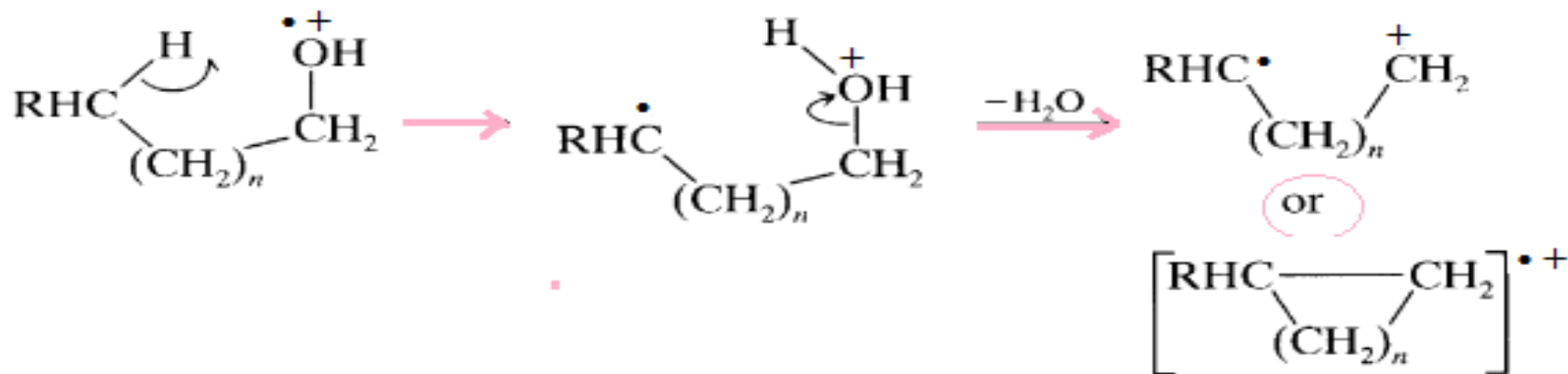
Process of fragmentations:



- The molecular ion peak of 1° and 2° alcohol is usually of low abundance. It is not detected in 3° alcohols.
- The fragmentation modes in alcohols depend upon the fact whether it is 1°, 2° or 3° alcohols.
- The fragmentation of C-C bond adjacent to oxygen atom (the bond next to the C-OH) is the preferred fragmentation mode i.e. α cleavage.(rule 8)

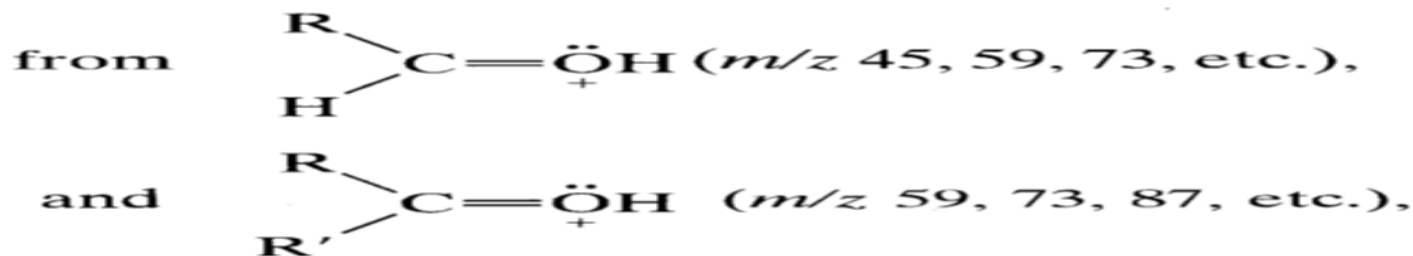


- 1° alcohols shows M-18 peaks, corresponding to the loss of water.

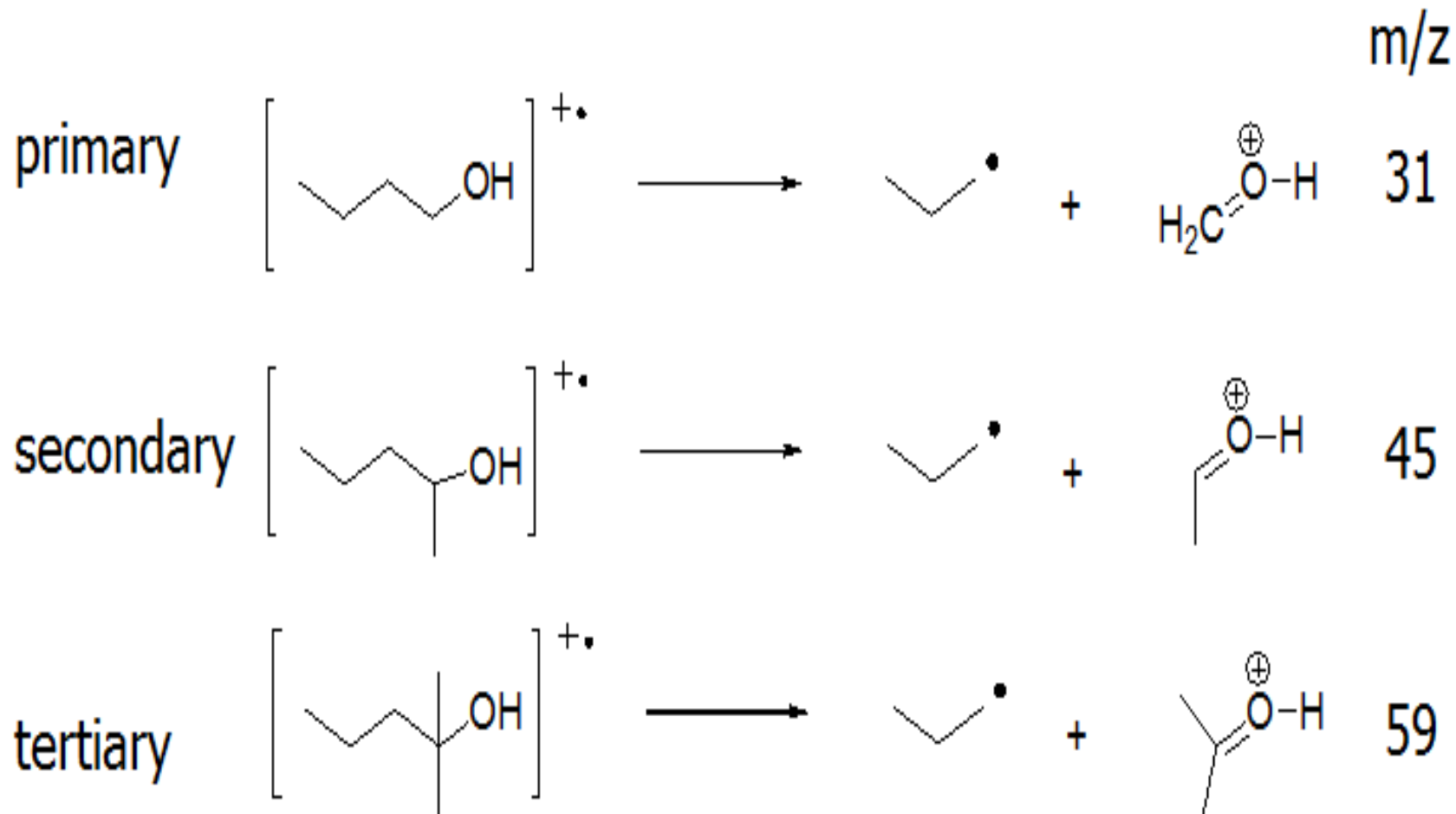


- Long chain members may show peaks corresponding to successive loss of H radicals at M-1, M-2 and M-3.
- The $\text{CH}_2=\text{O}^+\text{H}$ (m/z 31) is the most significant peak in the spectra of 1° alcohols.'

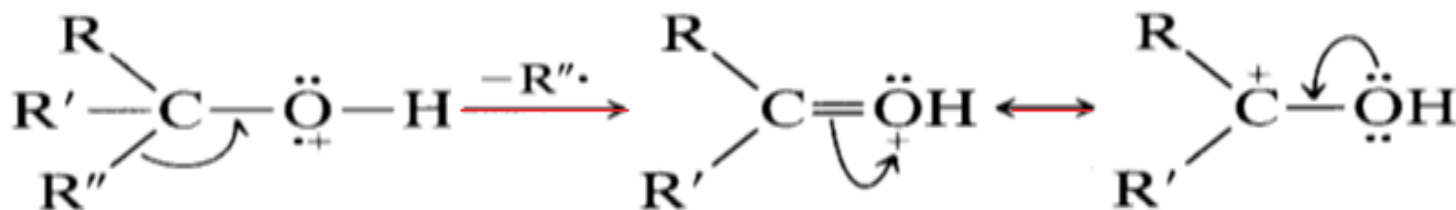
- Secondary alcohols cleave to give prominent peaks



The largest alkyl group is usually lost; the mode of cleavage typically is similar for all alcohols:



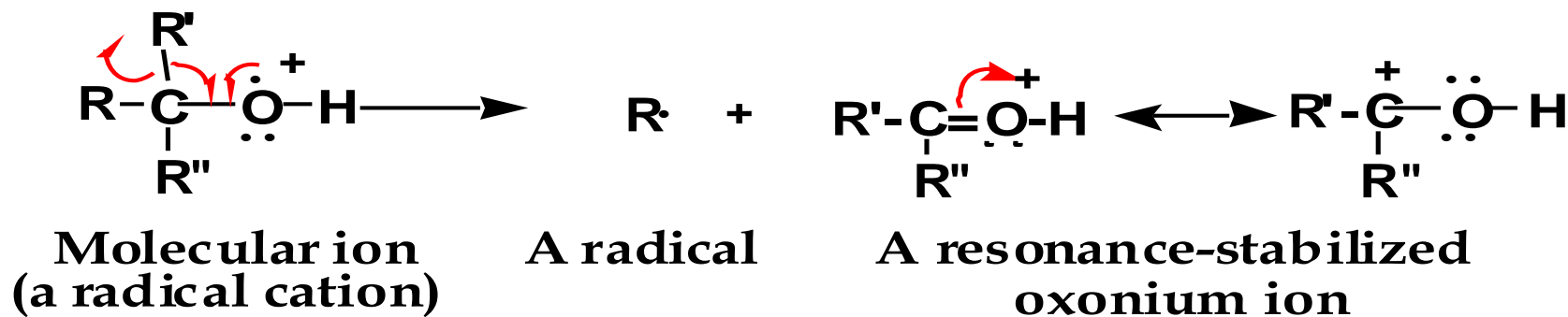
- The largest substituent is expelled most readily (rule 3).



• where $R'' > R'$ or R .

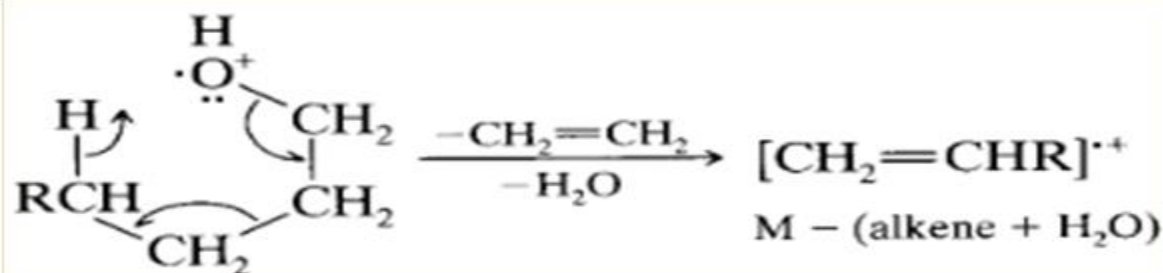
• When R and/or $R' = H$, an $M-1$ peak can usually be seen.

- Another common pattern is loss of an alkyl group from the carbon bearing the OH (β - Cleavage) to give a resonance – stabilized oxonium ion and an alkyl radical (largest R group lost as radical).



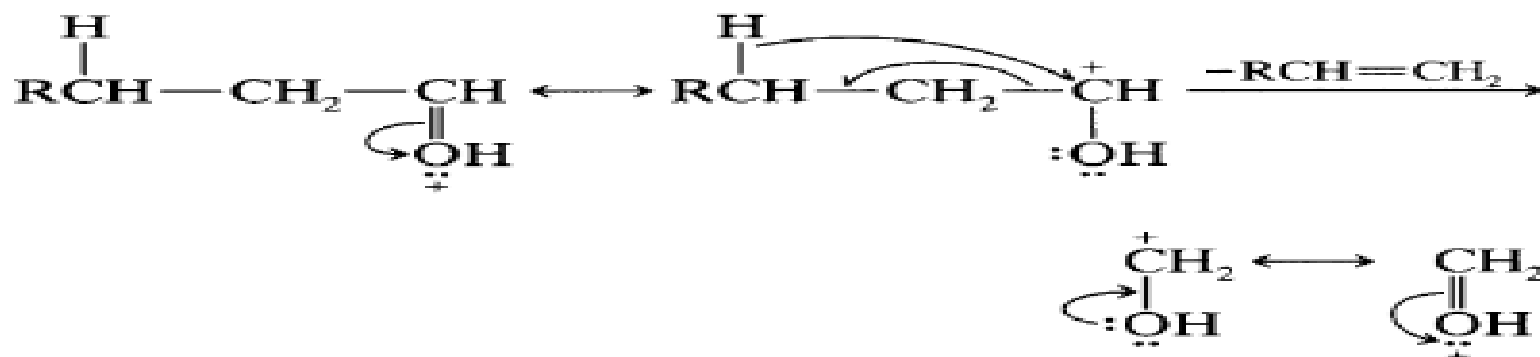
Elimination of water, together with elimination of an alkene from primary alcohols, accounts for the presence of a peak at $M - (\text{alkene} + \text{H}_2\text{O})$, that is, a peak at $M - 46$, $M - 74$, $M - 102$, The alkene ion then decomposes by successive eliminations of ethylene.

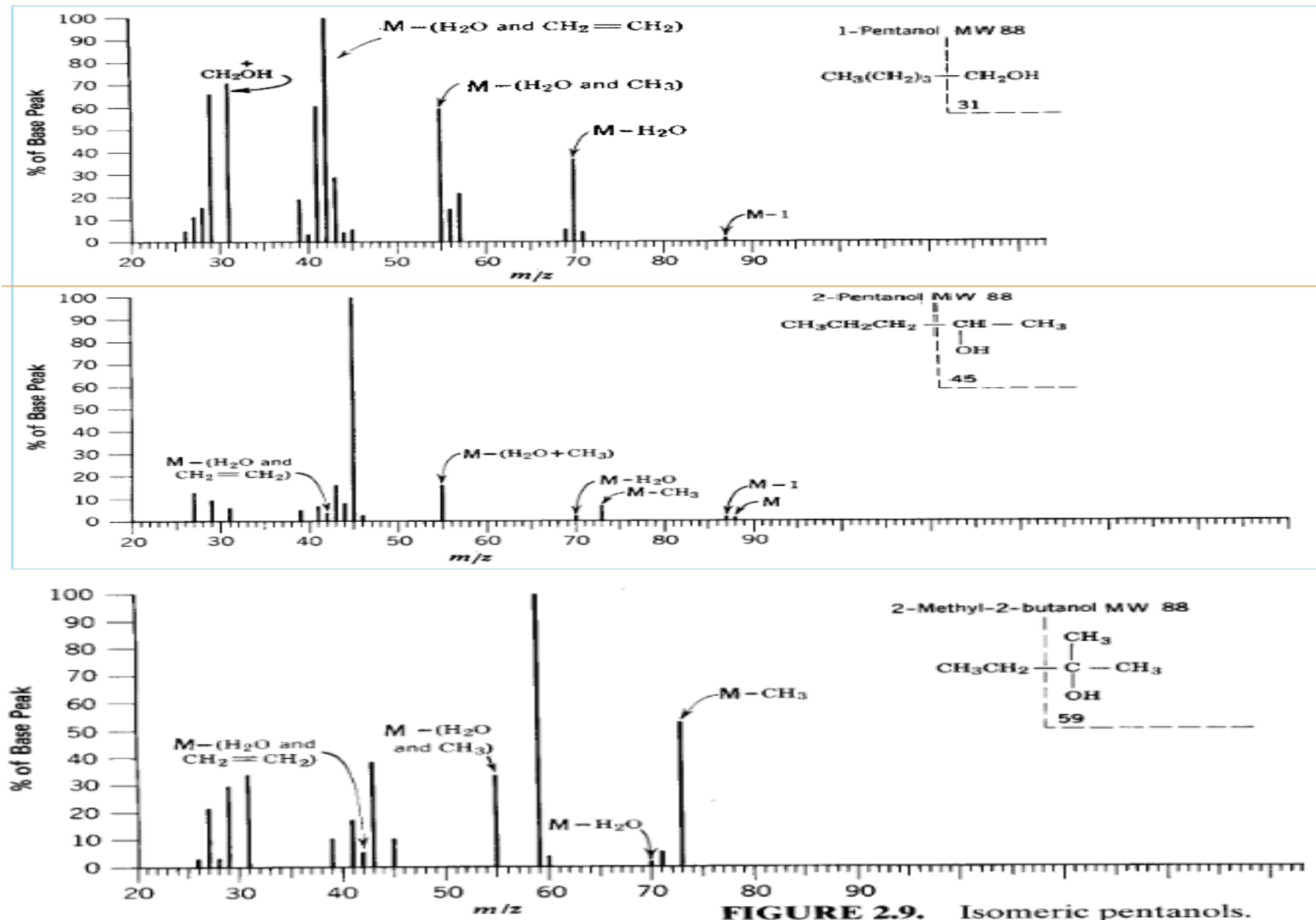
McLafferty type rearrangement



A peak at m/z 31 is quite diagnostic for a primary alcohol provided it is more intense than peaks at m/z 45, 59, 73

However, the first-formed ion of a secondary alcohol can decompose further to give a moderately intense m/z 31 ion.

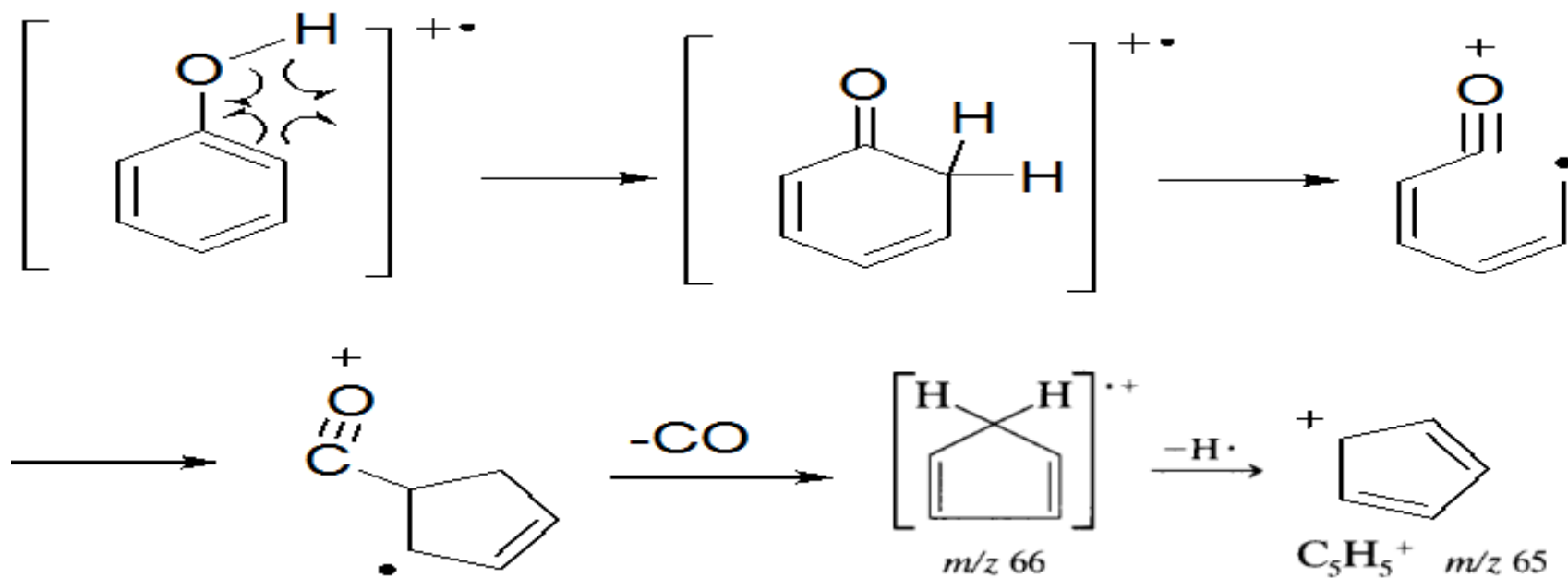




2-Phenol

In phenol itself :

- the molecular ion peak is the base peak,
- the $M - 1$ peak is small.
- A rearrangement peak at m/z 77 **phenyl cation**, and peaks resulting from loss of CO ($M - 28$) and CHO ($M - 29$) are usually found in phenols.



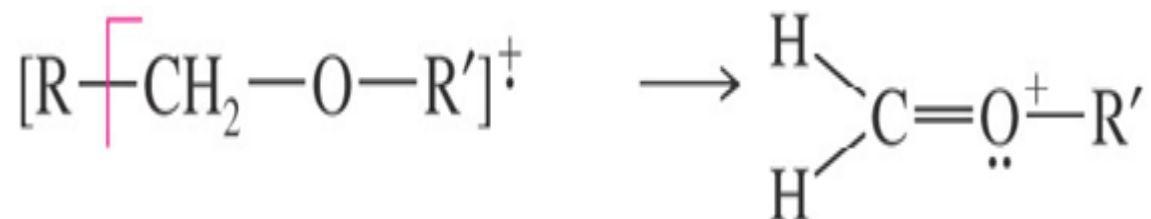
3- Ether

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.

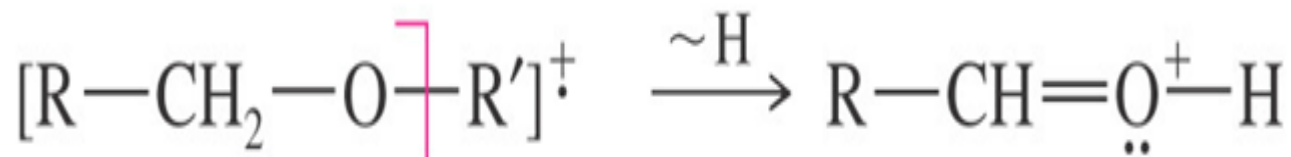
Fragmentation occurs in two principal ways:

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

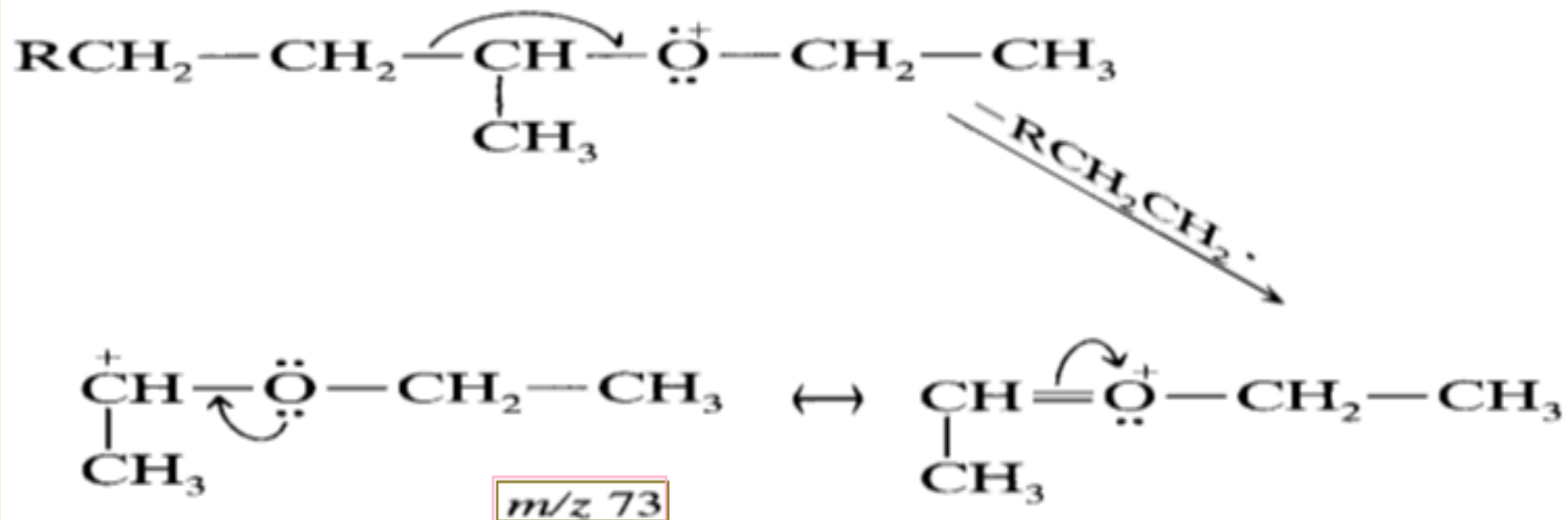
➤ Cleavage forming oxonium ion :



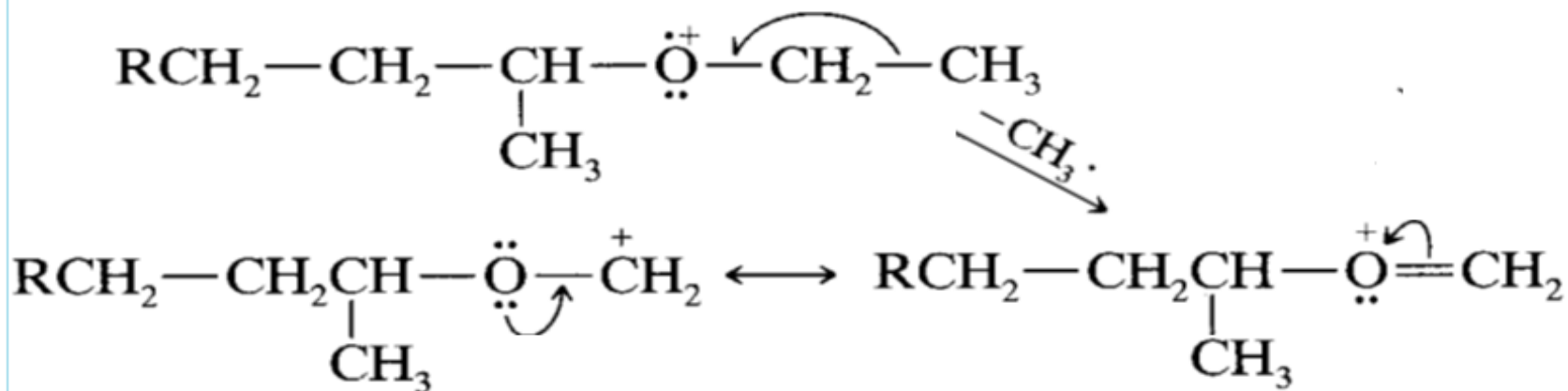
➤ Loss of alkyl group forming oxonium ion

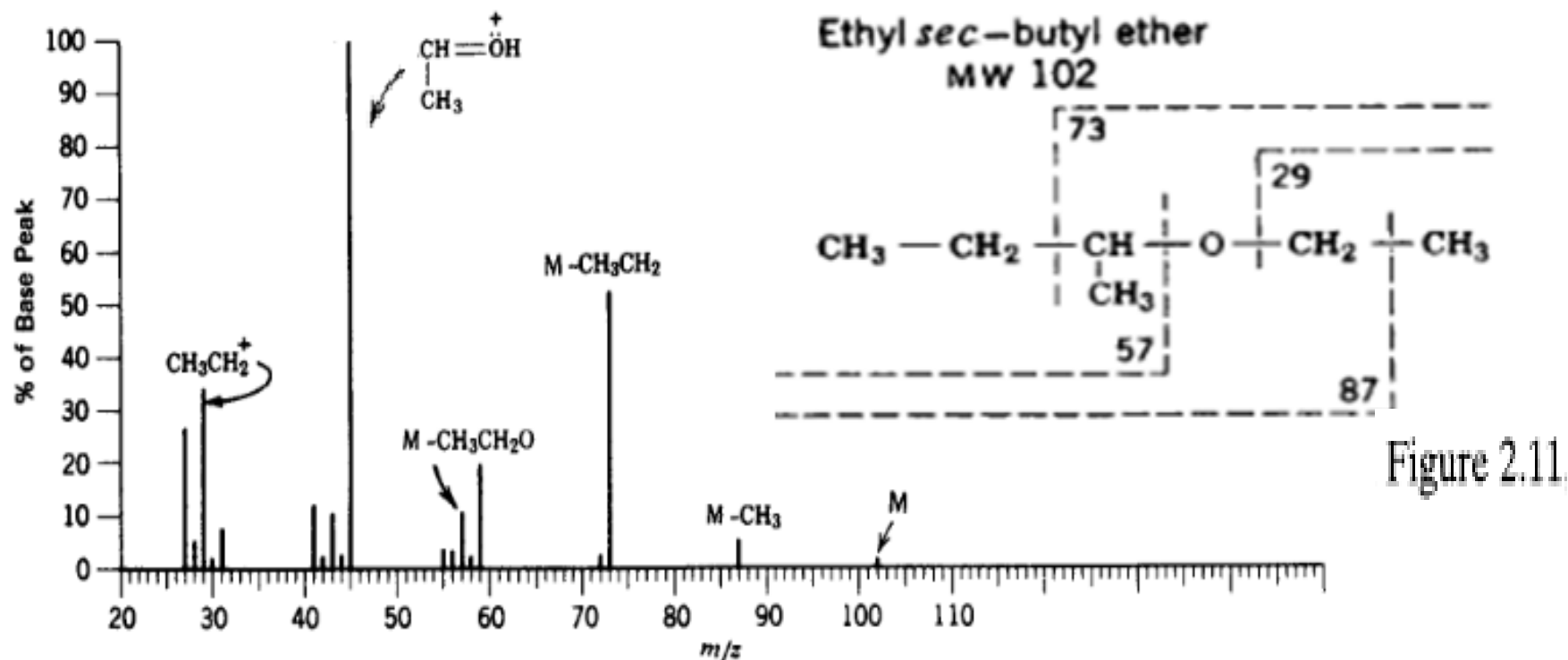


In Figure 2.11, R = H.

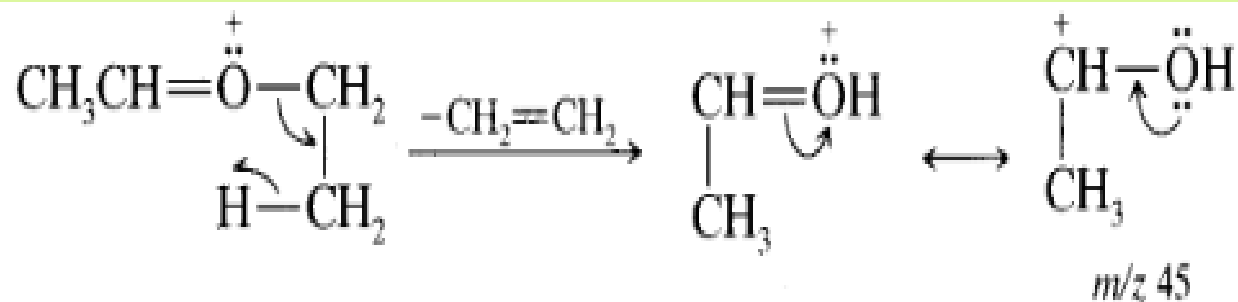


In Figure 2.11, R = H, m/z 87.



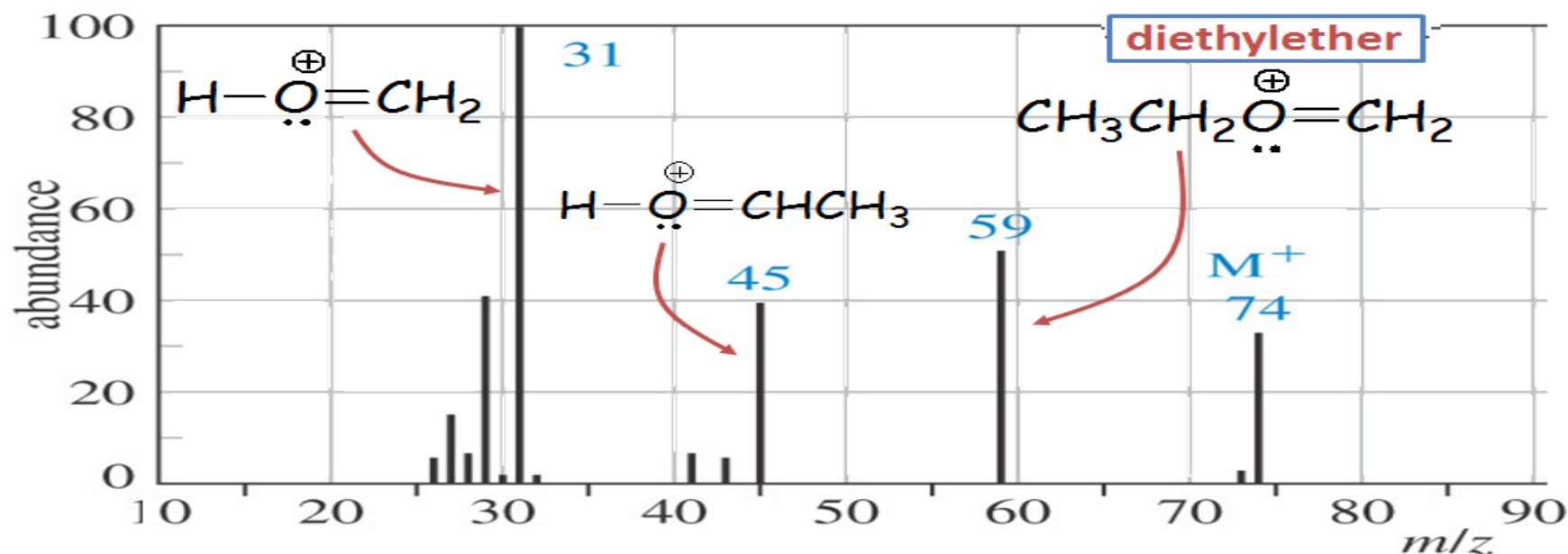
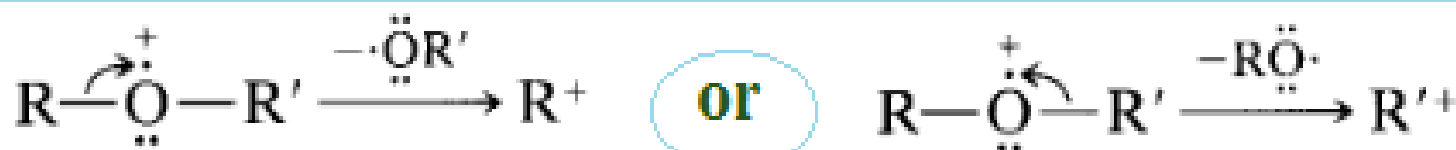
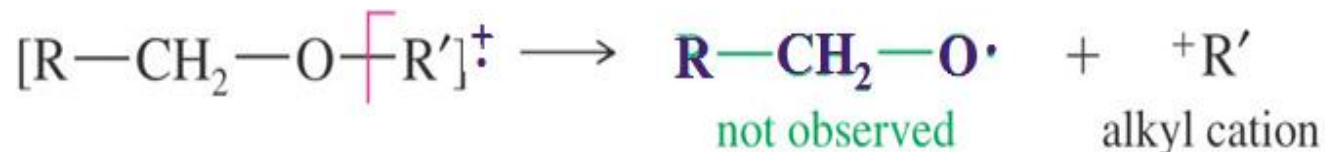


However, the first-formed fragment decomposes further ; the decomposition is important when the α carbon is substituted (McLafferty rearrangement).



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

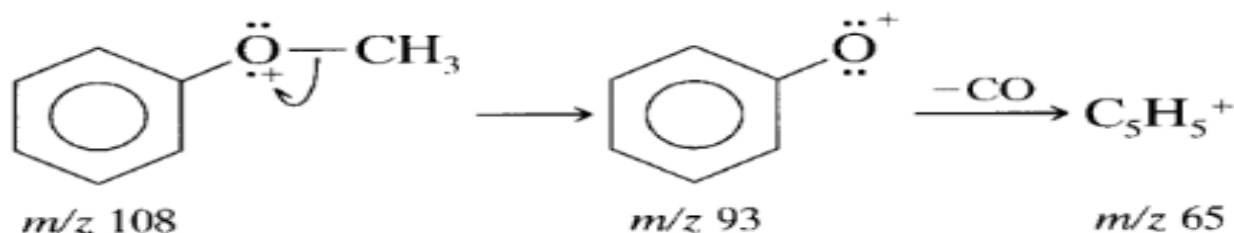
Loss of alkyl group forming a carbocation



Aromatic Ethers

The molecular ion peak of aromatic ethers is prominent. Primary cleavage occurs at the bond β to the ring, and the first-formed ion can decompose further.

Thus anisole, MW 108, gives ions of m/z 93 and 65.



Ketones

Aliphatic Ketones

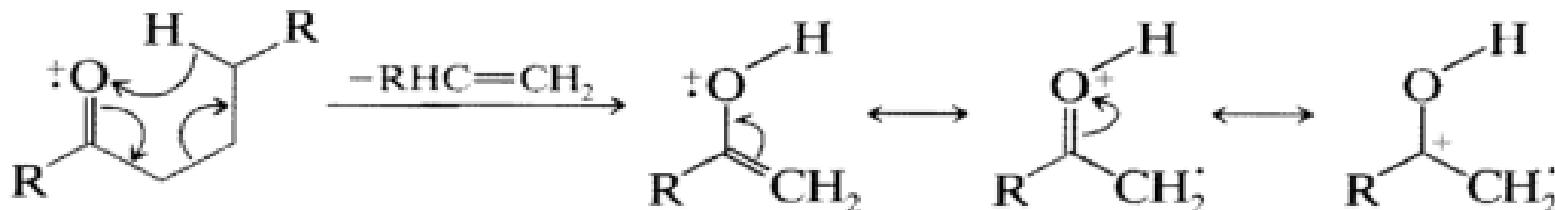
- The molecular ion peak of ketones is usually quite pronounced.
- Major fragmentation peaks result from cleavage at the C—C bonds adjacent to the oxygen atom.
- The charge remaining with the resonance-stabilized acylium ion.

Loss of R forming

acylium ion:



- This cleavage gives rise to a peak at m/z 43 or 57 or 71
- The base peak very often results from loss of the larger alkyl group.
- When one of the alkyl chains attached to the C=O group is C_3 or longer \Rightarrow McLafferty rearrangement,



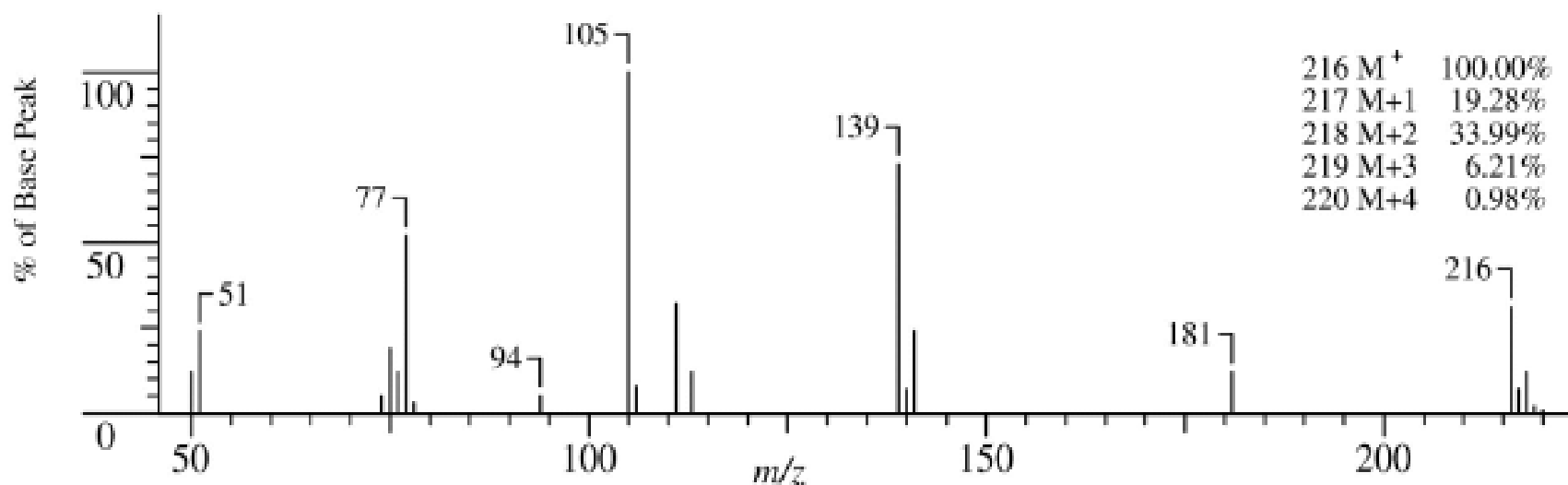
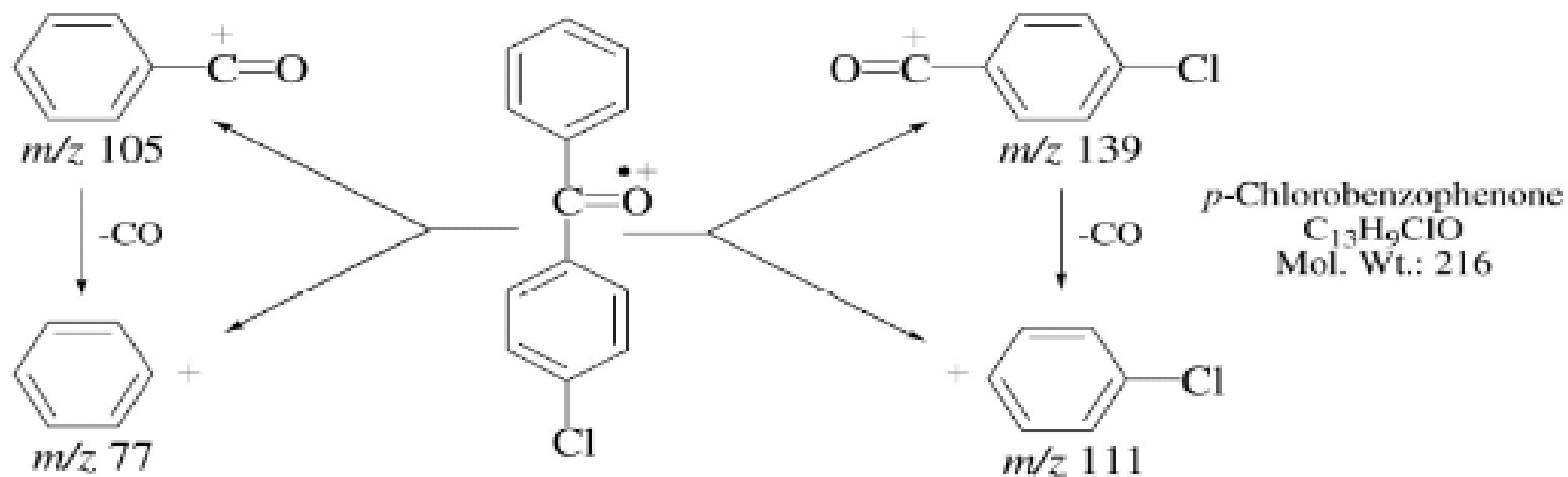
Reduction \Rightarrow corresponding hydrocarbon \Rightarrow carbon skeleton.

Cyclic Ketones.

- The molecular ion peak is prominent.
- The primary cleavage of cyclic ketones is adjacent to the C=O group, but the ion thus formed must undergo further cleavage in order to produce a fragment.
- The base peak of cyclopentanone and of cyclohexanone is m/z 55.

Aromatic Ketones.

- The molecular ion peak of an aromatic ketone is prominent.
- Cleavage occurs at the bond β to the ring, leaving a characteristic $\text{ArC}\equiv\text{O}^+$ fragment (m/z 105 when Ar = phenyl), which usually accounts for the base peak.
- Cleavage of the bond adjacent to the ring to form a $\text{RC}\equiv\text{O}^+$ fragment (R = alkyl) is less important though somewhat enhanced by electron-withdrawing groups.



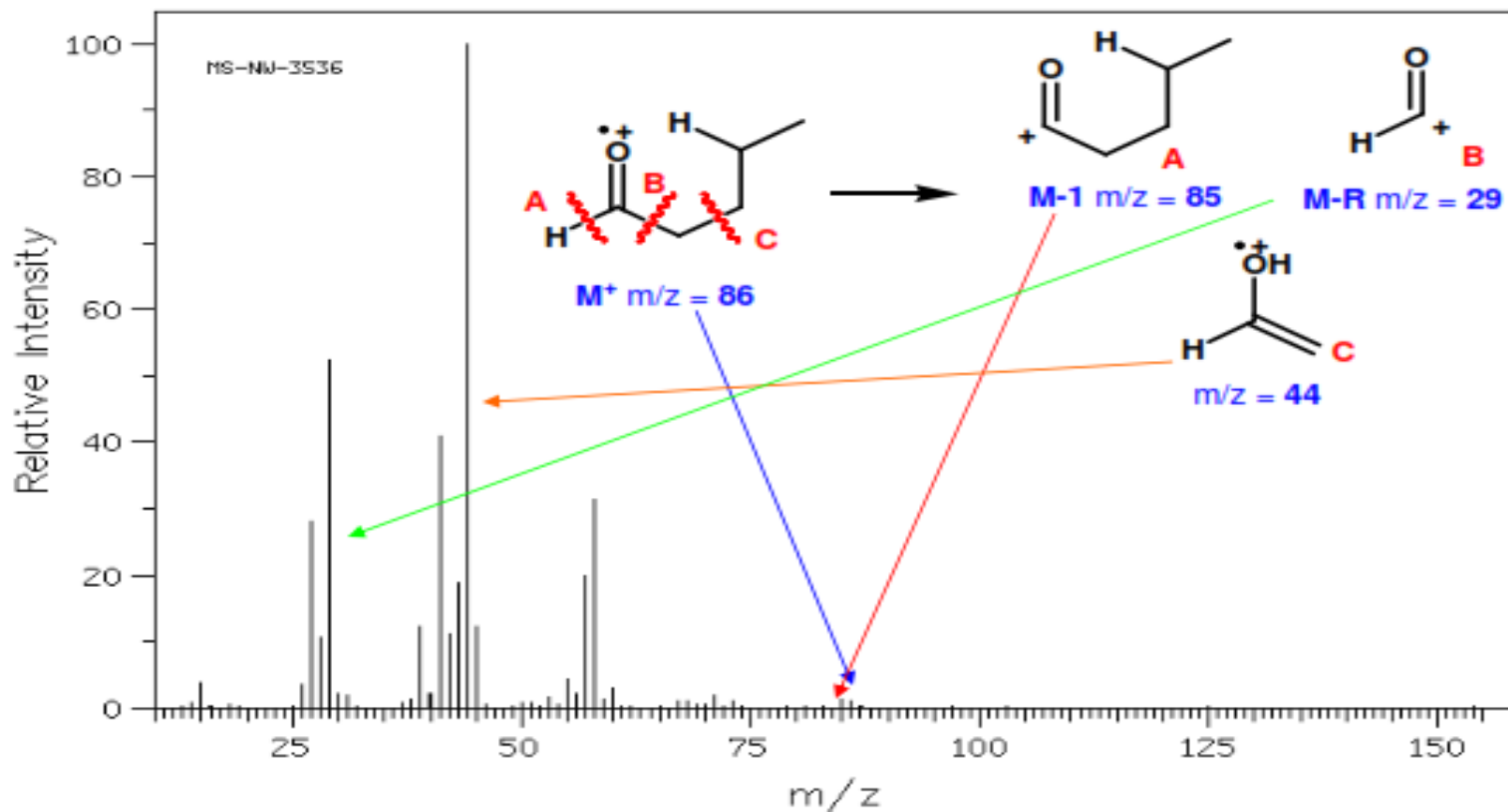
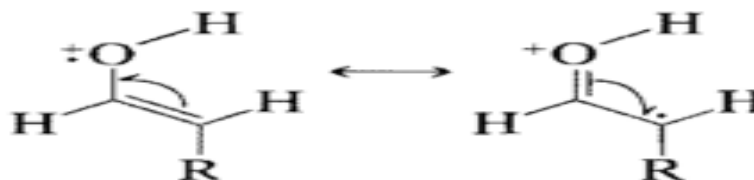
M^+ is evident. Primary cleavage is α to the carbonyl to give a strong ArCO^+ peak (m/z 105 when $\text{Ar} = \text{Ph}$). This will lose CO to give the phenyl cation (m/z 77).

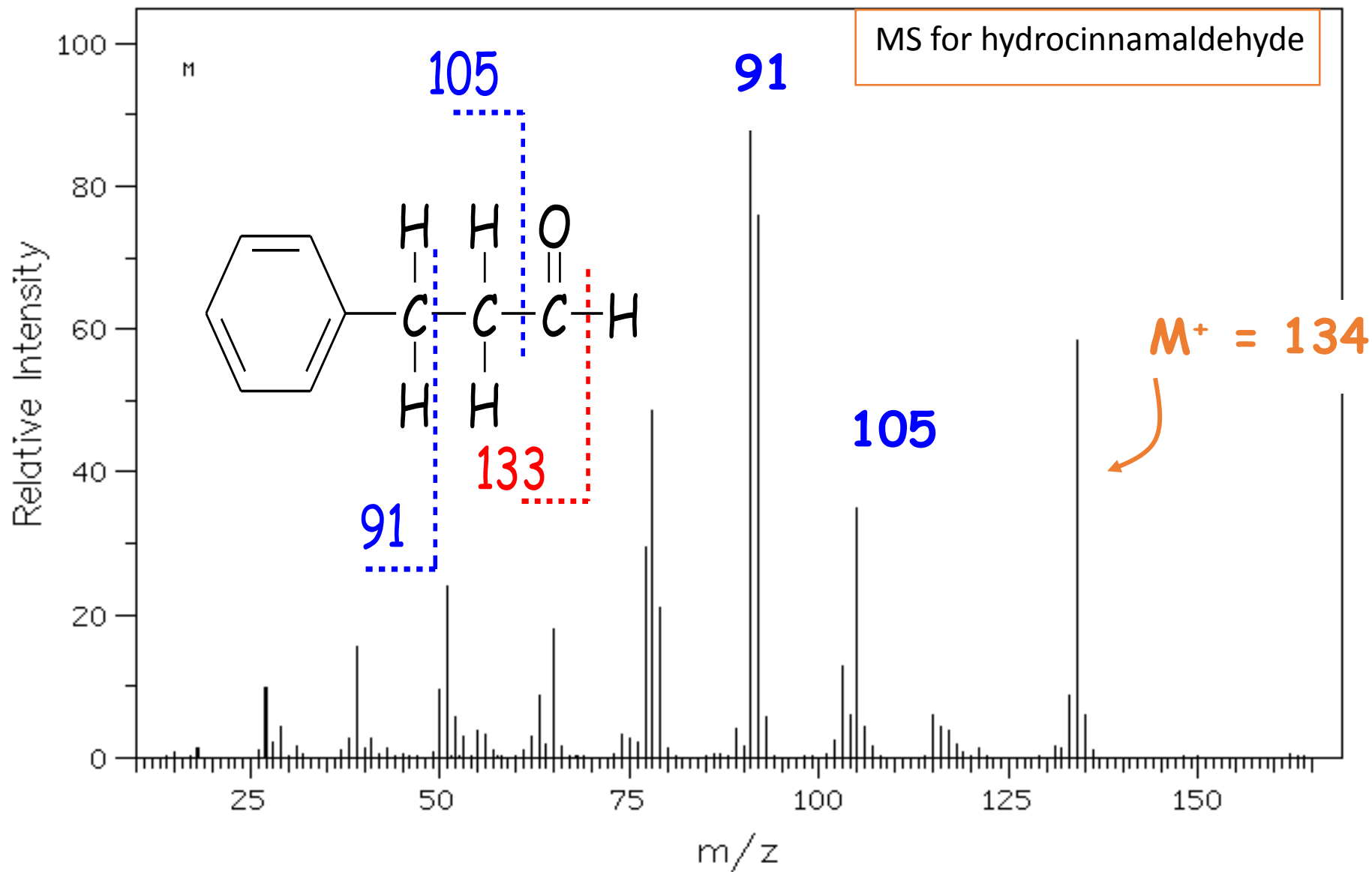
Aldehydes

Aliphatic Aldehydes.

- The molecular ion peak of aliphatic aldehydes is usually discernible.
- Cleavage of the C—H and C—C bonds next to the oxygen atom results in an $M - 1$ peak and in an $M - R$ peak (m/z 29, CHO^+).
- The $M - 1$ peak is a good diagnostic peak even for long-chain aldehydes, but the m/z 29 peak present in C_4 and higher aldehydes results from the hydrocarbon C_2H_5^+ ion.
- McLafferty cleavage of the α, β C—C bond occurs to give a major peak at m/z 44, 58, or 72, . . . , depending on the α substituents.
- In straight-chain aldehydes, the other unique, diagnostic peaks are at $M - 18$ (loss of water), $M - 28$ (loss of ethylene), $M - 43$ (loss of $\text{CH}_2=\text{CH}-\text{O}^{\cdot}$),

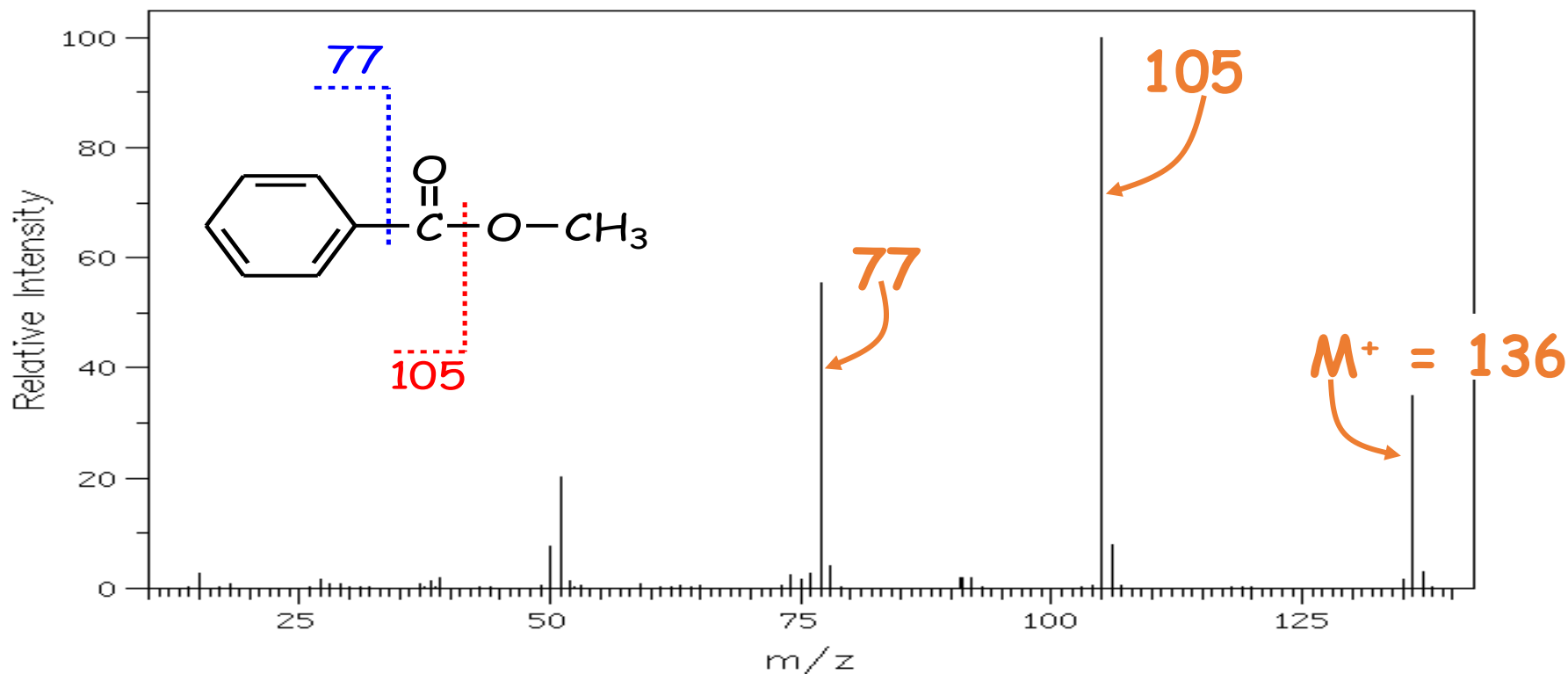
Aldehydes show weak but discernable M^+ peaks. Major pathways are α -cleavage and McLafferty Rearrangement.





Esters ($\text{RCO}_2\text{R}'$)

- Common fragmentation patterns include:
 - Loss of OR'
 - peak at $\text{M}^+ - \text{OR}'$
 - Loss of R'
 - peak at $\text{M}^+ - \text{R}'$



Carboxylic Acids

Aliphatic Acids.

- The molecular ion peak is weak but usually discernible.
- The most characteristic (sometimes the base) peak is m/z 60 resulting from the McLafferty rearrangement.
- In long-chain acids, the spectrum consists of two series of peaks resulting from cleavage at each C—C bond with retention of charge either on the oxygen-containing fragment (m/z 45, 59, 73, 87, ...) or on the alkyl fragment (m/z 29, 43, 57, 71, 85, ...).

