Chem-805

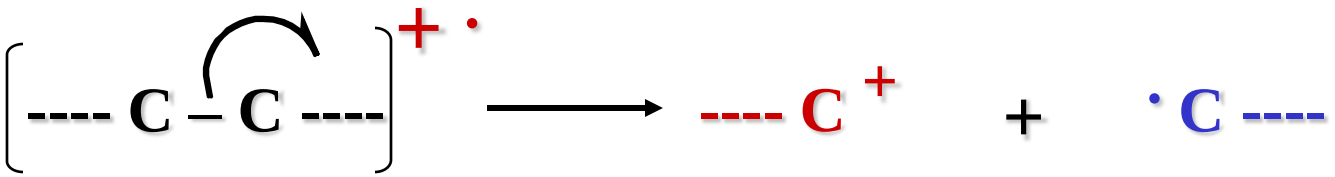
Identification of organic and inorganic compounds by spectroscopy

- **Mass Spectrometry**
  - **fragmentation**
- NMR
- Infrared

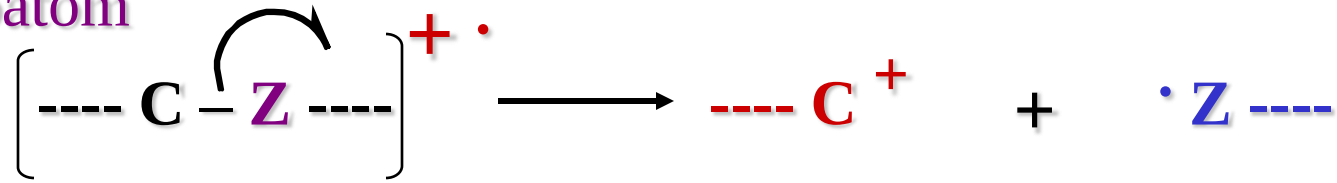
Fragmentation process

There are 3 type of fragmentations:

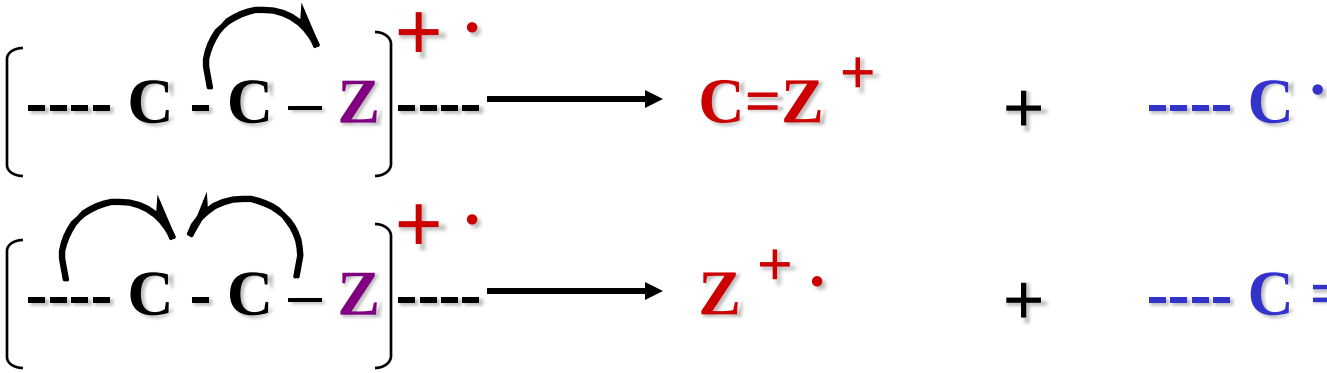
1) Cleavage of σ bond



At heteroatom



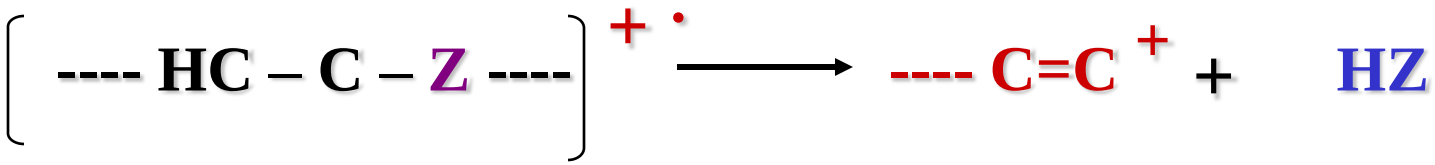
α to heteroatom



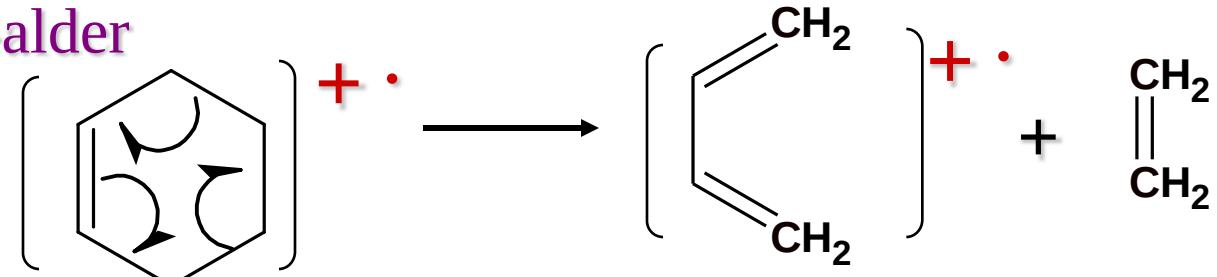
Fragmentation process

There are 3 type of fragmentations:

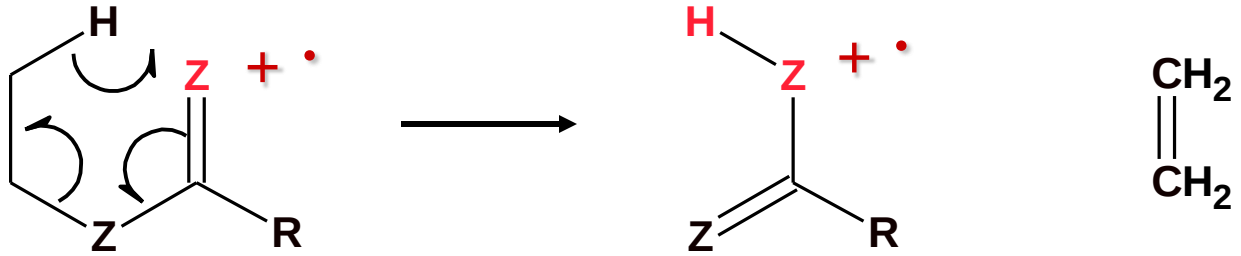
2) Cleavage of **2** σ bond (rearrangements)



Retro Diels-alder



McLafferty



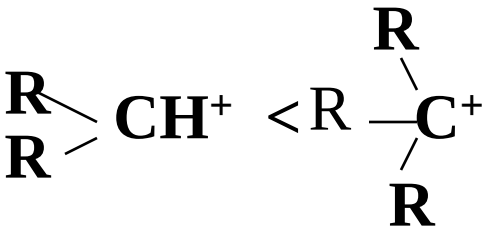
Fragmentation process

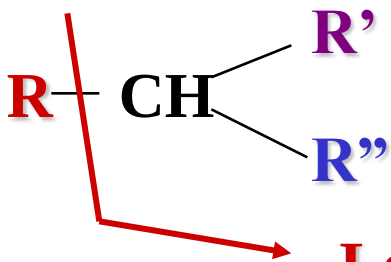
There are 3 type of fragmentations:

3) Cleavage of **Complex** rearrangements

Fragmentation rules in MS

1. Intensity of $M^{\cdot+}$ is Larger for linear chain than for branched compound
2. Intensity of $M^{\cdot+}$ decrease with Increasing M.W. (fatty acid is an exception)
3. Cleavage is favored at branching
   ➔ reflecting the Increased stability of the ion

Stability order: $CH_3^+ < R\text{-}CH_2^+ <$  $<$

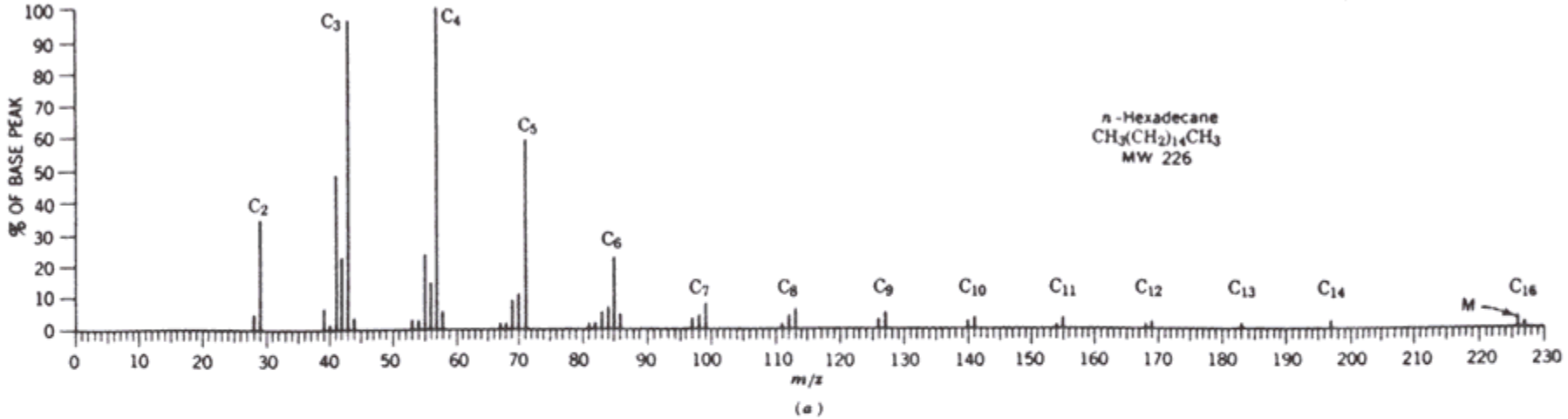


Loss of Largest Subst. Is most favored

Illustration of first 3 rules (large MW)

ALKANES

[M·+] Decrease with Increasing M.W.



Cleavage is Favored at Branching
=> Loss of Largest substituant

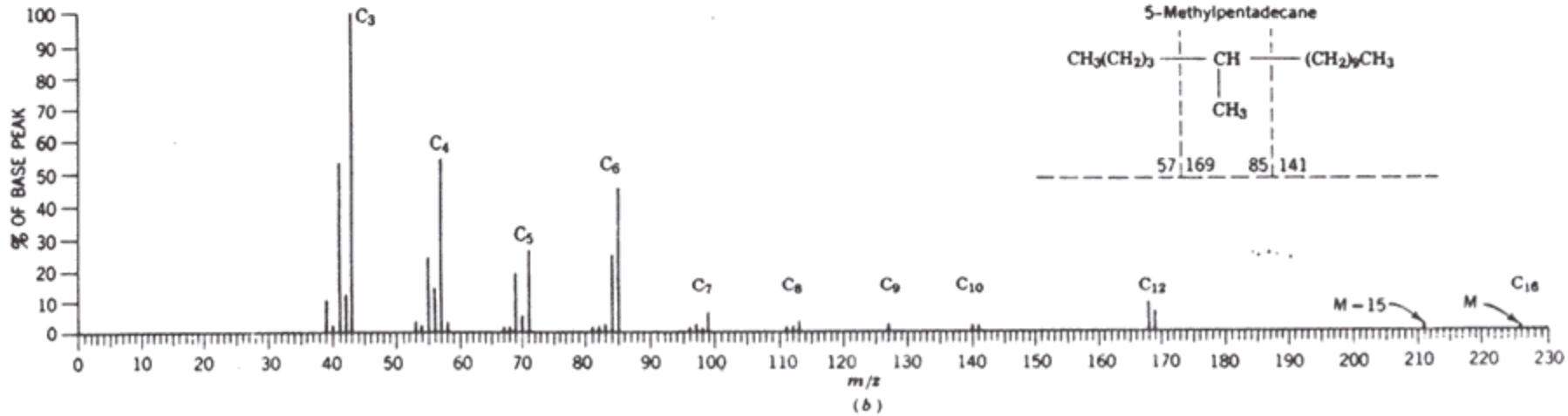
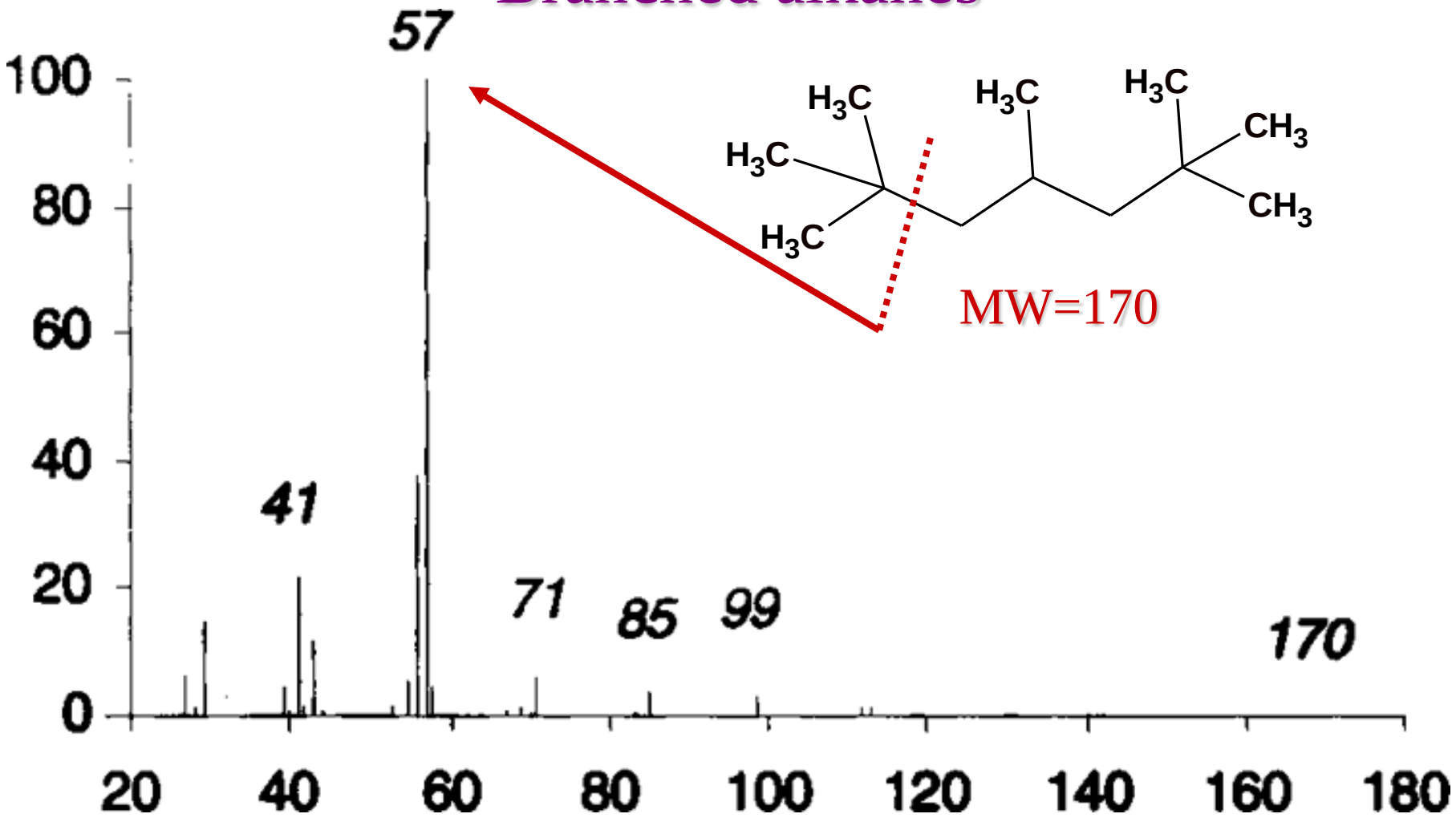


FIGURE 2.6 (*a*, *b*). Isomeric C_{16} hydrocarbons.

Branched alkanes

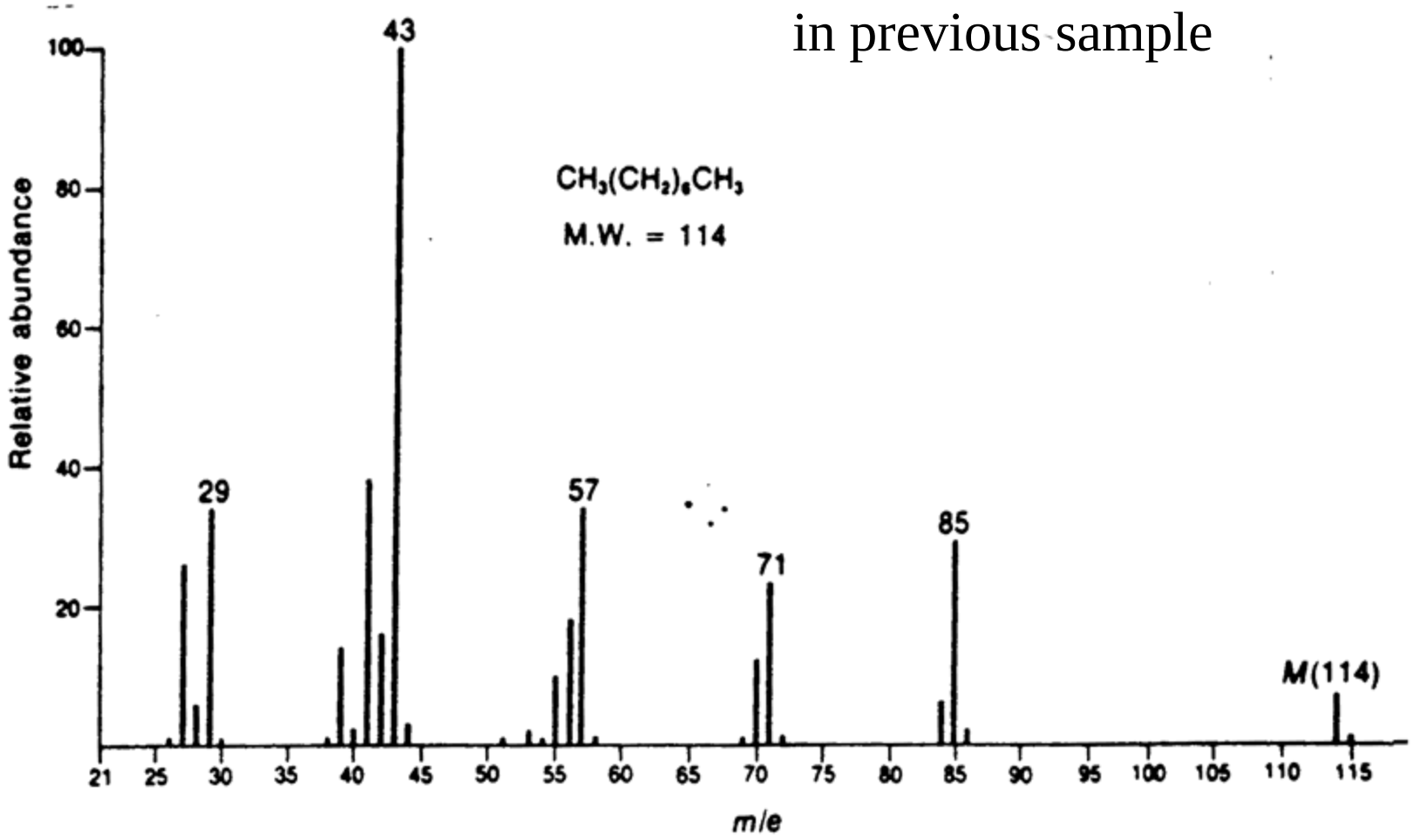


$M^{\cdot+}$ is absent with heavy branching

Fragmentation occur at branching: largest fragment loss

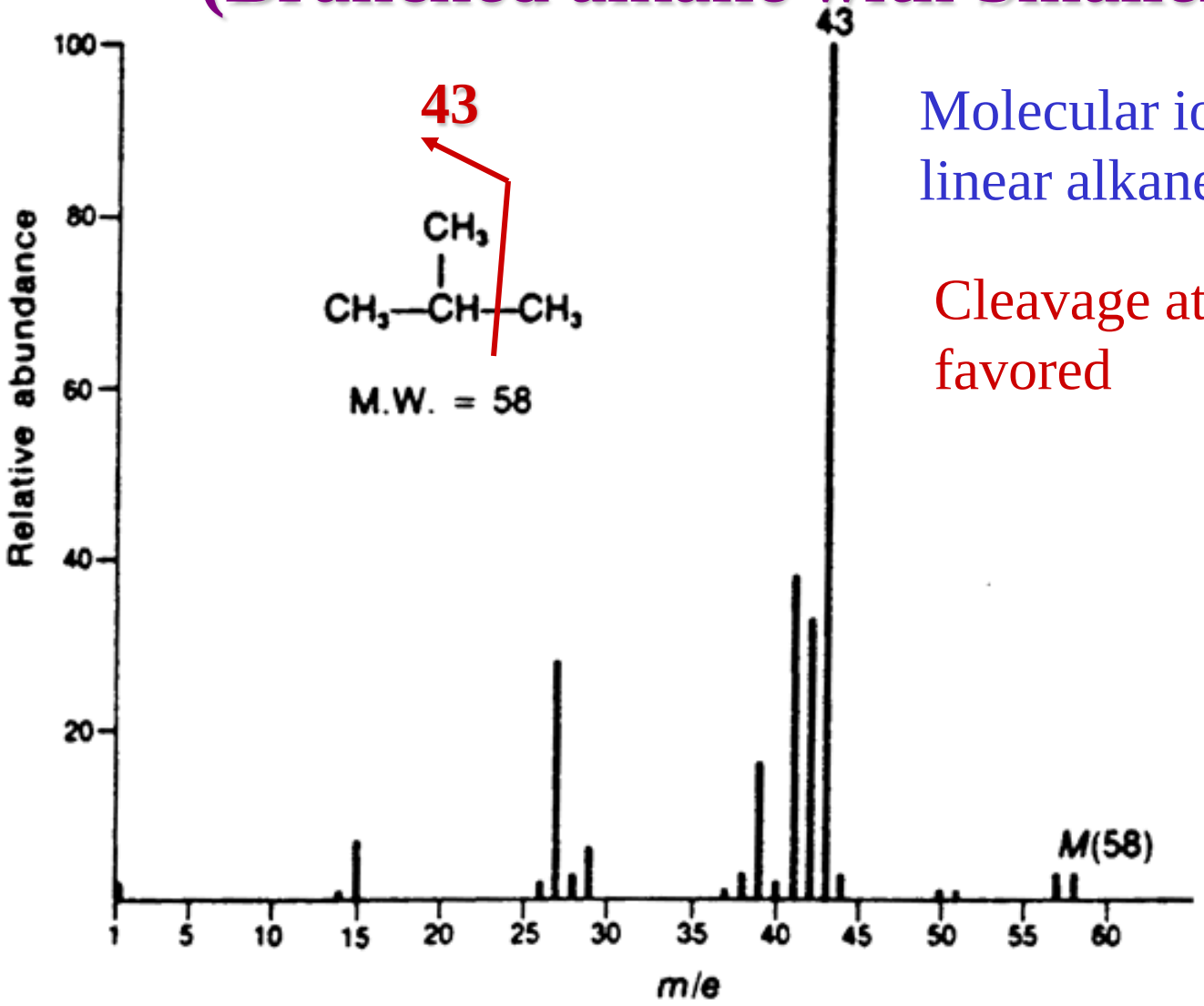
Illustration of first 3 rules (Linear alkane with Smaller MW)

Molecular ion is stronger than in previous sample



▶ **FIGURE 7.6** Mass spectrum of octane.

Illustration of first 3 rules (Branched alkane with Smaller MW)



Molecular ion smaller than linear alkane

Cleavage at branching is favored

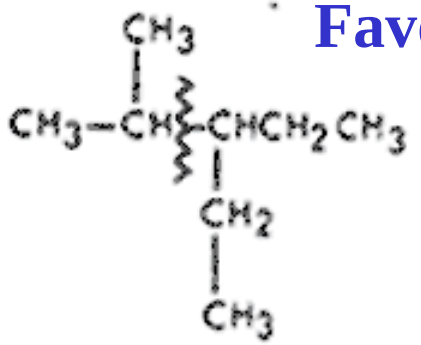
► **FIGURE 7.7** Mass spectrum of isobutane.

Rule 3

Alkanes

Cleavage Favored at branching

Loss of Largest substituent Favored



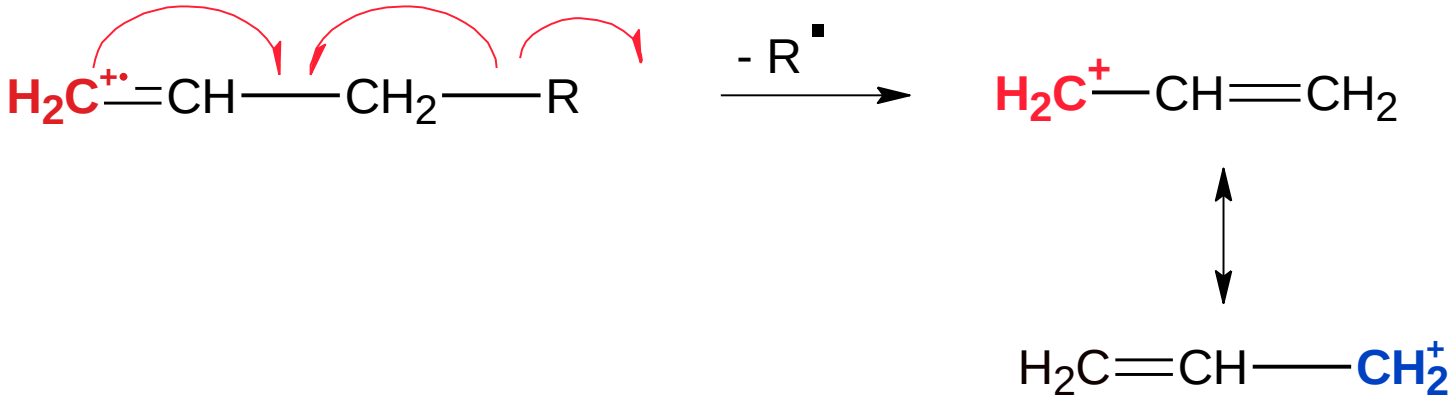
Rule1: intensity of $M^{\bullet+}$ is smaller with branching

Fig. 8.9

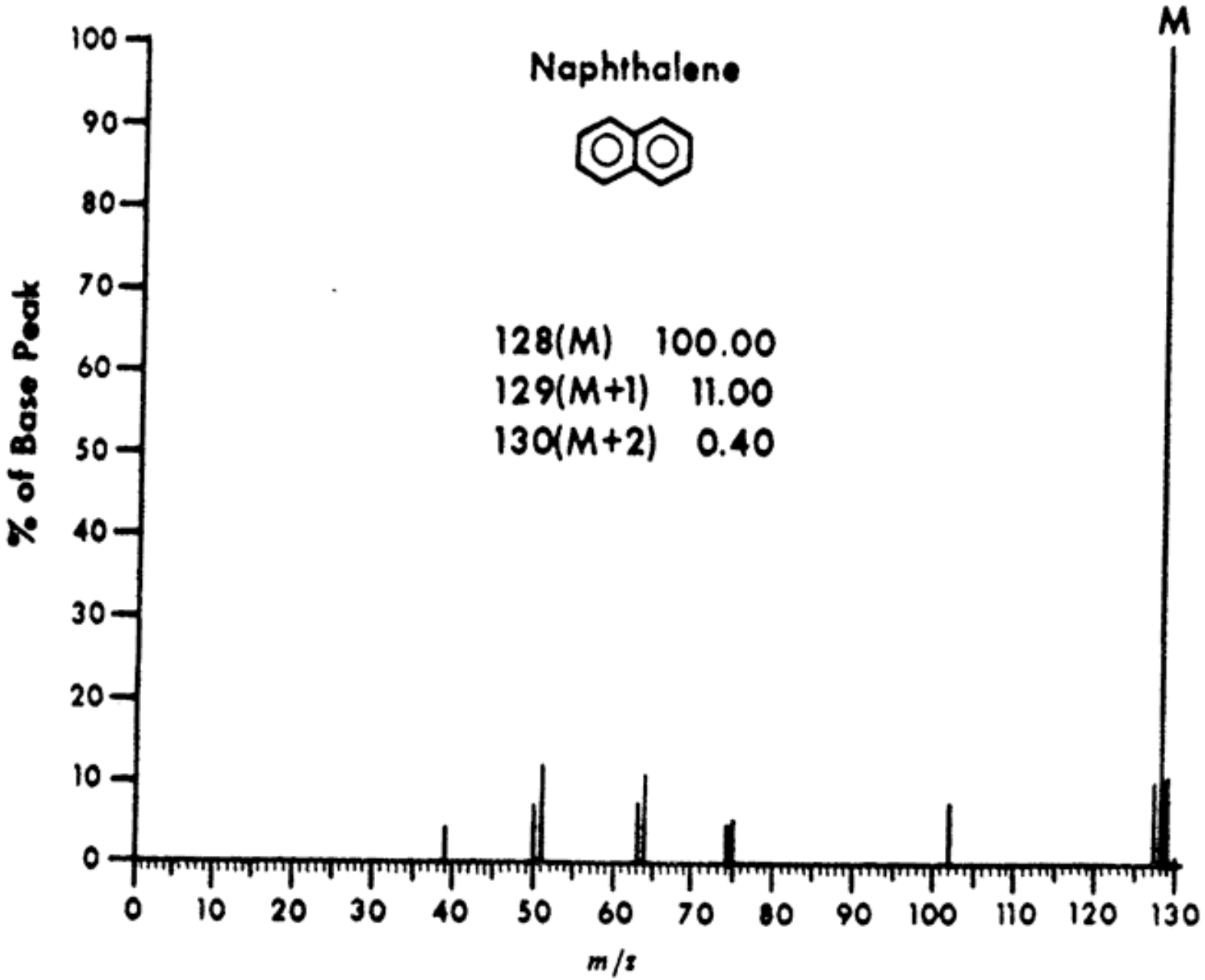
Fragmentation rules in MS

4. **Aromatic Rings, Double bond, Cyclic structures stabilize $M^{\cdot+}$**
5. **Double bond favor Allylic Cleavage**

➔ Resonance – Stabilized Cation



Aromatic ring has stable $M^{\cdot+}$



Cyclo Alkane

Cycloalkane ring has stable $M^{\cdot+}$

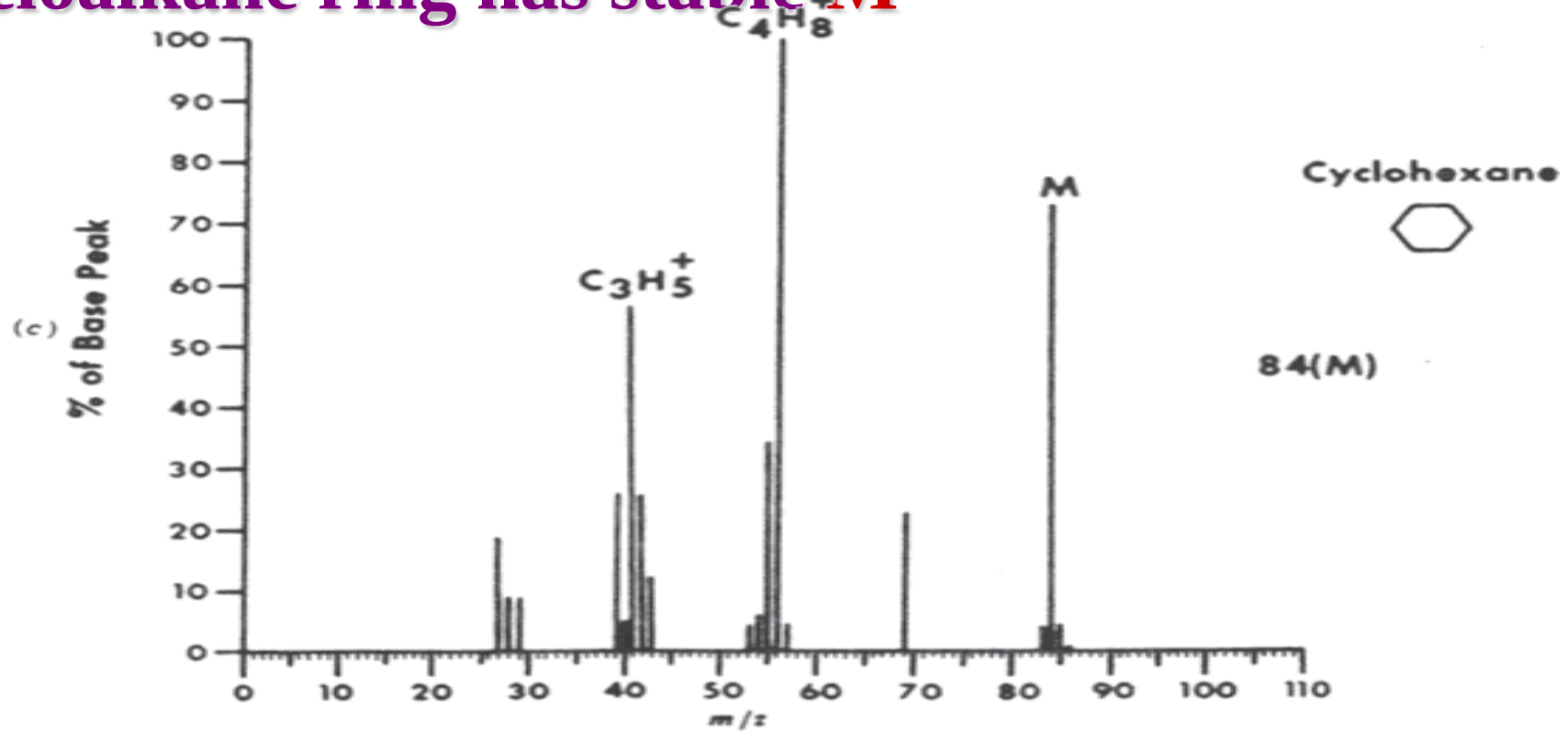
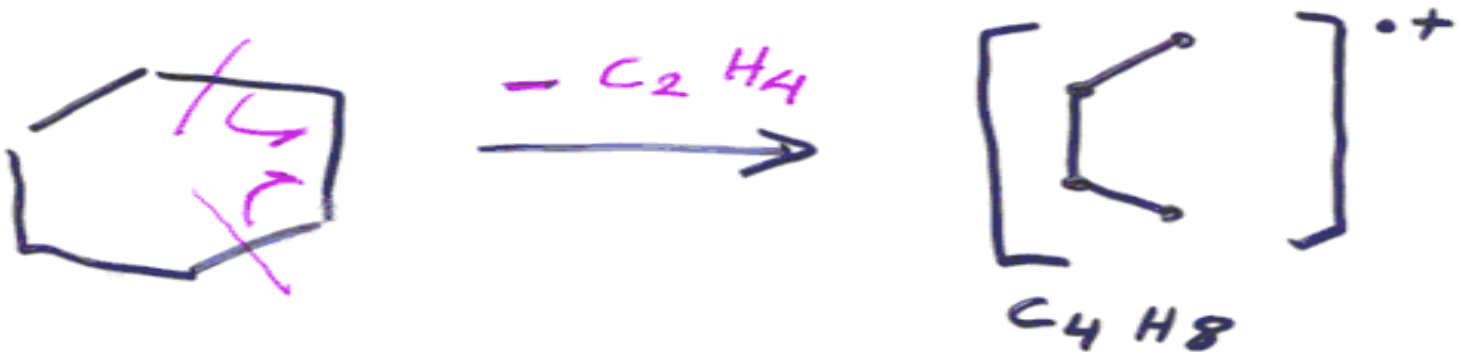
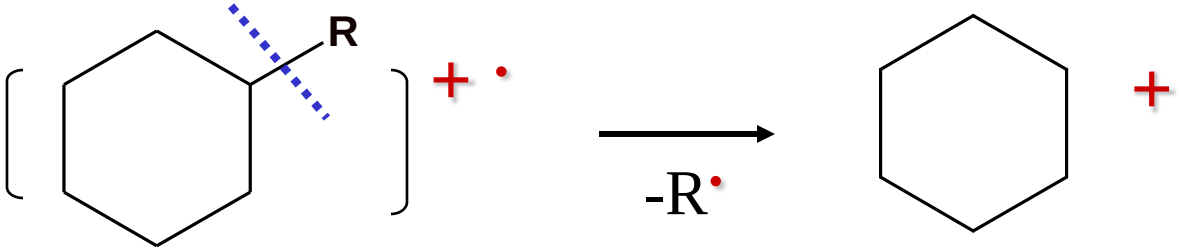


FIGURE 2.6 (*c*). Cyclohexane.

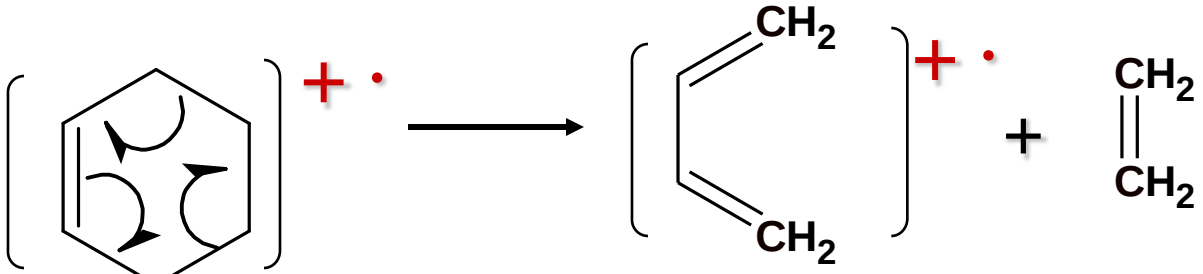


Fragmentation rules in MS

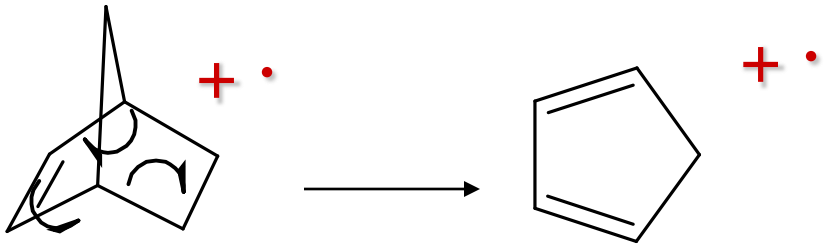
6. a) Saturated Rings lose α Alkyl Chain (case of branching)

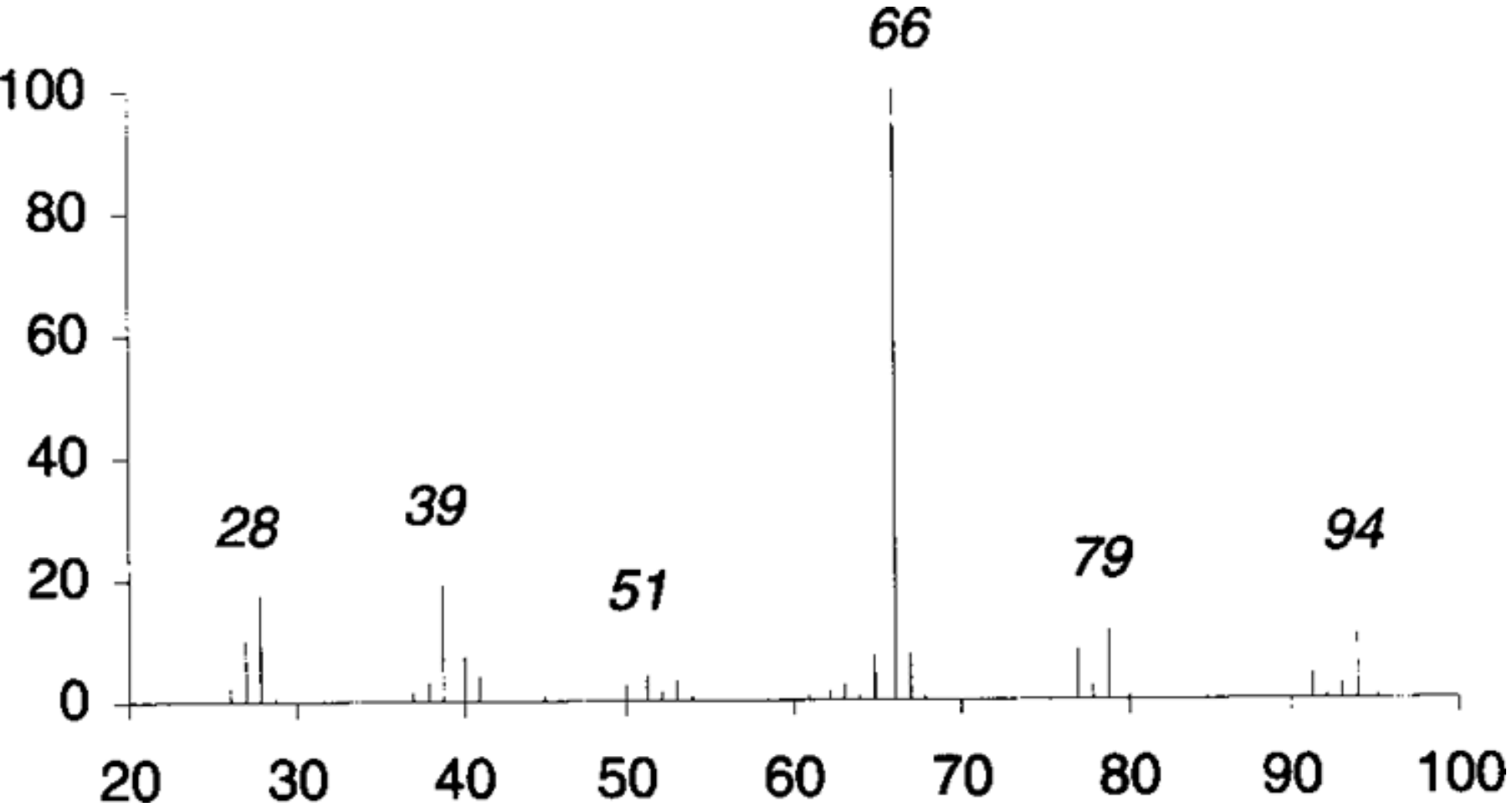


b) Unsaturated Rings ➔ Retro-Diels-Alder



Retro Diels-alder

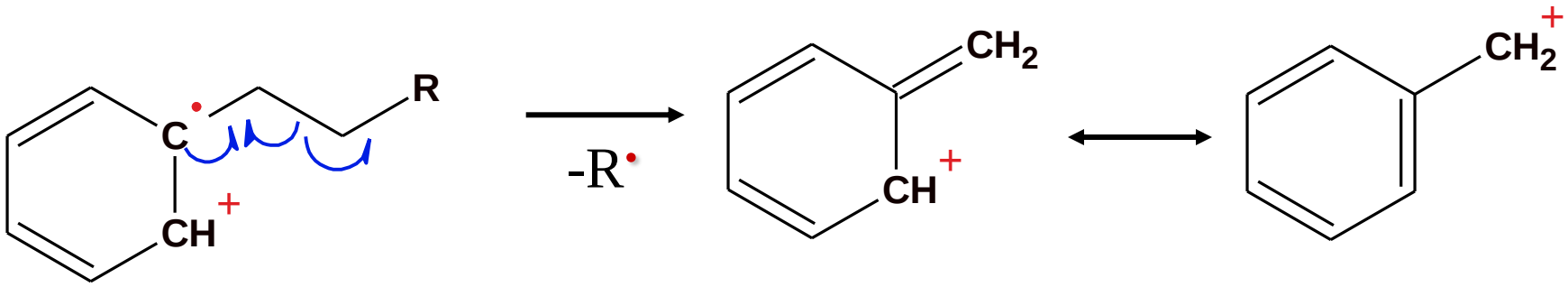




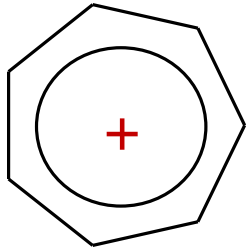
Fragmentation rules in MS

7. Aromatic Compounds Cleave in β

➔ Resonance Stabilized **Tropylium**

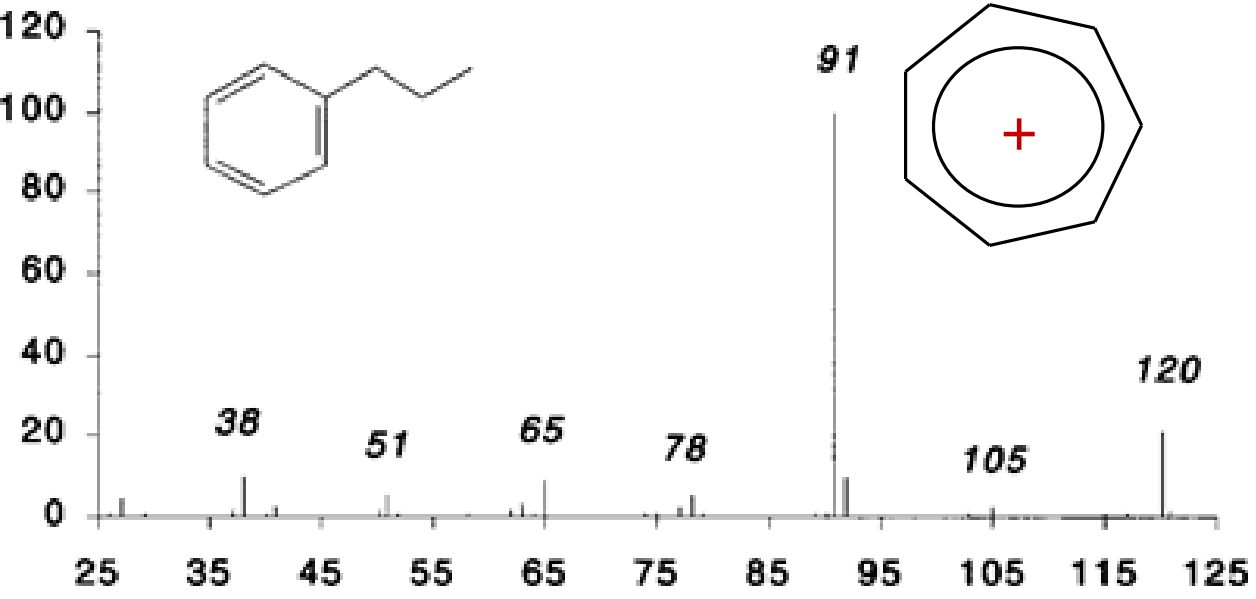


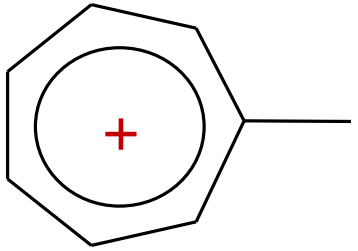
Tropylium ion

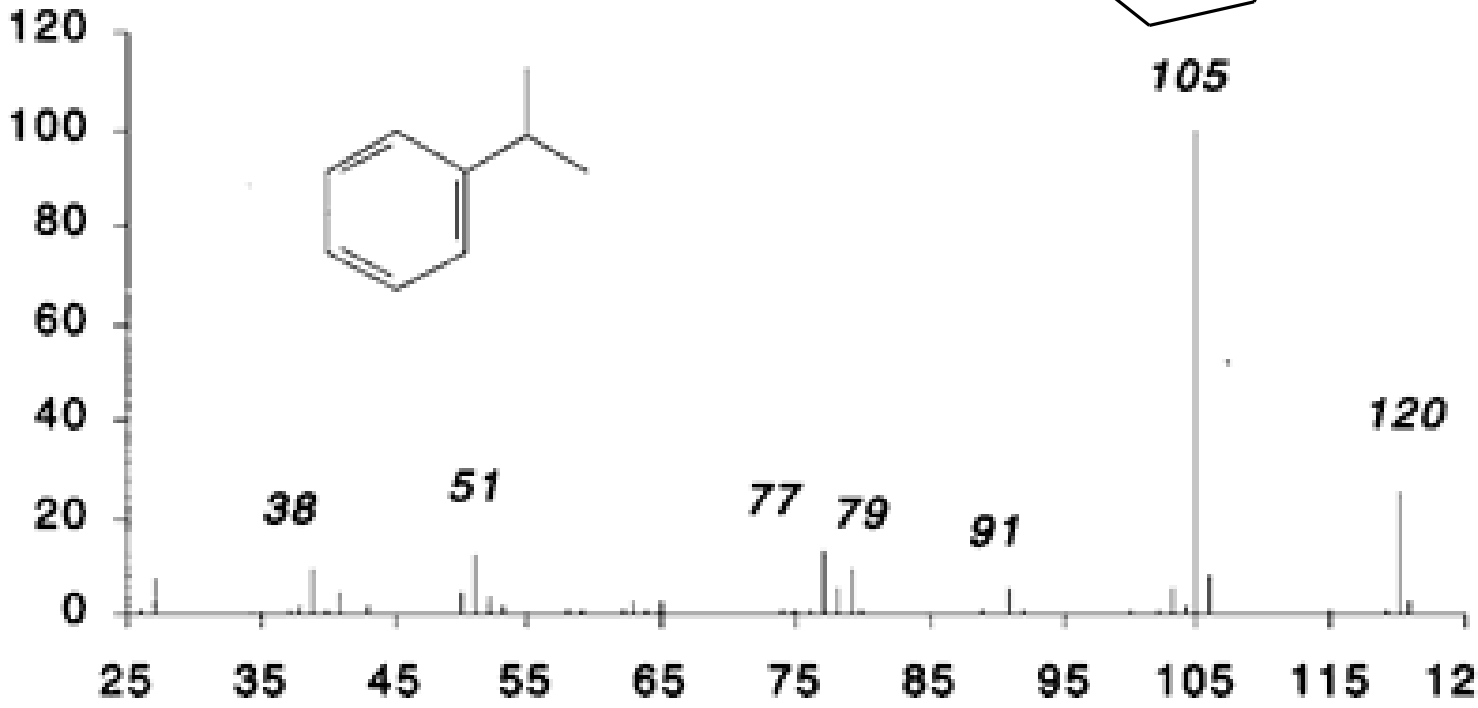


m/z 91

Tropylium ion

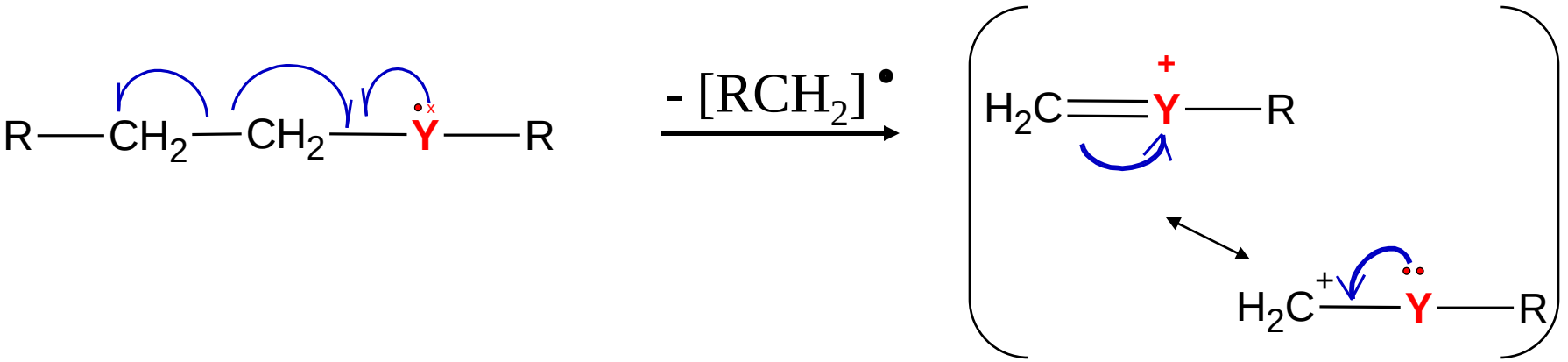


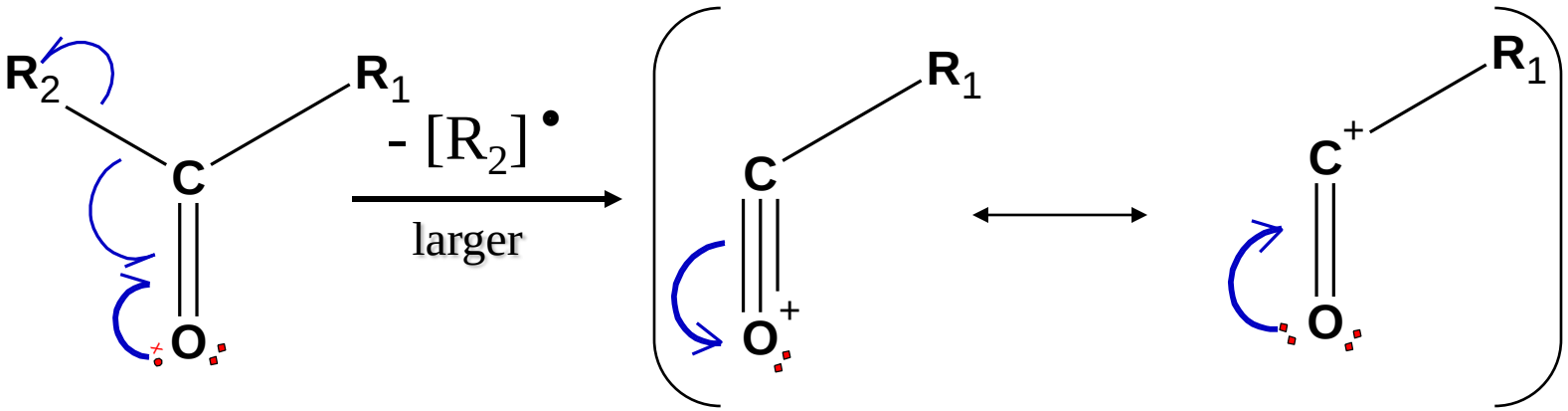




Fragmentation rules in MS

8. C-C Next to Heteroatom cleave leaving the **charge on the Heteroatom**

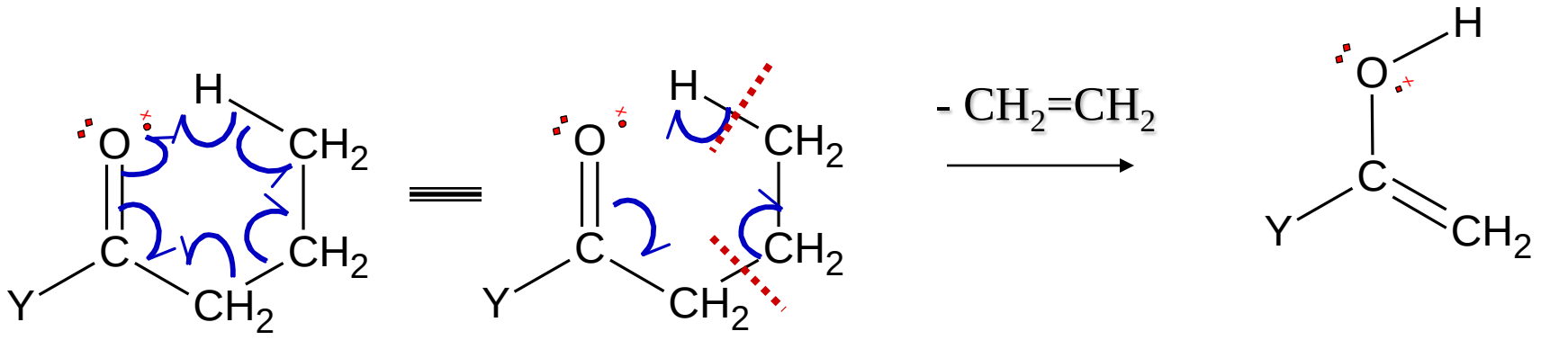




Fragmentation rules in MS

9. Cleavage of small neutral molecules (CO_2, CO, olefins, H_2O ….) Result often from rearrangement

McLafferty



Y ➔ H, R, OH, NR2

Ion Stabilized by resonance

Alkenes

Alkenes

Most intense peaks are often:

m/z 41, 55, 69

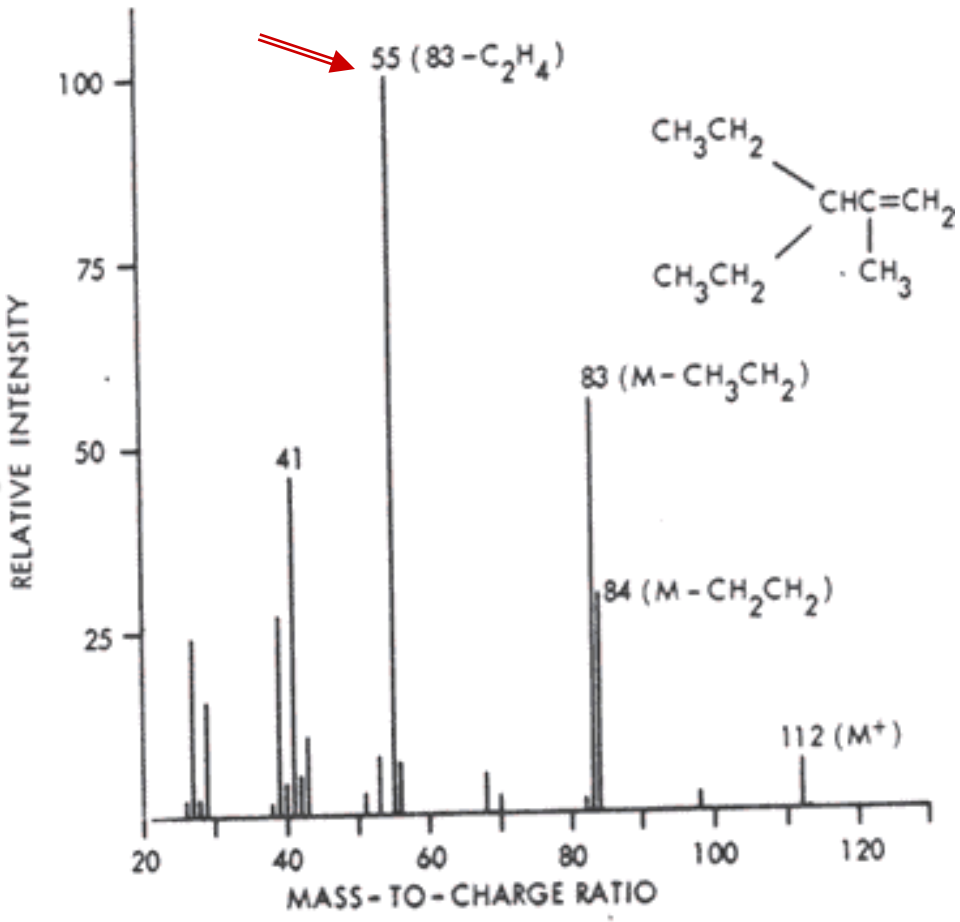
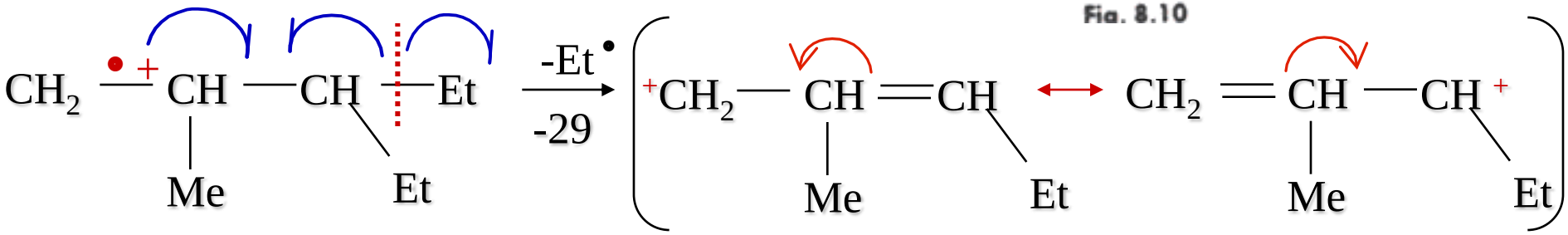


Fig. 8.10

Rule 4: Double Bond Stabilize $M^{\bullet}$

Rule 5: Double Bond favor
Allylic cleavage



$M^{\bullet +} = 112$

m/z = 83

Alkenes

Alkenes

Facile Migration of Double Bond
=> Difficult to localize Double Bond

Allylic Cleavage

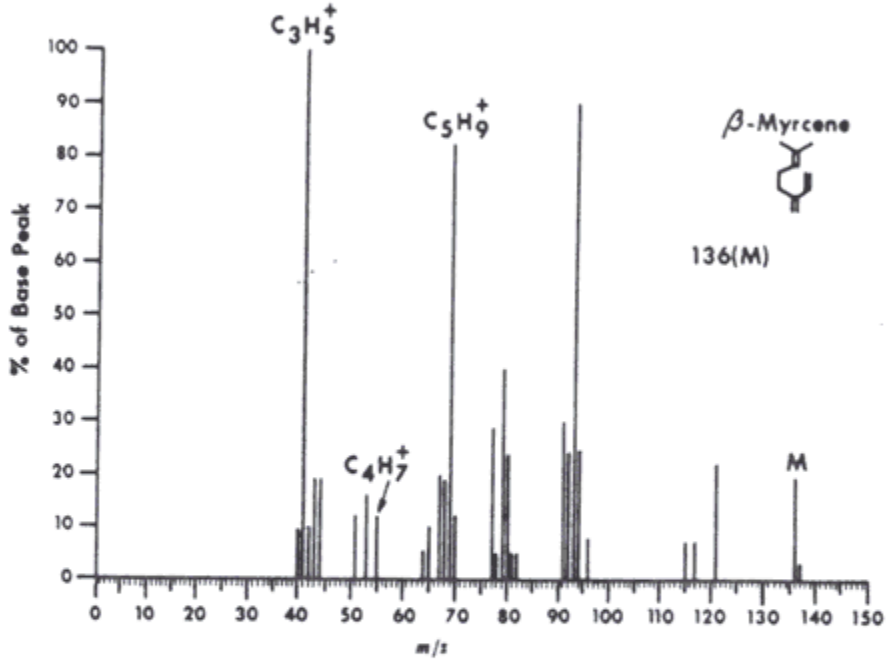
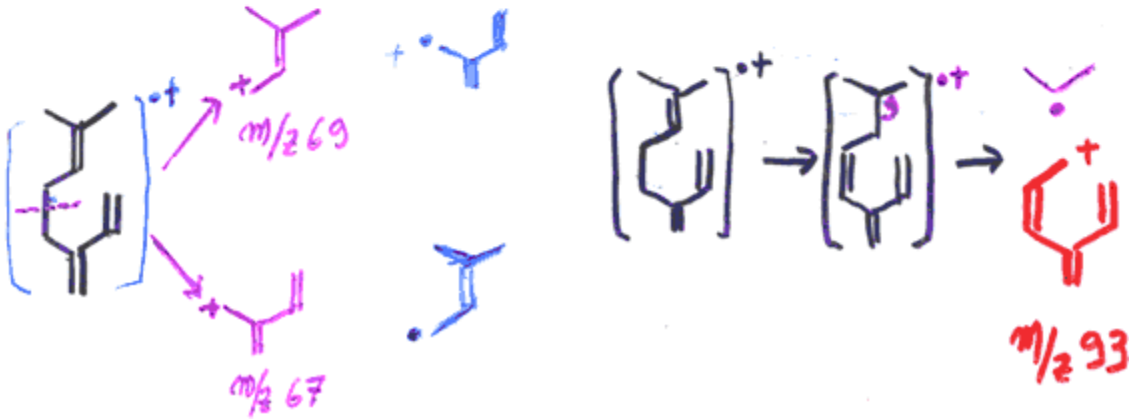


FIGURE 2.7. β-Myrcene.



Aromatic compound

$M^{\cdot+}$: stabilized

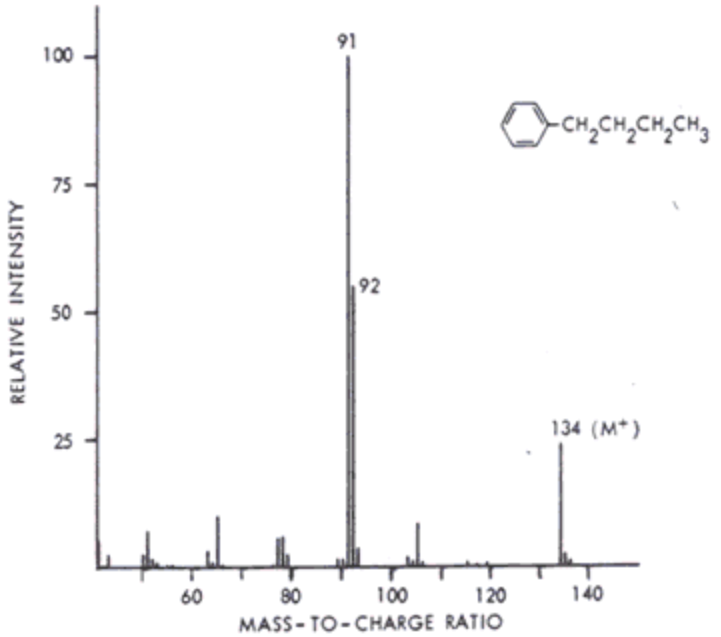
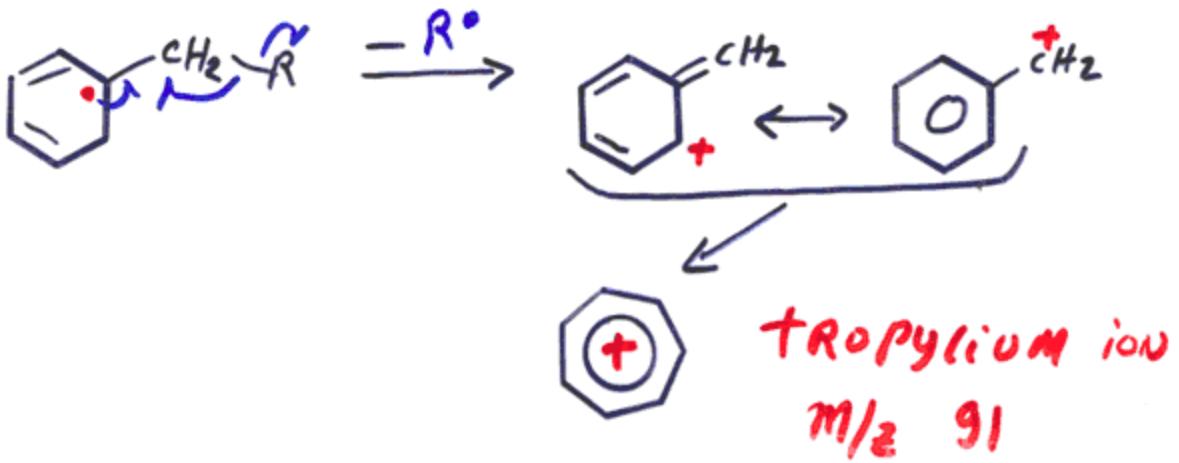


Fig. 8.11

Rule 7 :Cleavage in β of aromatic ring

-> Tropylium ion



Alcohols

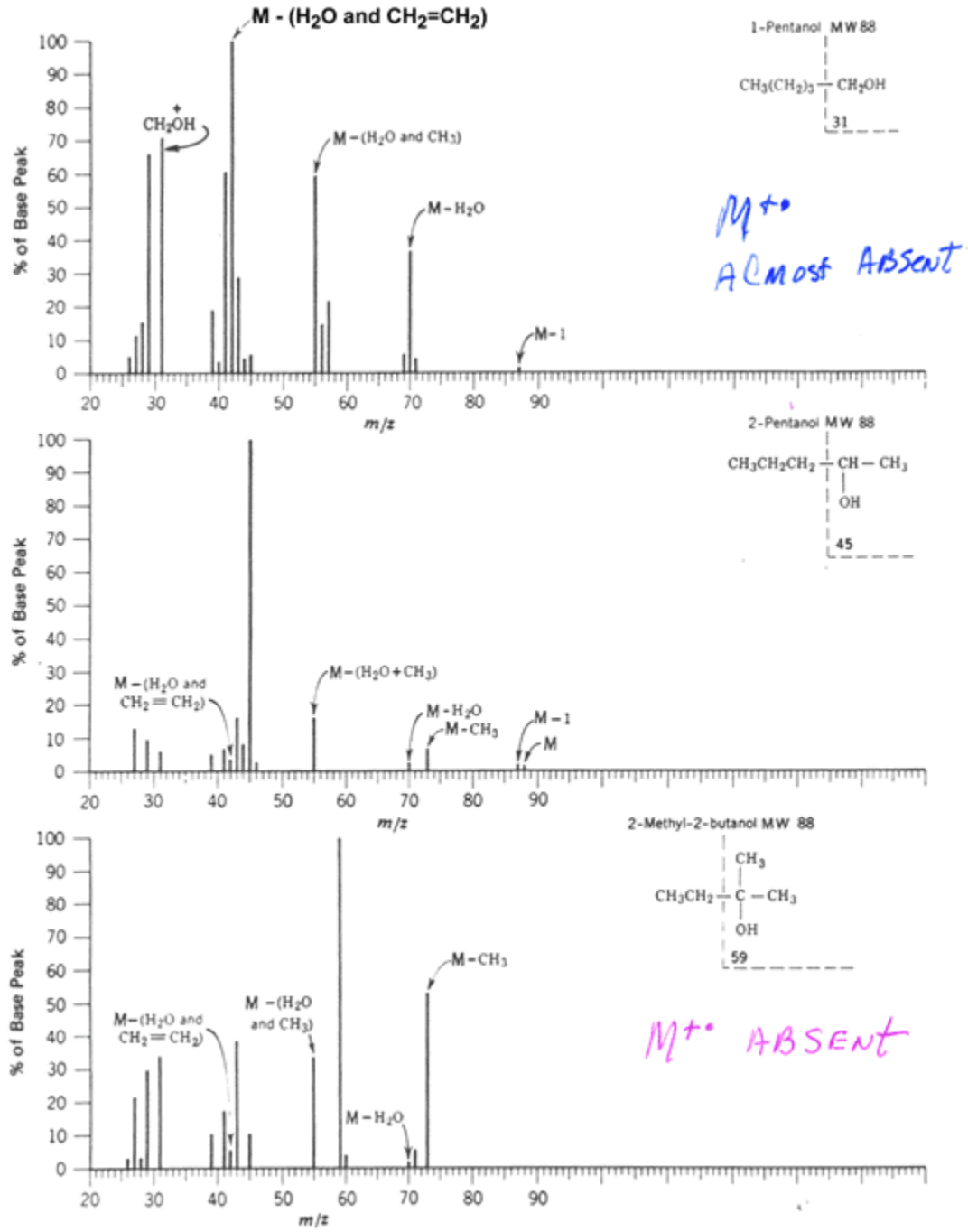
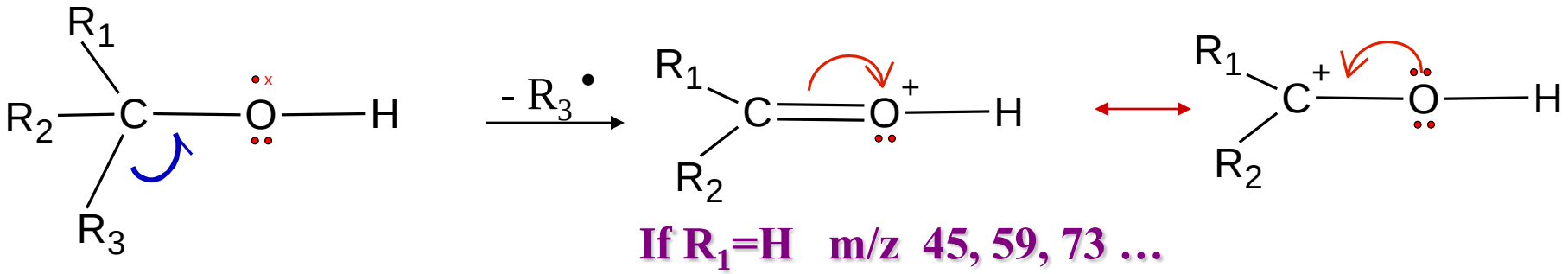


FIGURE 2.9. Isomeric pentanols.

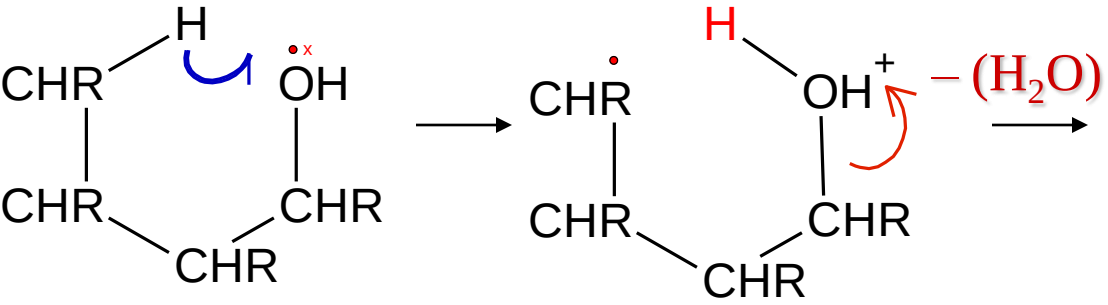
Hydroxy compounds

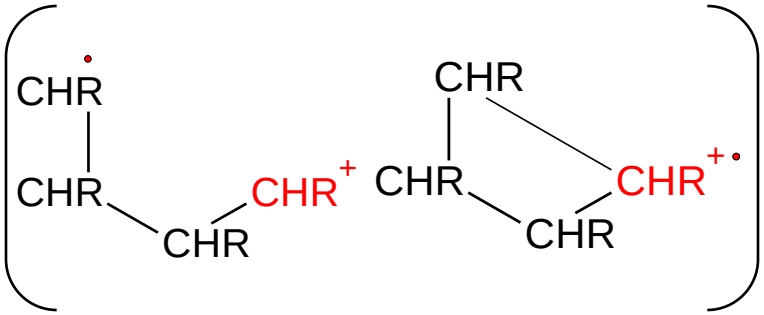


If R_1=H m/z 45, 59, 73 …

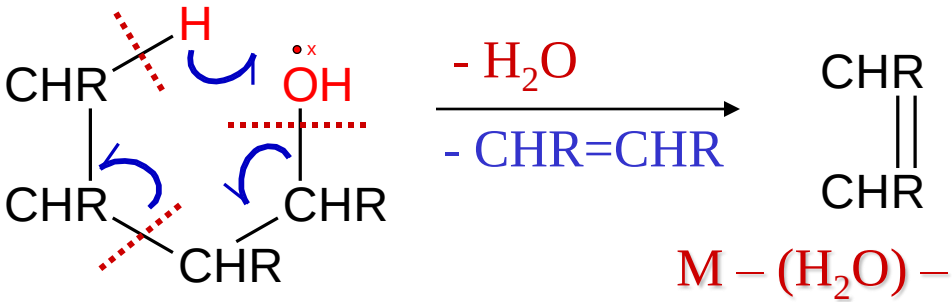
Loss of largest group

If R_1=alkyl m/z 59, 73, 87 …





$M - (H_2O)$



$M - (H_2O) - (C1{=}C2)$ Alkene

Phenol

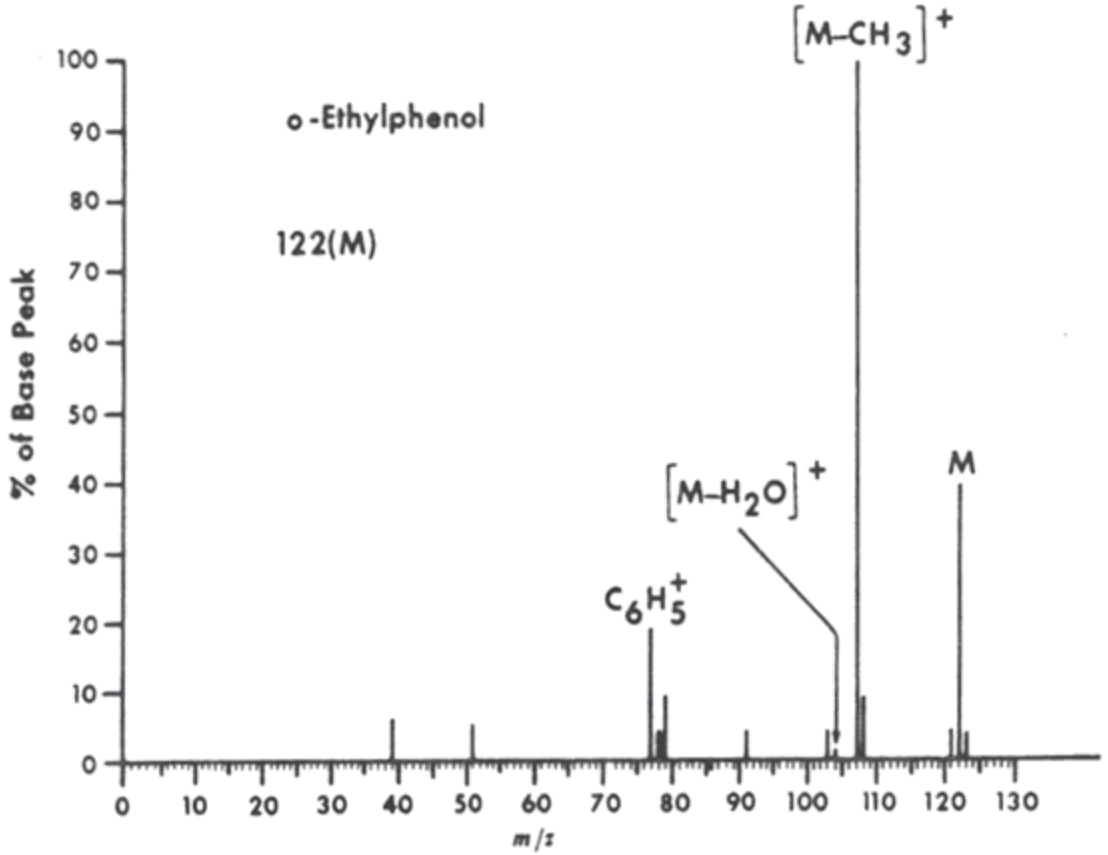
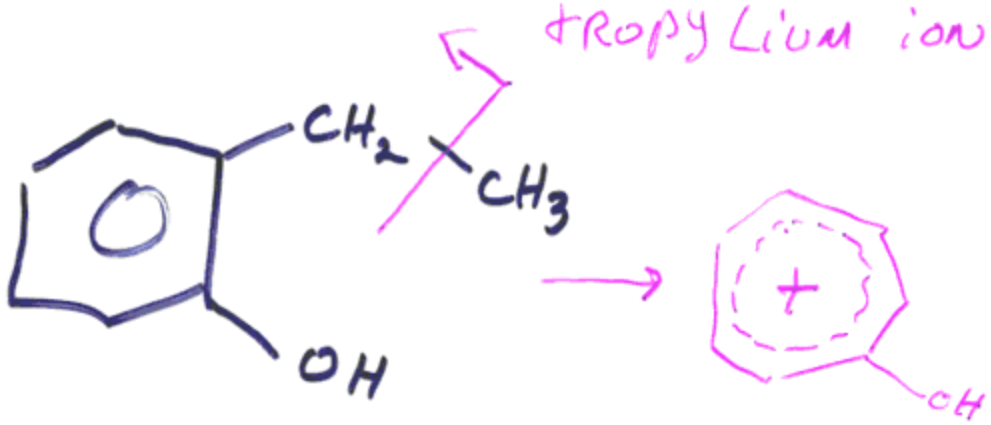


FIGURE 2.10. *o*-Ethylphenol.



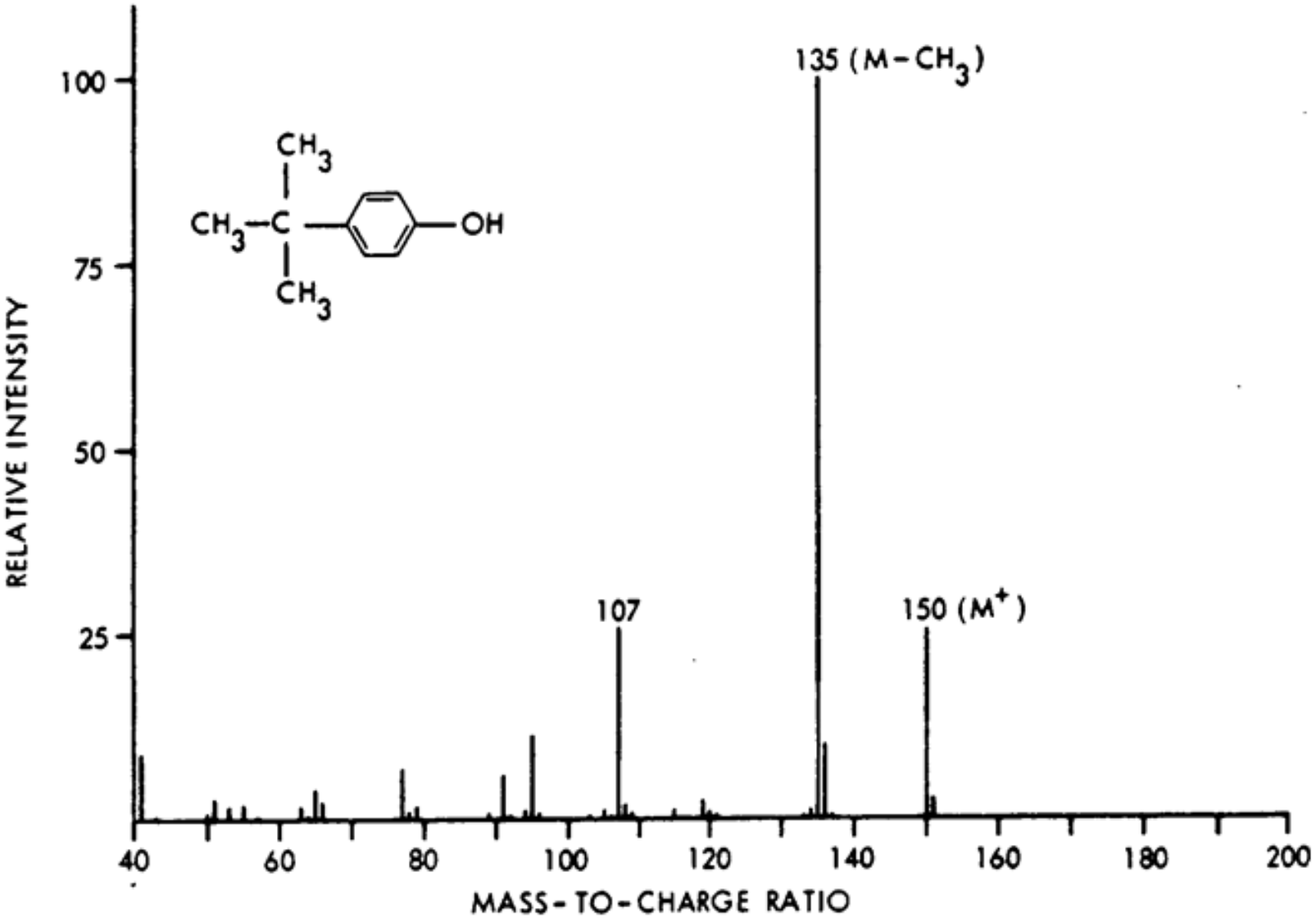
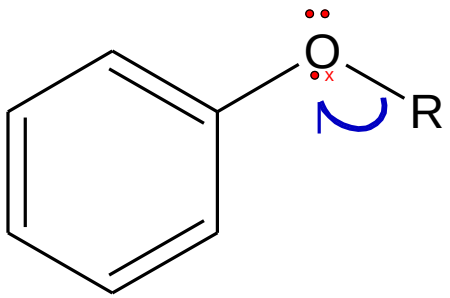

135 (M – CH3)
107
150 (M+)
100
75
50
25
RELATIVE INTENSITY
40
60
80
100
120
140
160
180
200
MASS-TO-CHARGE RATIO
CH3
CH3–C
OH
CH3

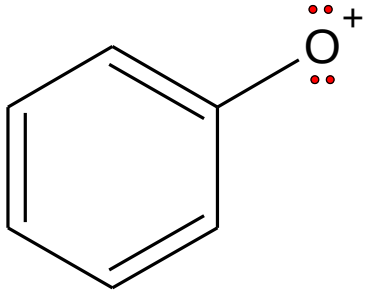
Fig. 8.17

Aromatic Ether Molecular ion is prominent

1)



- R •



m/z 93

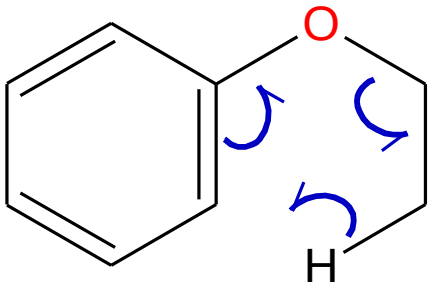
-CO

C_5H_5

m/z 65

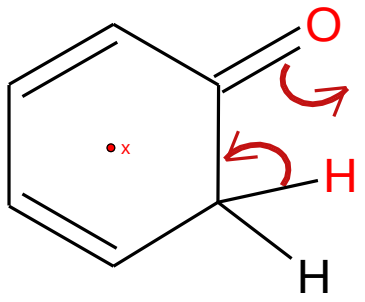
Cleavage in β of aromatic ring

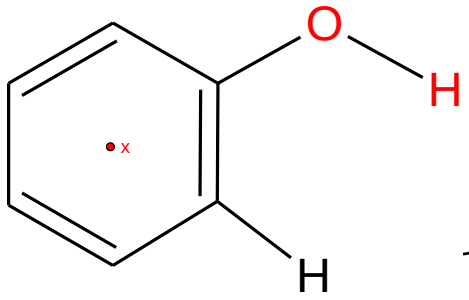
2)



Rearrangement

- $CH_2=CH_2$





m/z 94

Aliphatic Ether

Cleavage of C-C next ot Oxygen

Loss of biggest fragment

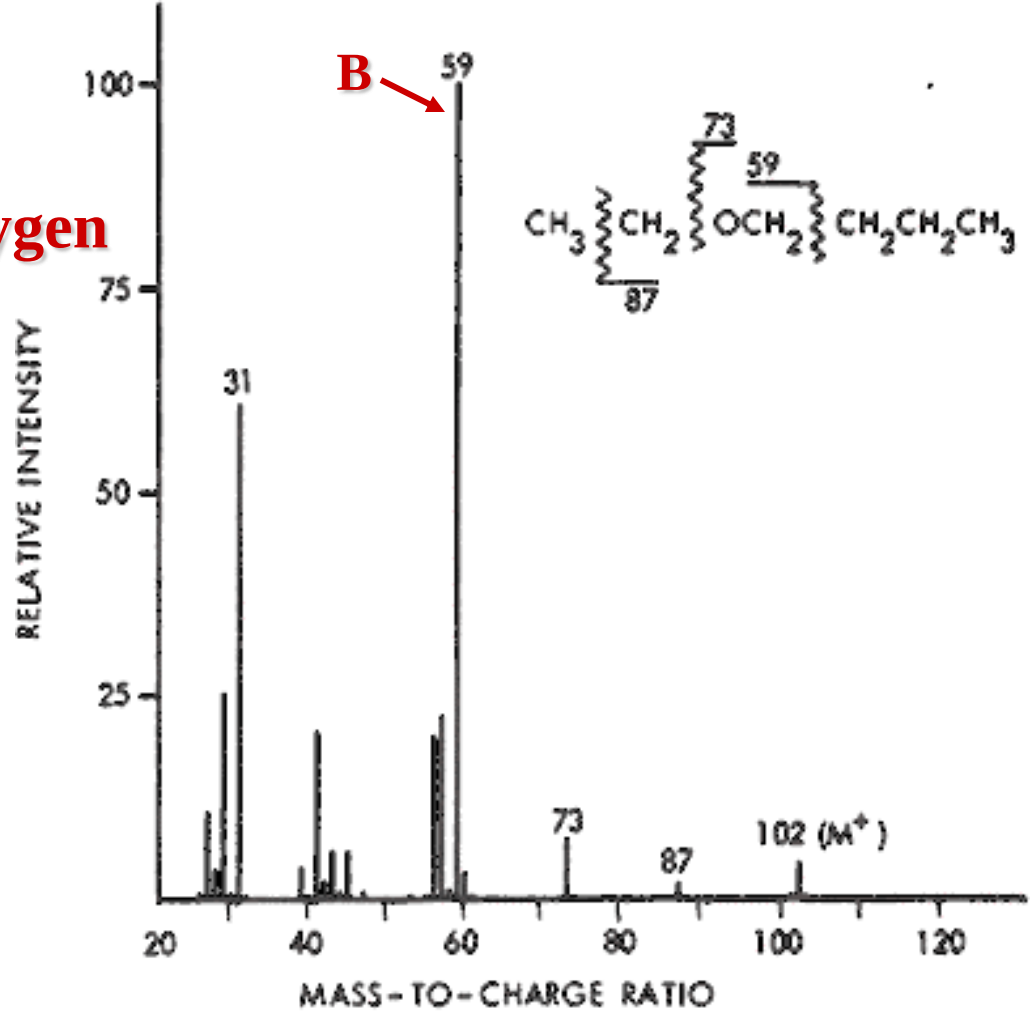
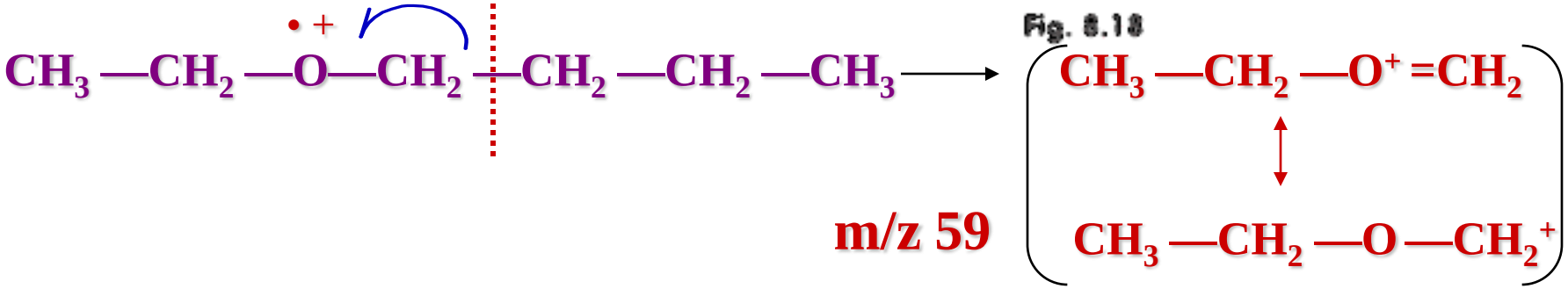
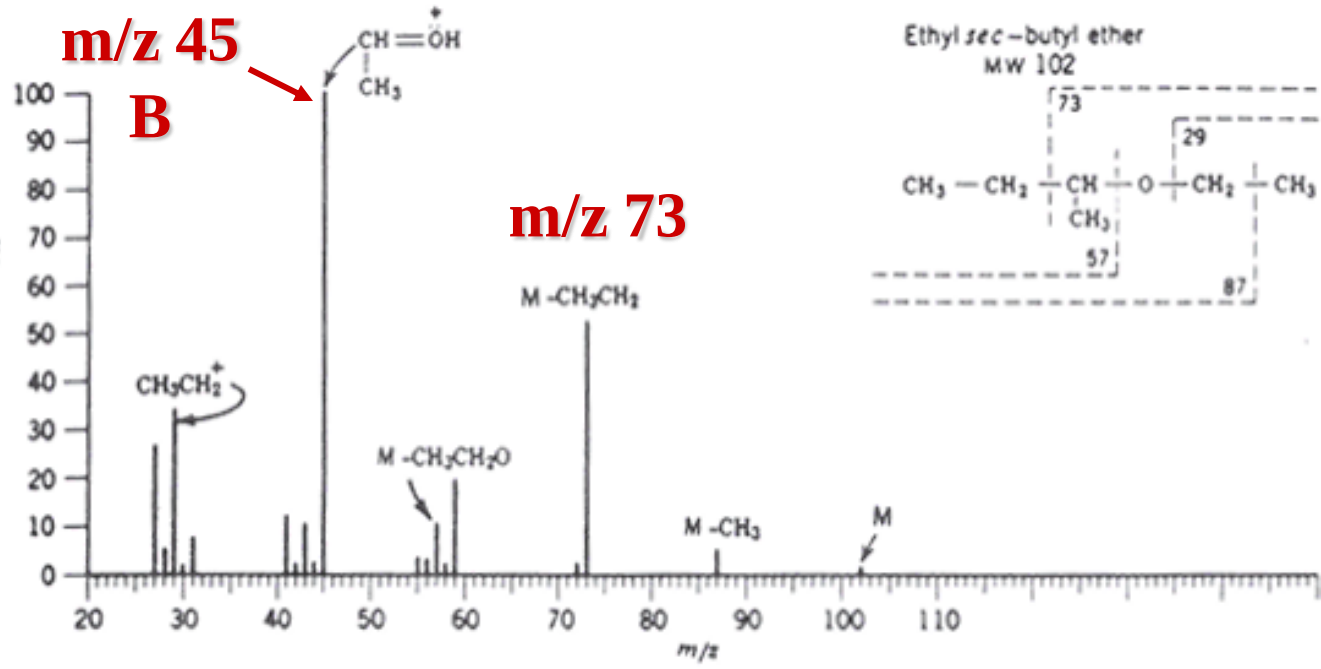


Fig. 8.18

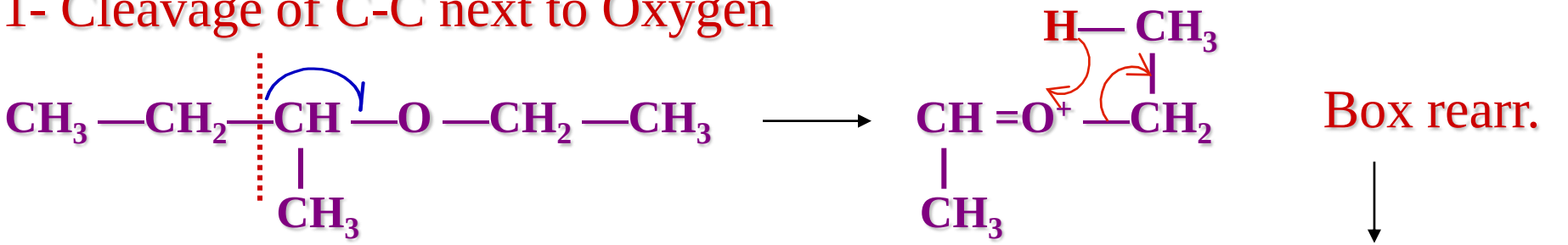


Ether Rearrangemer



GURE 2.11. Ethyl *sec*-butyl ether.

1- Cleavage of C-C next to Oxygen



2- Cleavage of C-O bond: charge on alkyl