Mass Spectrometry Interpretation

Interpretation of Mass Spectra

- Select a candidate peak for the molecular ion (M^+)
- Examine spectrum for peak clusters of characteristic isotopic patterns
- Test (M^+) peak candidate by searching for other peaks correspond to reasonable losses
- Look for characteristic low-mass fragment ions
- Compare spectrum to reference spectra

SOME COMMON AND REASONABLE LOSSES FROM THE MOLECULAR ION

M - 1	loss of hydrogen radical	M- $\cdot H$
M - 15	loss of methyl radical	M- $\cdot CH_3$
M - 29	loss of ethyl radical	M- $\cdot CH_2CH_3$
M - 31	loss of methoxyl radical	M- $\cdot OCH_3$
M - 43	loss of propyl radical	M- $\cdot CH_2CH_2CH_3$
M - 45	loss of ethoxyl radical	M- $\cdot OCH_2CH_3$
M - 57	loss of butyl radical	M- $\cdot CH_2CH_2CH_2CH_3$
M - 2	loss of hydrogen	M- H_2
M - 18	loss of water	M- H_2O
M - 28	loss of CO or ethylene	M- CO or M - CH_2H_4
M - 32	loss of methanol	M- CH_3OH
M - 44	loss of CO_2	M- CO_2
M - 60	loss of acetic acid	M- CH_3CO_2H
M - 90	loss of silanol: $HO\text{-}Si(CH_3)_3$	M- $HO - Si - (CH_3)_3$

Fragmentação

- Governada pela estabilidade do íon produzido
- consideração

  regra do octeto

  deslocalização por ressonância

  polarizabilidade e hiperconjugação

  eletronegatividade
- Regra de Stevenson:

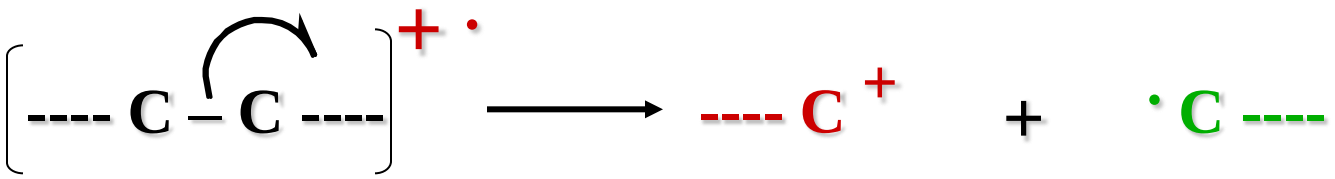
  Para quebra de uma ligações simples, o fragmento com o potencial de ionização mais baixo fica com a carga

  (em outras palavras, forma-se o íon mais estável)

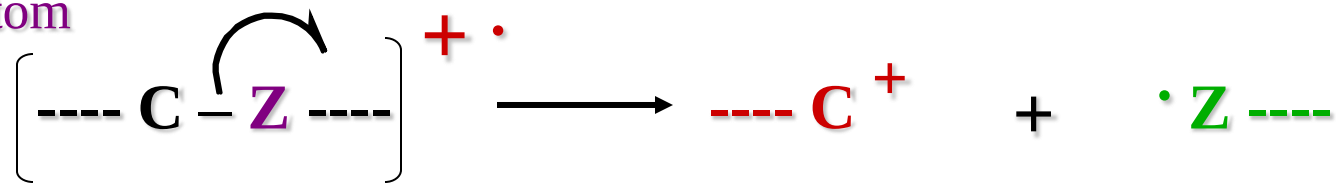
Fragmentation process

There are 3 type of fragmentations:

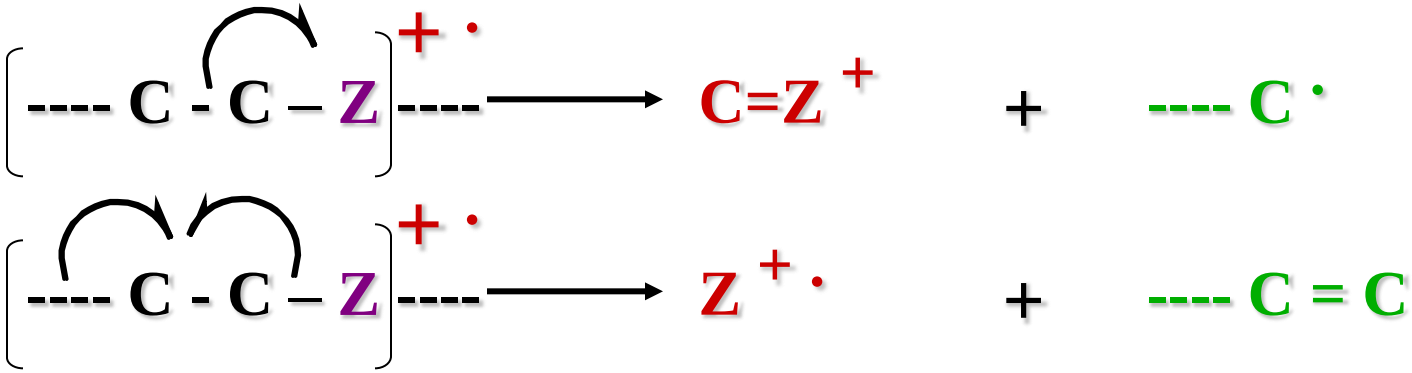
1) Cleavage of σ bond



At heteroatom

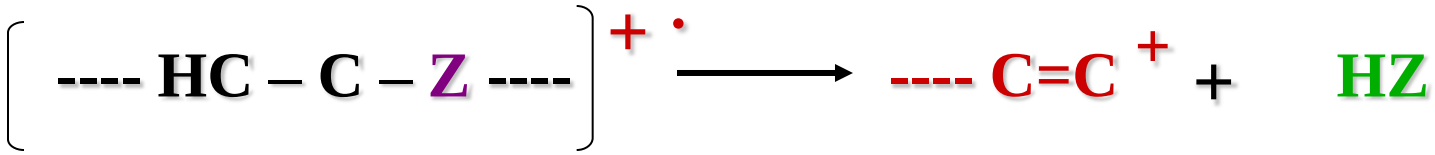


α to heteroatom

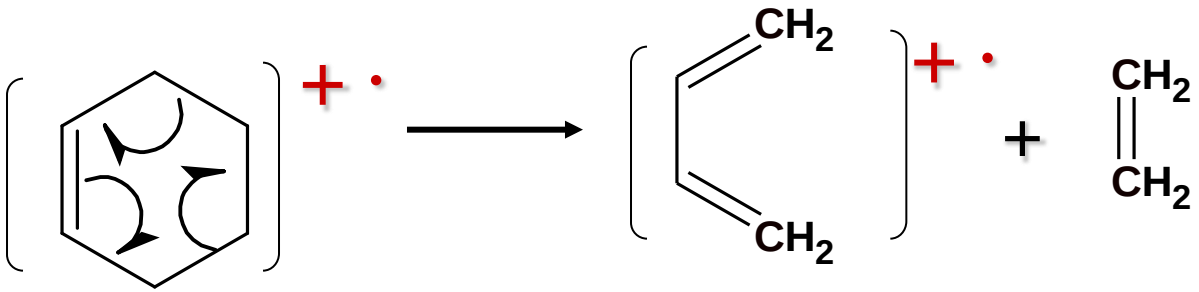


Fragmentation process

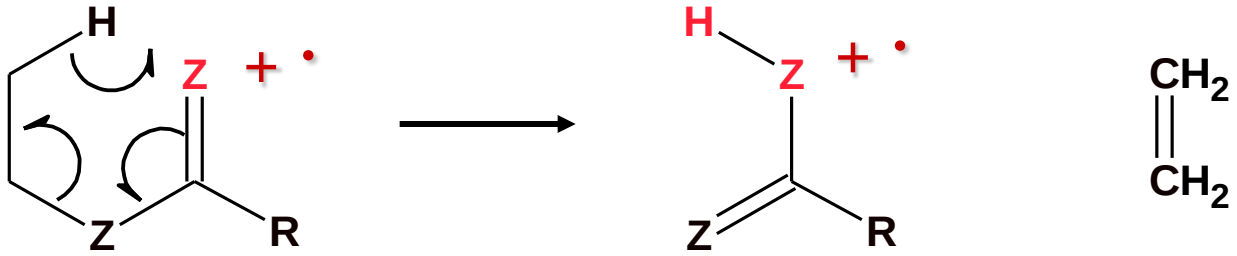
2) Cleavage of **2** σ bond (rearrangements)



Retro Diels-alder



McLafferty



3) Cleavage of **Complex** rearrangements

Regras Gerais de Fragmentação

Quebra de Uma Ligação (Quebras-α)

Quebra de Duas Ligações

- Eliminação de H-X
- retro Diels-Alder
- Rearranjo de McLafferty

FRAGMENTATION PATTERNS

ALKANES

The mass spectra of simple hydrocarbons have peaks at m/z values corresponding to the ions produced by breaking C-C bonds. Peaks can occur at ...

m/z	15	29	43	57	71	85	etc.
	CH_3^+	$C_2H_5^+$	$C_3H_7^+$	$C_4H_9^+$	$C_5H_{11}^+$	$C_6H_{13}^+$	

- **the stability of the carbocation formed affects its abundance**
- **the more stable the cation the higher the peak**
- **the more alkyl groups attached to the carbocation the more stable it is**

most stable **tertiary 3° > secondary 2° > primary 1°** **least stable**

alkyl groups are electron releasing and stabilise the cation

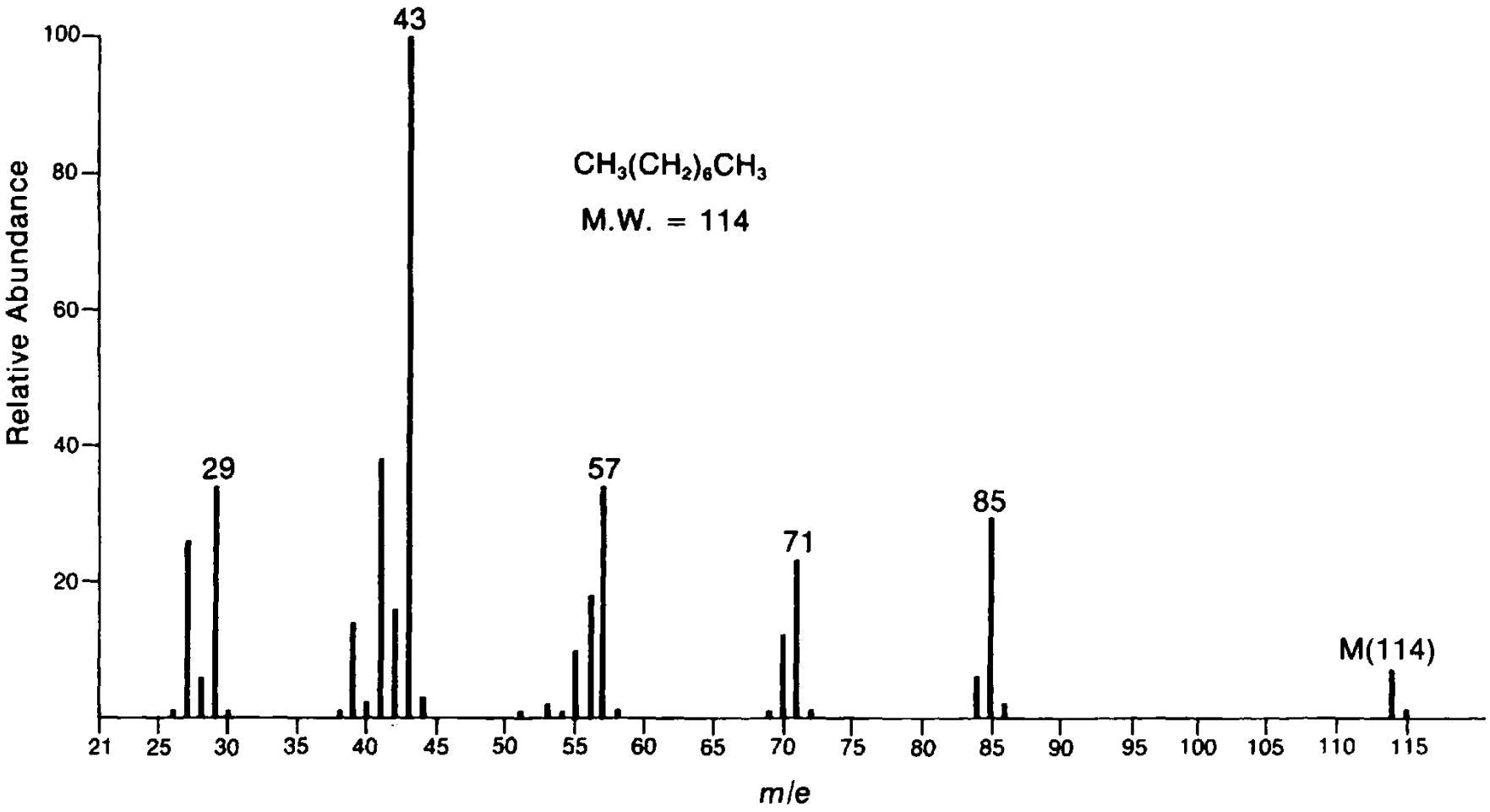
Alkane Fragmentation

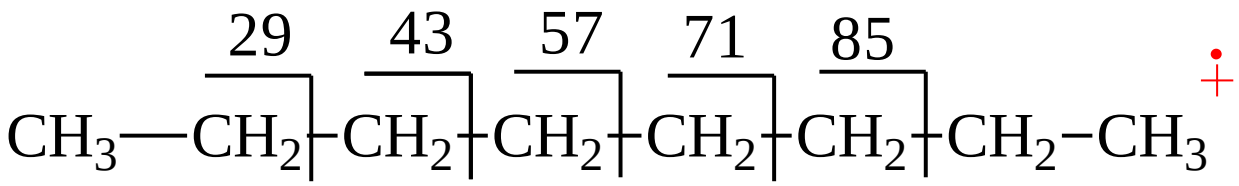
- Long chains give homologous series of m/z = 14 units
- Long chains rarely lose methyl radical
- Straight chain alkanes give primary carbocation
- branched alkanes have small or absent M^+
- enhanced fragmentation at branch points

Cycloalkanes

- loss of side chain
- loss of ethylene fragments

octane


43
100
80
60
40
20
Relative Abundance
CH3(CH2)6CH3
M.W. = 114
29
57
71
85
M(114)
21 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115
m/e

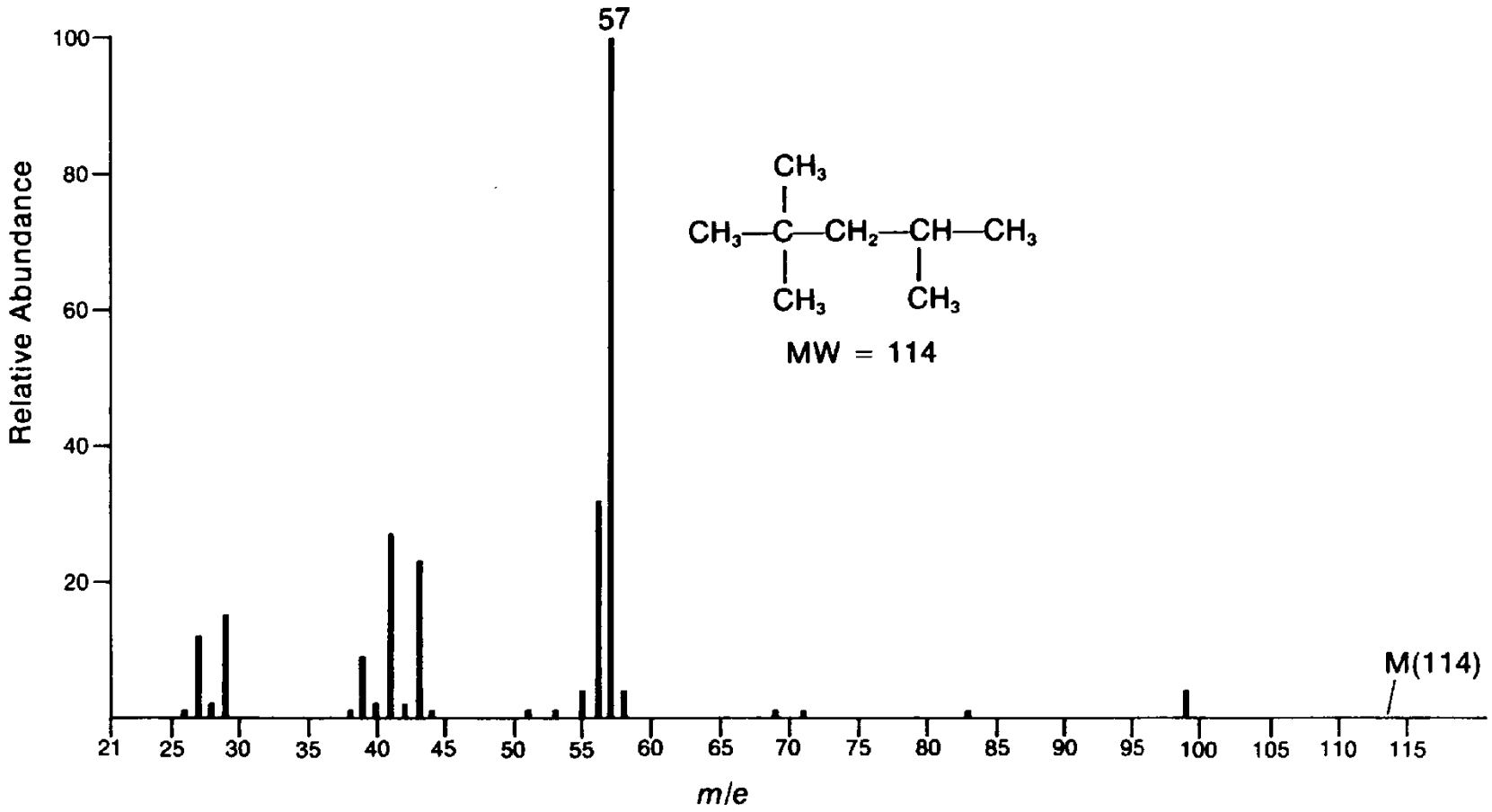


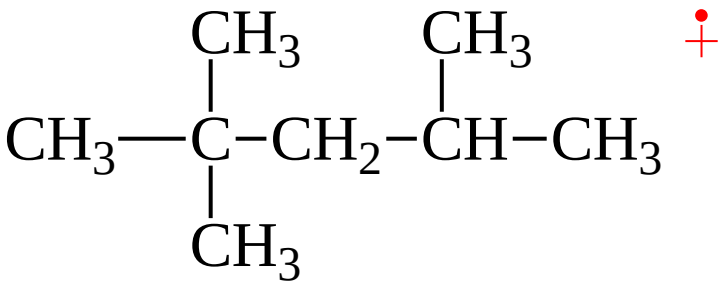
m/z = 114

linear alkane pattern

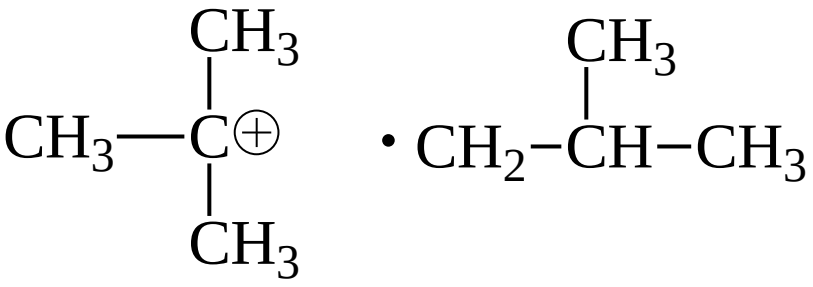
sequential peaks 14 mass units apart

isooctane

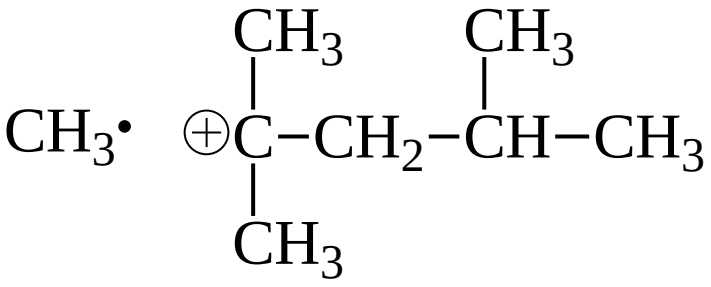

57
100
80
60
40
20
Relative Abundance
CH3
CH3—C—CH2—CH—CH3
CH3
CH3
MW = 114
M(114)
21 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115
m/e



m/z = 114



m/z = 57



m/z = 99

branched alkane - formation of most stable carbocation

Alkene Fragmentation

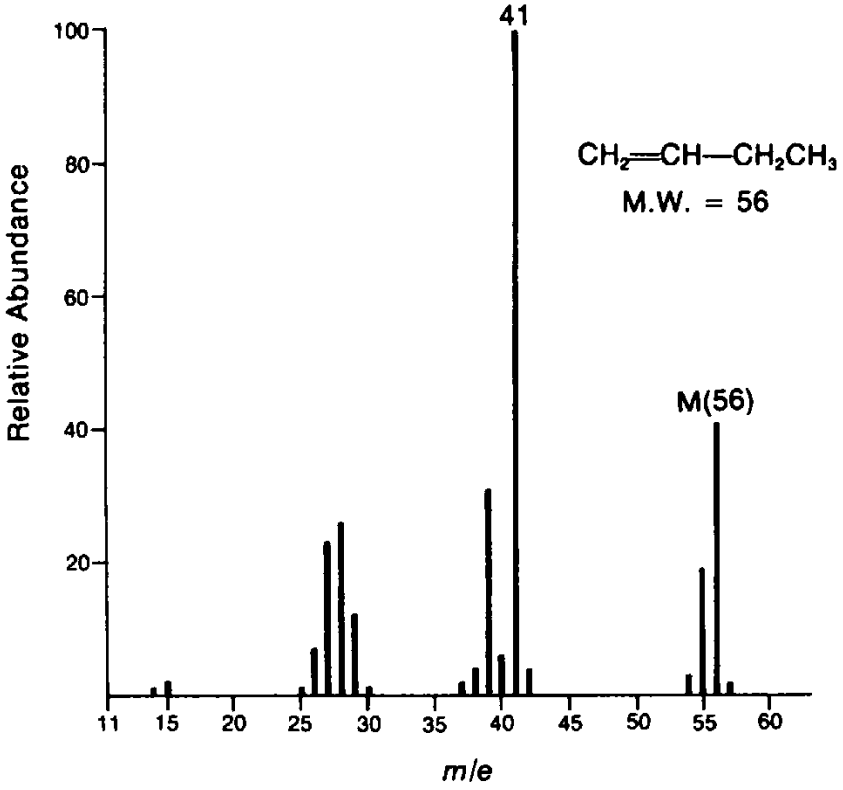
- Fairly prominent M^+
- fragment ions of $C_nH_{2n}^+$ and $C_nH_{2n-1}^+$
- terminal alkenes lose allyl cation if possible

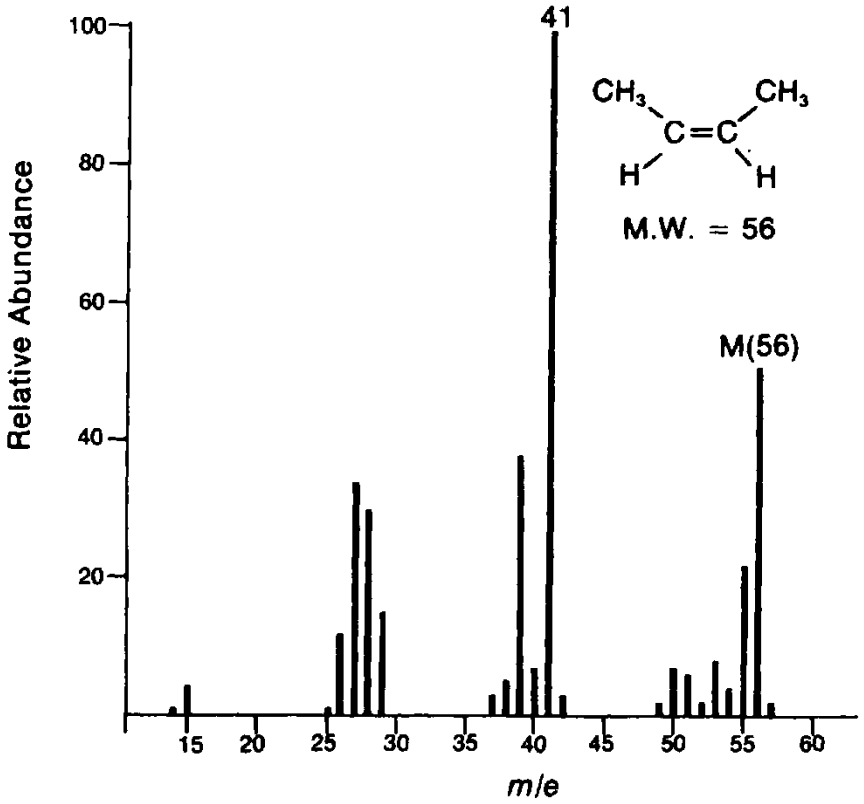
Cycloalkenes

- prominent molecular ion
- retro Diels-Alder cleavage

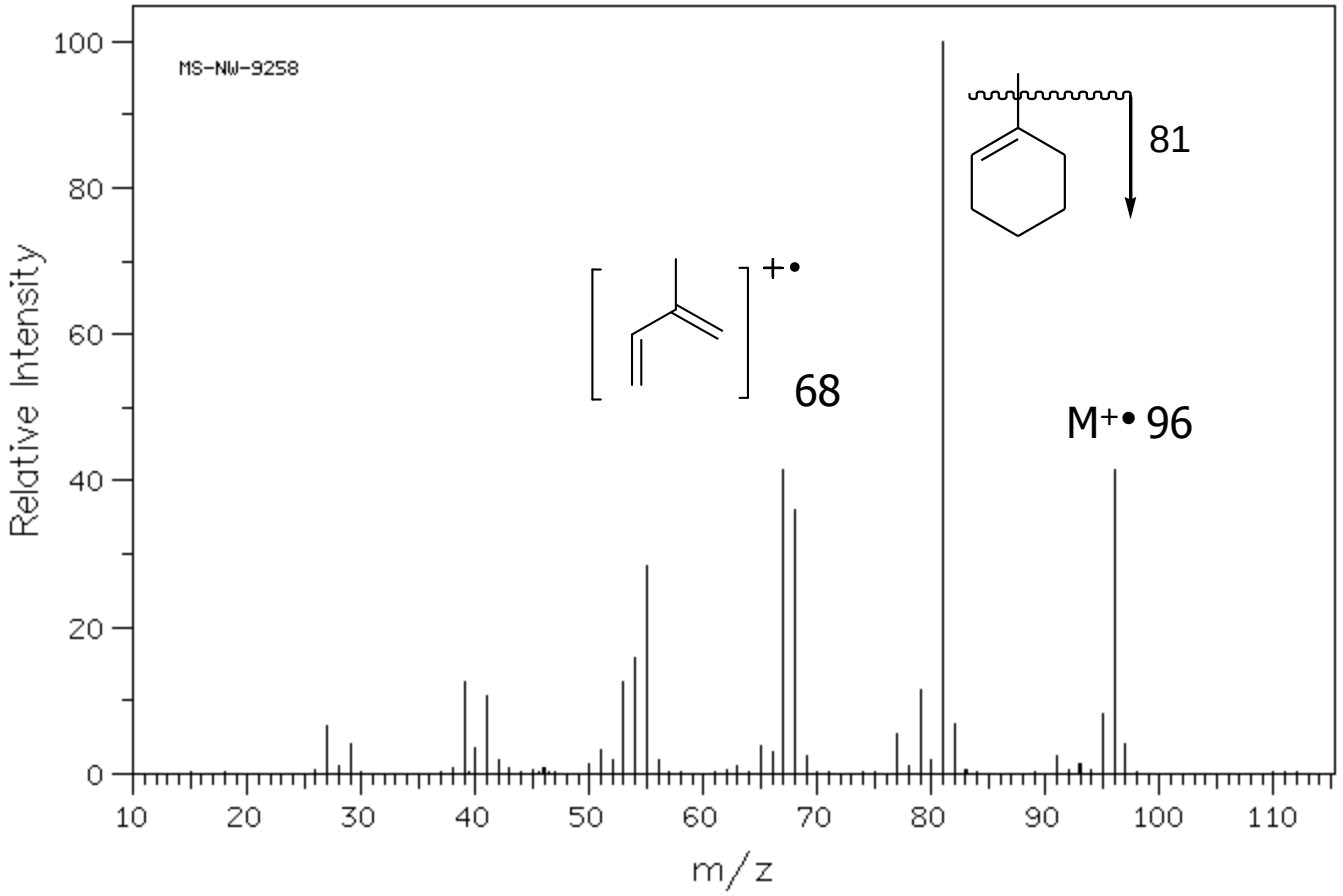
1-butene & 2-butene

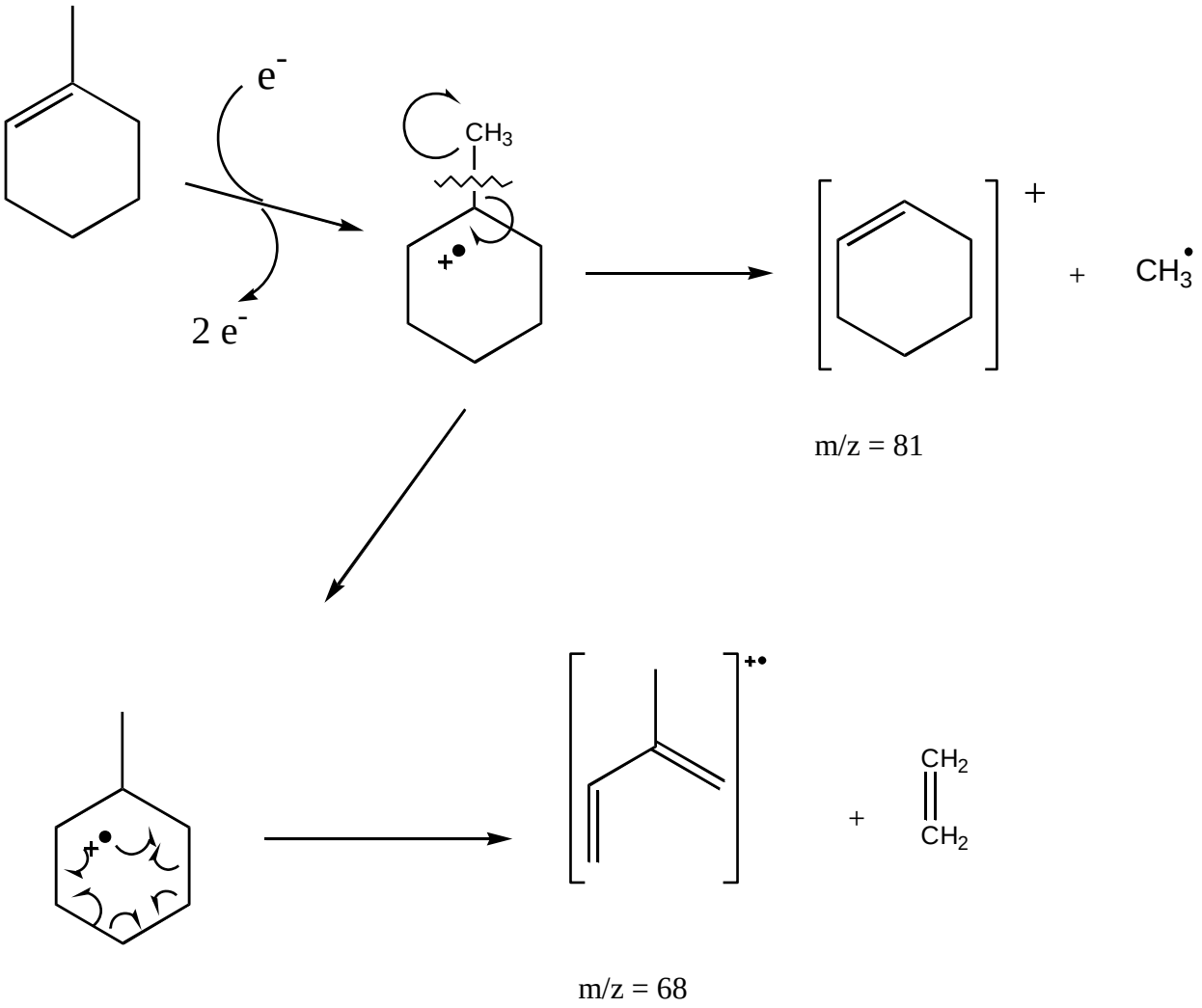
mass spectra are identical - not a good method for alkene isomers



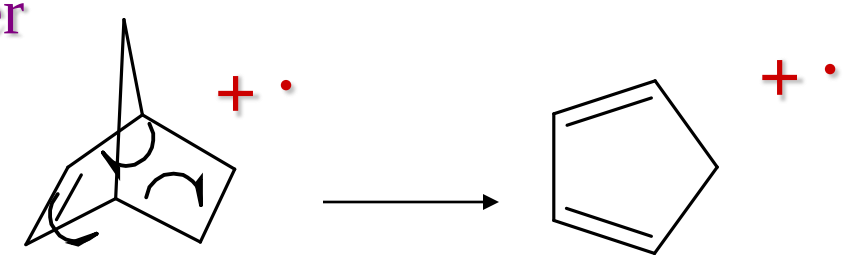


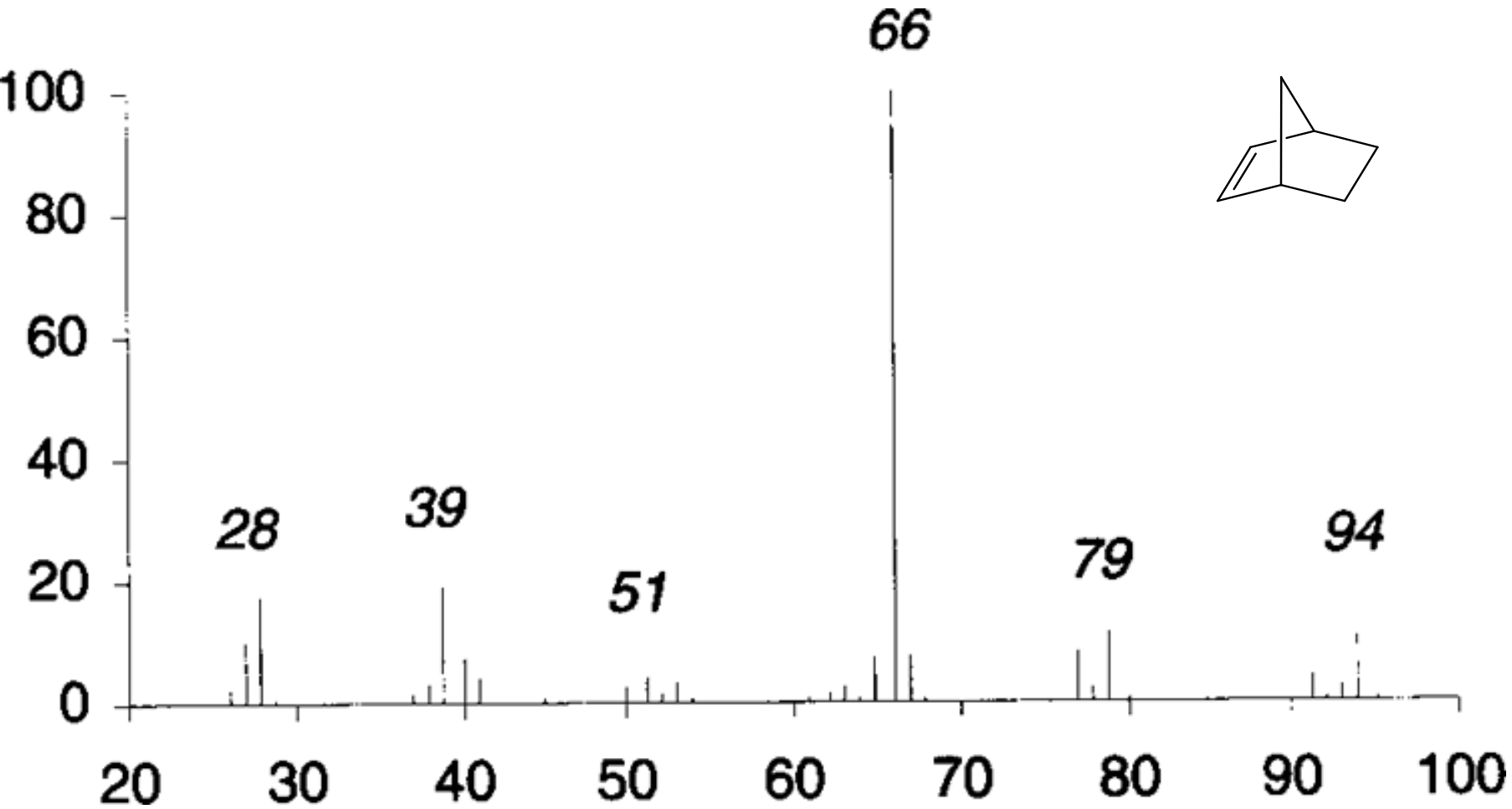
- **Cycloalkenes** –1-methyl-1-cyclohexene




e-
2 e-
CH3
+
+
CH3•
m/z = 81
+•
+
CH2
CH2
m/z = 68

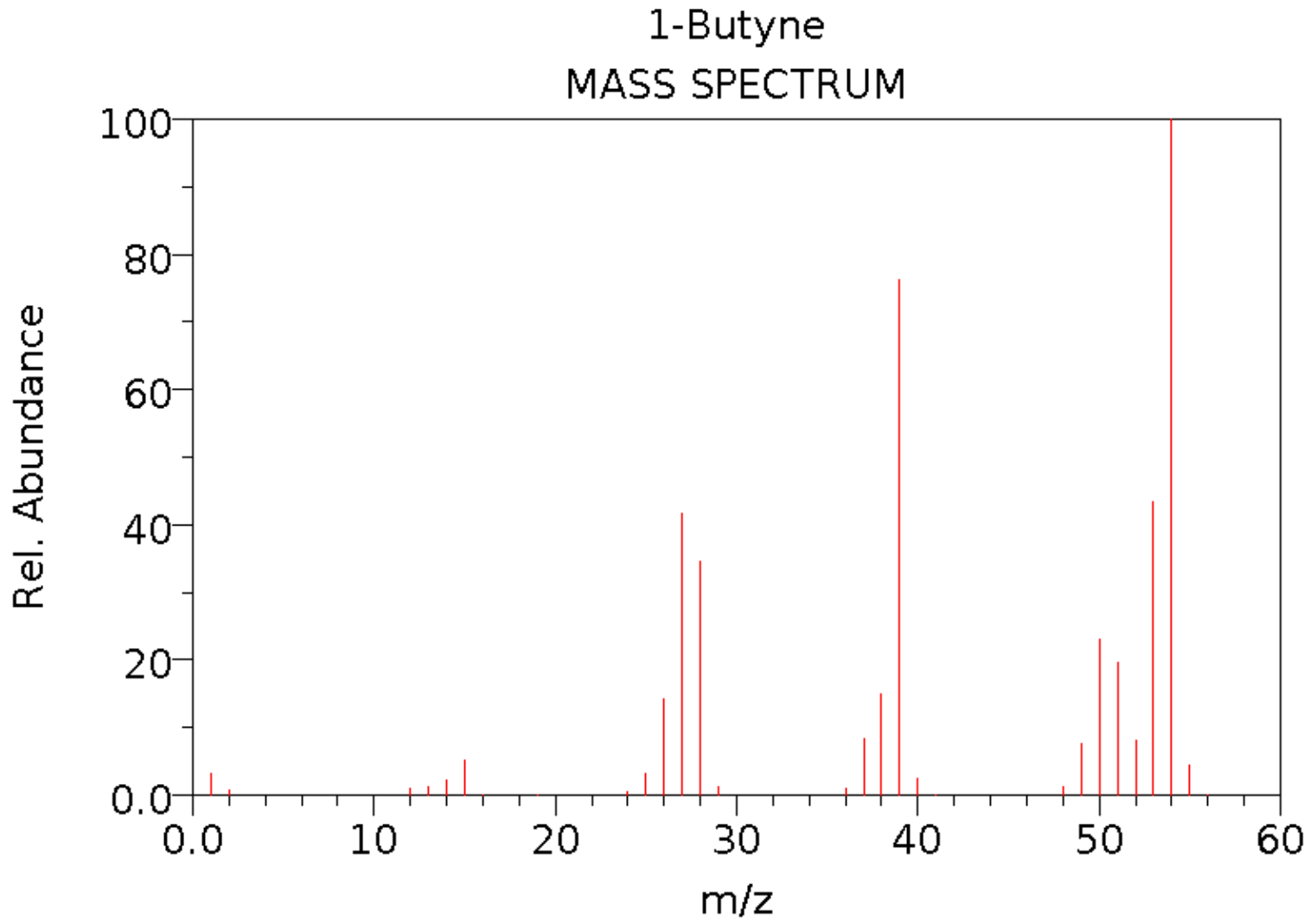
Retro Diels-alder





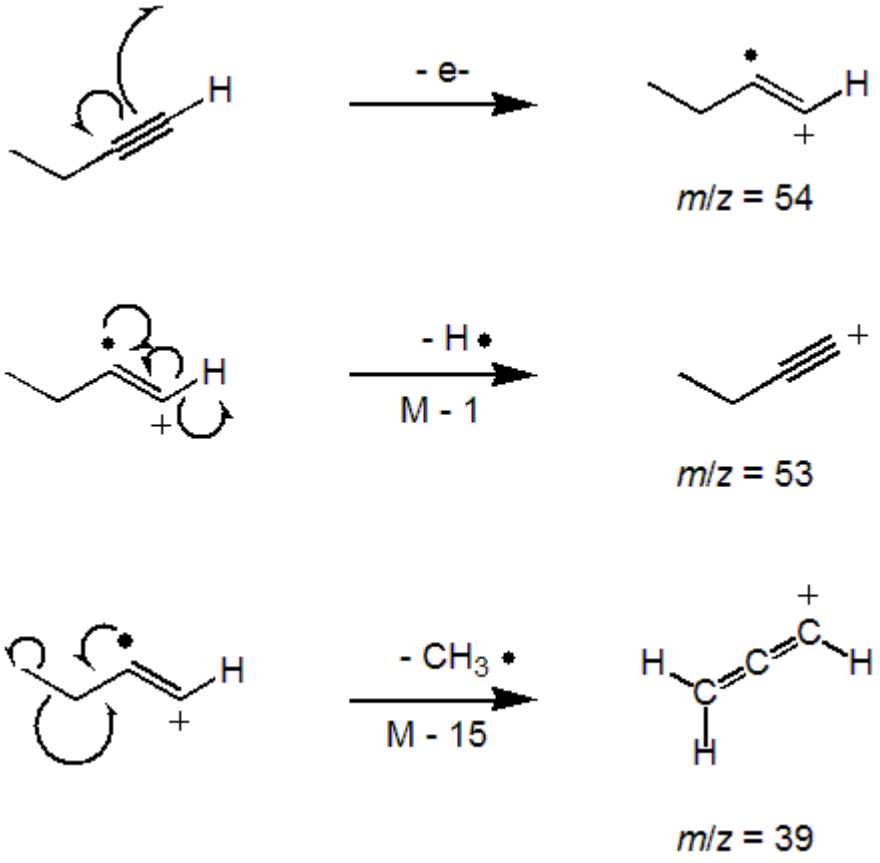
Alkyne Fragmentation

- Molecular ion readily visible
- terminal alkynes readily lose hydrogen atom
- terminal alkynes lose propargyl cation if possible

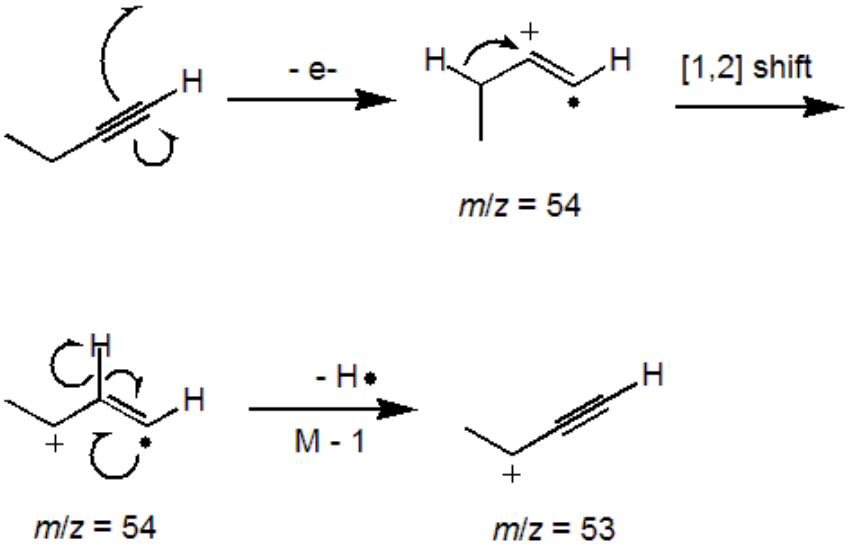


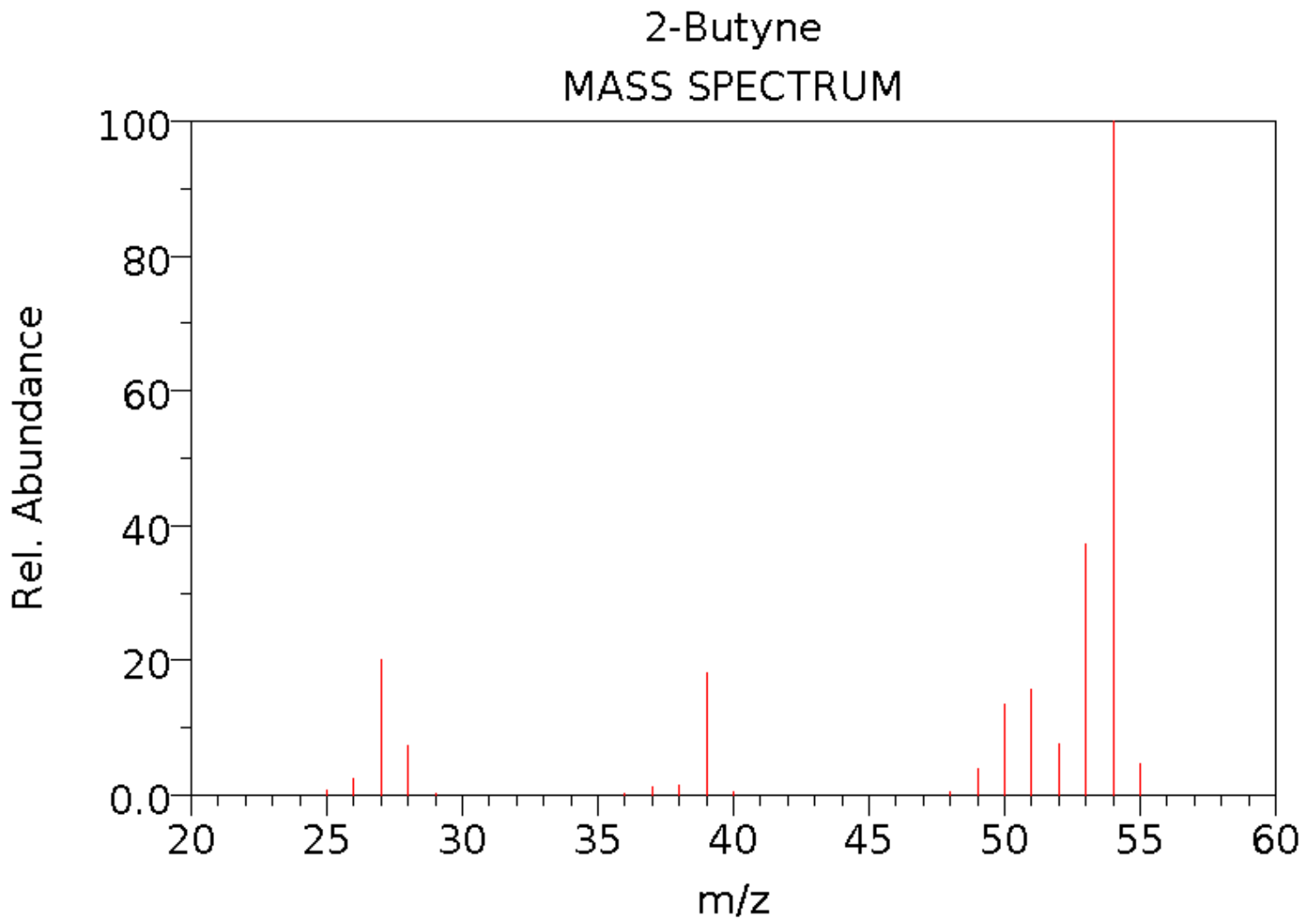
NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Proposta de Fragmentação



Proposta de Fragmentação Alternativa





NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Aromatic Hydrocarbon Fragmentation

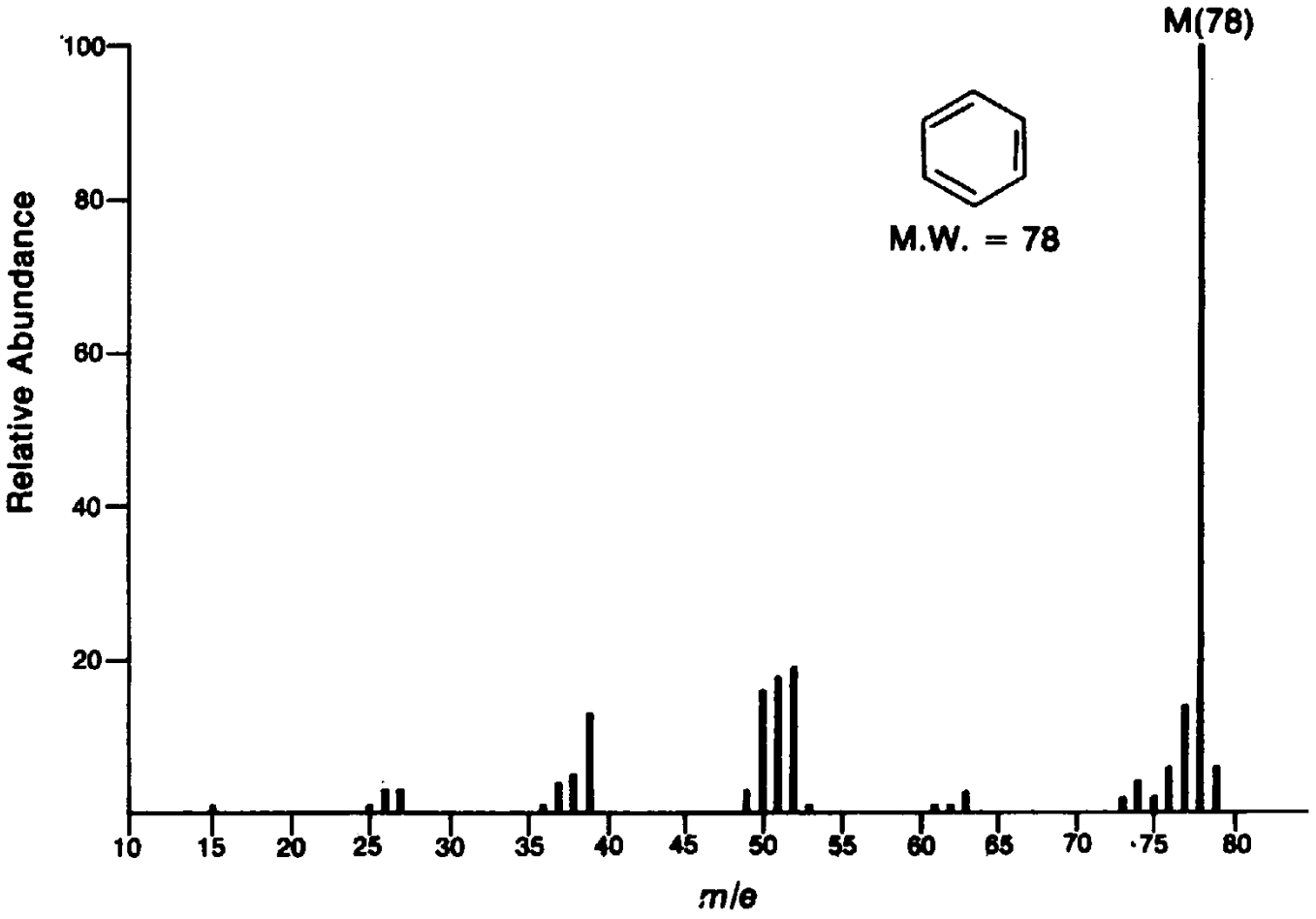
- Molecular ion usually strong
- alkylbenzenes cleave at benzylic carbon

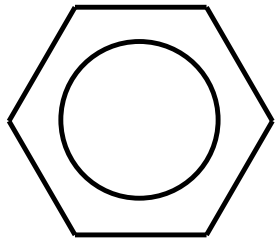
  tropylium ion formation

- McLafferty rearrangement of aromatics

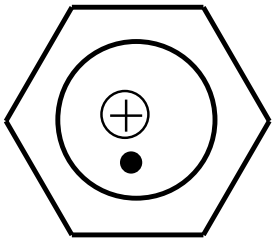
  need γ-hydrogens

benzene


M(78)
M.W. = 78
Relative Abundance
100
80
60
40
20
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
m/e



ei



+ $e^{\ominus}$

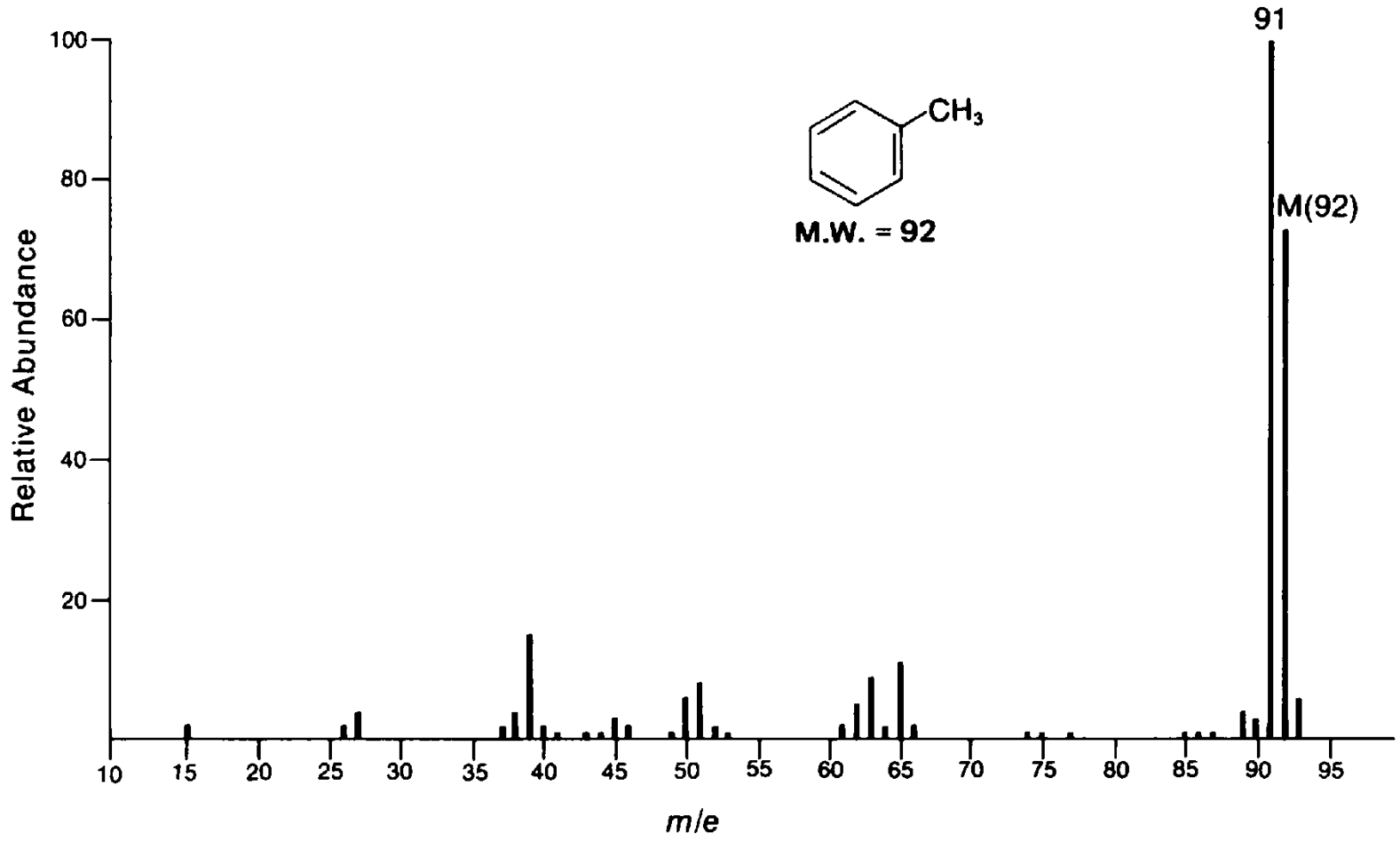
C_6H_6

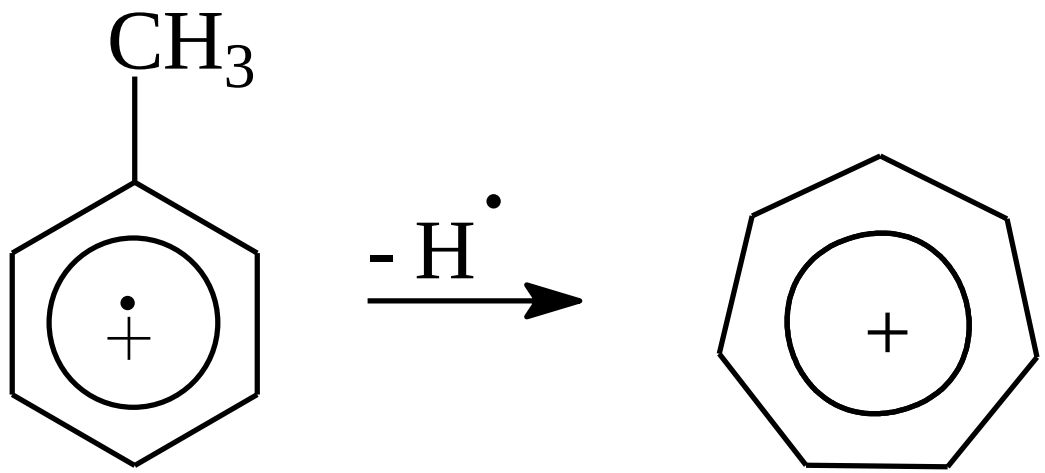
m/z = 78

closed shell
(paired electrons)

open shell
(odd electron ion)

toluene


91
M(92)
CH3
M.W. = 92
Relative Abundance
100
80
60
40
20
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
m/e



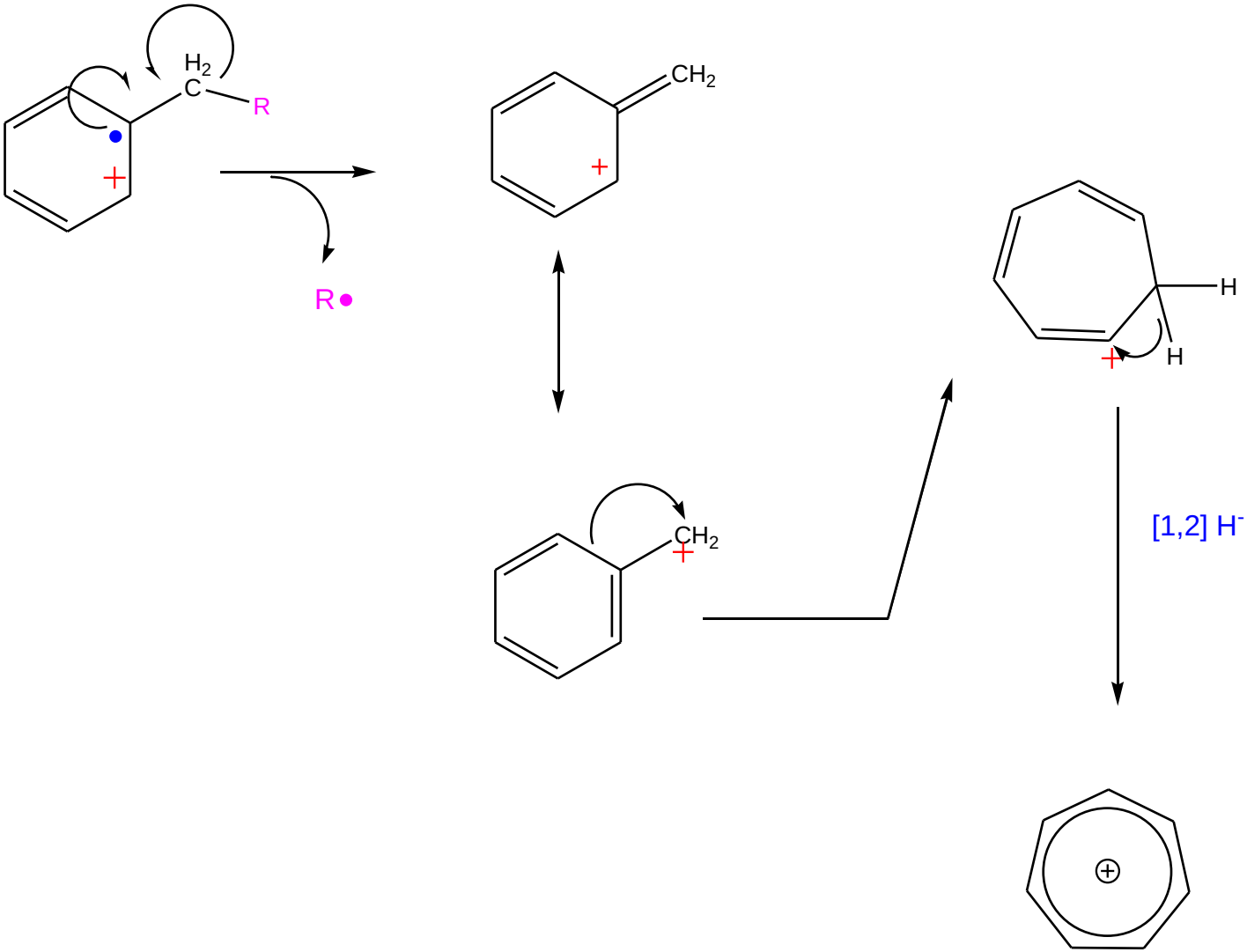
m/z = 92

m/z = 91

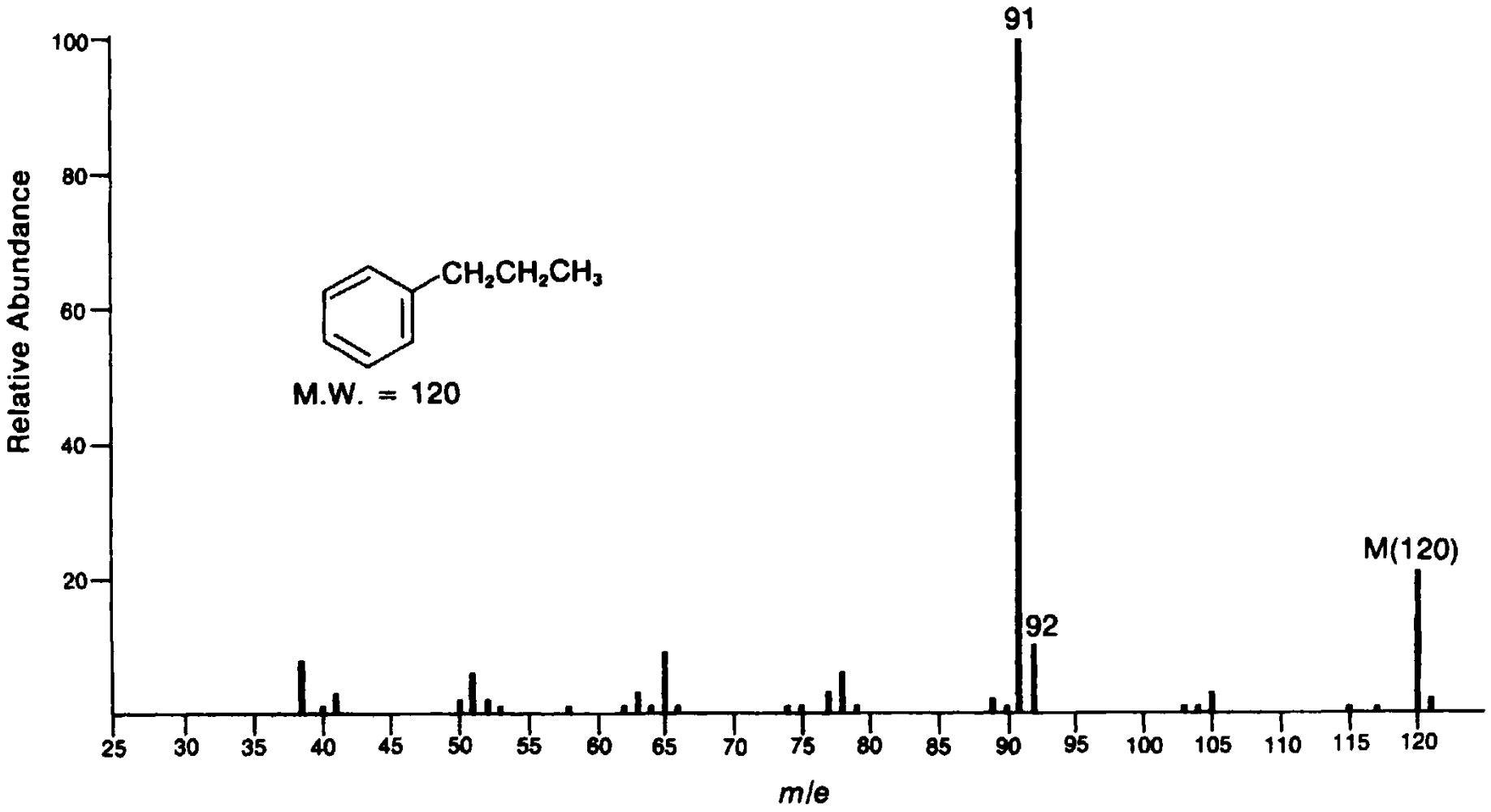
C_7H_7

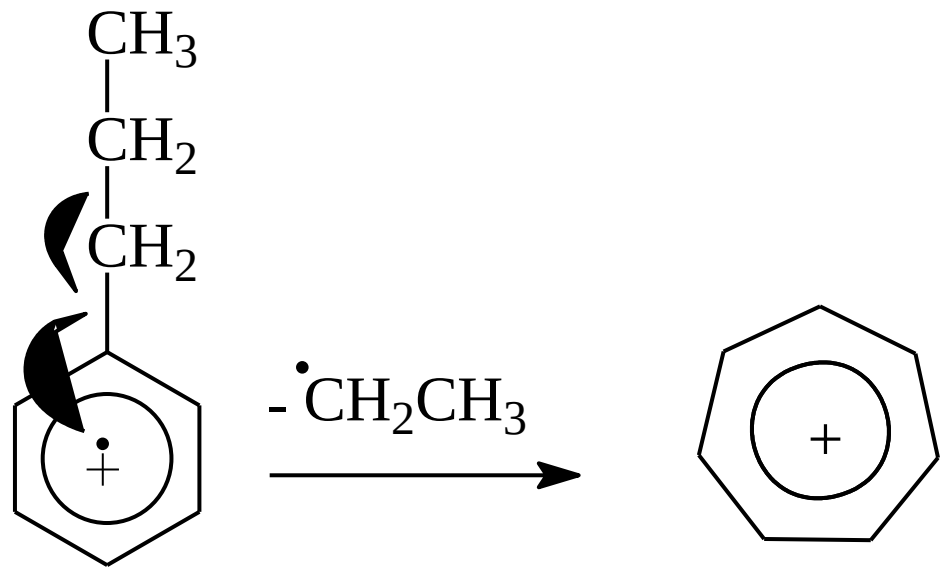
tropylium ion

FORMAÇÃO DO ÍON TROPÍLIO



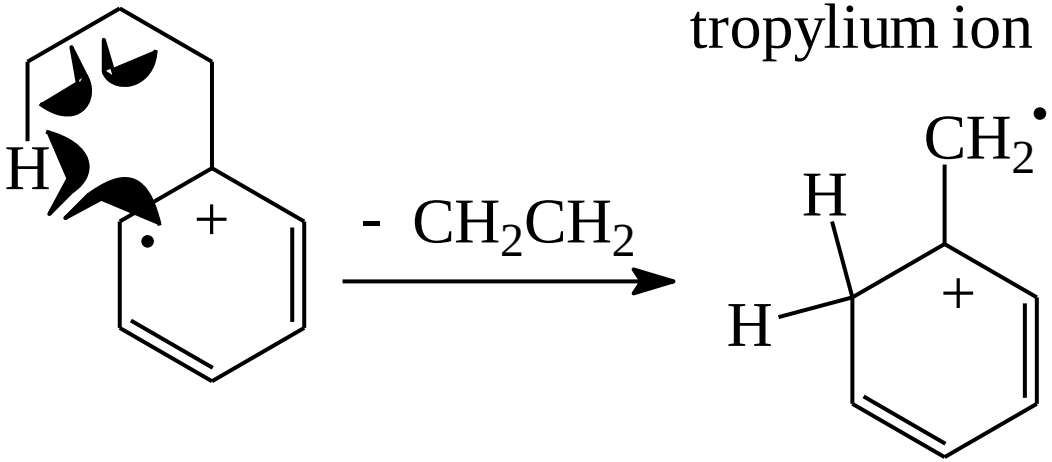
n-propylbenzene





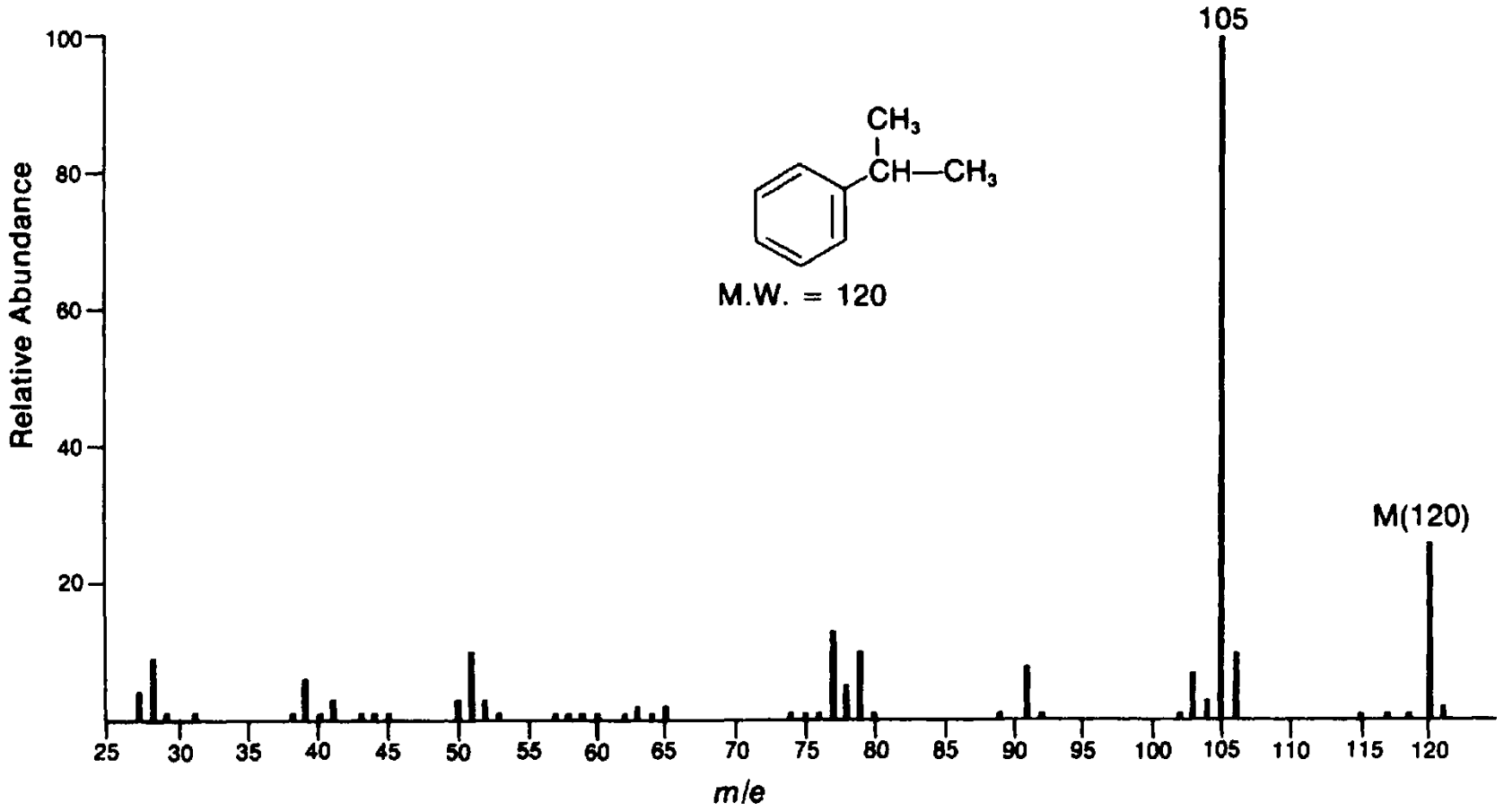
m/z = 120

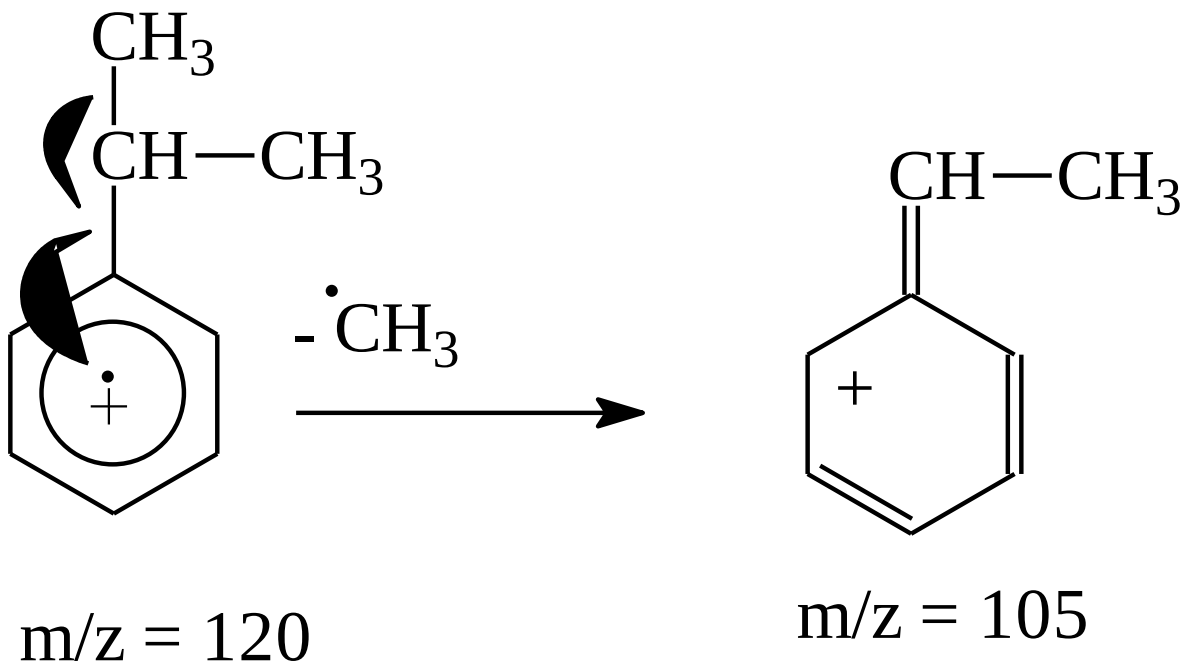
m/z = 91
C_7H_7
tropylium ion



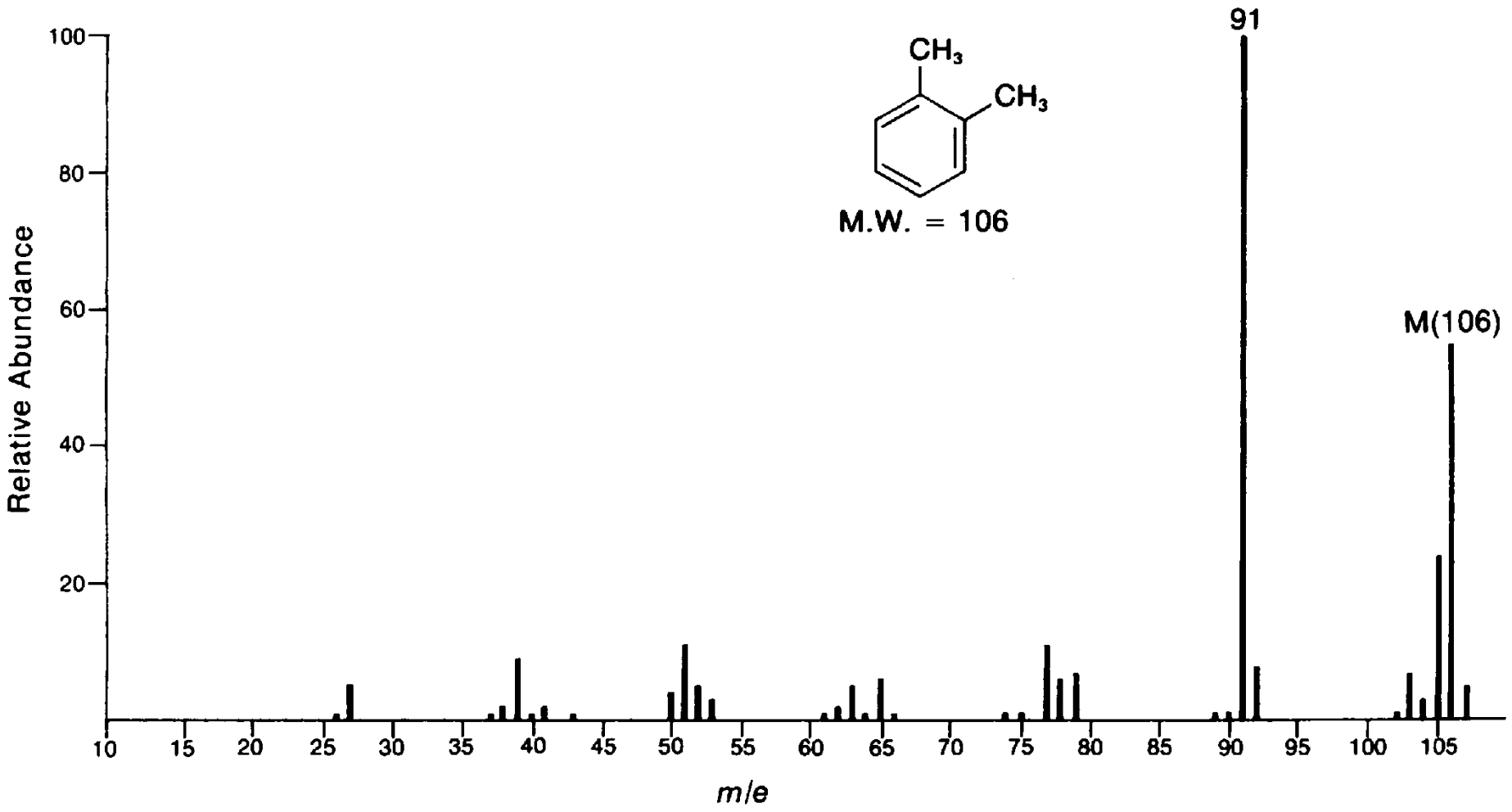
m/z = 92

isopropylbenzene

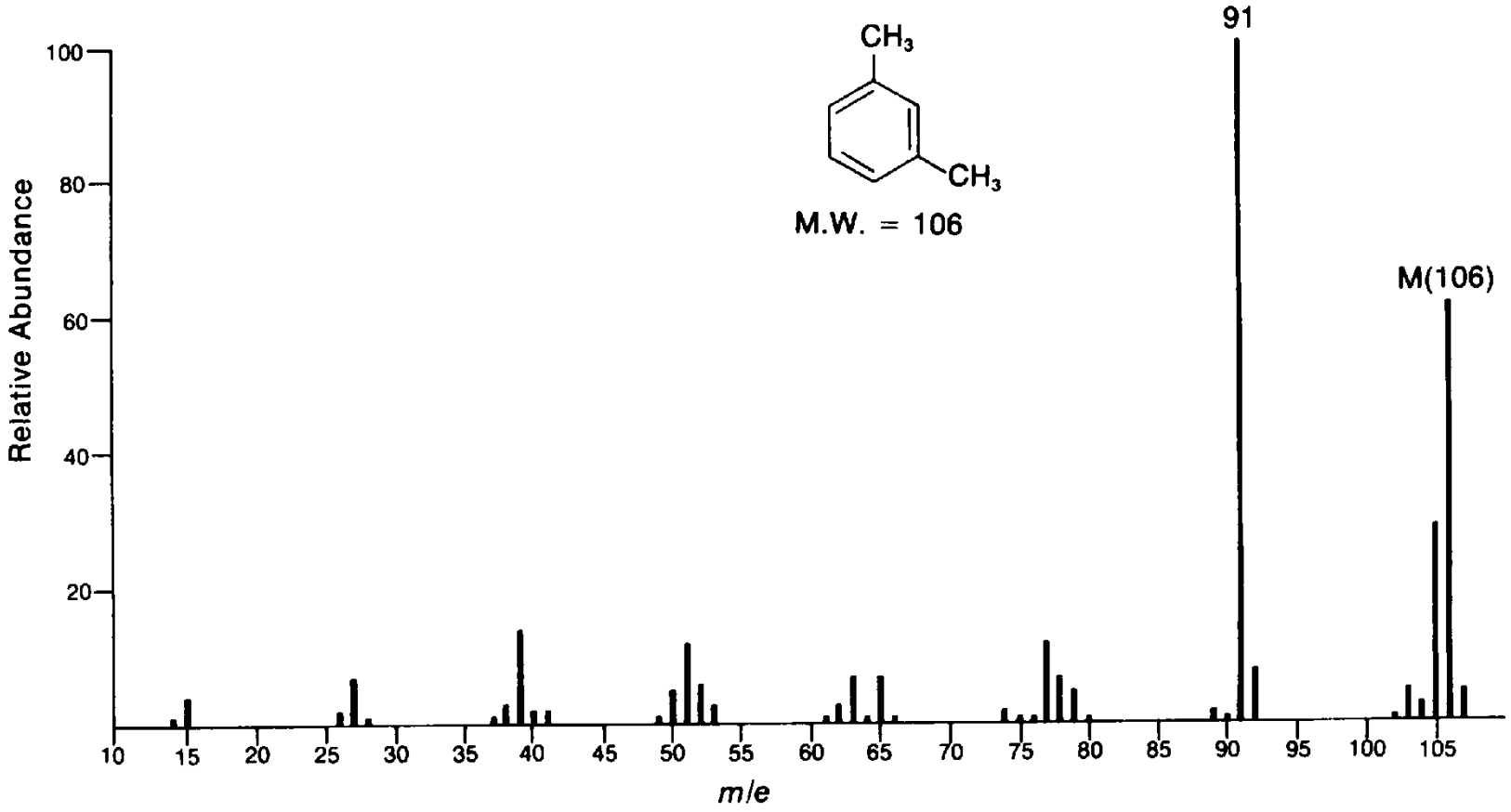



CH3
CH—CH3
- ·CH3
CH—CH3
+
m/z = 120
m/z = 105

o-xylene


91
M(106)
CH3
CH3
M.W. = 106
Relative Abundance
100
80
60
40
20
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105
m/e

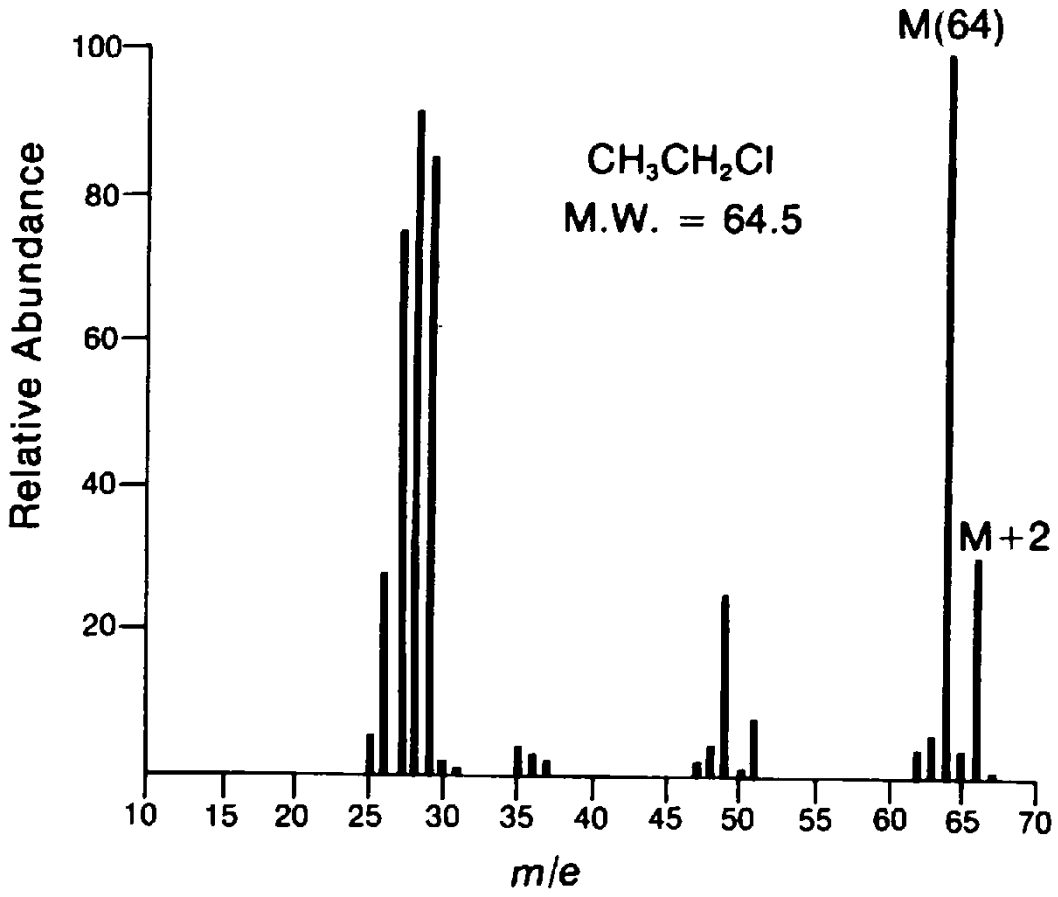
m-xylene

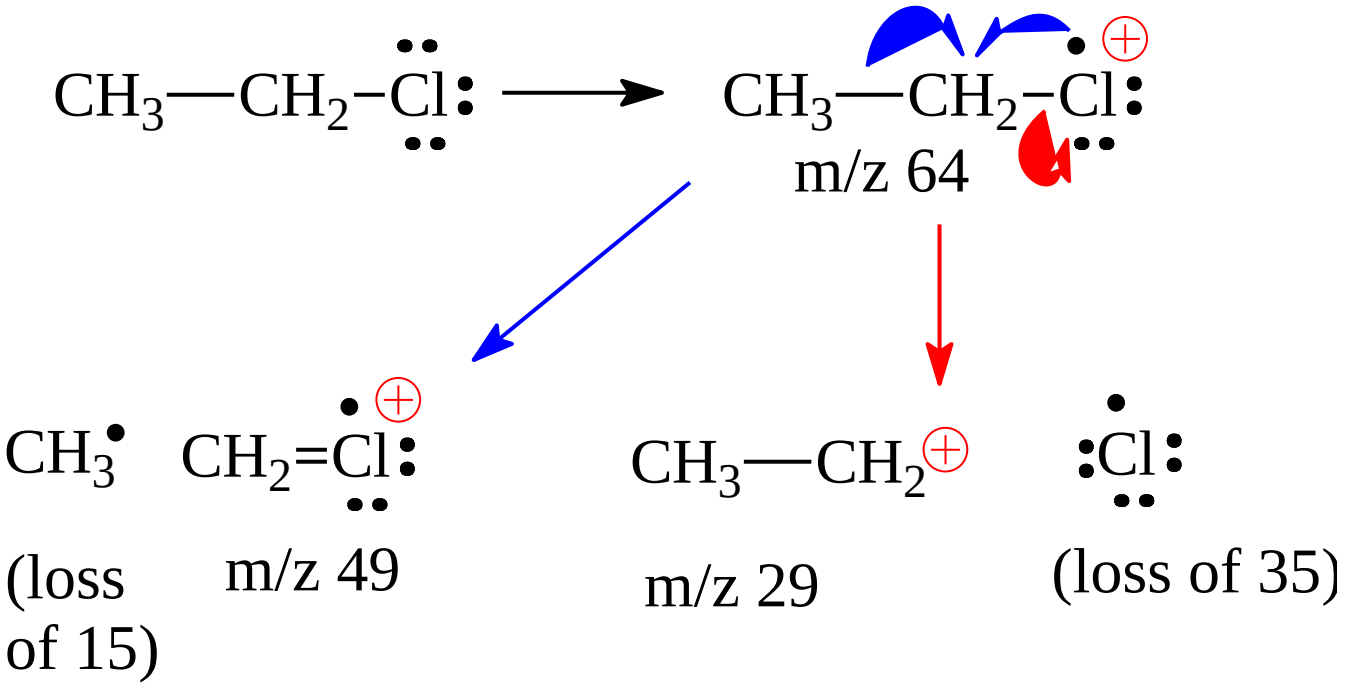

CH3
CH3
M.W. = 106
91
M(106)
Relative Abundance
100
80
60
40
20
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
m/e

Halide Fragmentation

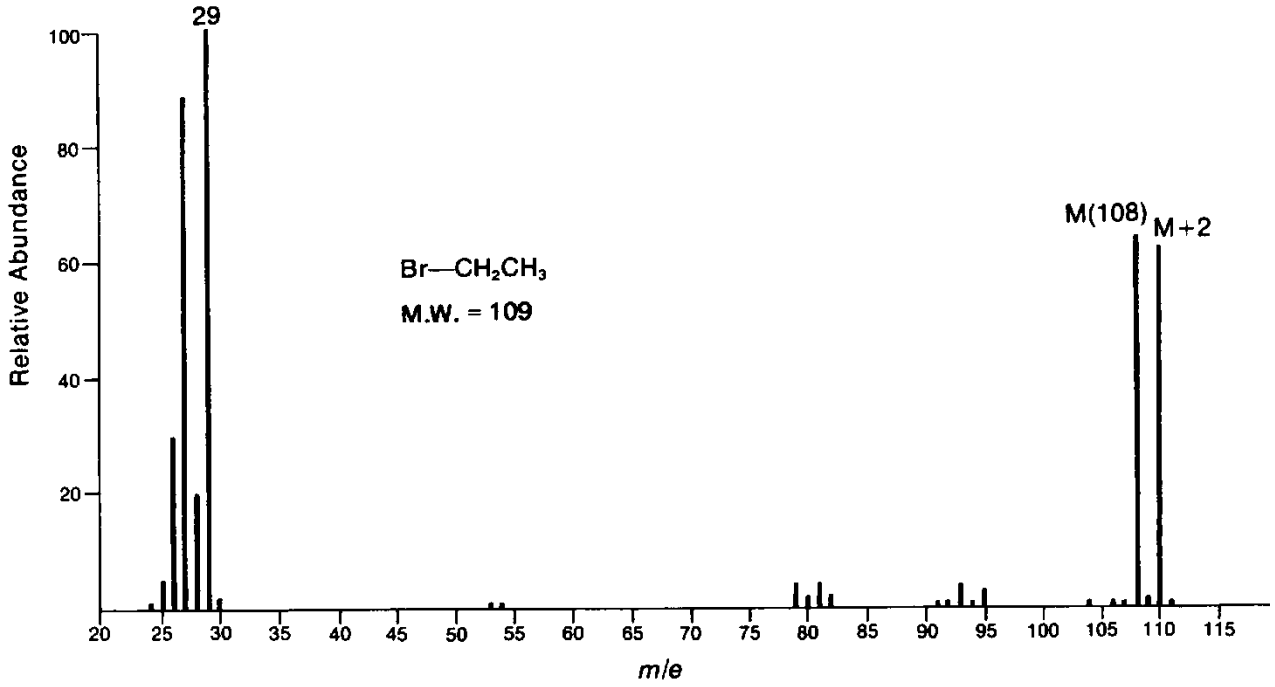
- Loss of halogen atom
- Elimination of HX
- alpha-cleavage
- 1,4-rearrangement

chloroethane

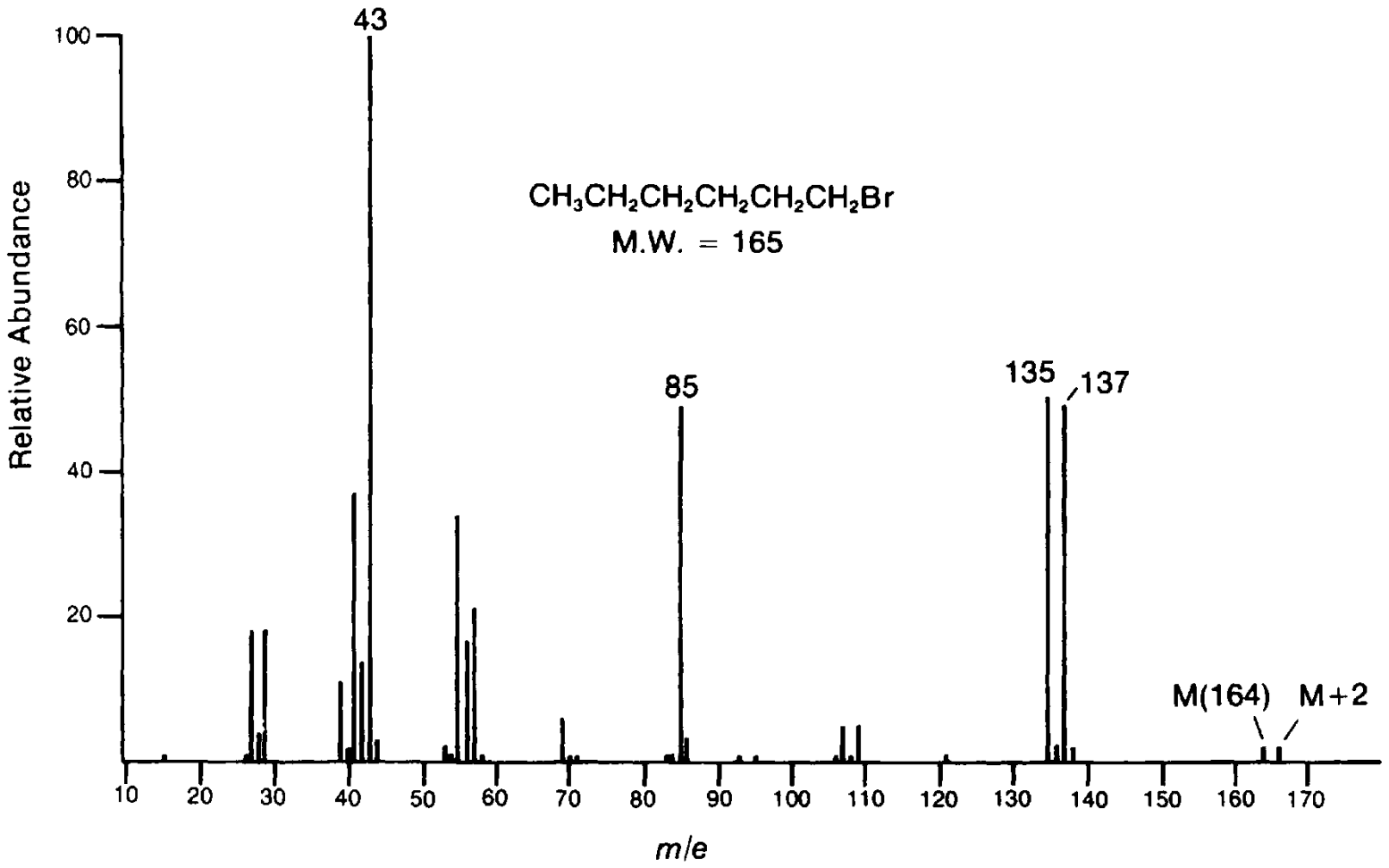


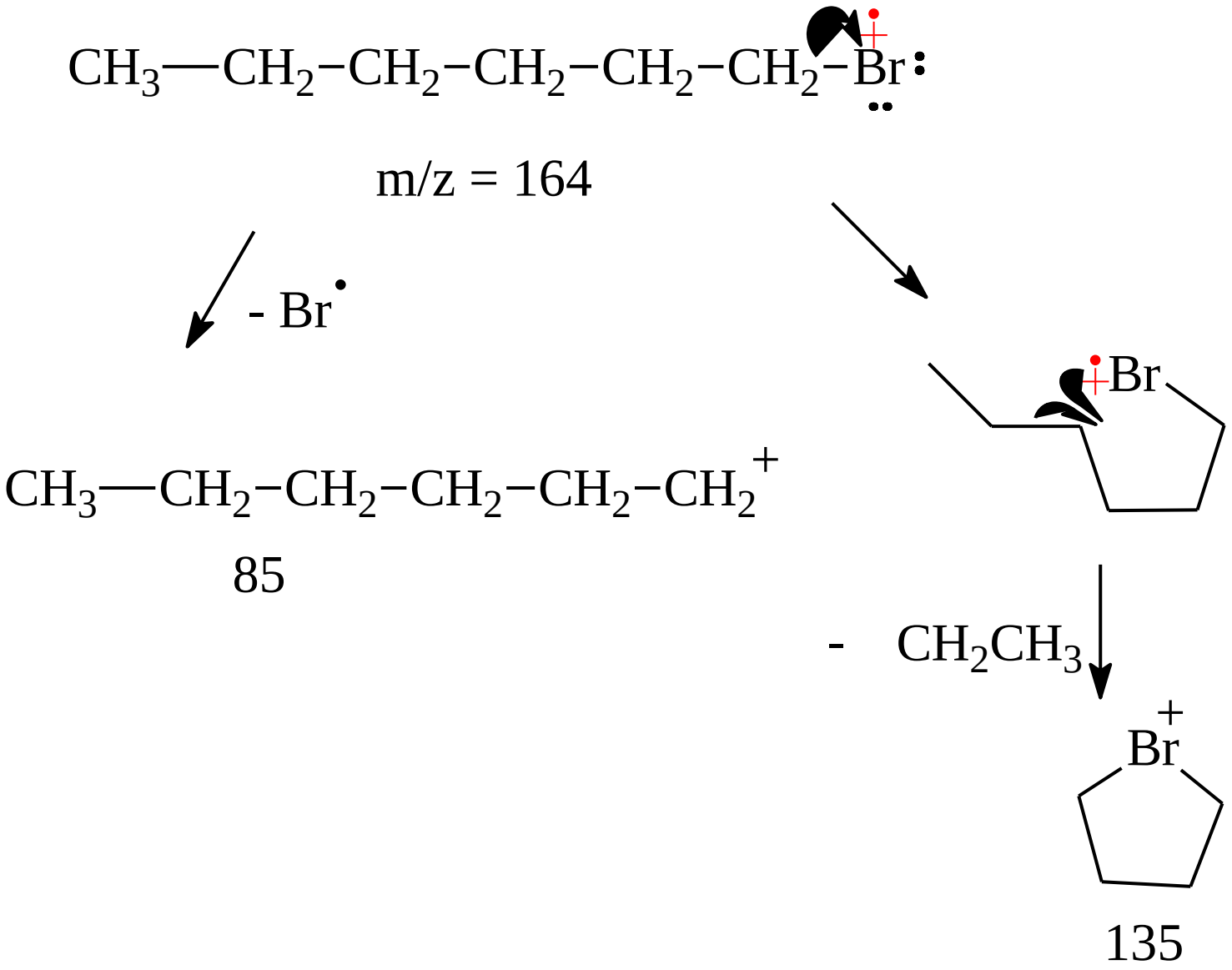

CH3—CH2–Cl
CH3—CH2–Cl
m/z 64
CH3
(loss of 15)
CH2=Cl
m/z 49
CH3—CH2
m/z 29
Cl
(loss of 35)

bromoethane



bromohexane




CH3—CH2−CH2−CH2−CH2−CH2−Br
m/z = 164
- Br•
CH3—CH2−CH2−CH2−CH2−CH2+
85
Br
- CH2CH3
Br+
135

Alcohol Fragmentation

- Molecular ion strength depends on substitution

primary alcohol	weak M^+
secondary alcohol	VERY weak M^+
tertiary alcohol	M^+ usually absent

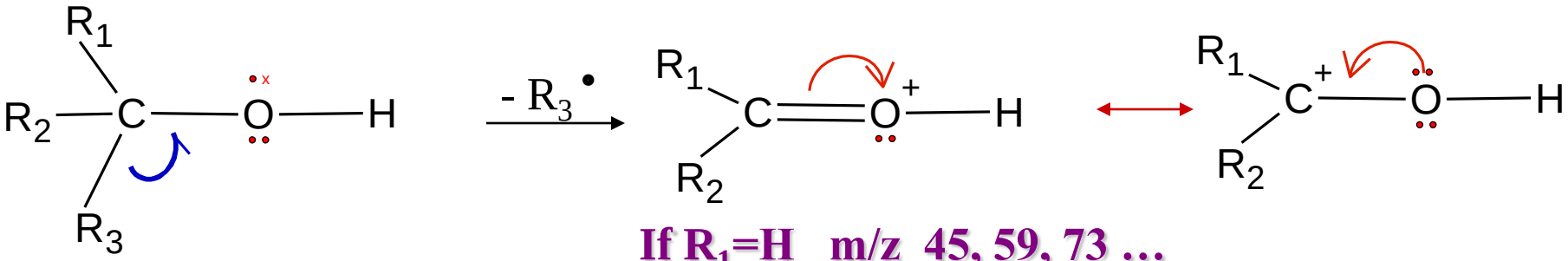
- Dehydration fragmentation

  thermal vs. 1,4-dehydration of M^+

- Loss of alkyl group

  largest R group lost as radical

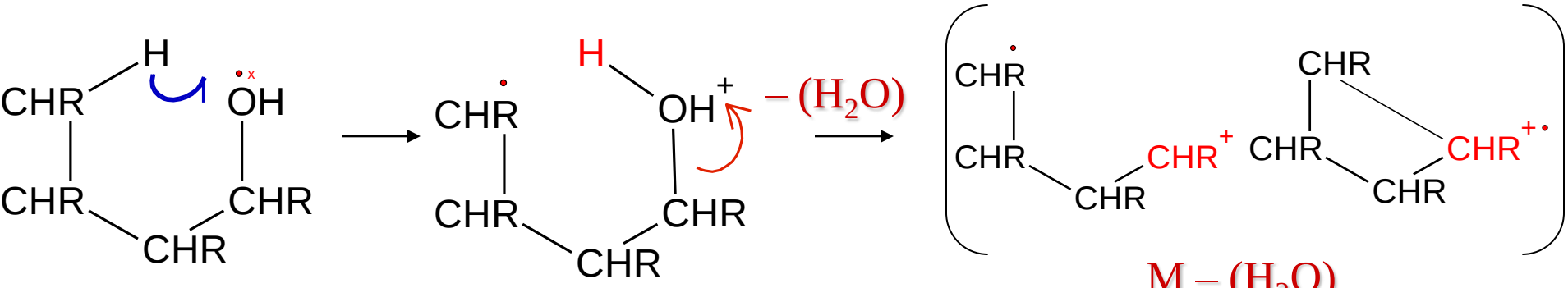
Hydroxy compounds



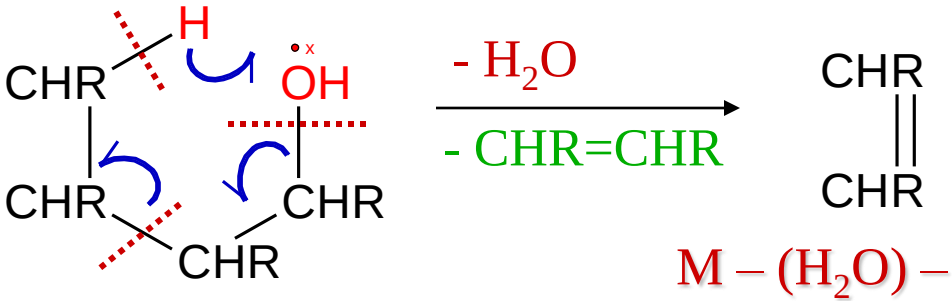
If R_1=H m/z 45, 59, 73 …

Loss of largest group

If R_1=alkyl m/z 59, 73, 87 …

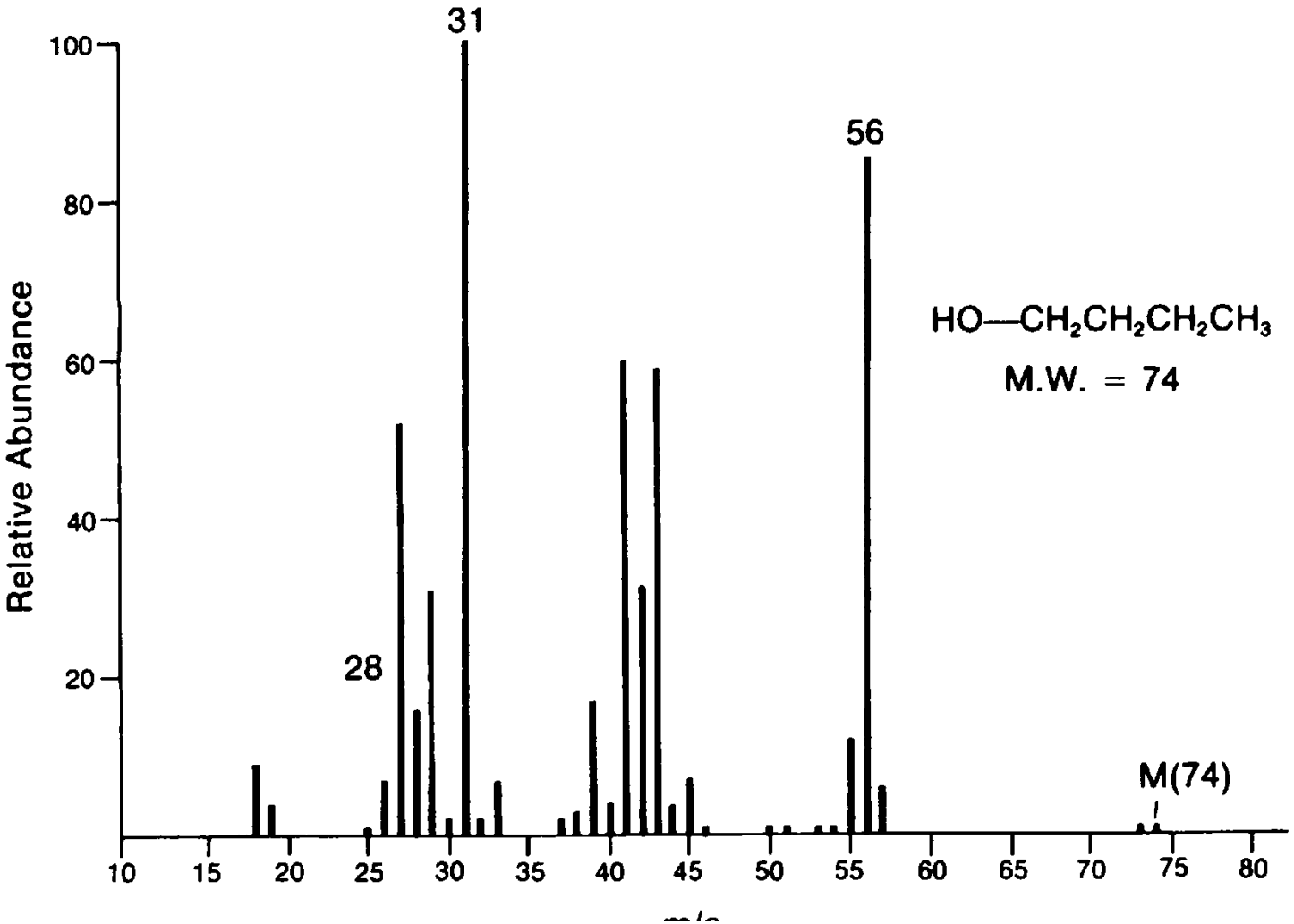


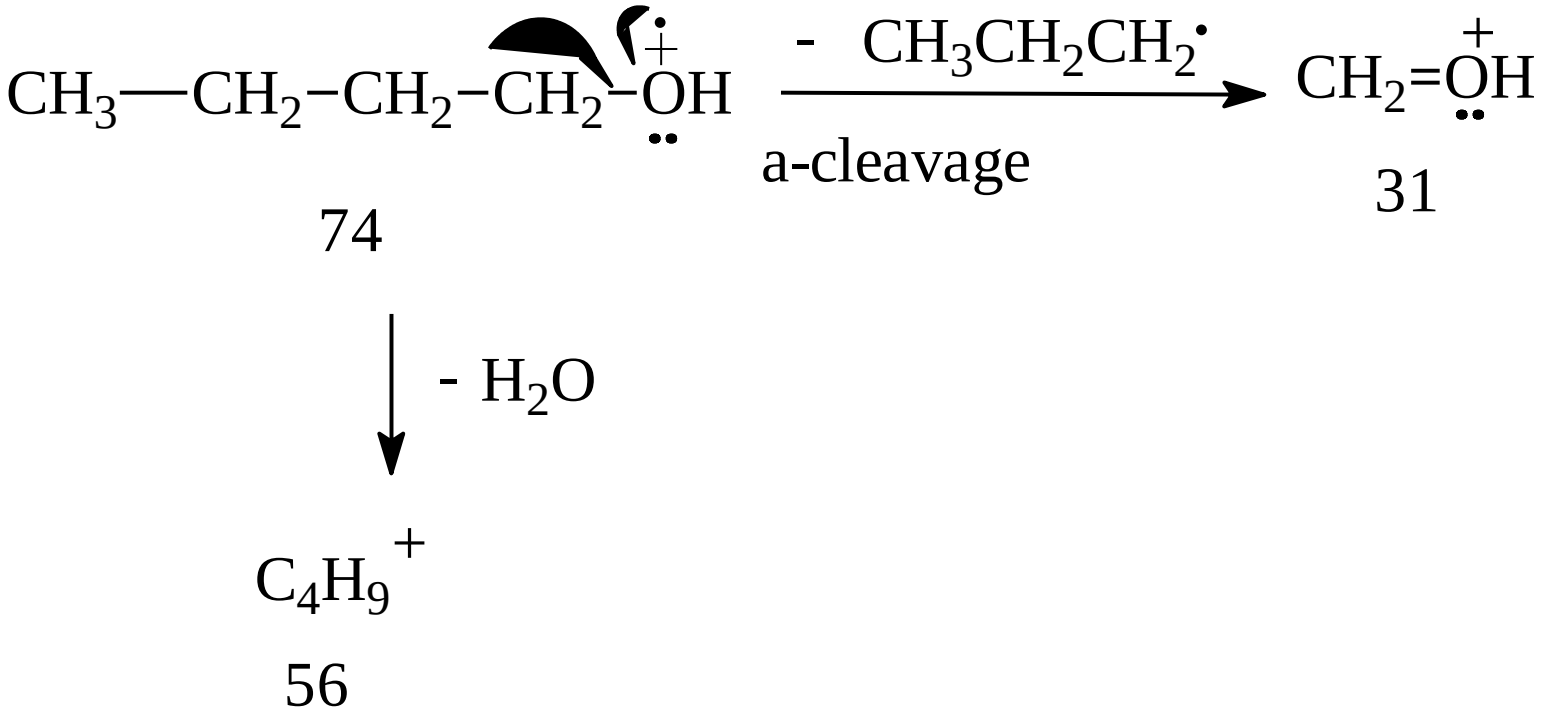
M – (H_2O)



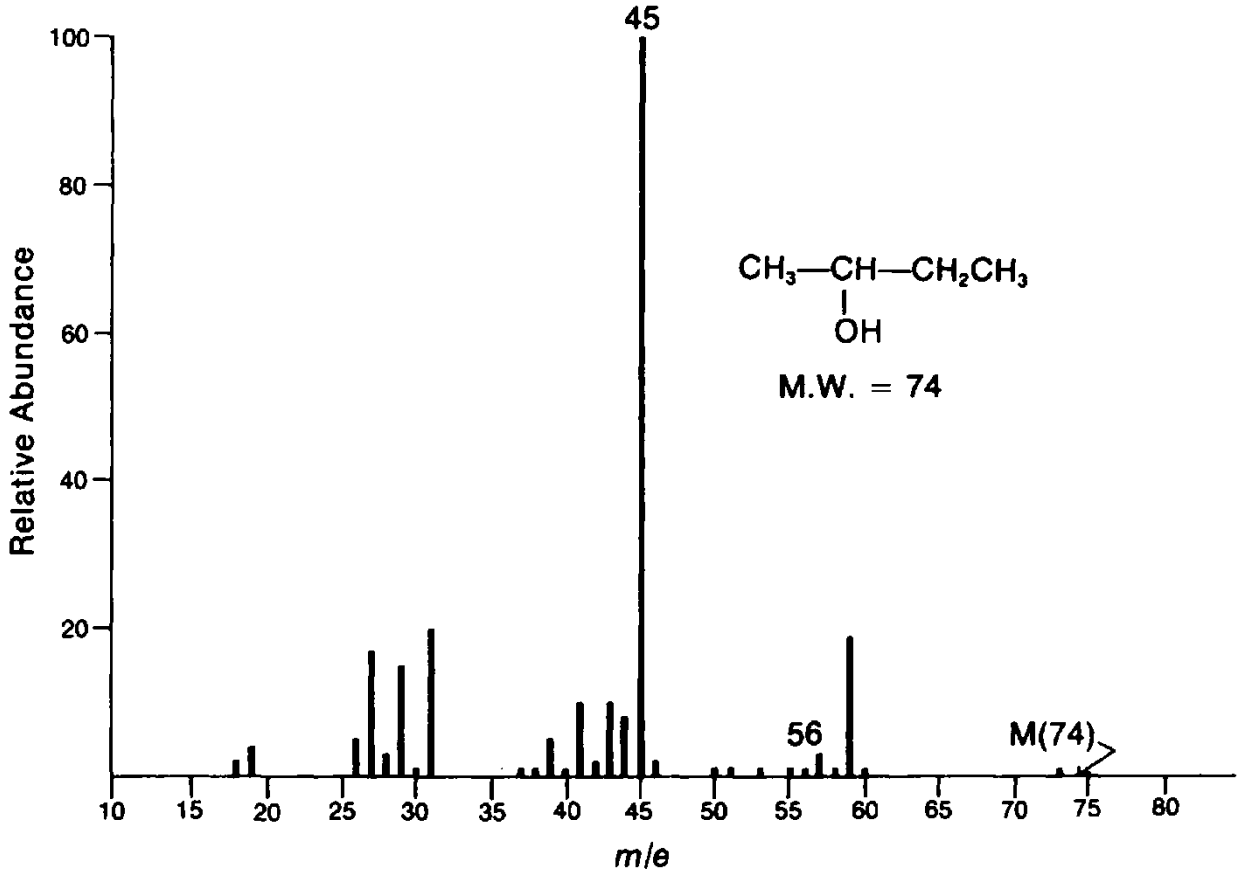
M – (H_2O) – (C1=C2) Alkene

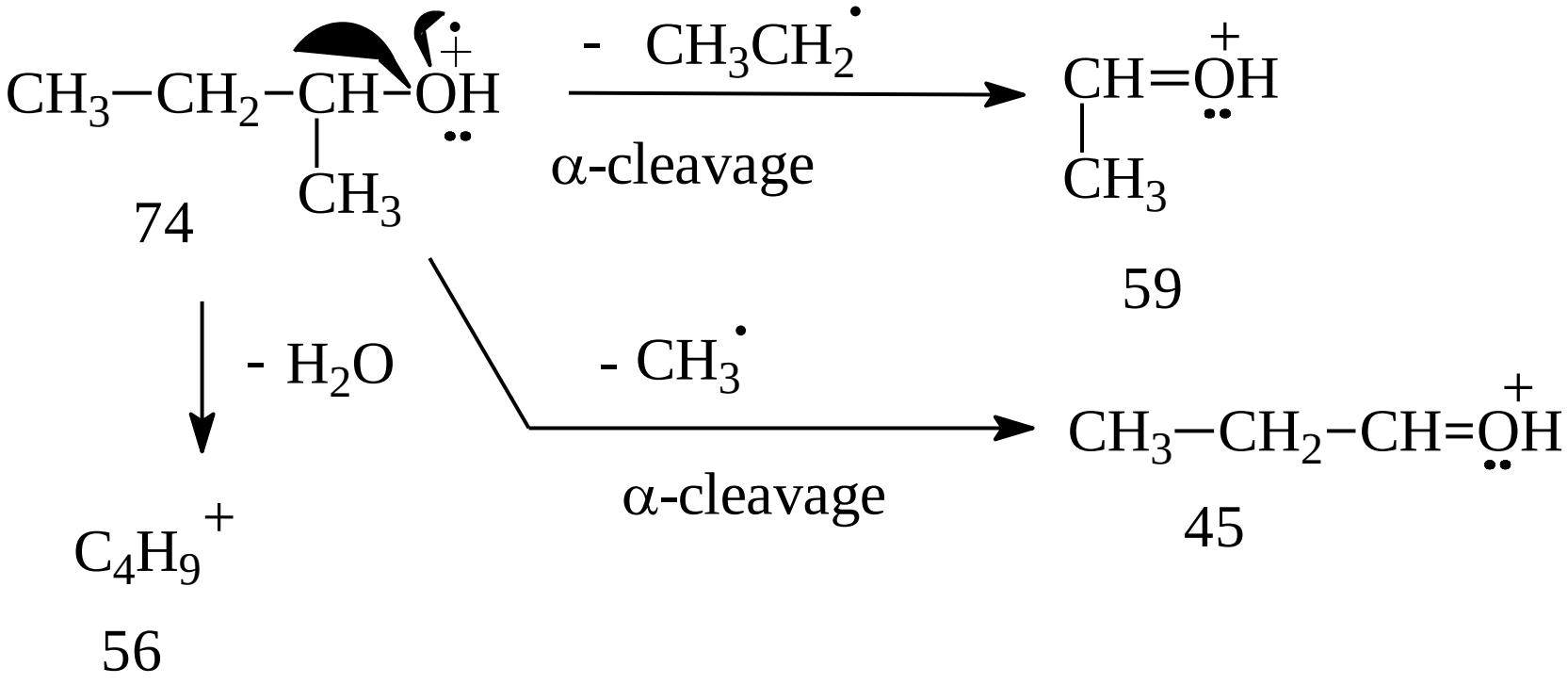
1-butanol


31
56
28
M(74)
100
80
60
40
20
Relative Abundance
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
HO—CH2CH2CH2CH3
M.W. = 74

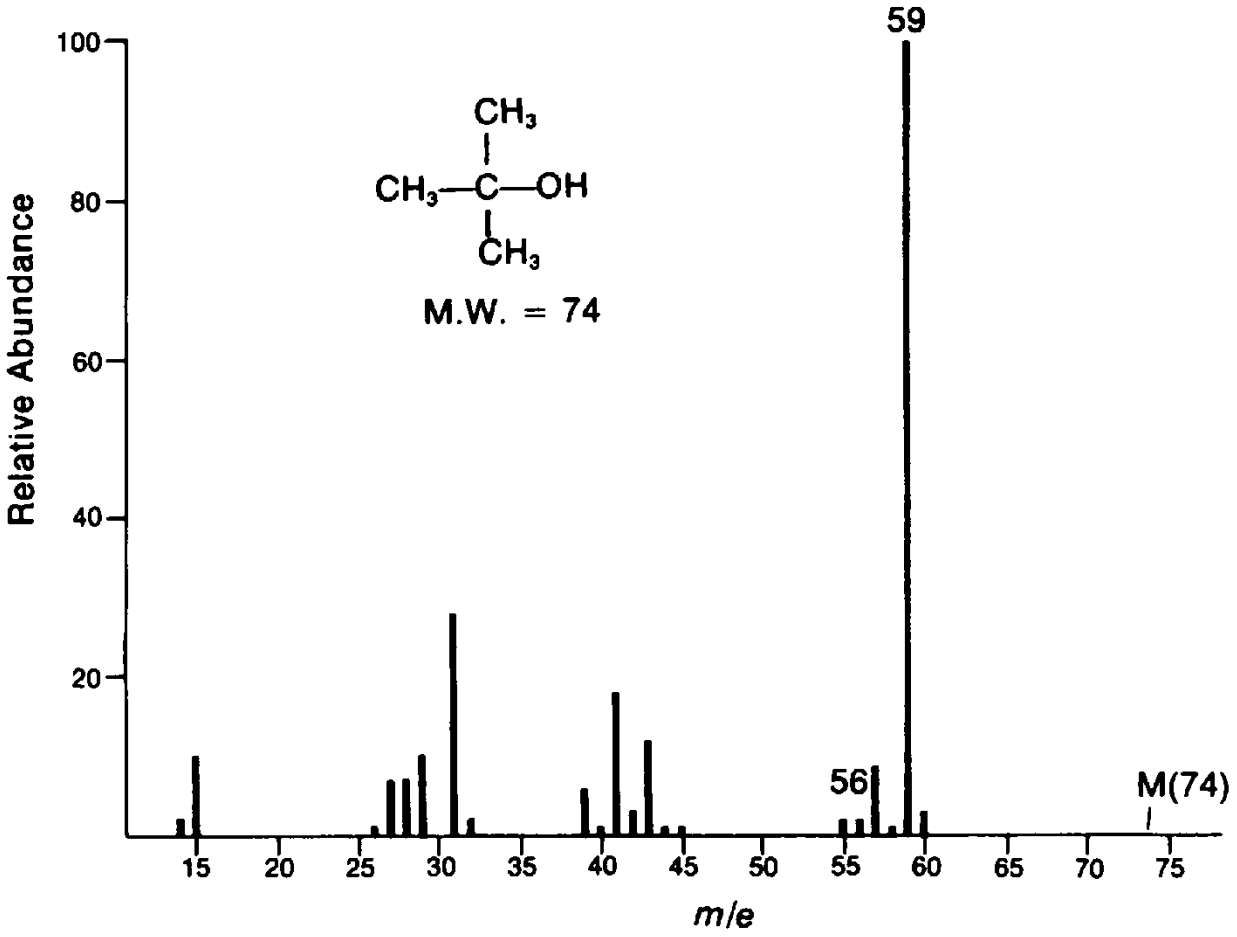

CH3—CH2−CH2−CH2−OH
- CH3CH2CH2•
a-cleavage
CH2=OH
74
31
- H2O
C4H9+
56

2-butanol

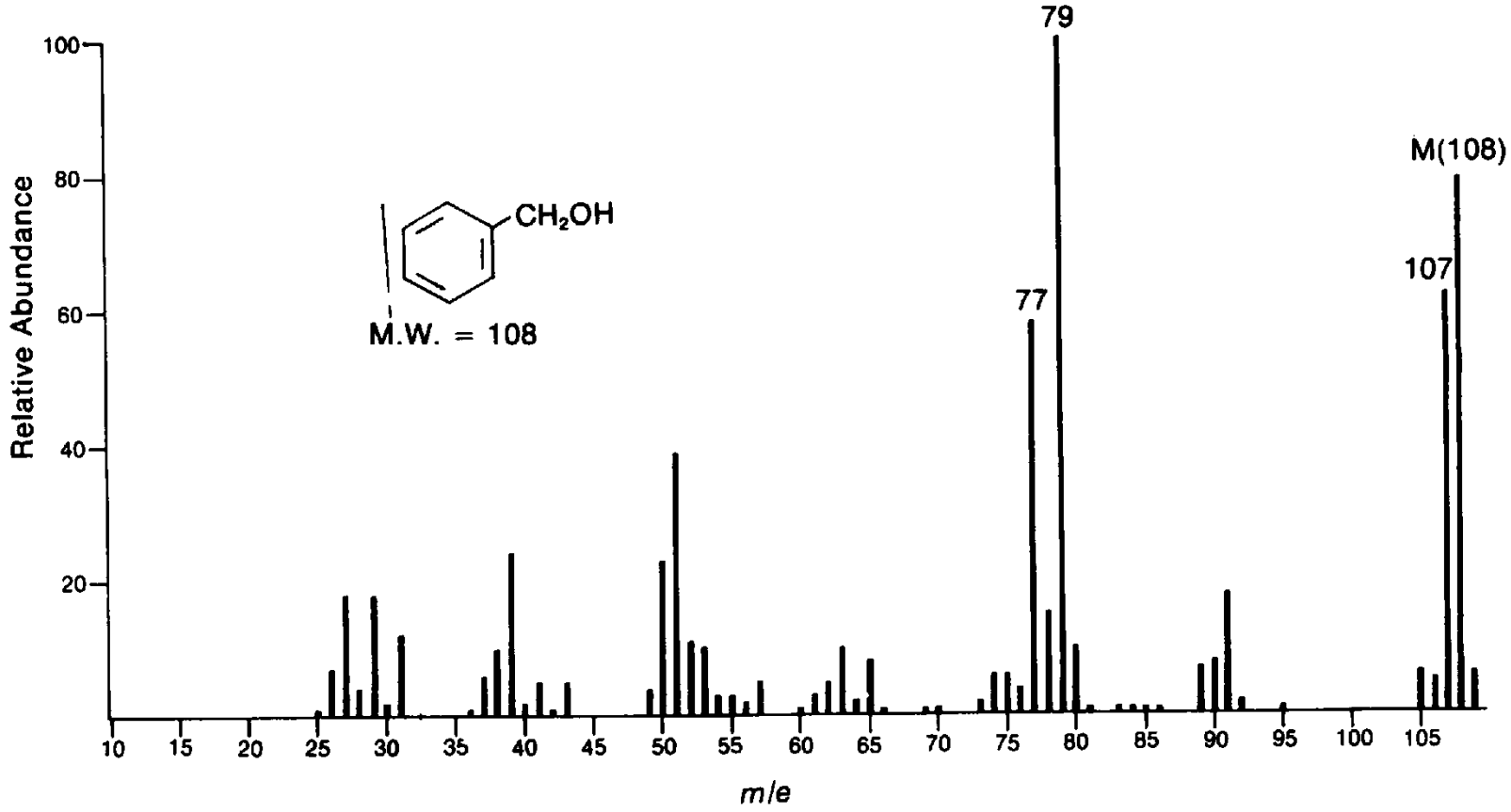

45
100
80
60
40
20
Relative Abundance
CH3—CH—CH2CH3
OH
M.W. = 74
56
M(74)
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
m/e

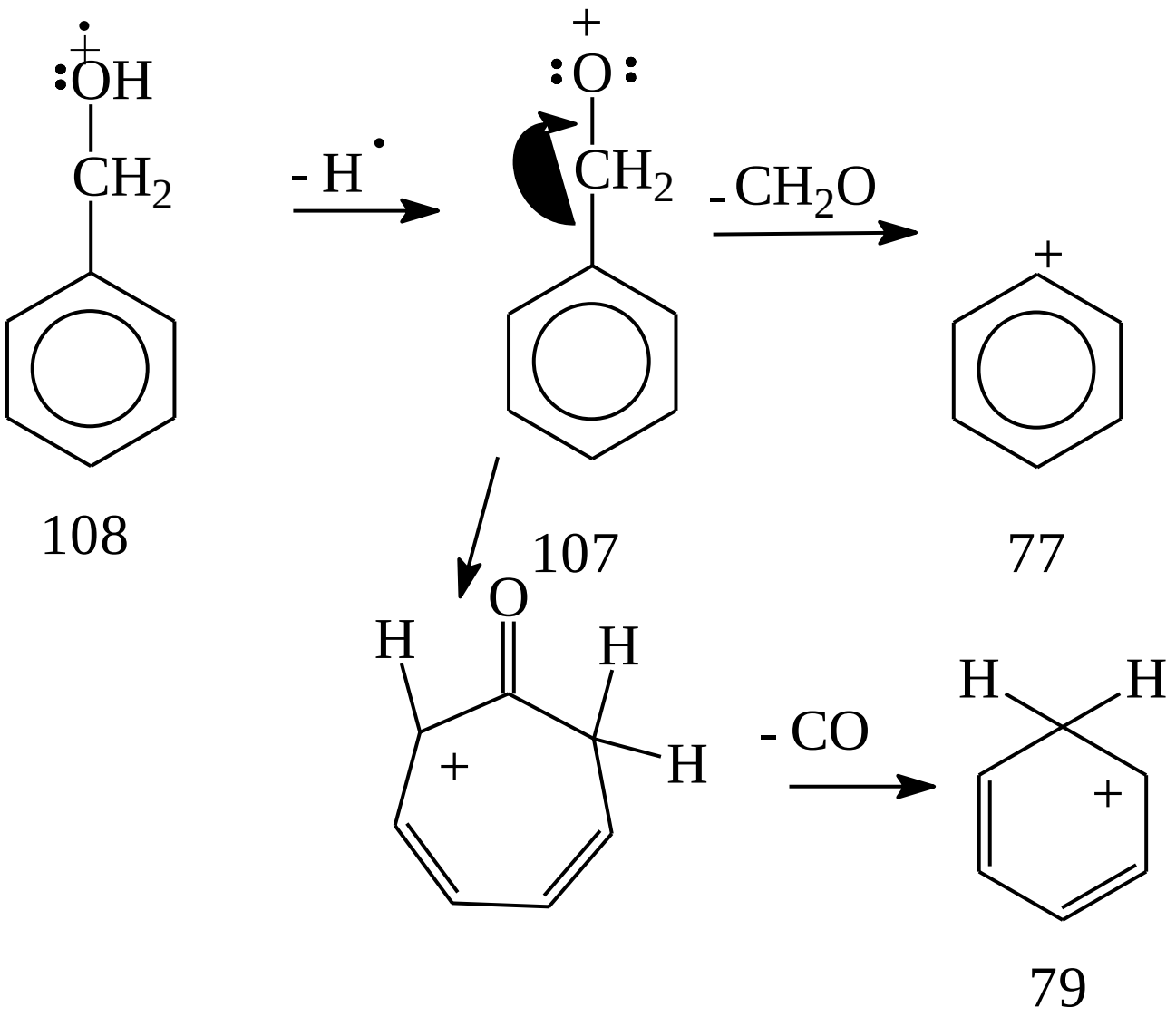

CH3−CH2−CH−OH
CH3
74
- CH3CH2•
α-cleavage
CH=OH
CH3
59
- H2O
C4H9+
56
- CH3•
α-cleavage
CH3−CH2−CH=OH
45

t-butanol

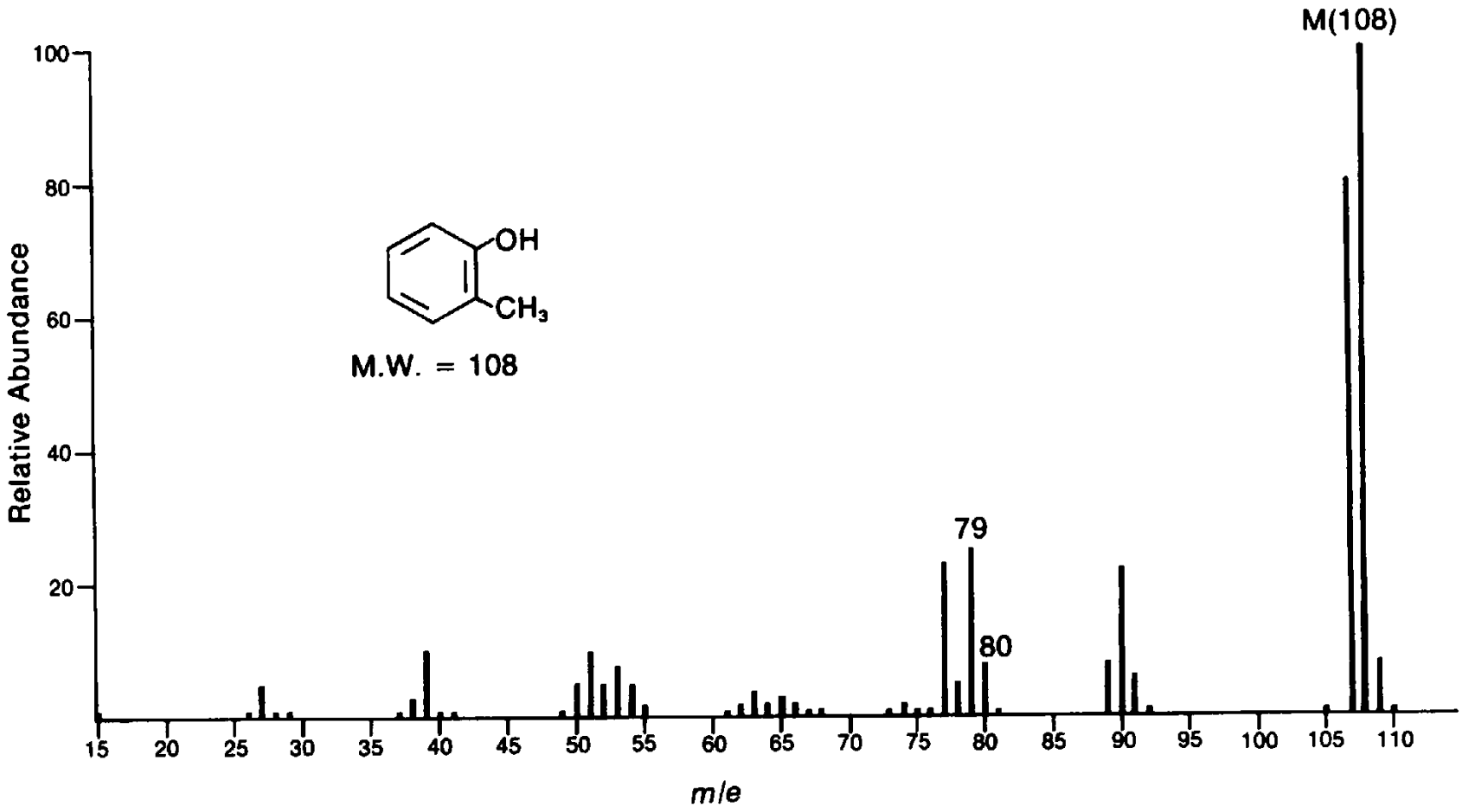

59
100
80
60
40
20
Relative Abundance
CH3
CH3—C—OH
CH3
M.W. = 74
56
M(74)
15
20
25
30
35
40
45
50
55
60
65
70
75
m/e

benzyl alcohol

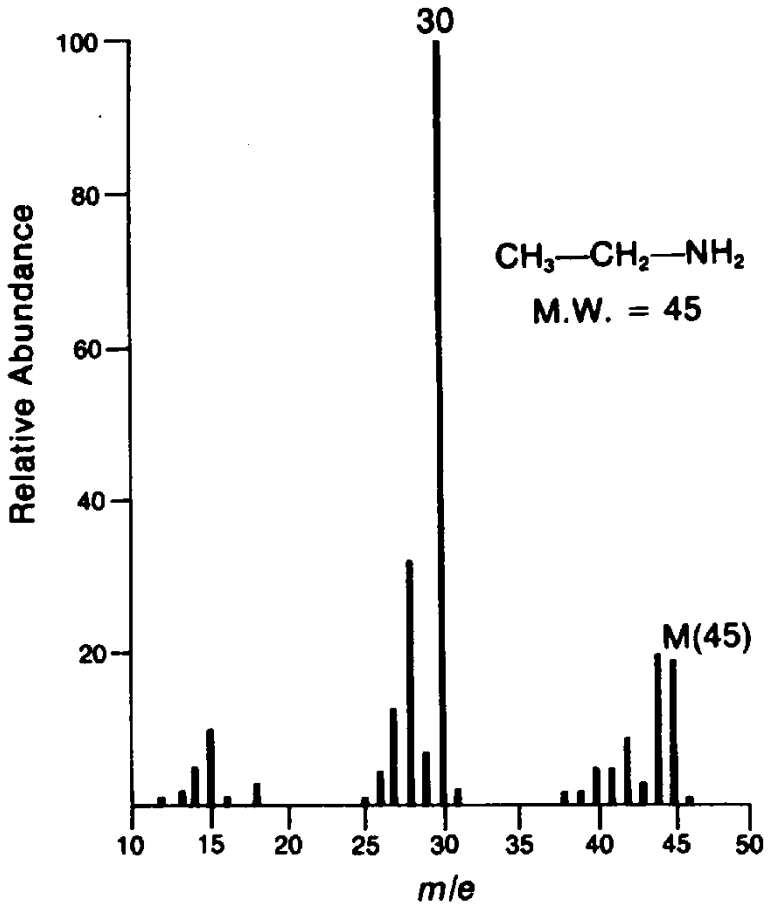


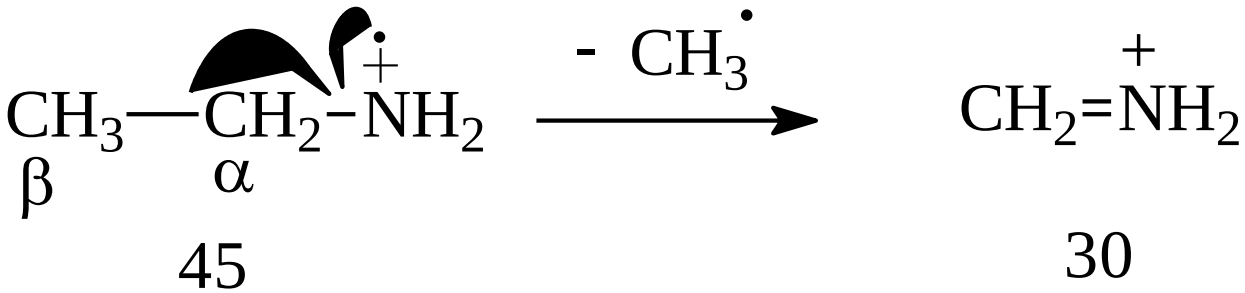

OH
CH2
- H
O
CH2
- CH2O
108
107
77
O
H
H
H
+
- CO
H
H
+
79

o-cresol


M(108)
100
80
60
40
20
Relative Abundance
OH
CH3
M.W. = 108
79
80
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
m/e

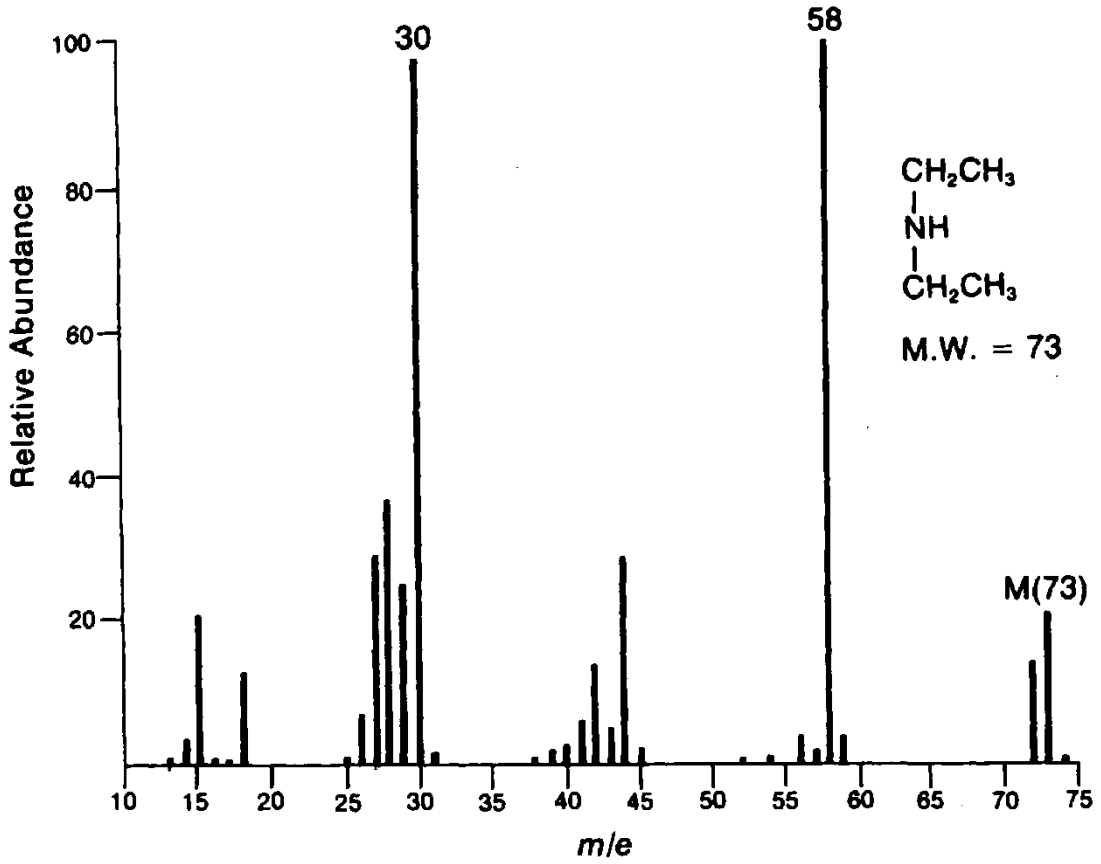
ethylamine

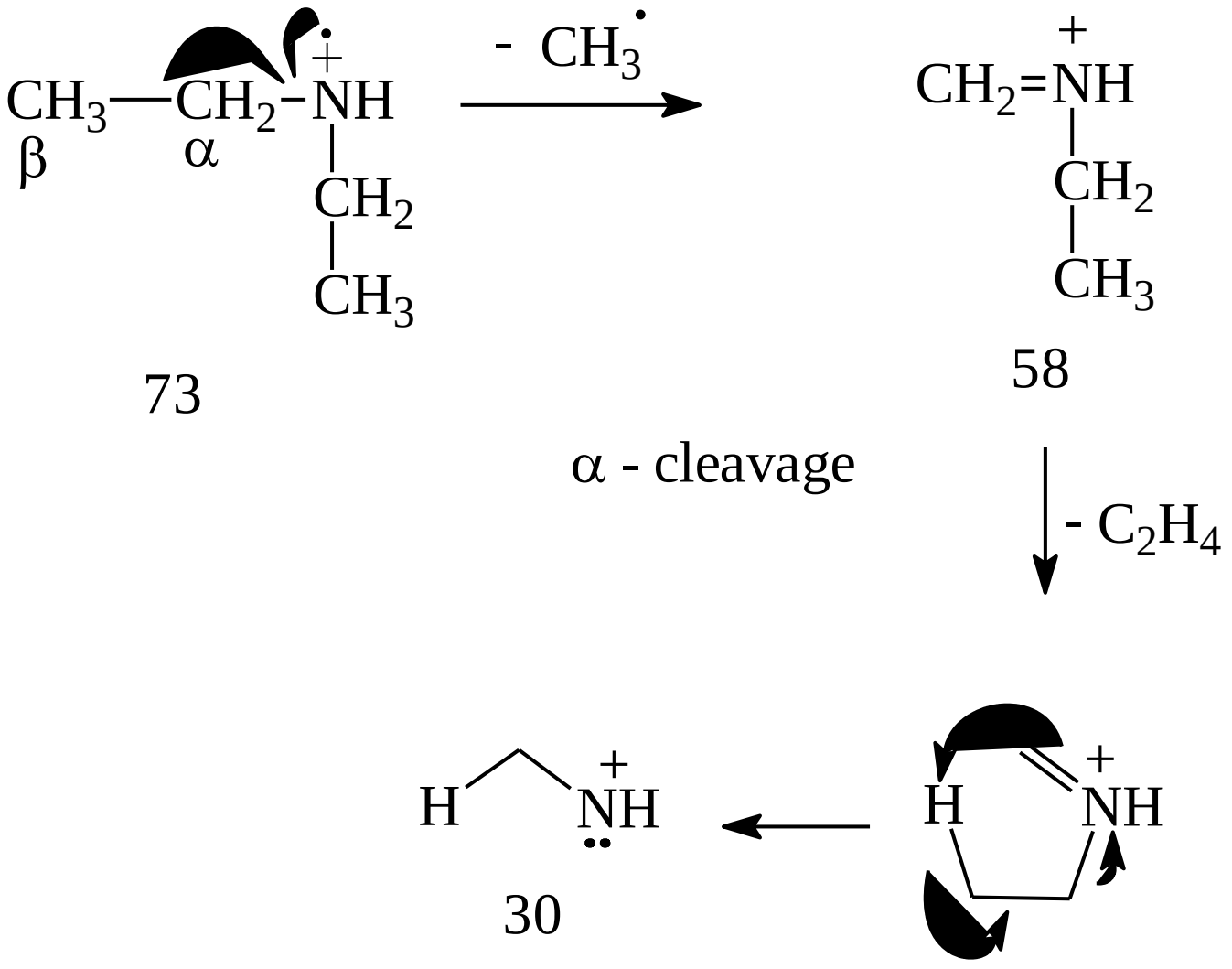

30
100
80
60
40
20
Relative Abundance
CH3—CH2—NH2
M.W. = 45
M(45)
10
15
20
25
30
35
40
45
50
m/e



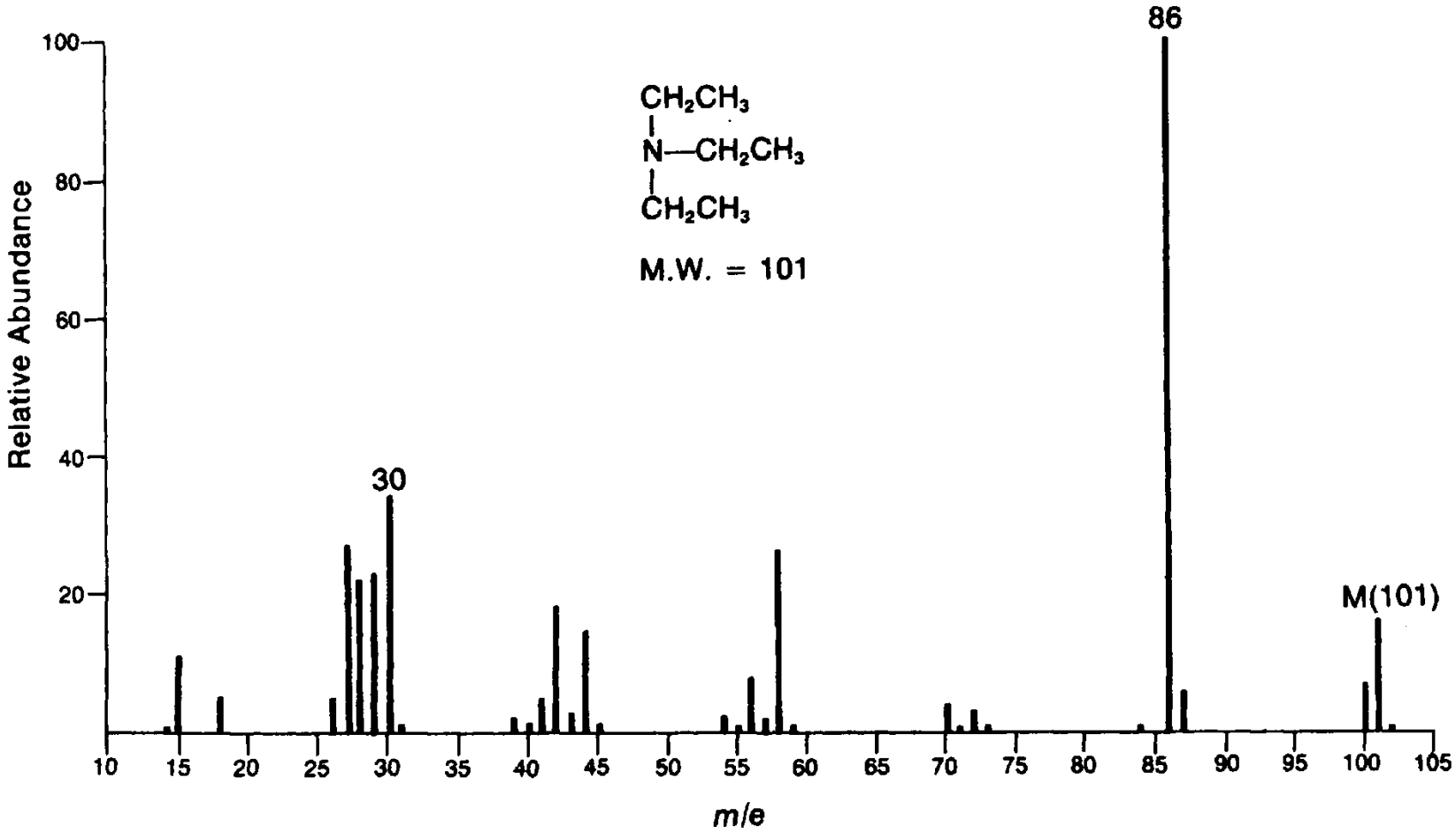
α - cleavage

diethylamine




- CH3•
CH3—CH2–NH
β
α
CH2
CH3
+
CH2=NH
CH2
CH3
73
58
α - cleavage
- C2H4
H
NH
+
30

triethylamine



Carbonyl Compounds

Dominant fragmentation pathways:

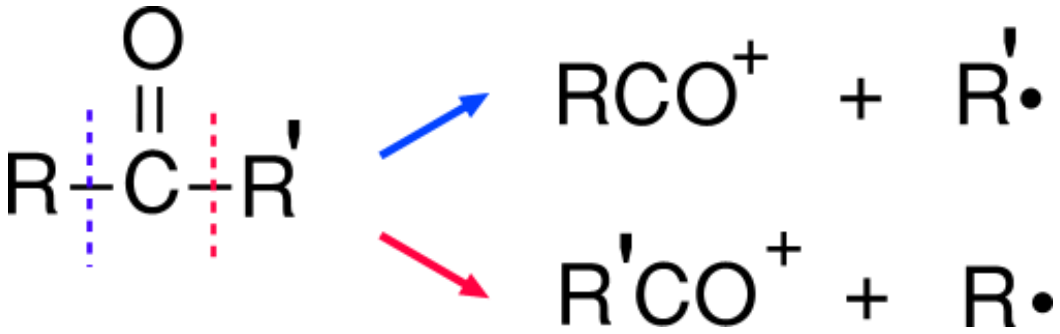
- α-cleavage
- β-cleavage
- McLafferty rearrangement

FRAGMENTATION PATTERNS

ALDEHYDES AND KETONES

Cleavage of bonds next to the carbonyl group (C=O) is a characteristic fragmentation of aldehydes and ketones. A common fragment is carbon monoxide (CO) but as it is a molecule and thus uncharged it will not produce a peak of its own. However, it will produce an m/z drop of 28 somewhere in the spectrum.

The position of the carbonyl group influences the fragmentation pattern because the molecular ion fragments either side of the carbonyl group

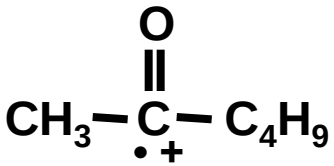


the more stable the acylium ion RCO^+, the more abundant it will be and the more abundant the species the taller its peak in the mass spectrum

FRAGMENTATION PATTERNS

Aldehydes and ketones

The position of the carbonyl group influences the fragmentation pattern because the molecular ion fragments either side of the carbonyl group.

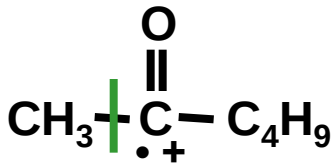


MOLECULAR ION
has m/z = 100

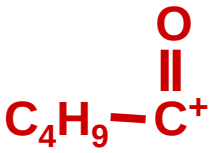
FRAGMENTATION PATTERNS

Aldehydes and ketones

The position of the carbonyl group influences the fragmentation pattern because the molecular ion fragments either side of the carbonyl group.

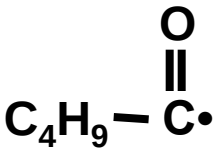


MOLECULAR ION has m/z = 100



m/z = 85

$CH_3\bullet$



CH_3^+

m/z = 15

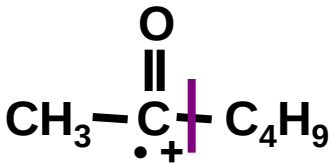
Breaking the bond between the methyl group and the carbonyl group produces two possible ions, depending on how the bond breaks.

Two peaks at m/z values 15 and 85 will appear in the mass spectrum.

FRAGMENTATION PATTERNS

Aldehydes and ketones

The position of the carbonyl group influences the fragmentation pattern because the molecular ion fragments either side of the carbonyl group.



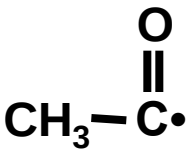
MOLECULAR ION has m/z = 100

Breaking the bond between the butyl group and the carbonyl group produces two further ions, depending on how the bond breaks.

$C_4H_9\bullet$

m/z = 43

Two peaks at m/z values 43 and 57 will appear in the mass spectrum.



$C_4H_9^+$

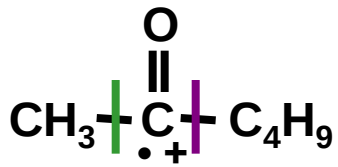
m/z = 57

FRAGMENTATION PATTERNS

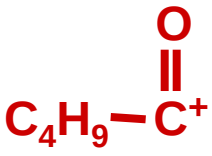
Aldehydes and ketones

The position of the carbonyl group influences the fragmentation pattern because the molecular ion fragments either side of the carbonyl group.

Example;

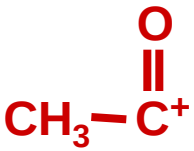


MOLECULAR ION has m/z = 100



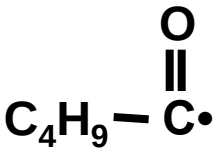
m/z = 85

$CH_3\bullet$



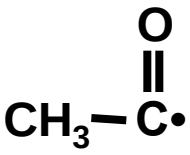
m/z = 43

$C_4H_9\bullet$



CH_3^+

m/z = 15

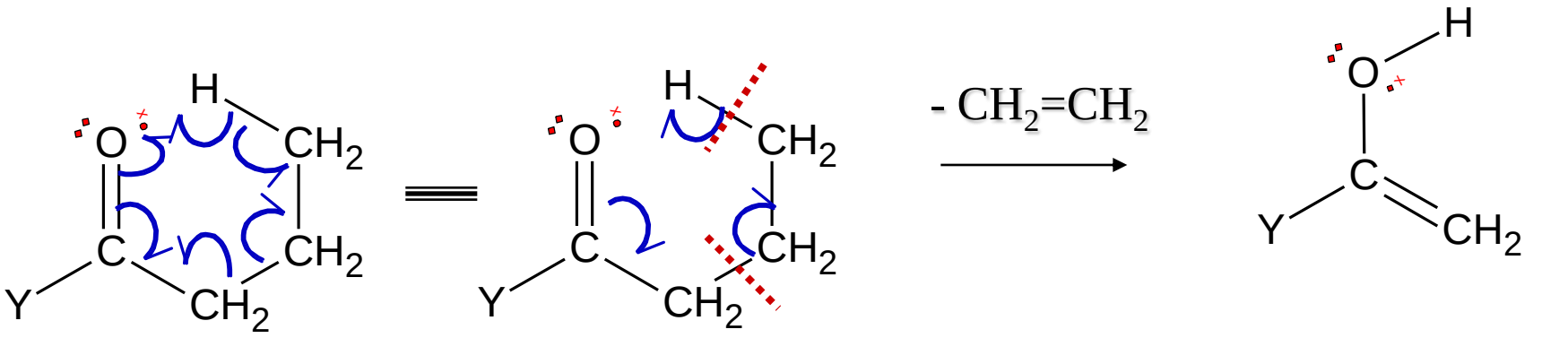


$C_4H_9^+$

m/z = 57

A further peak occurs at m/z = 72 (100-28) due to loss of CO

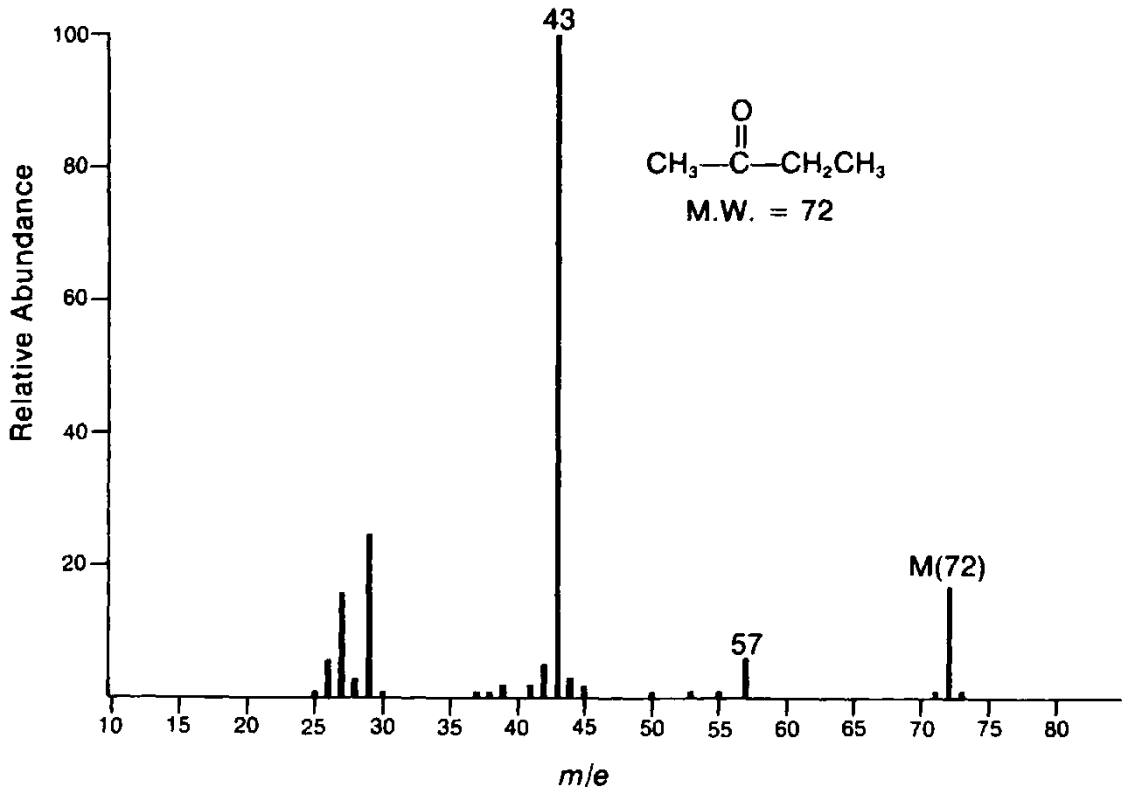
Rearranjo de McLafferty



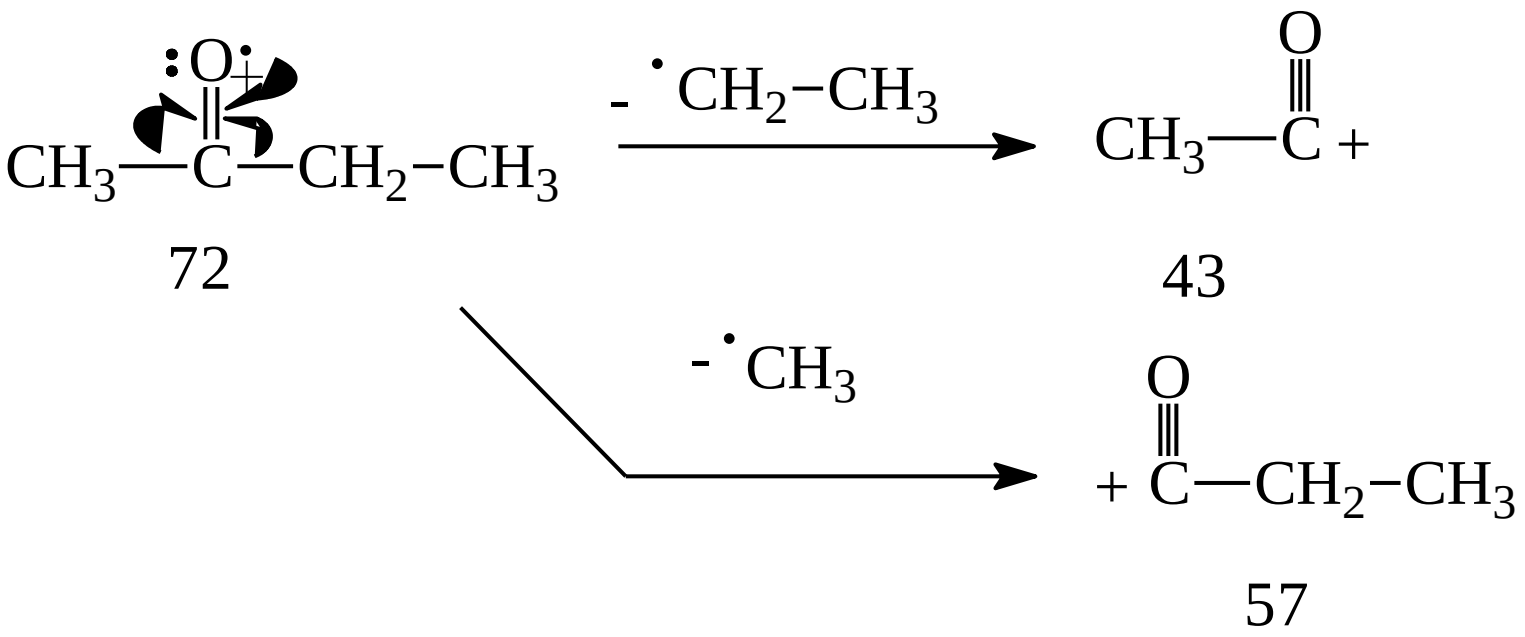
Y ➔ H, R, OH, NR2

Ion Stabilized by resonance

2-butanone

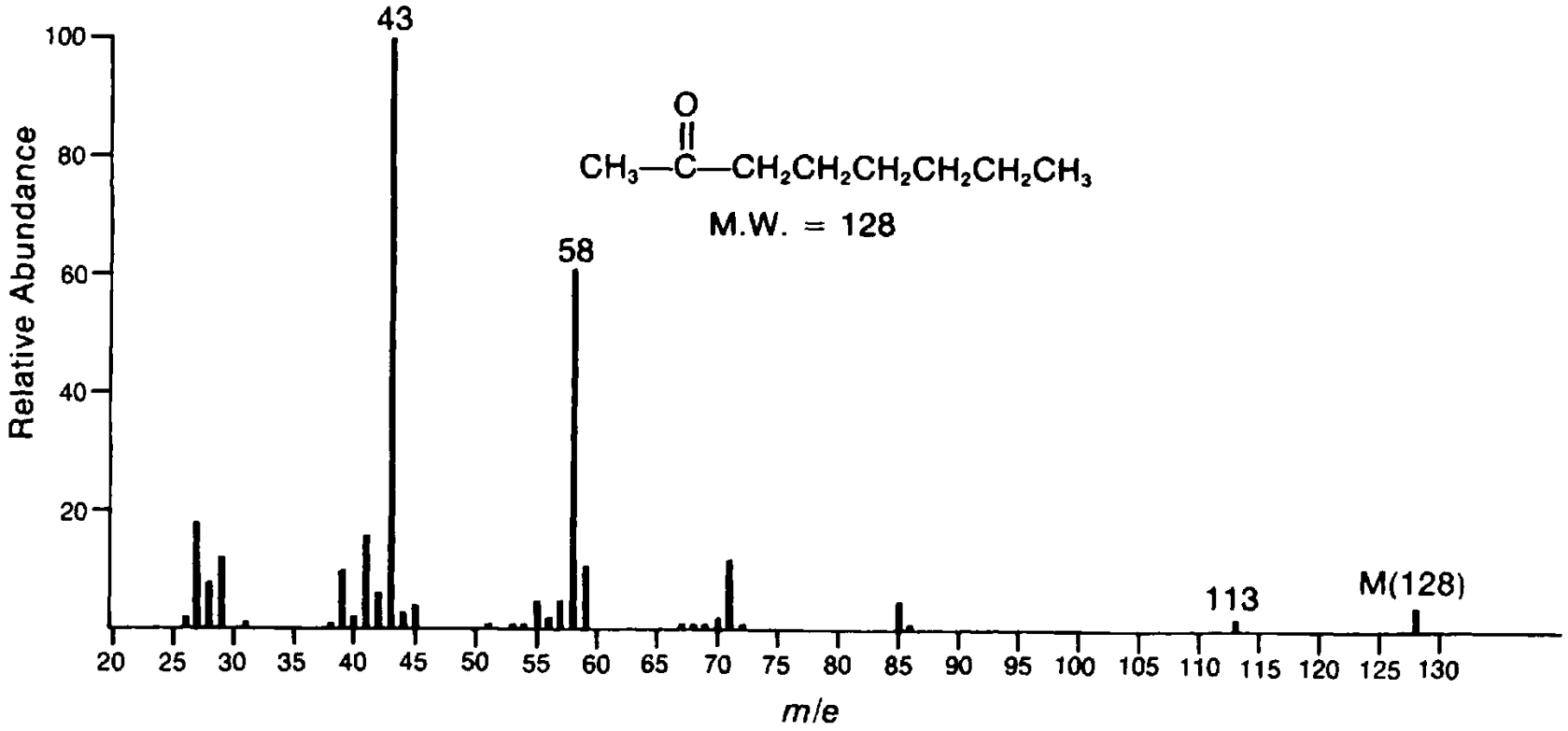

43
100
80
60
40
20
Relative Abundance
O
CH3—C—CH2CH3
M.W. = 72
M(72)
57
10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
m/e

α-cleavage

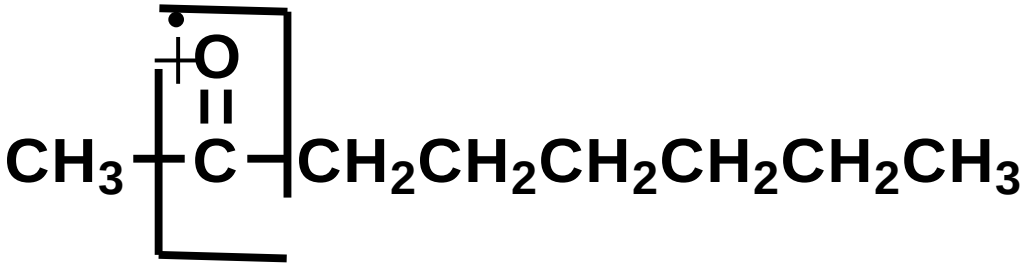


favor loss of larger radical

2-octanone

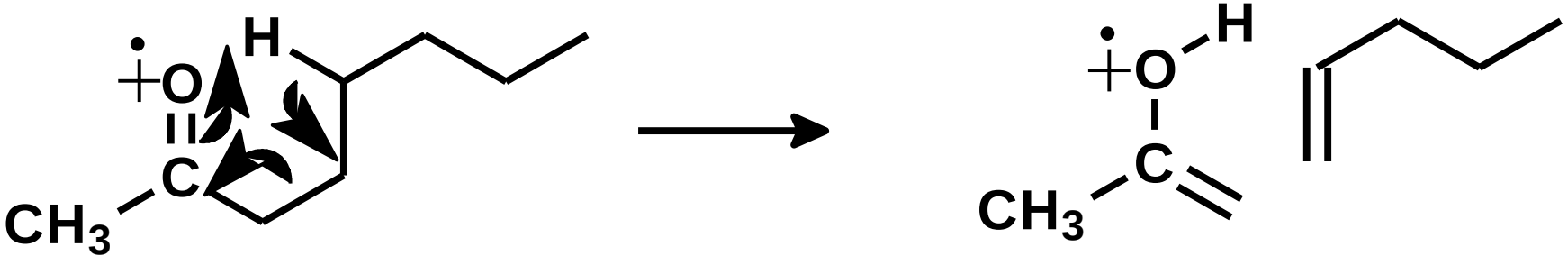

43
58
113
M(128)
100
80
60
40
20
Relative Abundance
20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130
m/e
O
CH3—C—CH2CH2CH2CH2CH2CH3
M.W. = 128

43



113

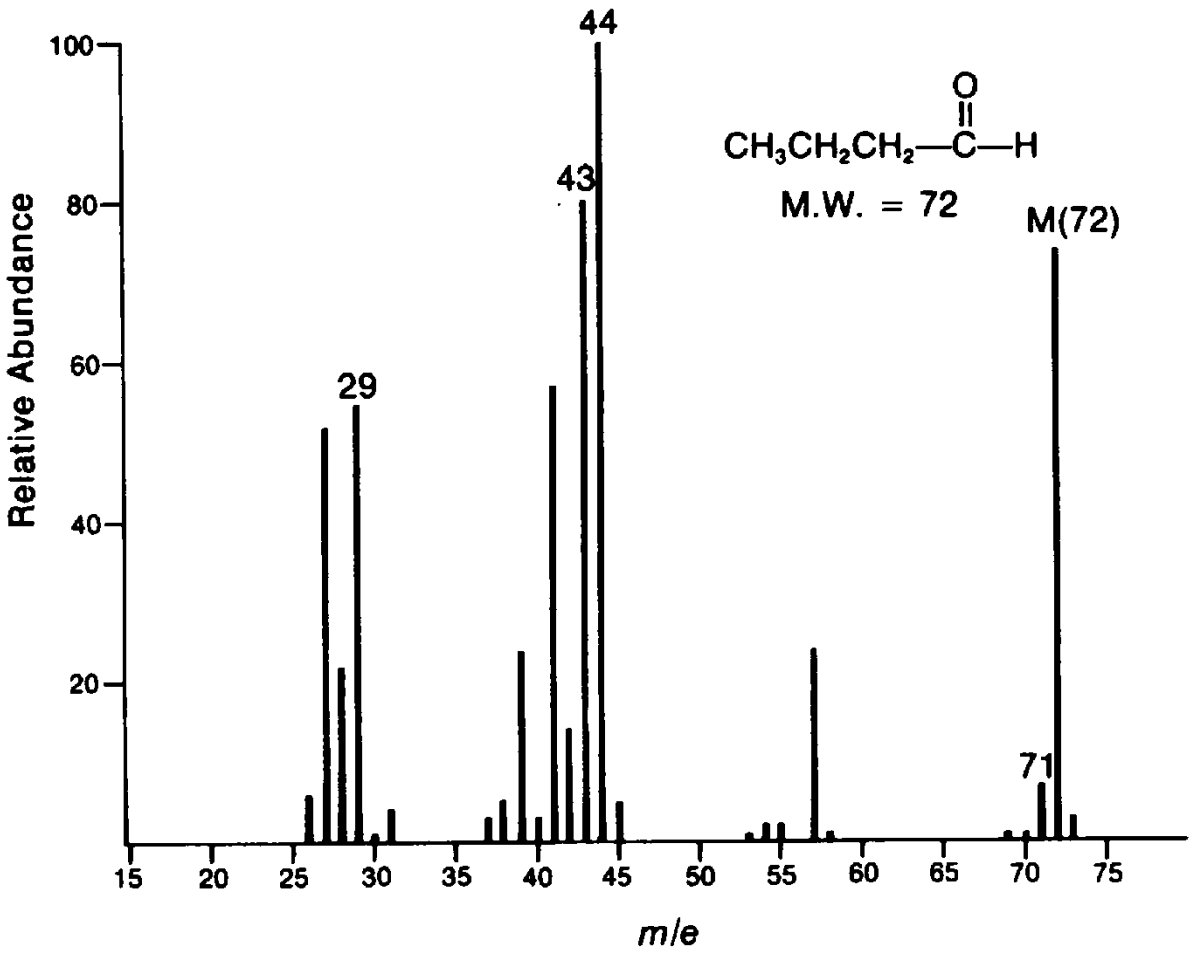
128



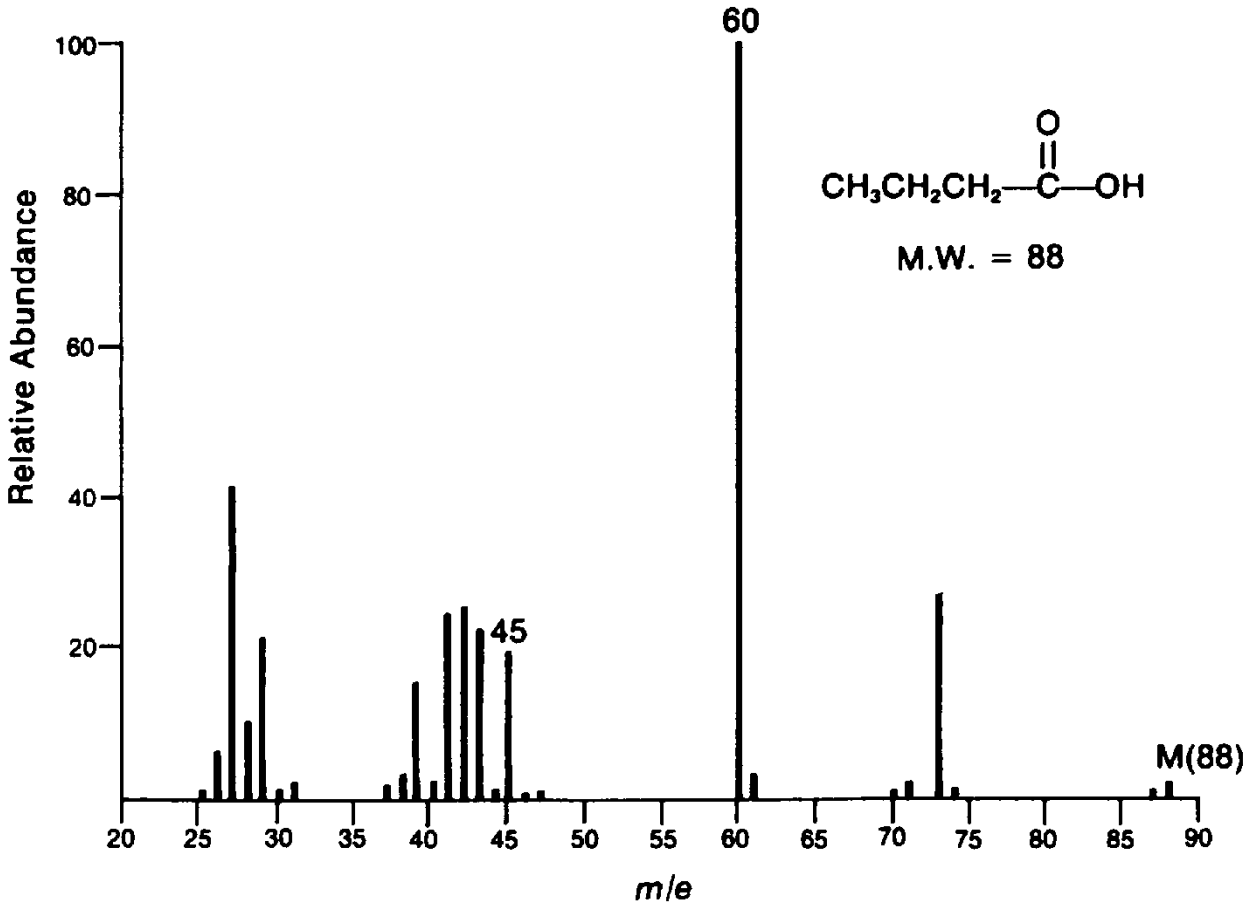
58

McLafferty Rearrangement

butyraldehyde



butyric acid



p-anisic acid