

Aldehyde

SPECTRAL ANALYSIS BOX — Aldehydes

MOLECULAR ION

M^+ weak, but observable (aliphatic)

M^+ strong (aromatic)

FRAGMENT IONS

Aliphatic:

$m/z = 29, M - 29,$

$M - 43, m/z = 44$

Aromatic:

$M - 1, M - 29$

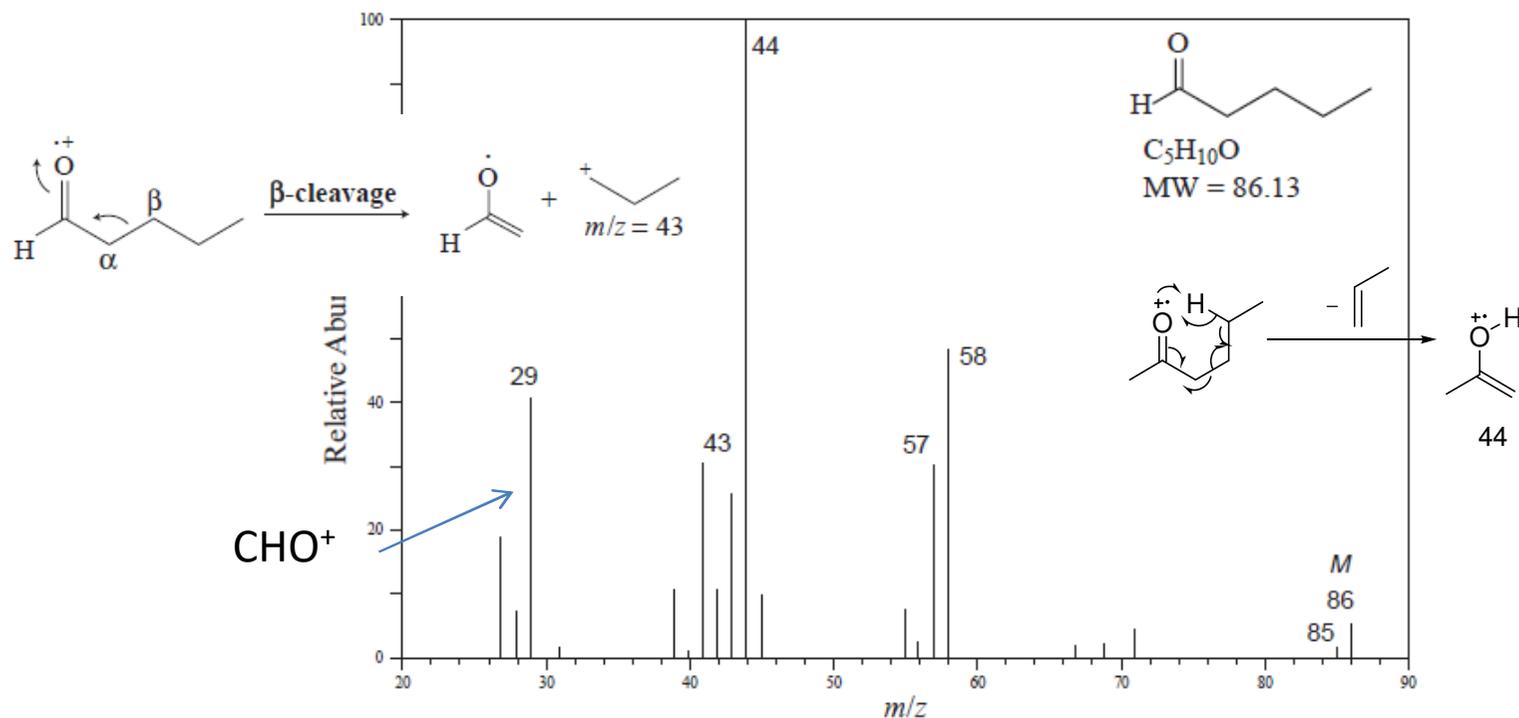


FIGURE 8.58 EI MS of valeraldehyde

Aromatic aldehyde

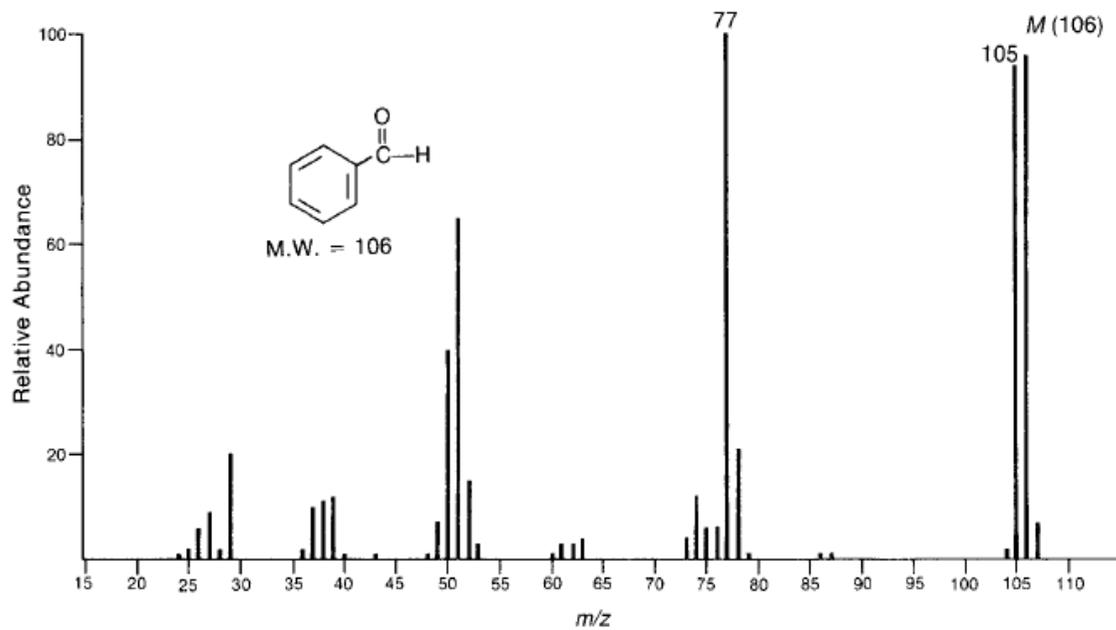
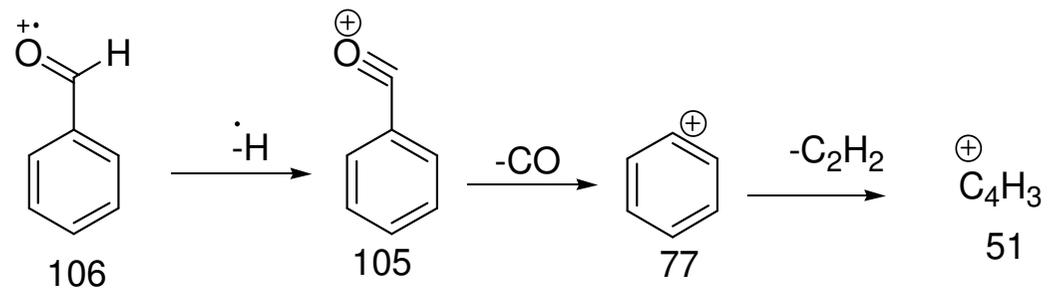


FIGURE 8.59 EI-MS of benzaldehyde.



Aliphatic Ketone

MOLECULAR ION

M^+ strong

FRAGMENT IONS

Aliphatic:

$M - 15, M - 29, M - 43, \text{etc.}$

$m/z = 43$

$m/z = 58, 72, 86, \text{etc.}$

$m/z = 42, 83$

Aromatic:

$m/z = 105, 120$

CH_3CO^+

1. Loss of alkyl group from both side of alkyl group observed
2. Loss of large alkyl group is preferred
3. McLafferty rearrangement will always possible if gamma H is present.

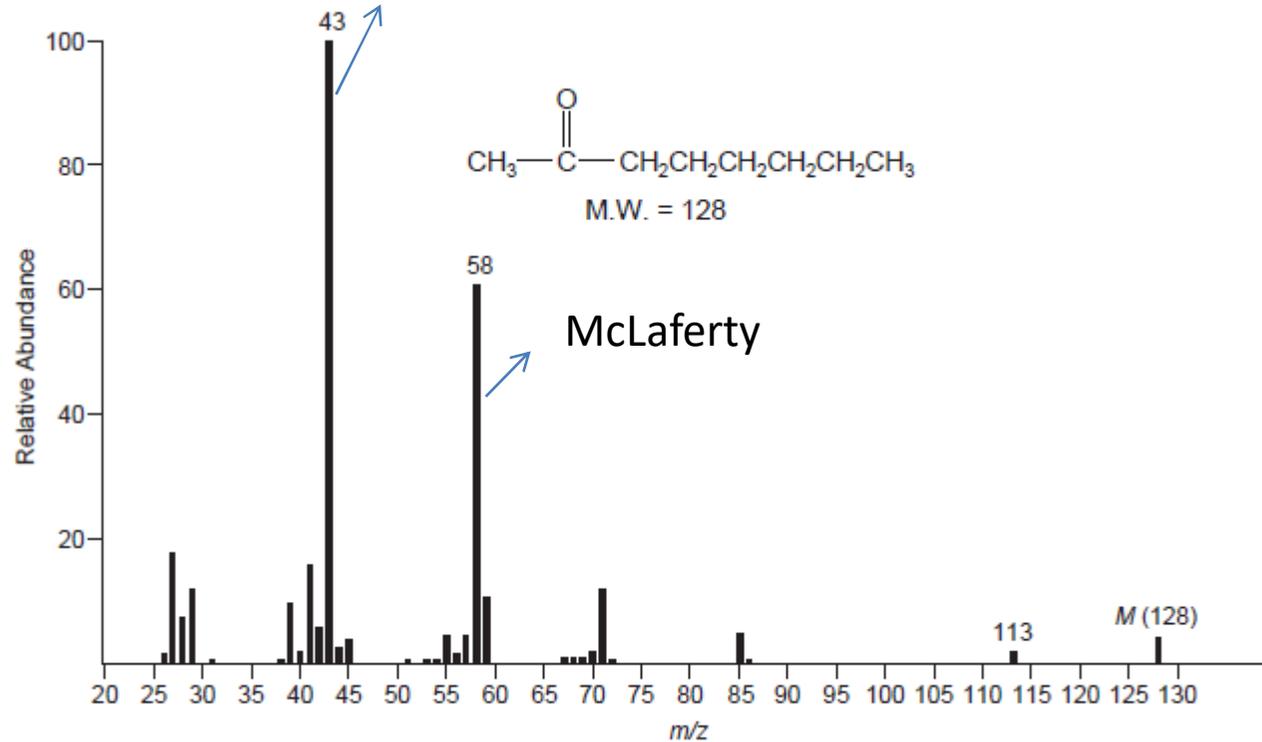
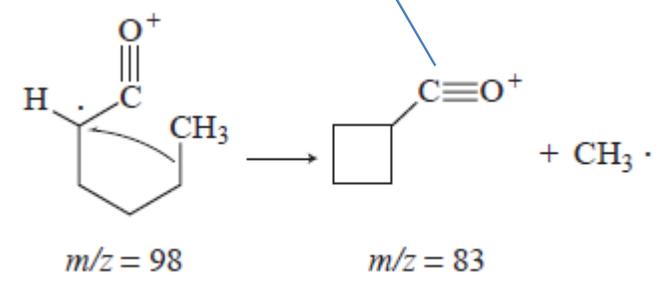
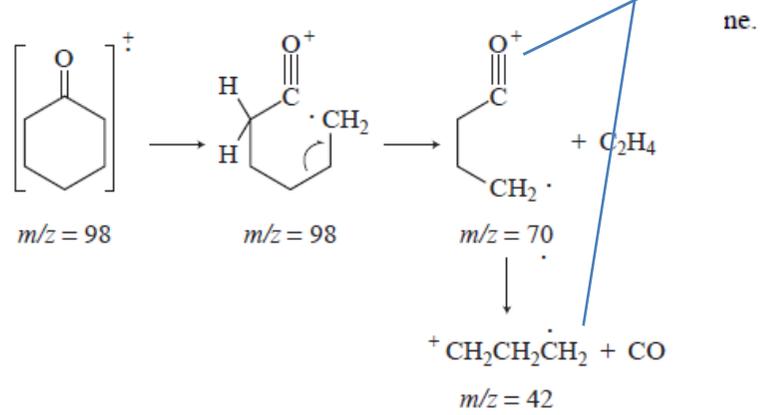
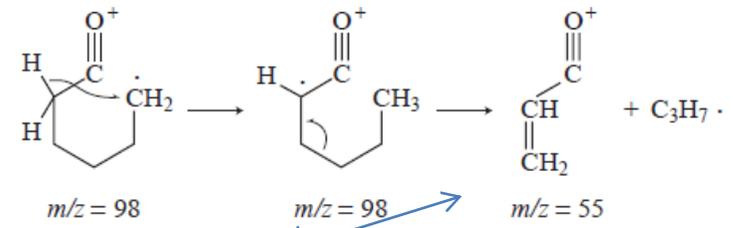
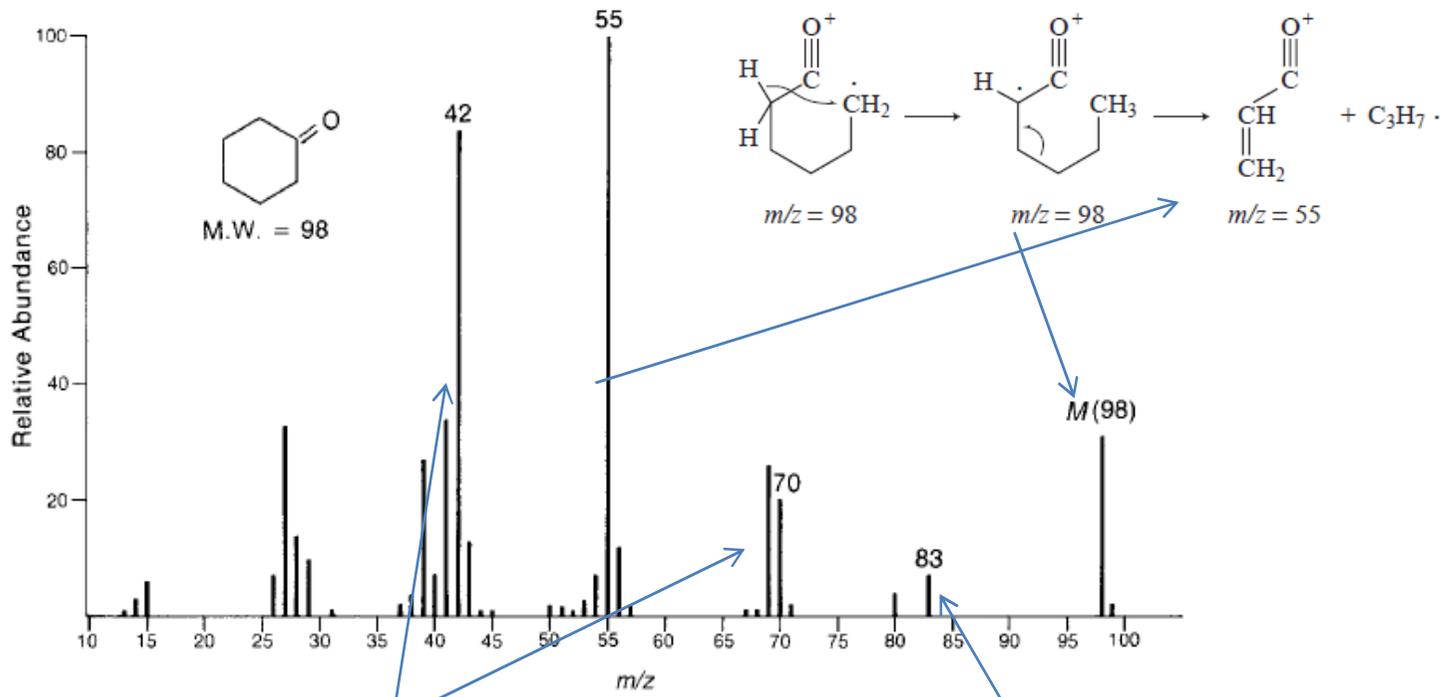


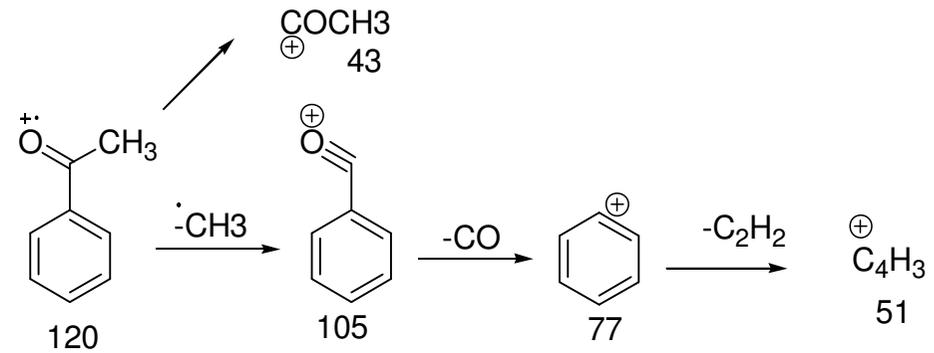
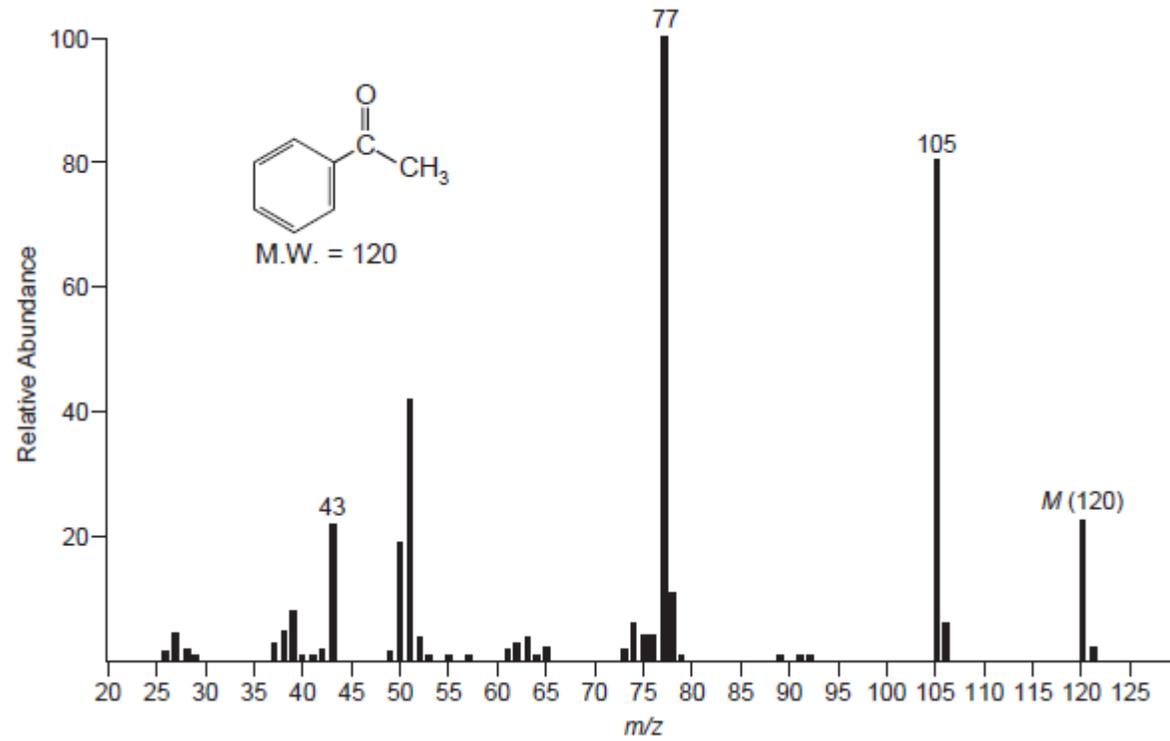
FIGURE 8.61 EI-MS of 2-octanone.

Cyclic ketone

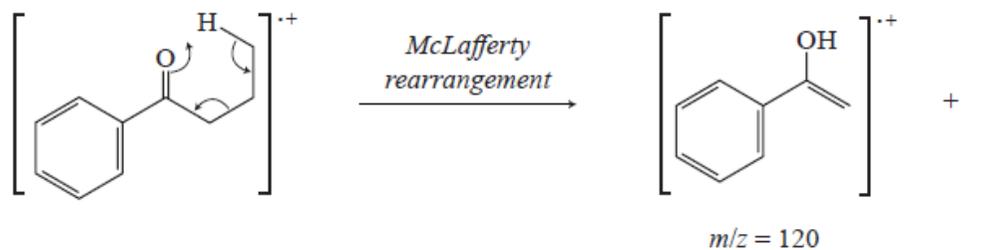
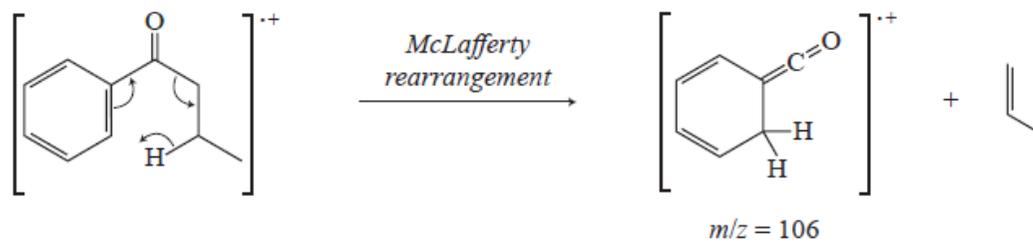
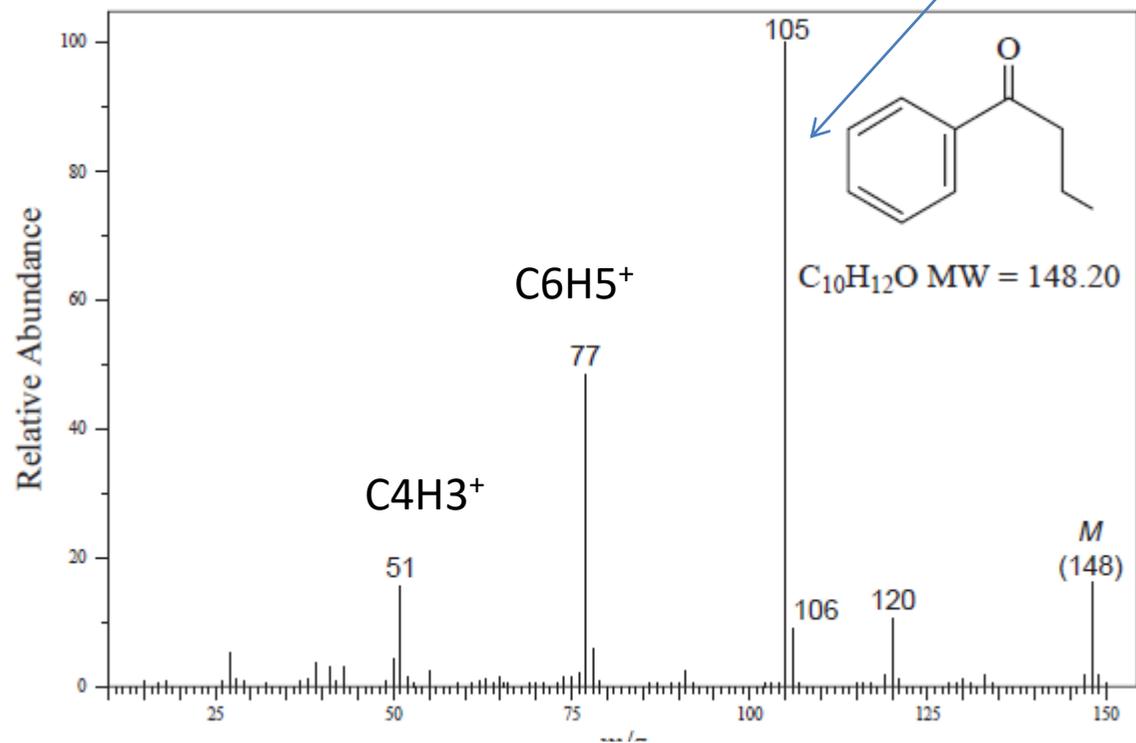


ne.

Aromatic ketone



Due to loss of alkyl group



Aliphatic Ester

MOLECULAR ION

M^+ weak, but generally observable

FRAGMENT IONS

Methyl esters:

$M - 31, m/z = 59, 74$

Higher esters:

$M - 45, M - 59, M - 73$

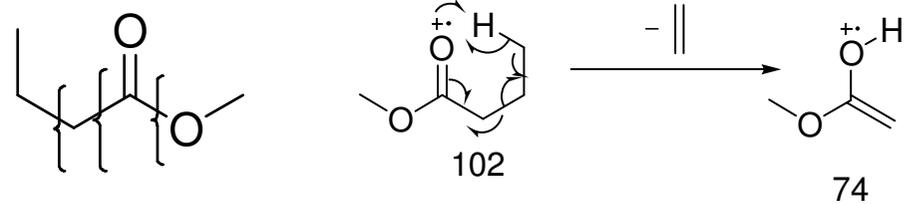
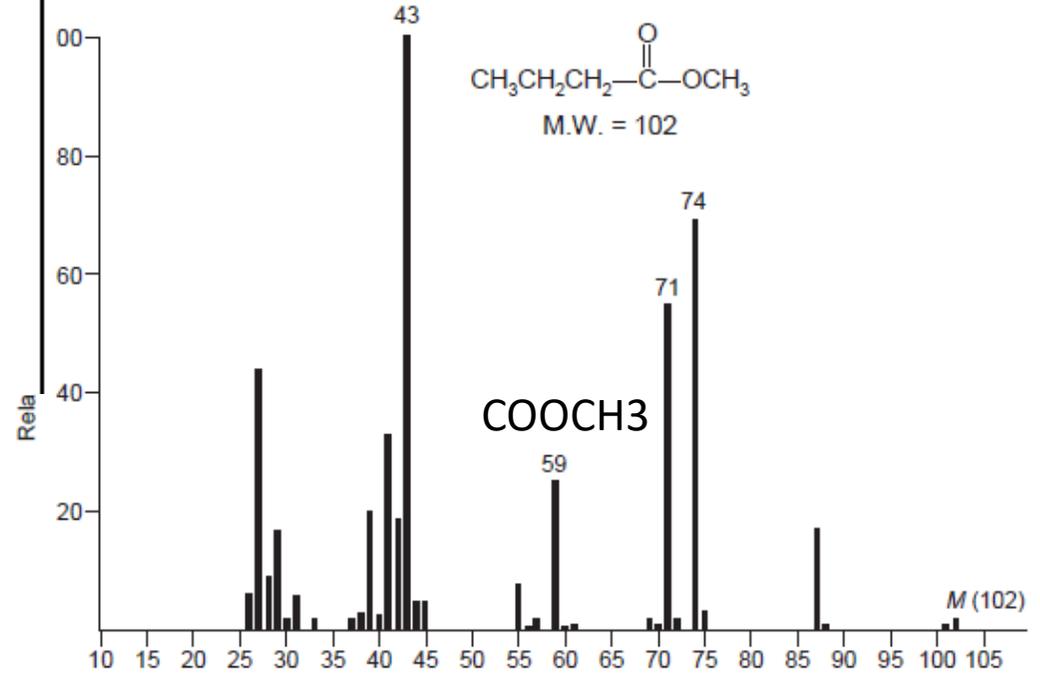
$m/z = 73, 87, 101$

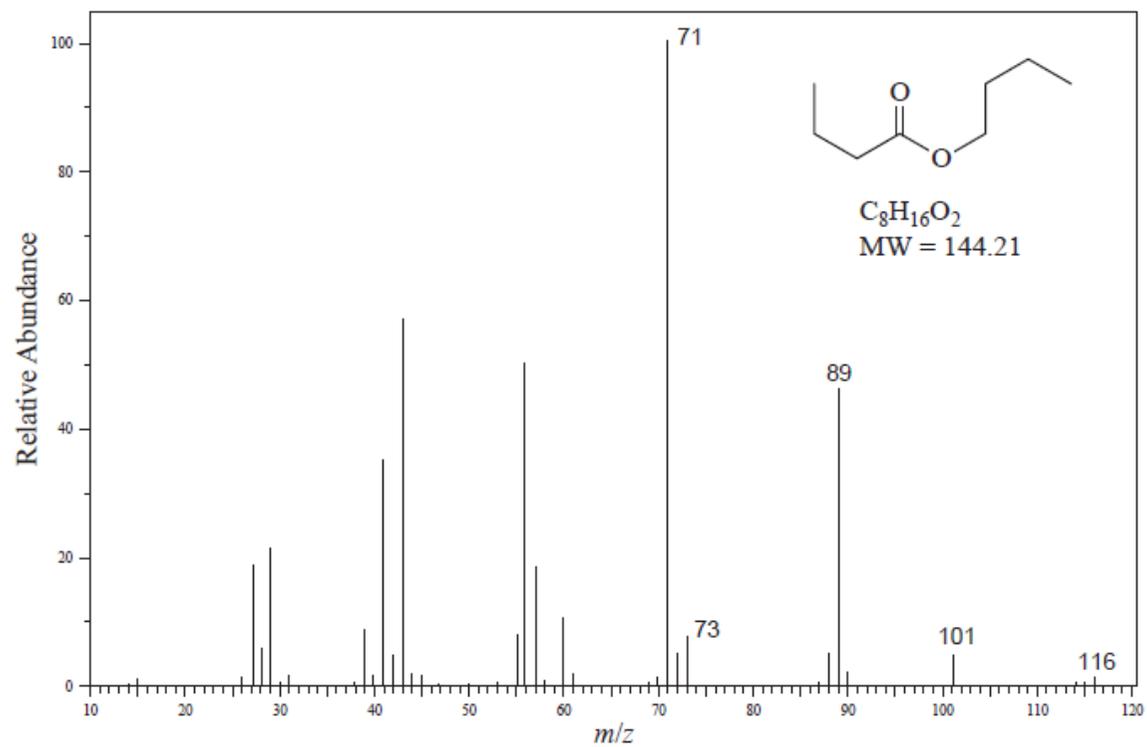
$m/z = 88, 102, 116$

$m/z = 61, 75, 89$

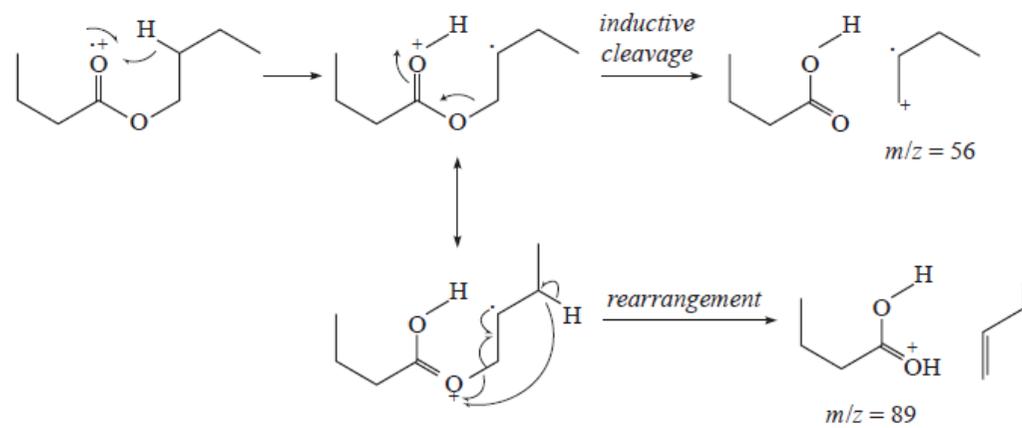
$m/z = 77, 105, 108$

$M - 32, M - 46, M - 60$

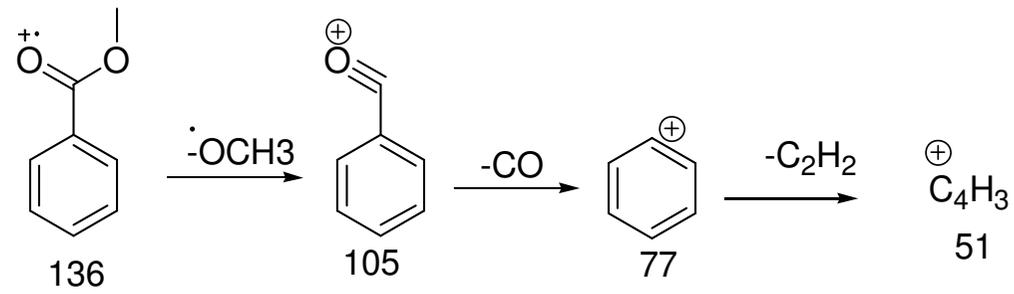
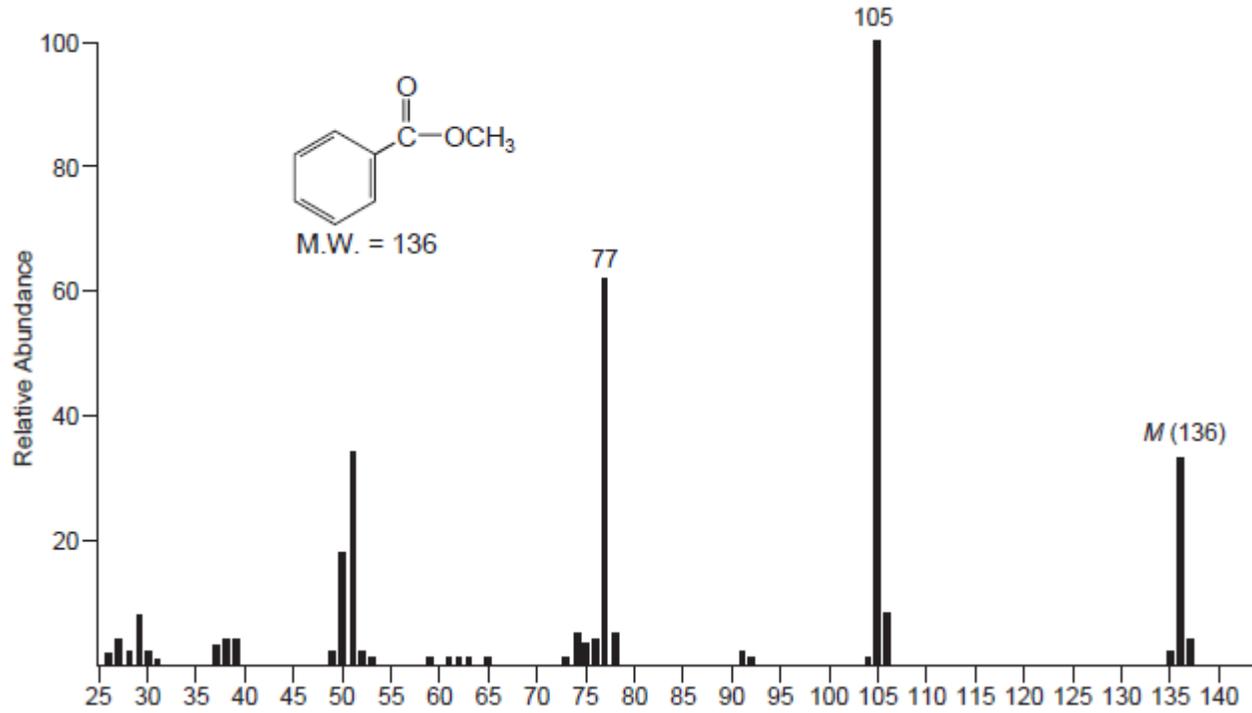




FIG



Aromatic ester



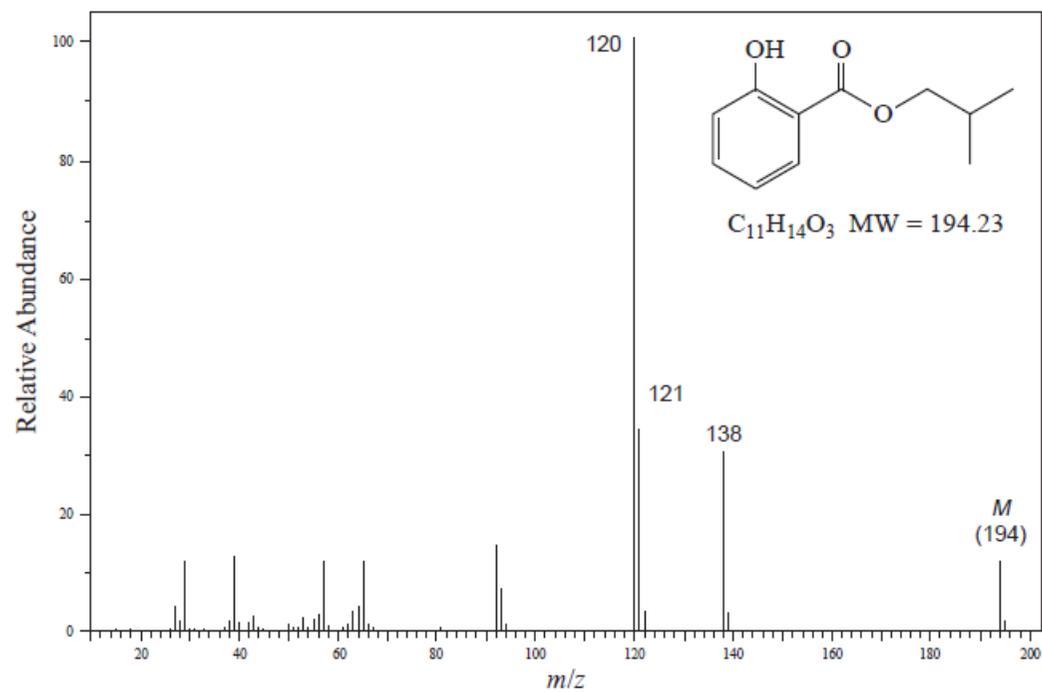
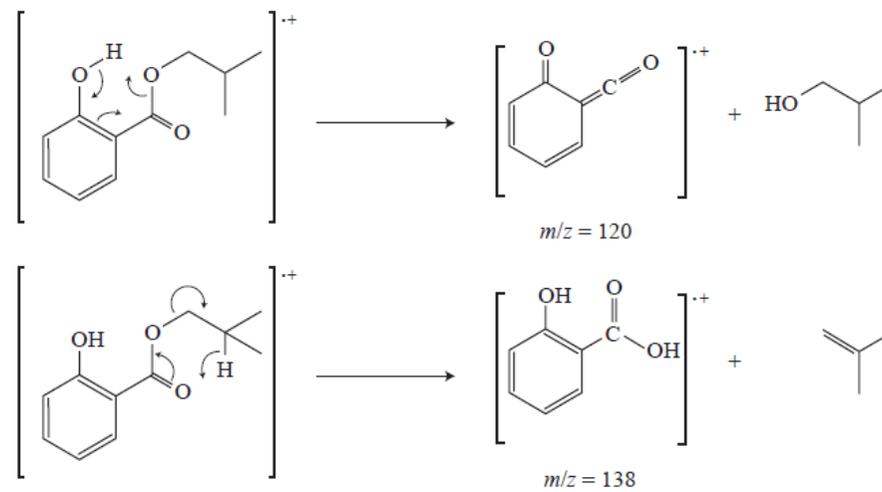


FIGURE 8.69 EI-MS of isobutyl salicylate.

Carboxylic acid

SPECTRAL ANALYSIS BOX — Carboxylic Acids

MOLECULAR ION

Aliphatic carboxylic acids:

M^+ weak, but observable

Aromatic carboxylic acids:

M^+ strong

FRAGMENT IONS

Aliphatic carboxylic acids:

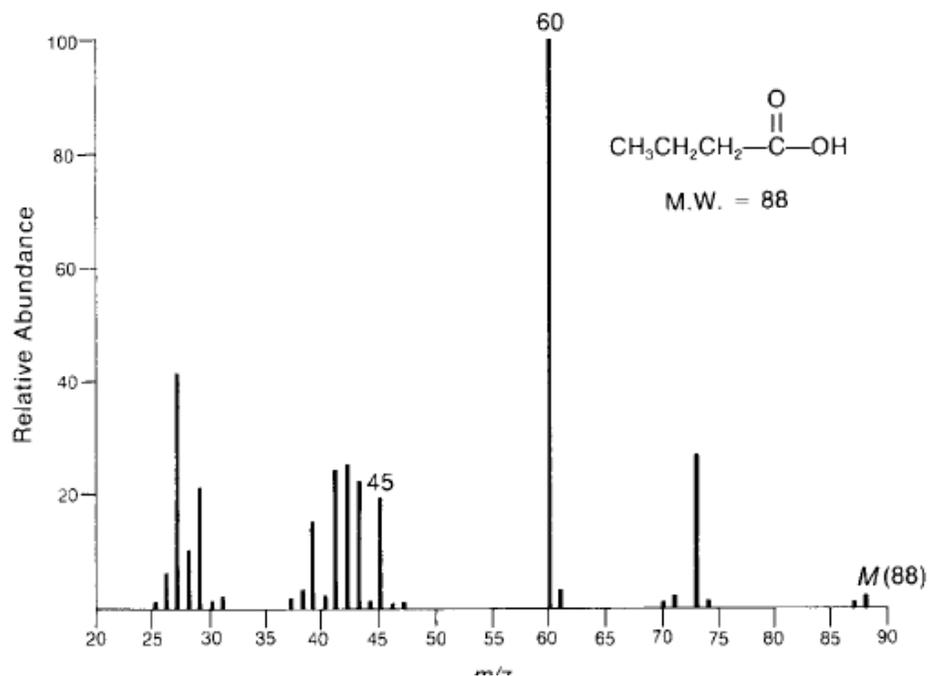
$M - 17$, $M - 45$

$m/z = 45, 60$

Aromatic carboxylic acids:

$M - 17$, $M - 45$

$M - 18$



Peak at 45 is COOH

152-17-28-26 = 135, 107

M-OH-CO-C₂H₂

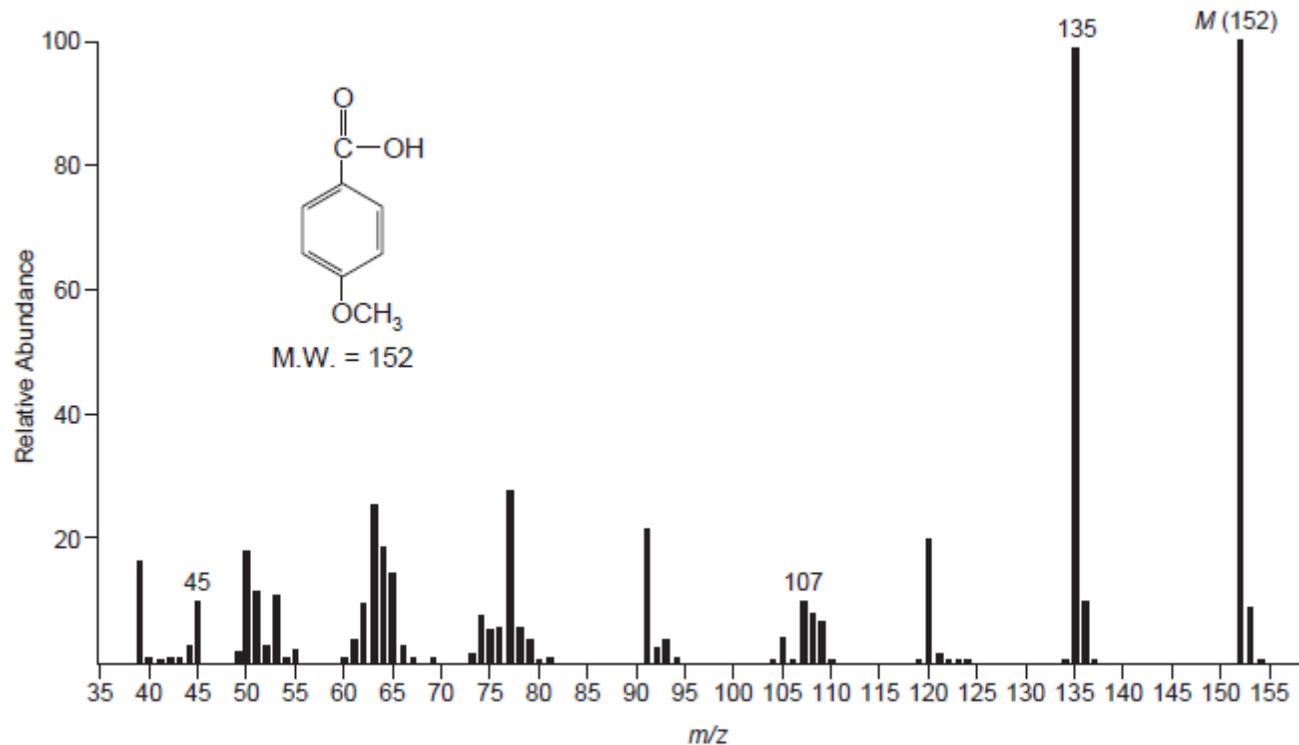


FIGURE 8.71 EI-MS of *para*-anisic acid.

It will also give ether fragments in addition

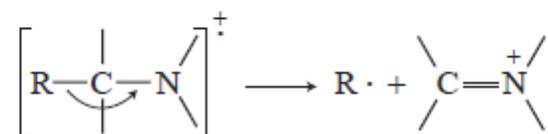
1. Loss of Me group, loss of CO

Amine

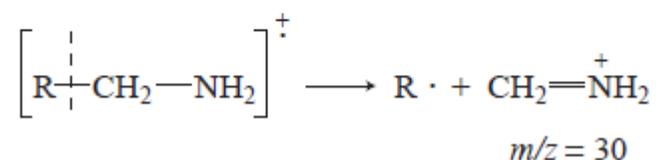
STRUCTURAL ANALYSIS FOR AMINES

MOLECULAR ION	FRAGMENT IONS
M ⁺ weak or absent	α -Cleavage
Nitrogen Rule obeyed	$m/z = 30$

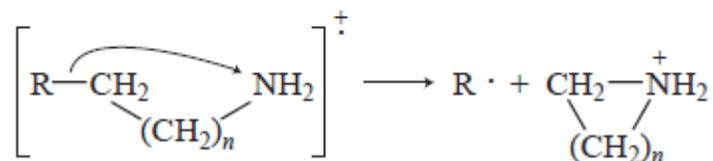
The most intense peak in the mass spectrum of an aliphatic amine arises from α -cleavage:

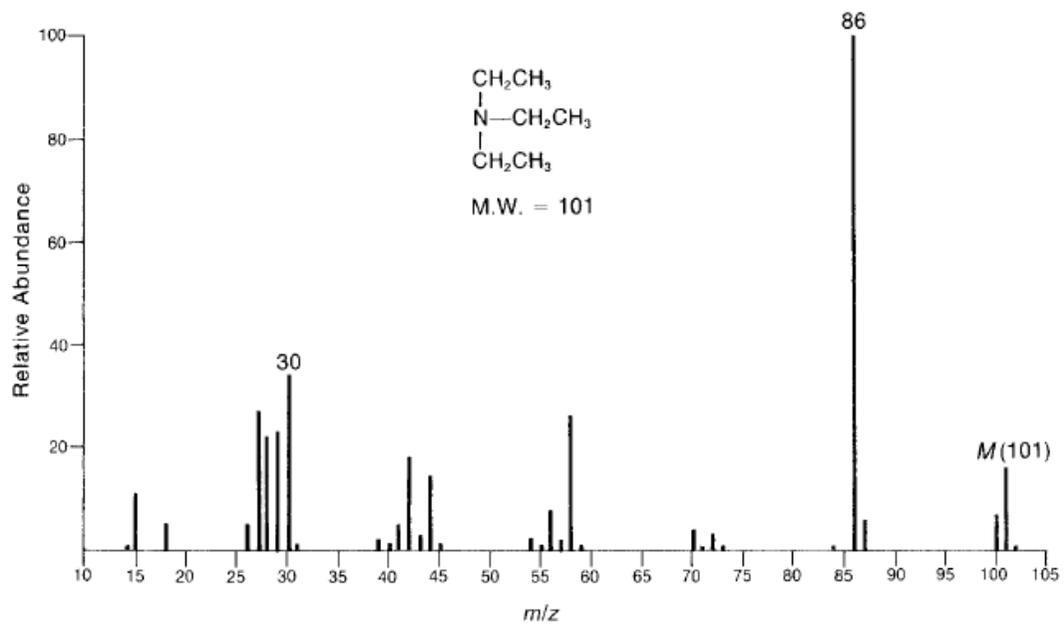
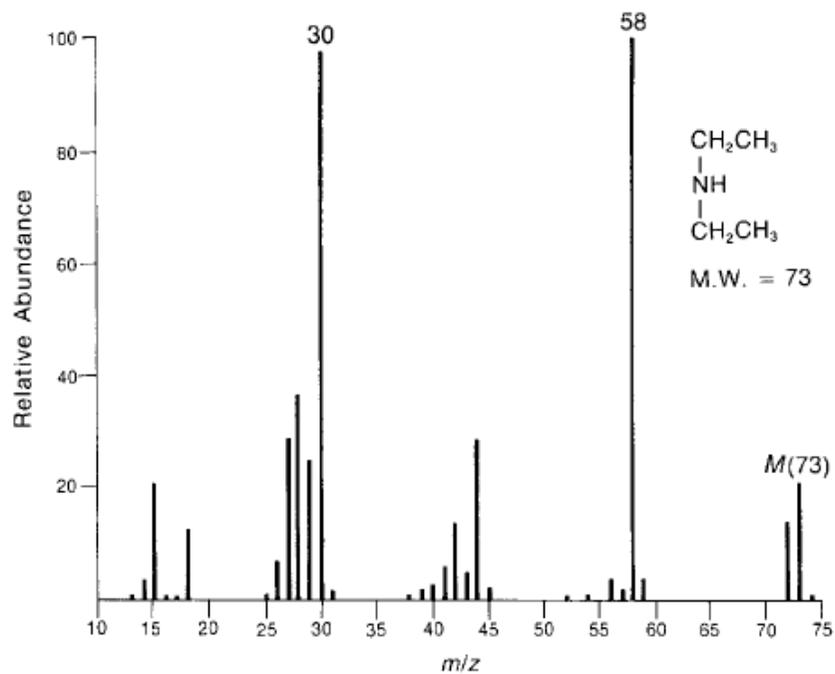
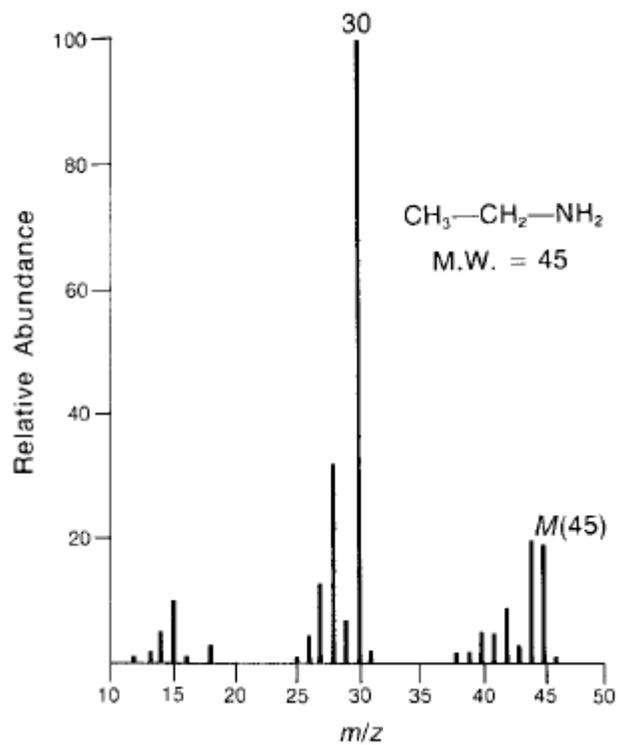


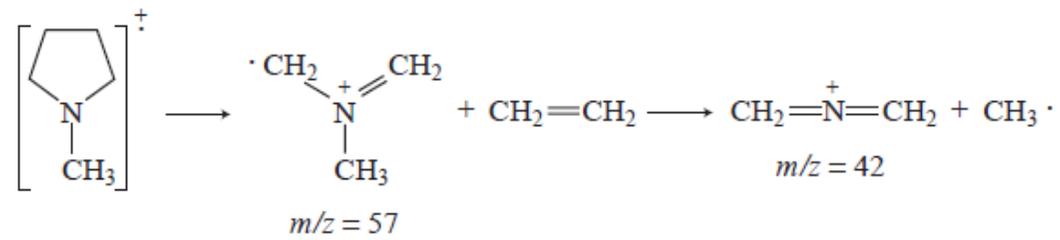
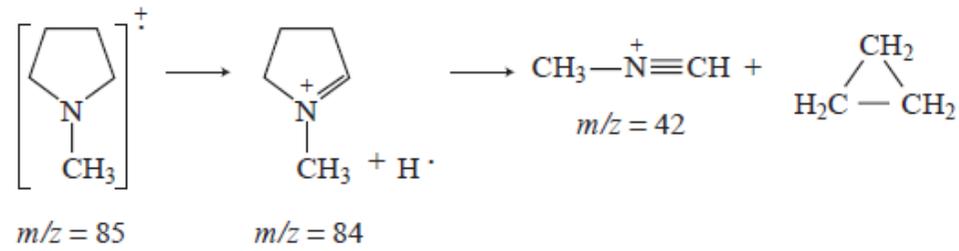
When there is a choice of R groups to be lost through this process, the largest R group is lost preferentially. For primary amines that are not branched at the carbon next to the nitrogen, the most intense peak in the spectrum occurs at $m/z = 30$. It arises from α -cleavage:



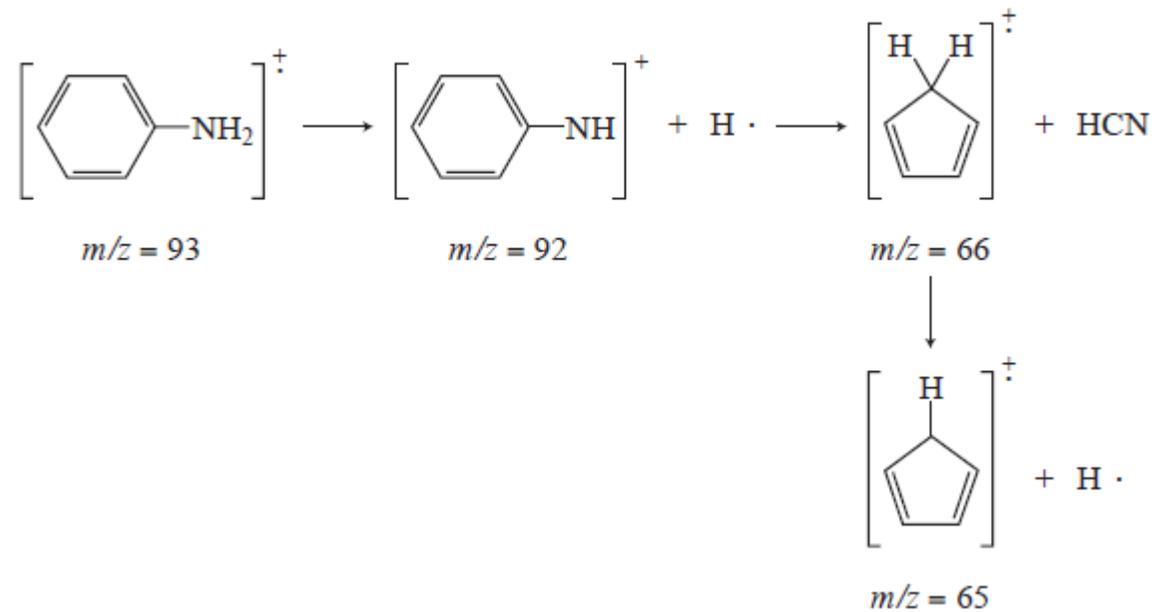
The same β -cleavage peak can also occur for long-chain primary amines. Further fragmentation of the R group of the amine leads to clusters of fragments 14 mass units apart due to sequential loss of CH₂ units from the R group. Long-chain primary amines can also undergo fragmentation via the process



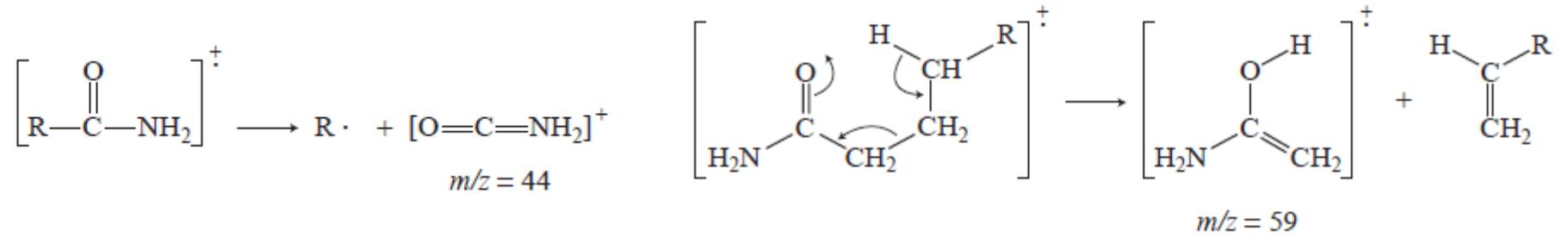




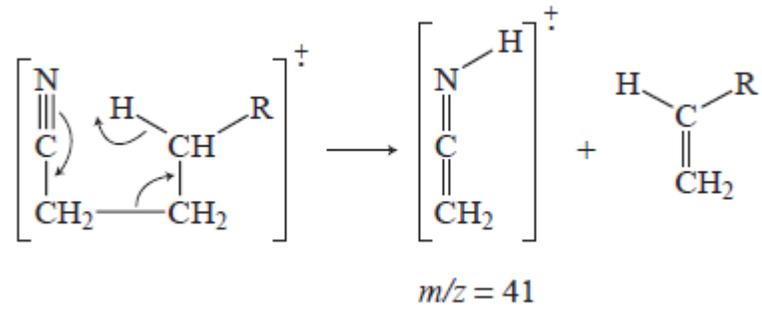
Arc



Amides

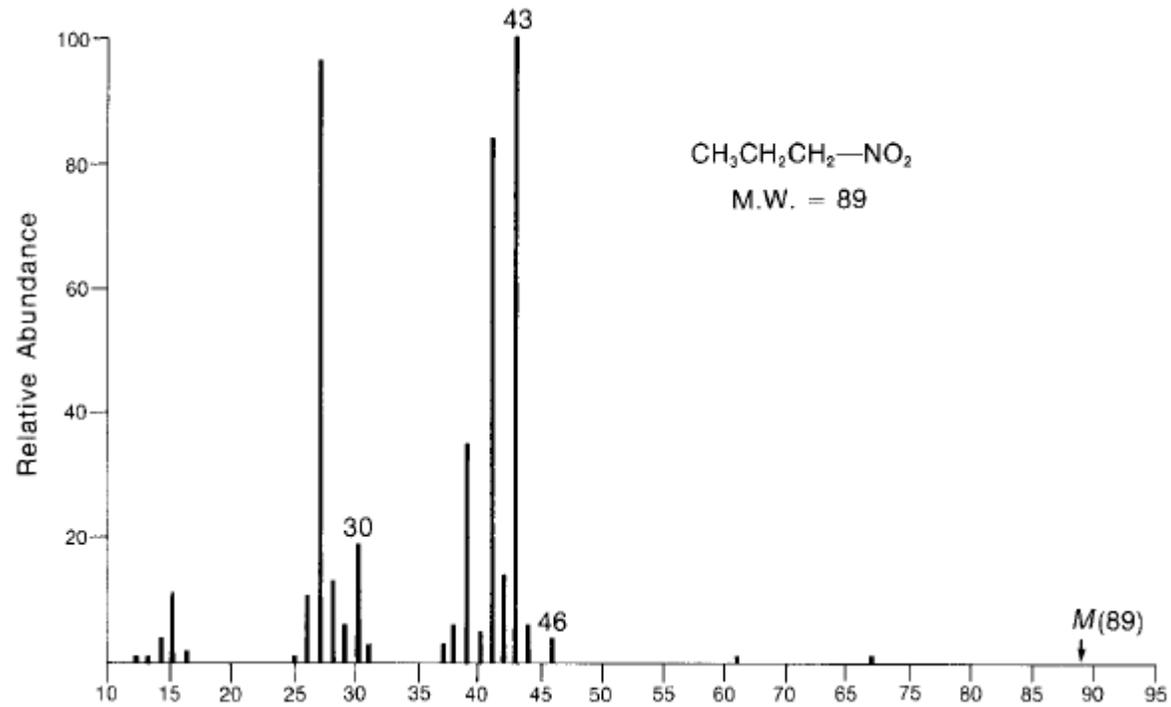


Nitriles

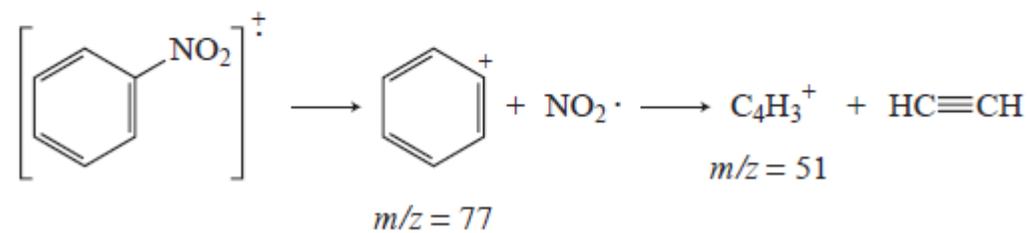
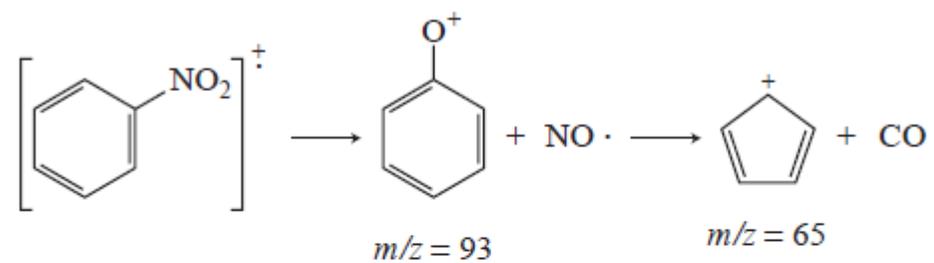


Aliphatic nitro compounds

weaker peak at $m/z = 46$, corresponding to the NO_2^+ ion. These peaks appear in the mass spectrum of 1-nitropropane (Fig. 8.78). The intense peak at $m/z = 43$ is due to the C_3H_7^+ ion.



Aromatic nitro compounds



Alkyl chloride and bromide

SPECTRAL ANALYSIS BOX — Alkyl Halide

MOLECULAR ION

Strong $M + 2$ peak
 (for Cl, $M/M + 2 = 3:1$;
 for Br, $M/M + 2 = 1:1$)

FRAGMENT IONS

Loss of Cl or Br
 Loss of HCl
 α -Cleavage

