

Apart from above general fragmentation each class of molecules have some specific fragmentation pattern and discussed category-wise

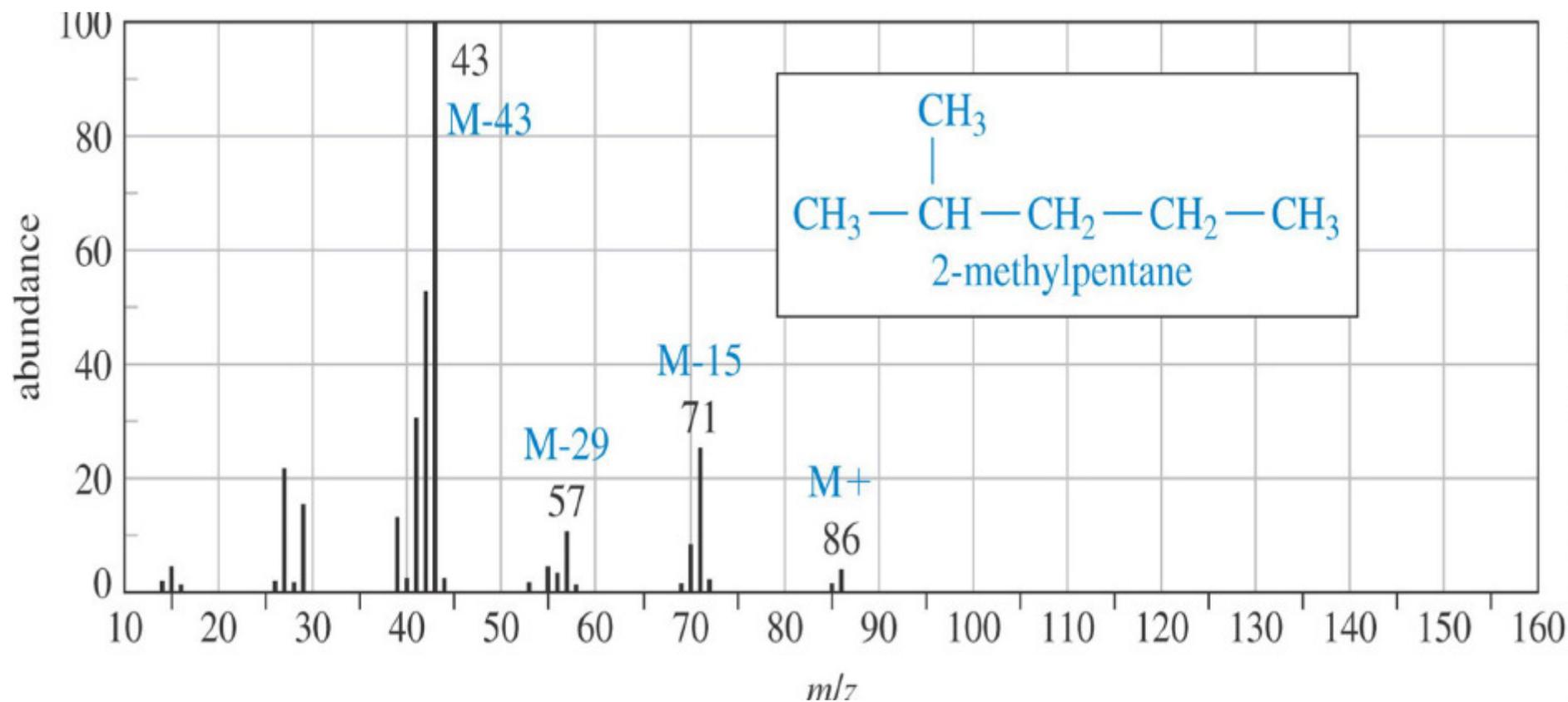
Fragmentation of Alkane

Alkanes

- Fragmentation often splits off simple alkyl groups:

<input type="checkbox"/> Loss of methyl	$M^+ - 15$
<input type="checkbox"/> Loss of ethyl	$M^+ - 29$
<input type="checkbox"/> Loss of propyl	$M^+ - 43$
<input type="checkbox"/> Loss of butyl	$M^+ - 57$

- Branched alkanes tend to fragment forming the most stable carbocations.



Both loss of methyl and propyl radical provides 2° Cation but loss of propyl radical provides base peak

Cycloalkane

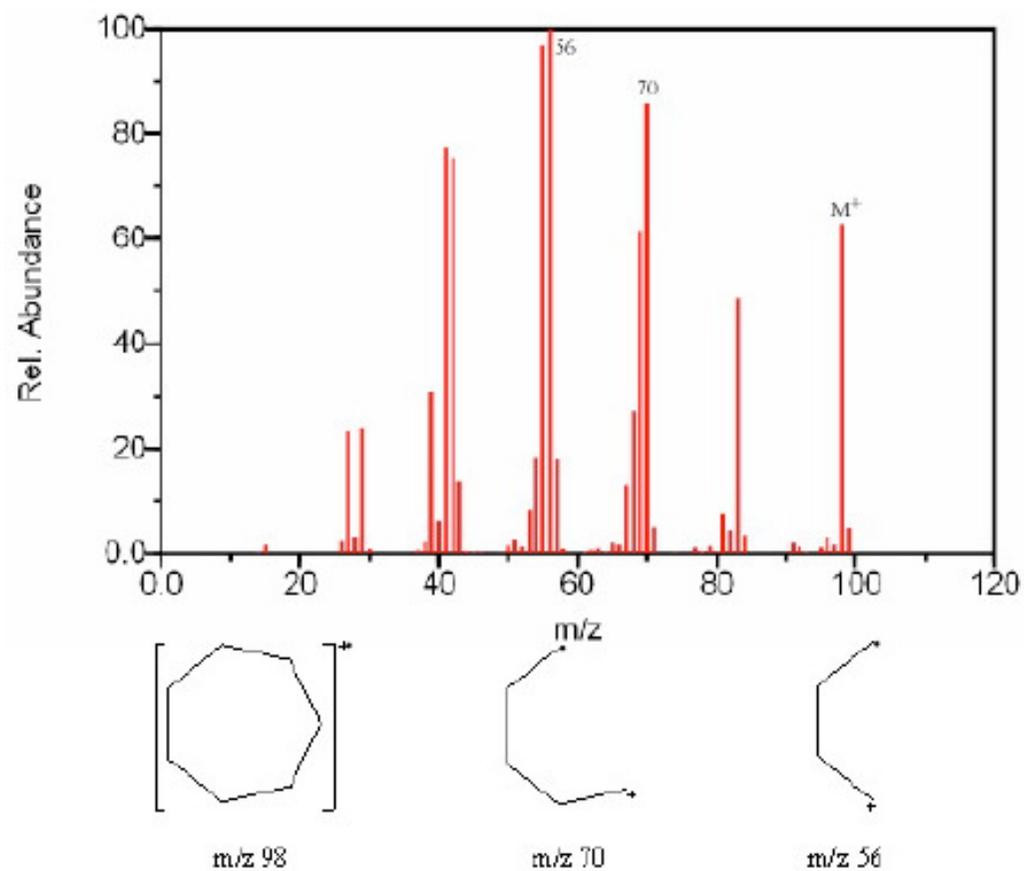
MOLECULAR ION

Strong M^+

FRAGMENT IONS

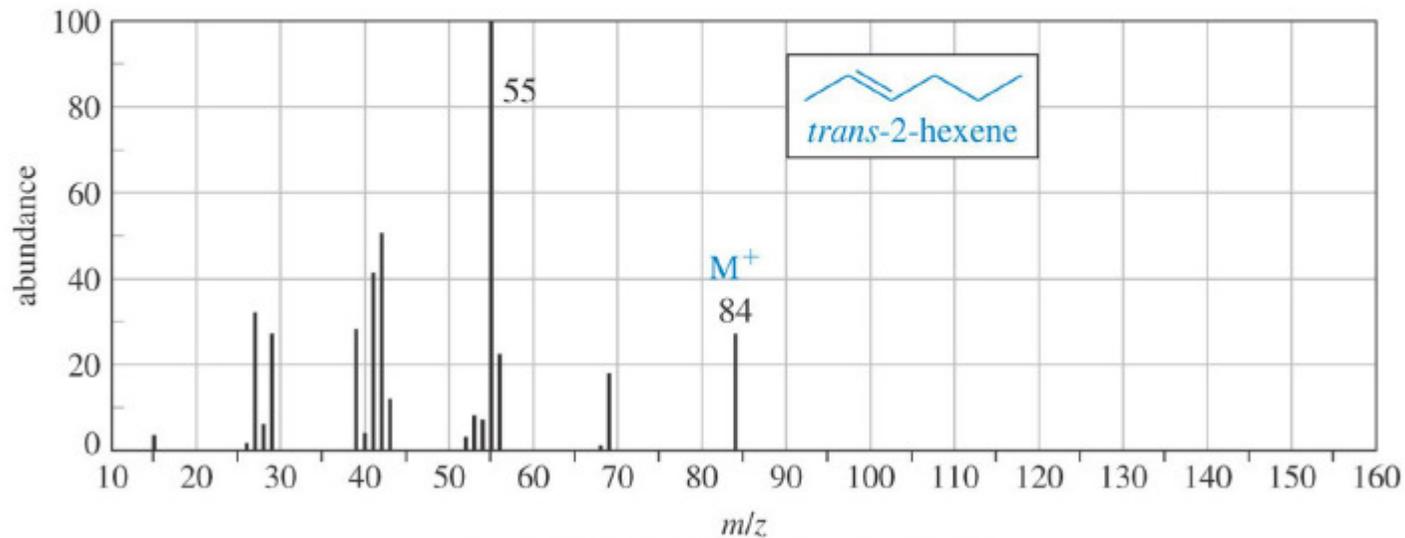
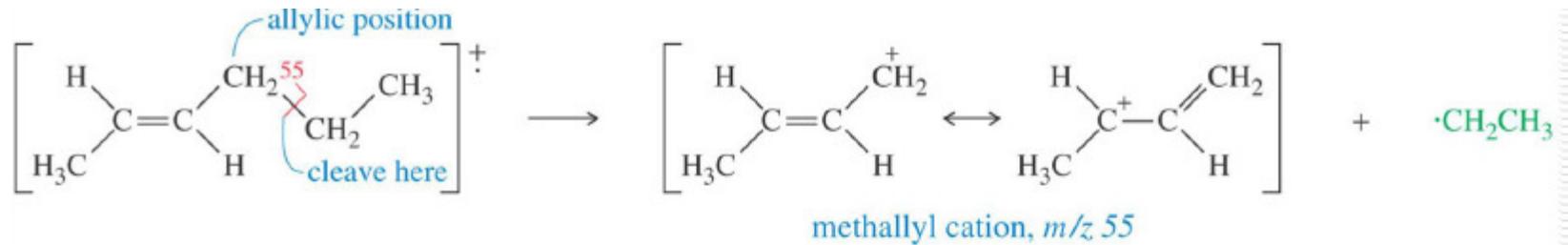
$M - 28$

A series of peaks: $M - 15$, $M - 29$, $M - 43$, $M - 57$, etc.



Fragmentation of Alkene

1. Most stable fragmentation occur at allylic position and usually appear as base peak.
2. If gamma H present wrt to double bond, McLafferty rearrangement also occur Peak at 56.
3. Other fragmentation like normal alkane occurs.



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MOLECULAR ION

Strong M^+

FRAGMENT IONS

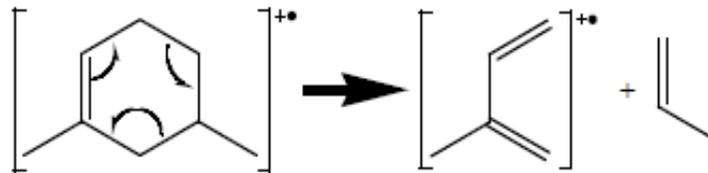
$m/z = 41$

A series of peaks: $M - 15$, $M - 29$, $M - 43$, $M - 57$, etc.

Cycloalkene

1 If gamma H present outside wrt to double bond, Mclaferty rearrangement also occur Peak at 56.

3. Other fragmentation like normal alkane occurs.



Alkynes

MOLECULAR ION

Strong M^+

FRAGMENT IONS

$m/z = 39$

Strong $M - 1$ peak

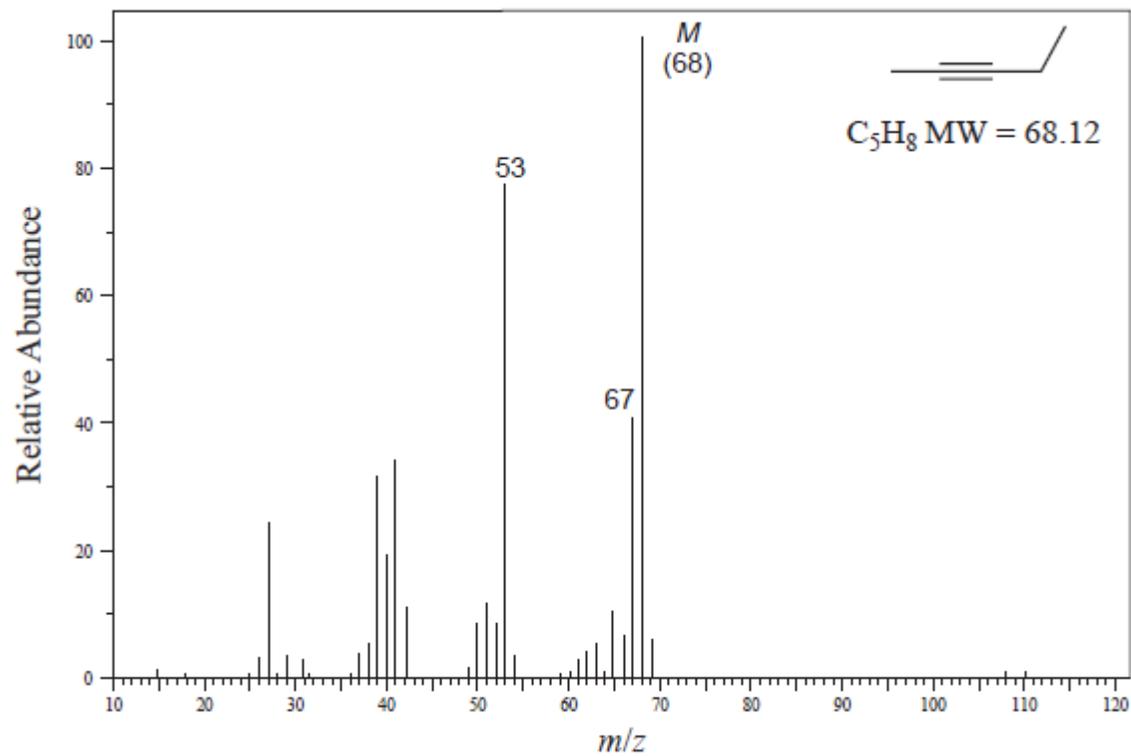


FIGURE 8.37 EI-MS spectrum of 2-pentyne.

Aromatic hydrocarbon compounds

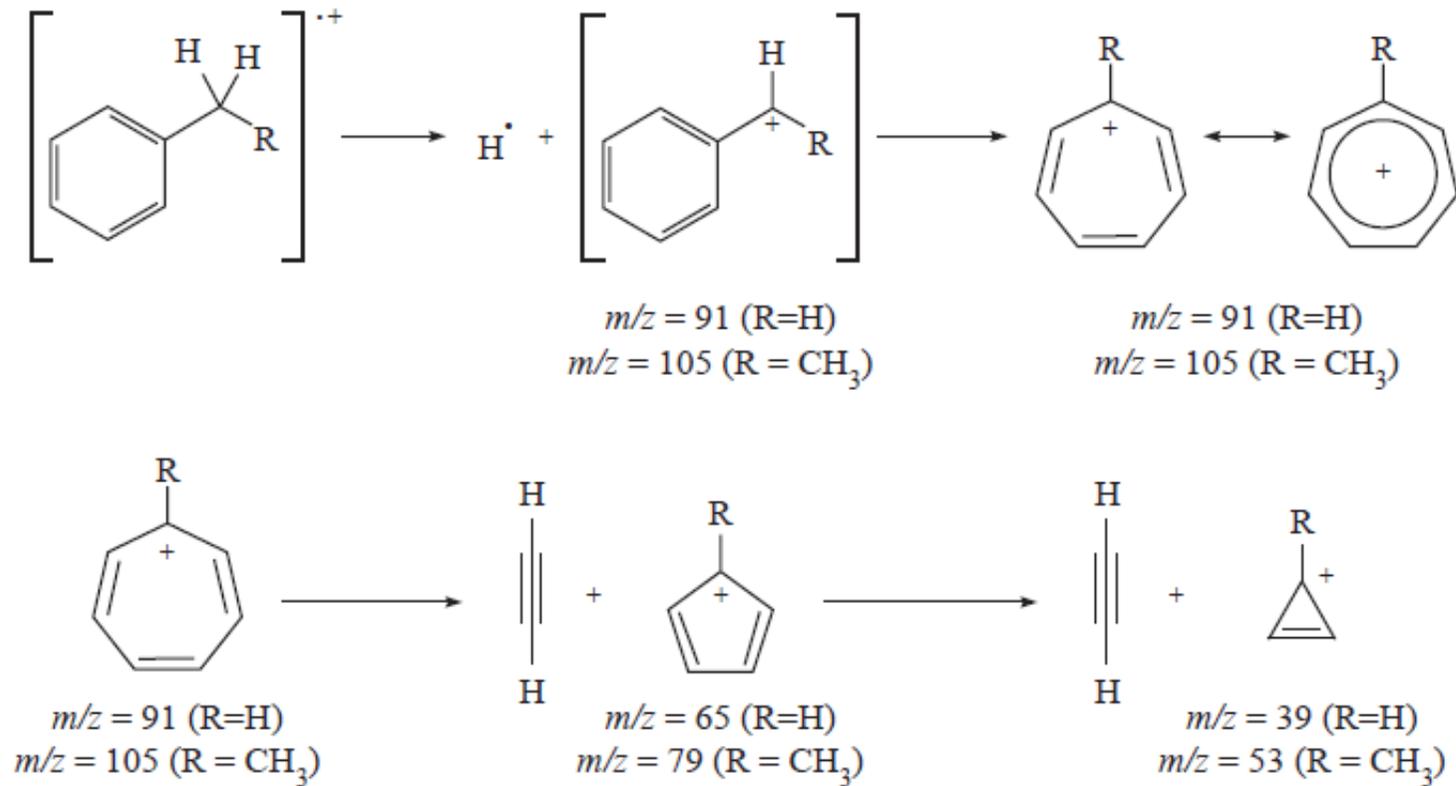


FIGURE 8.43 Formation and fragmentation of the tropylium ion.

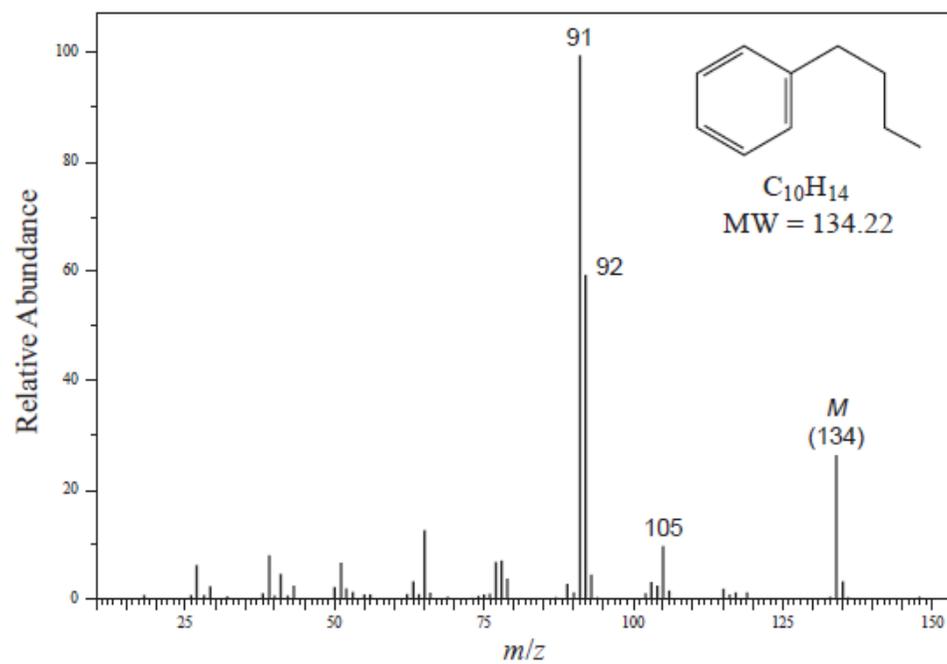
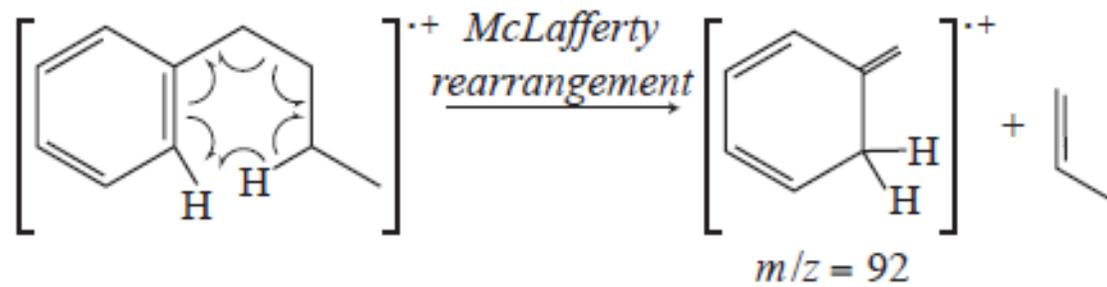


FIGURE 8.44 EI-MS of butylbenzene.

Alcohol and phenol

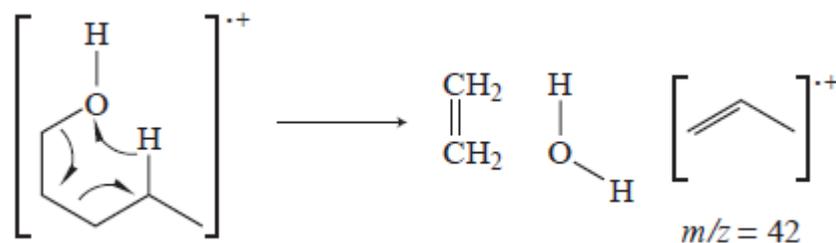
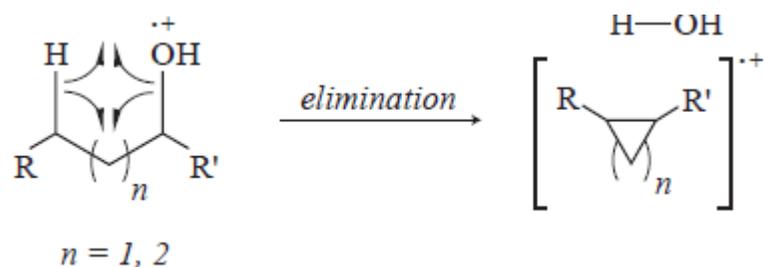
MOLECULAR ION

M^+ weak or absent

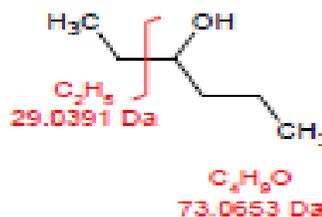
FRAGMENT IONS

Loss of alkyl group

$M - 18$



Cleavage at α to hydroxy group occur and if 2 possibility exist larger radical ion lost



Cyclic Alcohol

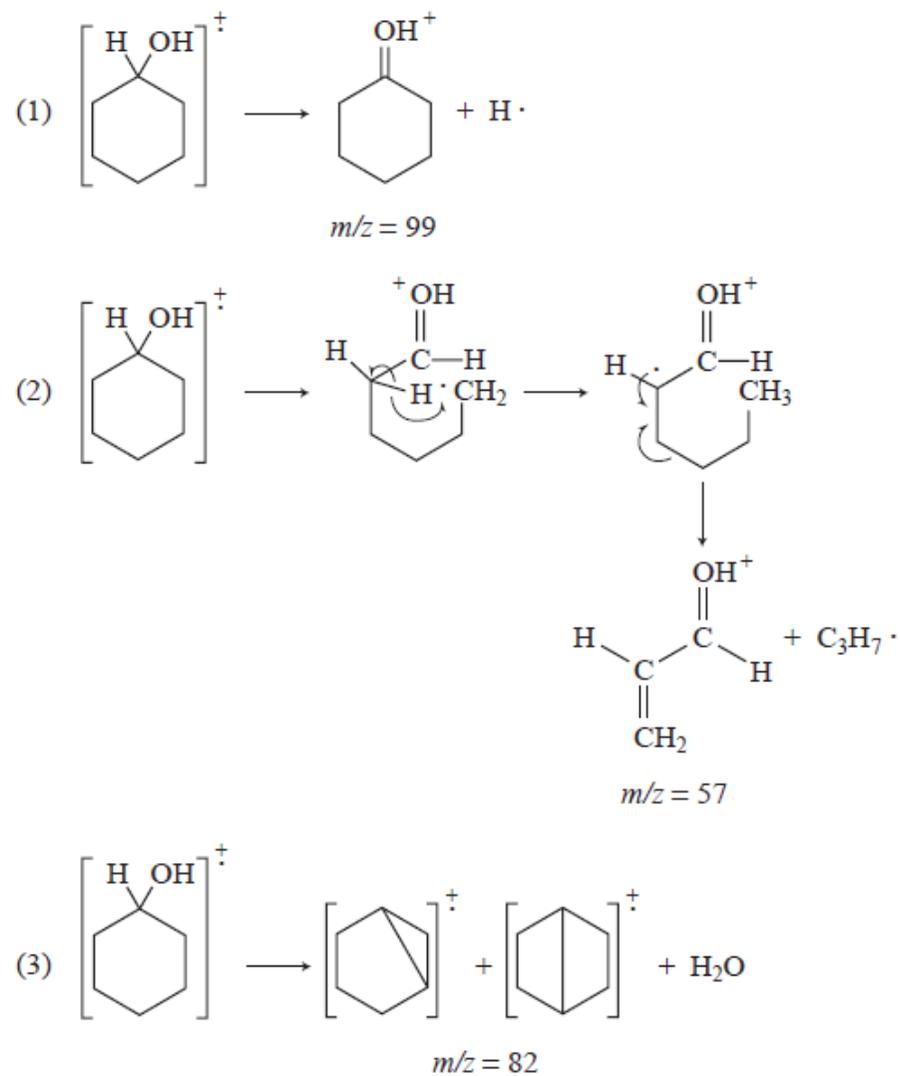


FIGURE 8.49 Fragmentation pathways for cyclohexanol.

Benzyl Alcohol

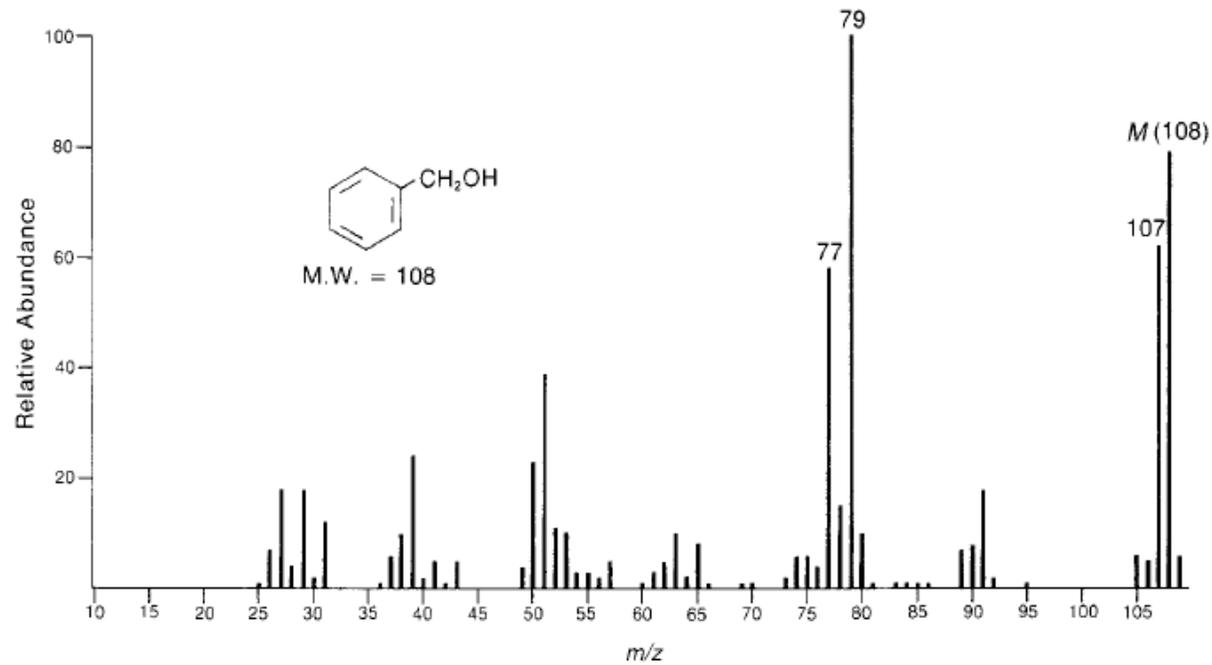
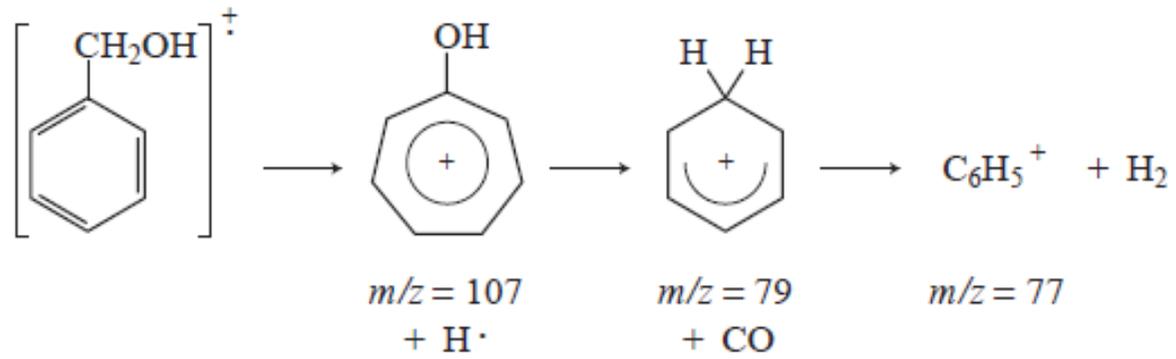


FIGURE 8.51 EI-MS of benzyl alcohol.

Phenol

MOLECULAR ION

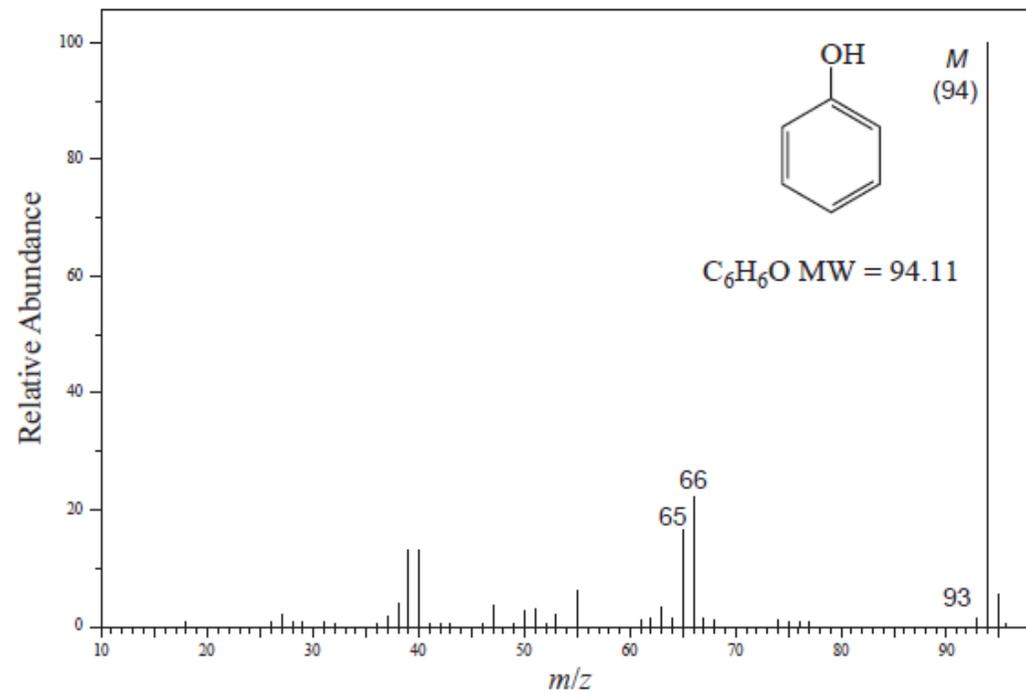
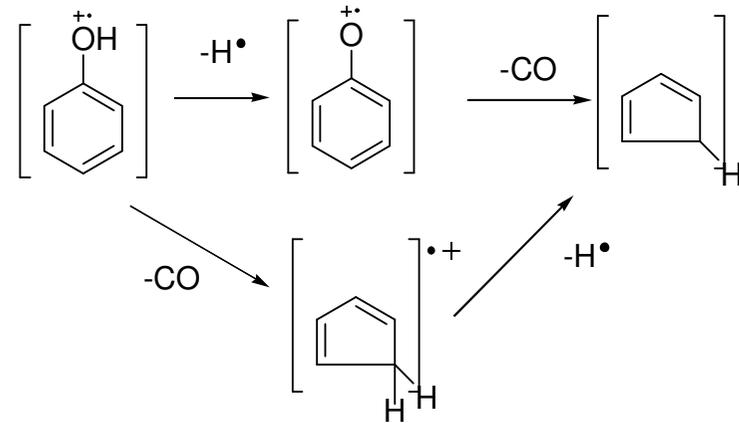
M^+ strong

FRAGMENT IONS

$M - 1$

$M - 28$

$M - 29$



Both fragmentation as Phenol and toluene will occur

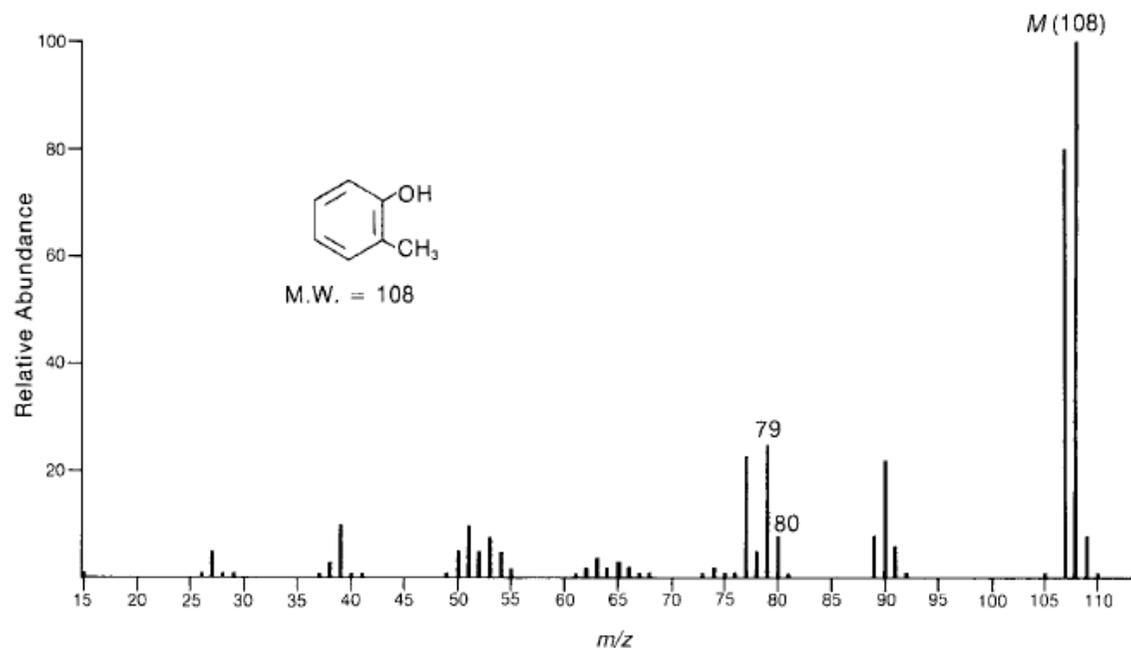
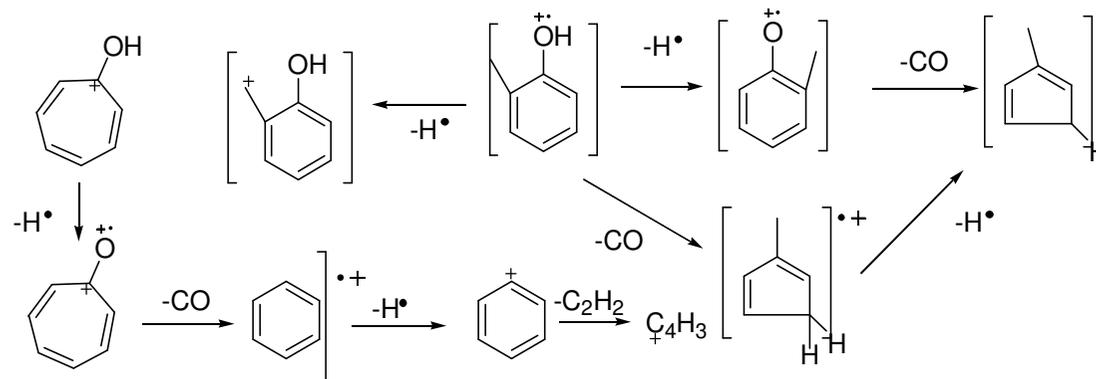


FIGURE 8.53 EI-MS of 2-methylphenol (*ortho*-cresol).

Ether fragmentation

MOLECULAR ION	FRAGMENT IONS
M^+ weak, but observable	α -Cleavage
	$m/z = 43, 59, 73, \text{ etc.}$
	$M - 31, M - 45, M - 59, \text{ etc.}$

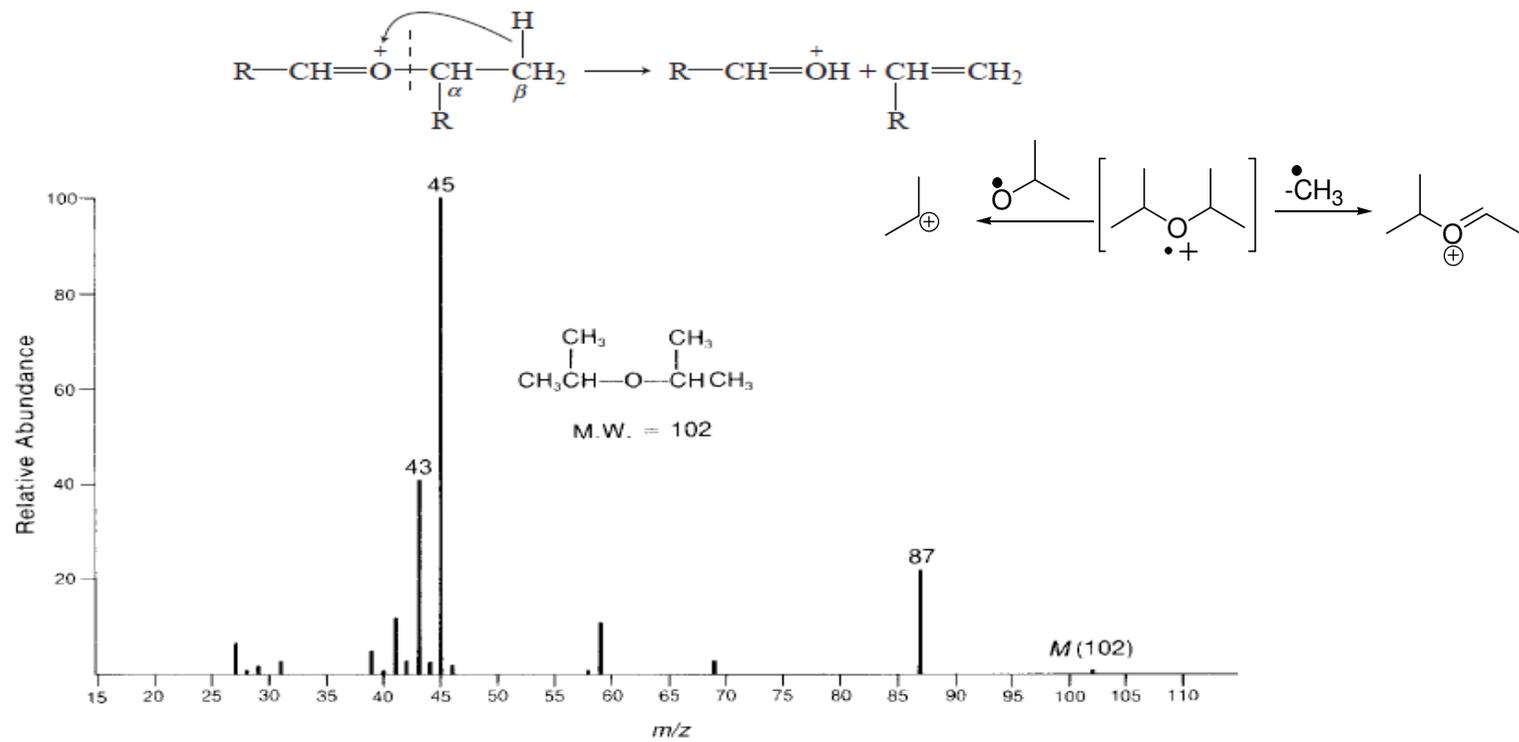
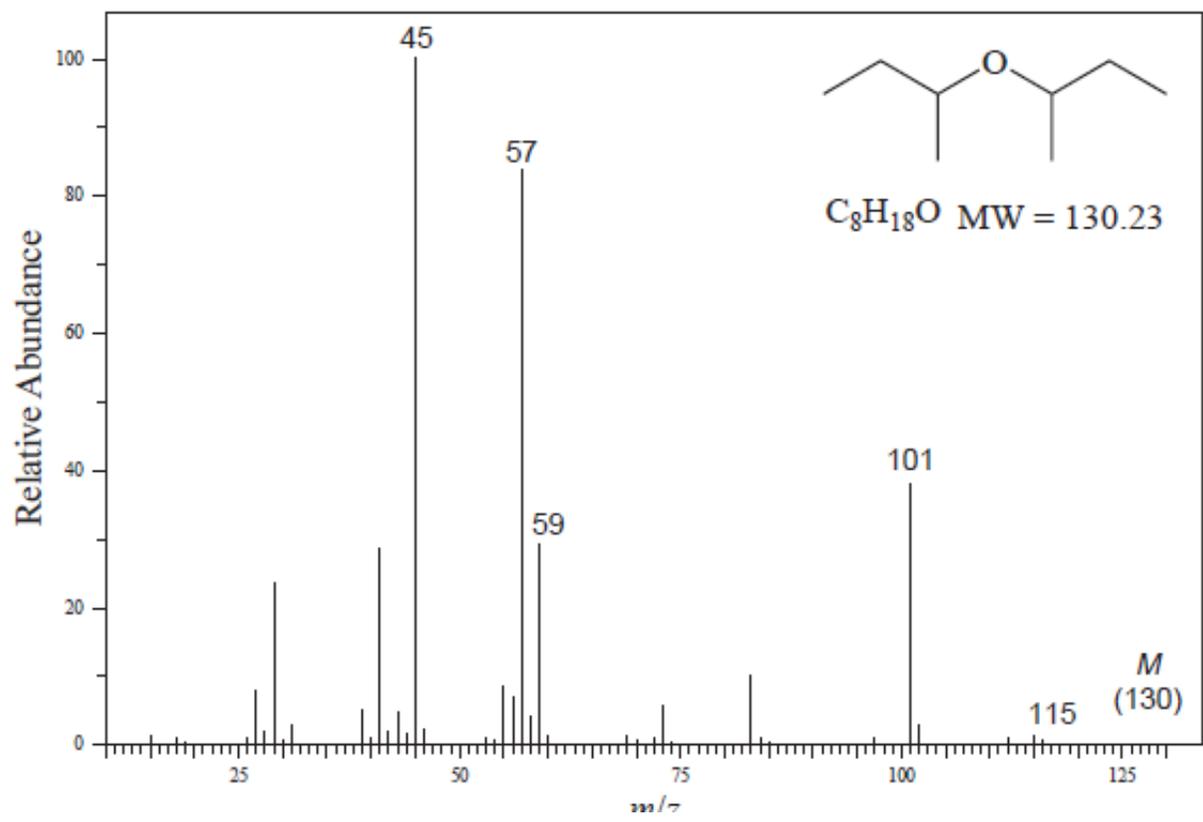
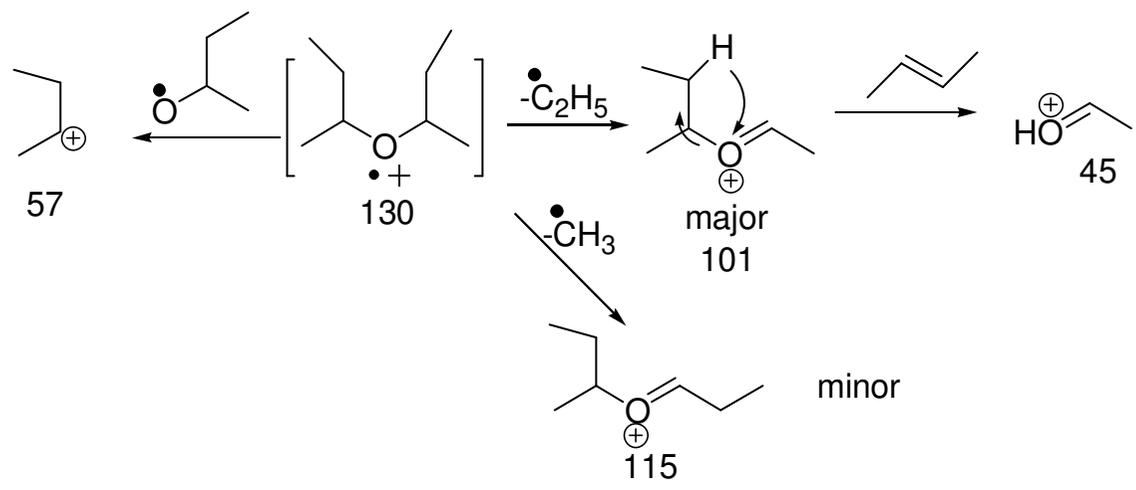


FIGURE 8.54 EI-MS of diisopropyl ether.



Aromatic ether

1. Aromatic ethers involve loss of the alkyl group to form $C_6H_5O^+$ ions.
2. These fragment ions then lose carbon monoxide to form cyclopentadienyl cations ($C_5H_5^+$).
3. In addition, an aromatic ether may lose the entire alkoxy group to yield phenyl cations ($C_6H_5^+$).
4. The mass spectrum of ethyl 4-methylphenyl ether (*p*-methylphenetole) exhibits a strong molecular ion at $m/z = 136$ as well as a fragment at $m/z = 107$ from loss of an ethyl radical (Fig. 8.57).
5. The base peak at $m/z = 108$ arises from loss of ethene via a McLafferty rearrangement.

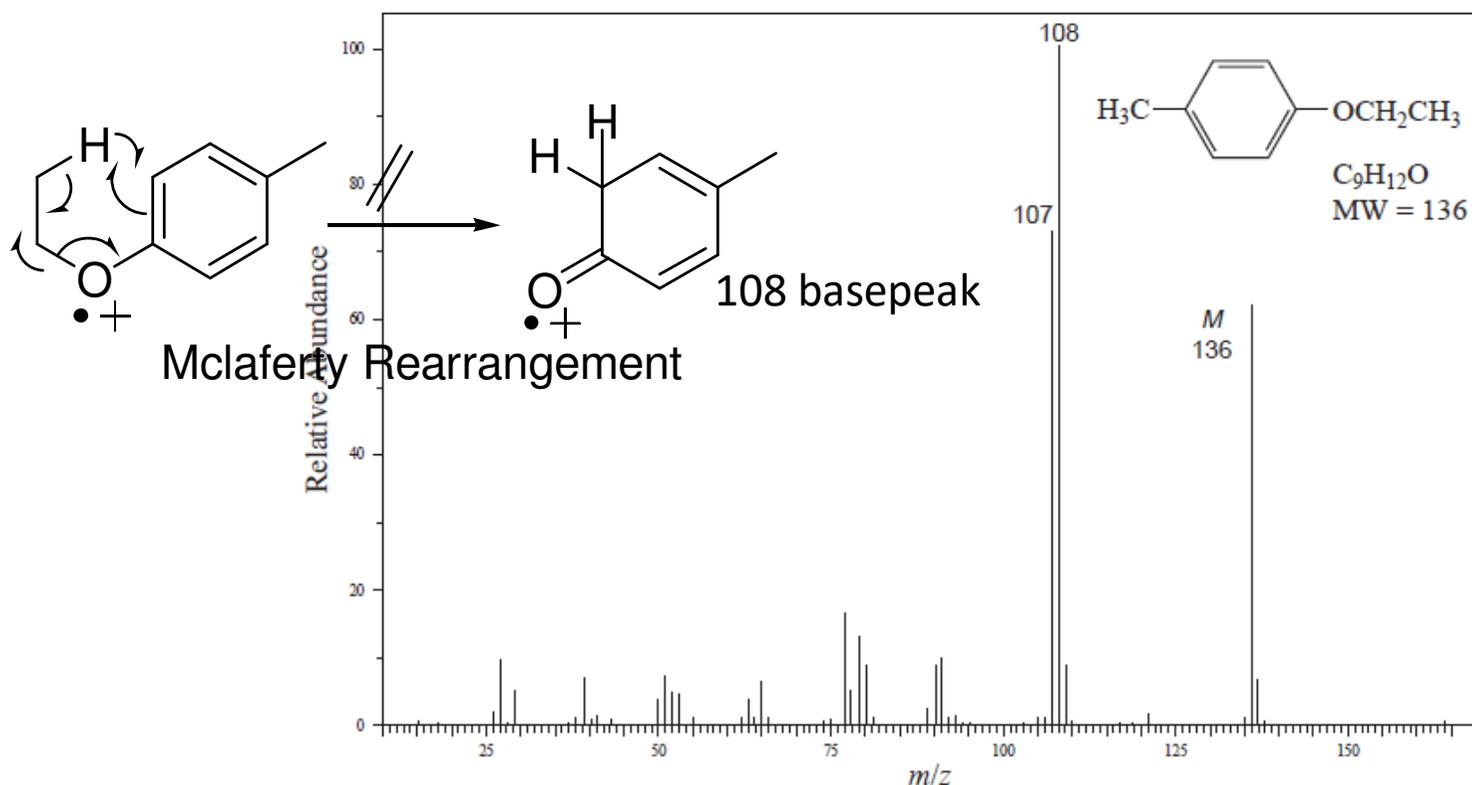


FIGURE 8.57 EI-MS of 4-methylphenetole.