

## Lecture # 7

# MASS SPECTROMETRY

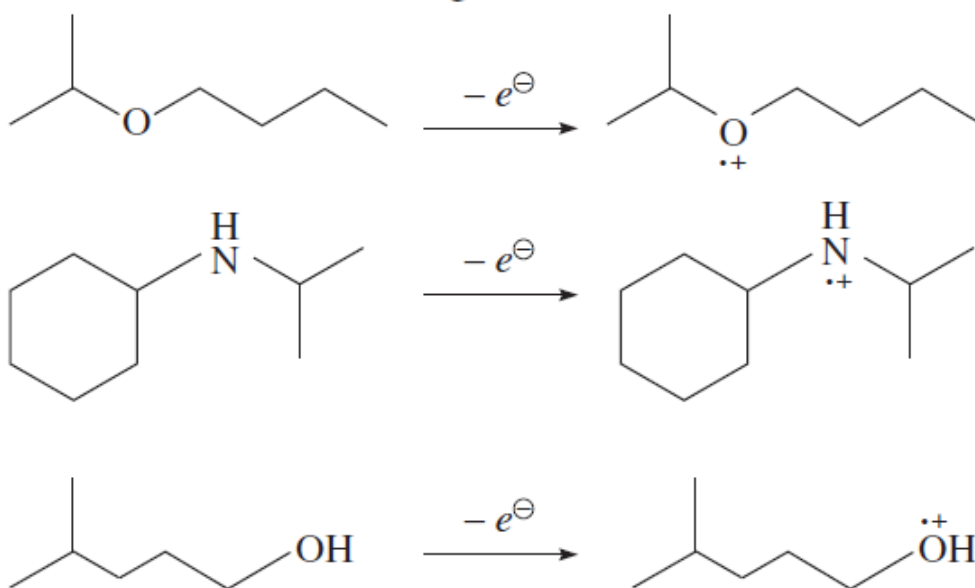
## Part Two: Fragmentation and Structural Analysis

If the lifetime of the molecular ion is greater than  $10^{-5}$  sec, a peak corresponding to the molecular ion will appear in the mass spectrum. However, molecular ions with lifetimes less than  $10^{-5}$  sec break apart into fragments before they are accelerated within the ionization chamber and enter the mass analyzer.

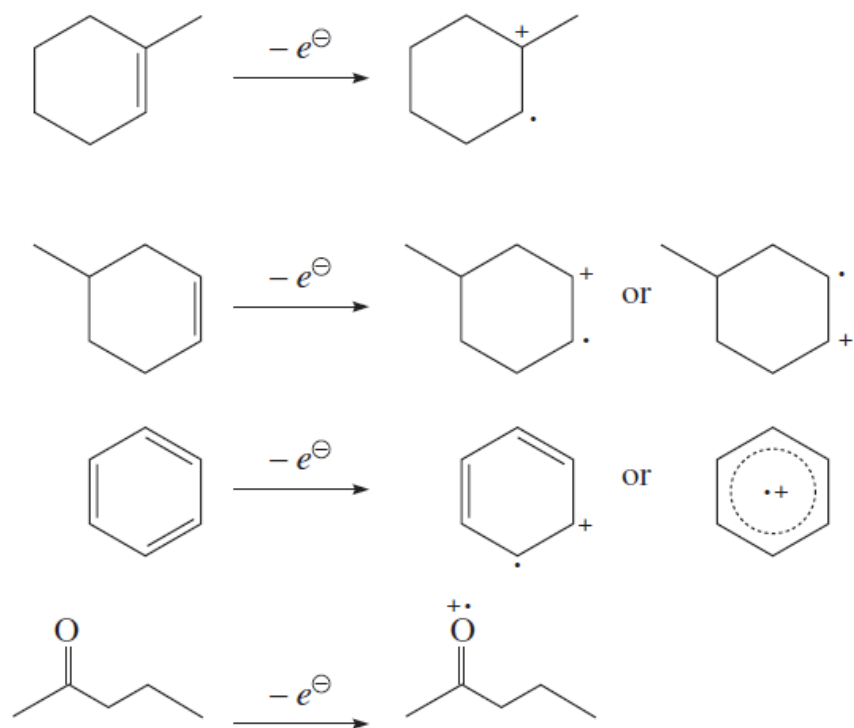
Odd electron ions ( $OE^{\bullet+}$ ) have even mass (if no nitrogen is

present in the compound; Section 3.6) and thus even electron ions ( $EE^+$ ) will have odd mass.

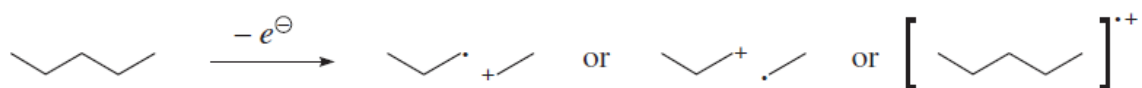
Loss of an electron from a non-bonding orbital:



Loss of an electron from a  $\pi$  orbital:

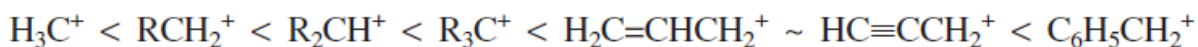


Loss of an electron from a  $\sigma$  orbital:



## 4.2 FUNDAMENTAL FRAGMENTATION PROCESSES

The unimolecular processes that are energetically most favorable give rise to the most fragment ions. This is the idea behind **Stevenson's Rule**: The most probable fragmentation is the one that leaves the positive charge on the fragment with the lowest ionization energy. In other words, fragmentation processes that lead to the formation of more stable ions are favored over processes that lead to less stable ions.



*difficult*

*easy*

### Radical-Site-Initiated Cleavage: $\alpha$ -Cleavage

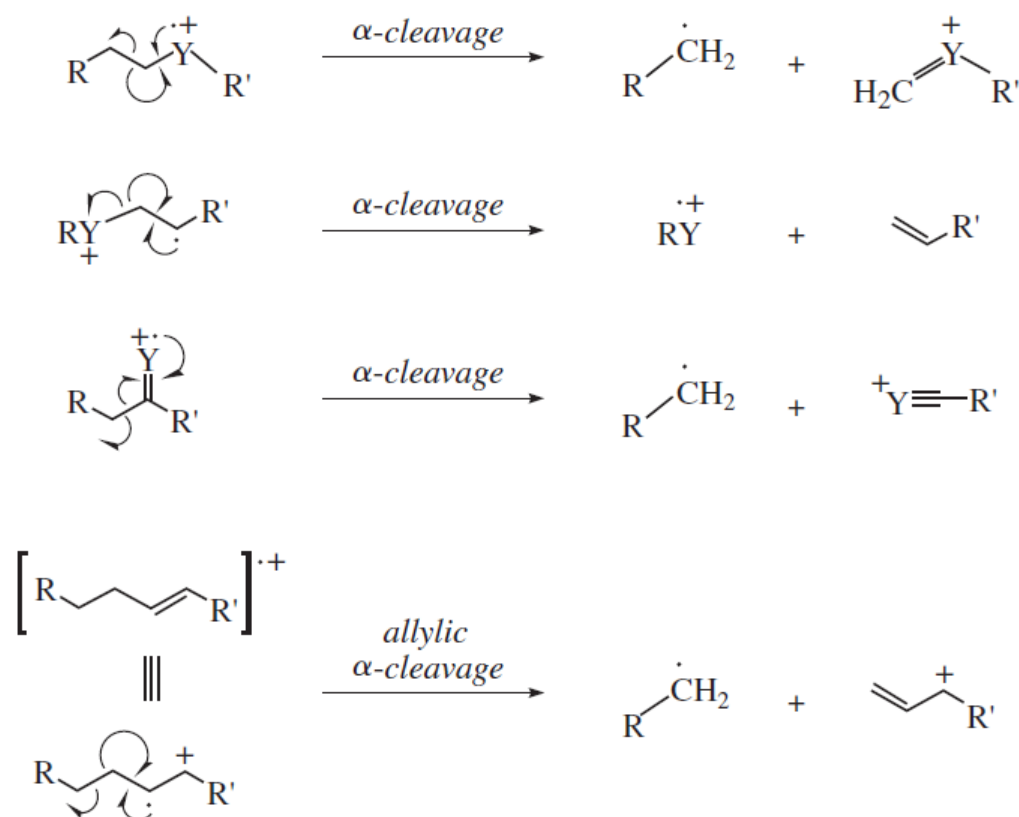


FIGURE 4.1 Representative  $\alpha$ -cleavage fragmentations ( $\text{Y}$  = heteroatom).



## Retro Diels-Alder Cleavage

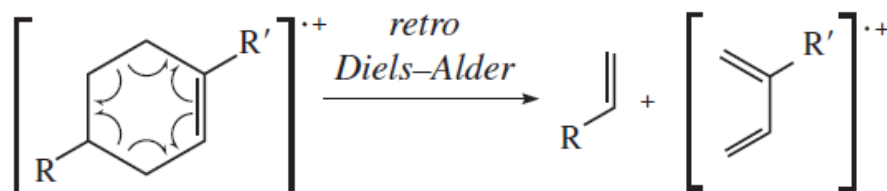


FIGURE 4.4 A retro Diels–Alder fragmentation.

## McLafferty Rearrangements

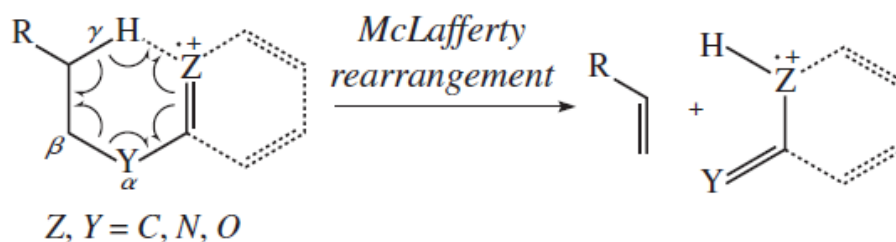


FIGURE 4.5 The McLafferty rearrangement.

## Other Cleavage Types

In addition to these processes, fragmentation processes involving rearrangements, migrations of groups, and secondary fragmentations of fragment ions are also possible. These modes of fragmentation occur less often than the two cases already described, and additional discussion of them will be reserved for the compounds in which they are important.

## 4.3 FRAGMENTATION PATTERN OF HYDROCARBONS

### A. Alkanes

The mass spectra of alkanes are characterized by strong molecular ion peaks and a regular series of fragment ion peaks separated by 14 amu.

For a straight-chain, or “normal,” alkane, a peak corresponding to the molecular ion can be observed as in the mass spectra of butane (Fig. 4.6) and octane (Fig. 4.7). As the carbon skeleton becomes more highly branched, the intensity of the molecular ion peak decreases. Straight-chain alkanes have fragments that are always primary carbocations. Since these ions are rather unstable, fragmentation is not favored. A significant number of the original molecules survive electron bombardment without fragmenting. Consequently, a molecular ion peak of significant intensity is observed. You will

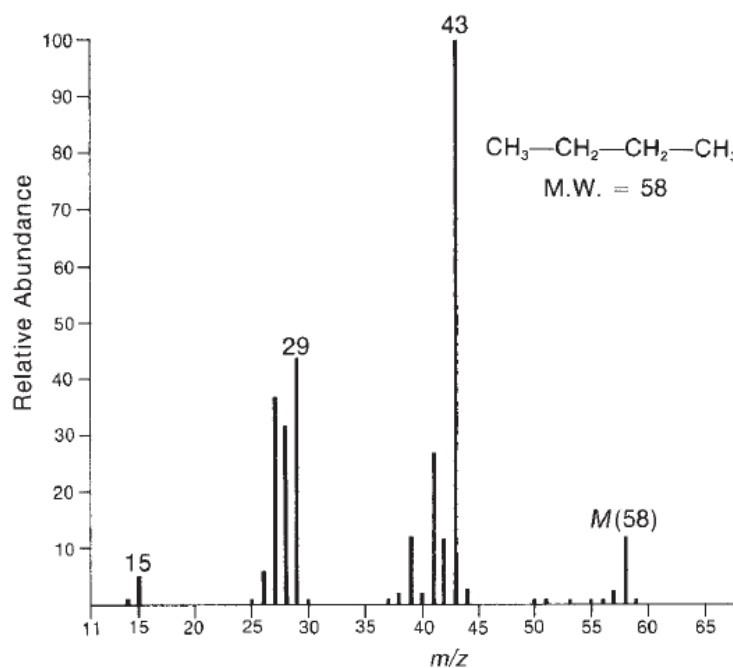


FIGURE 4.6 Mass spectrum of butane.

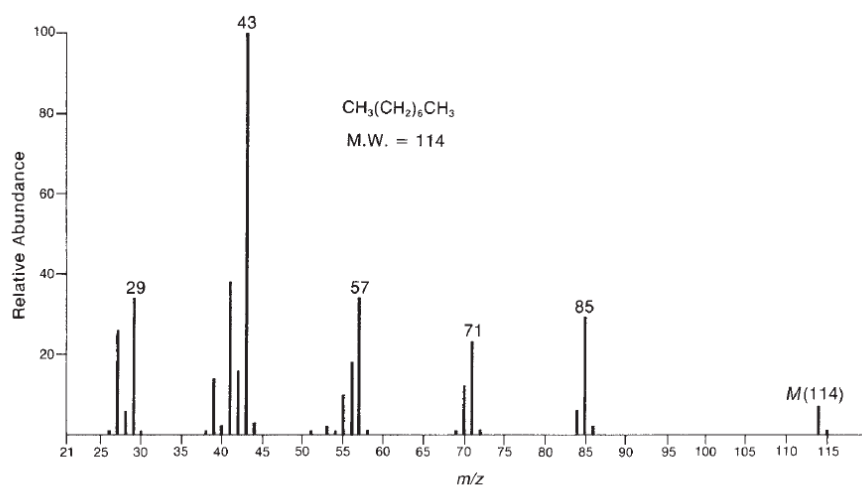


FIGURE 4.7 EI mass spectrum of octane.

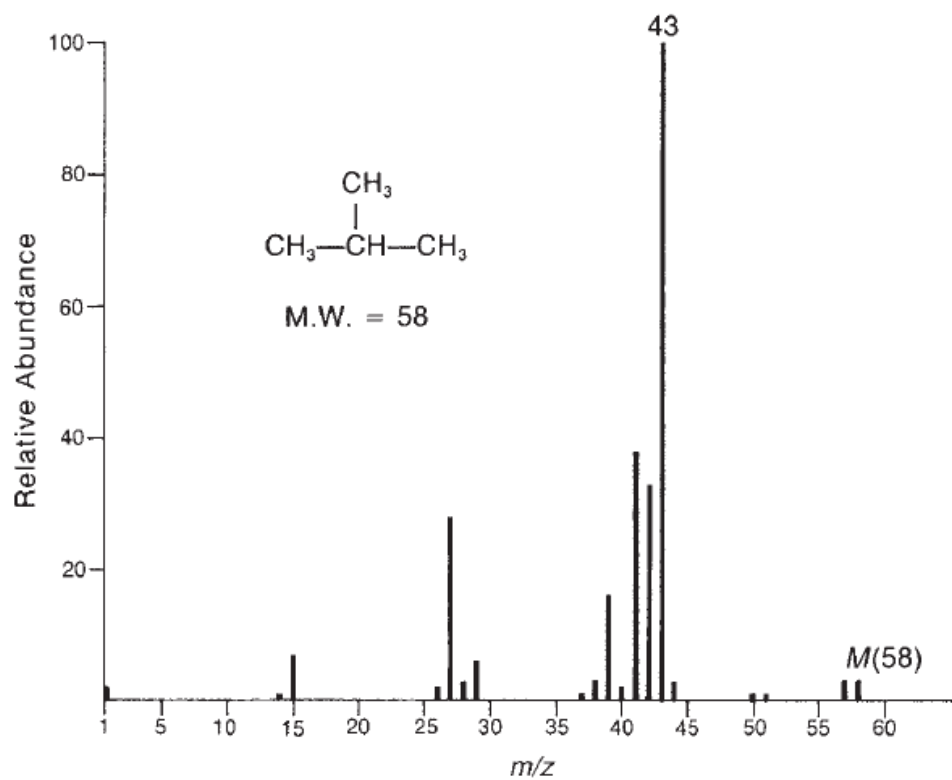


FIGURE 4.8 EI mass spectrum of isobutane.

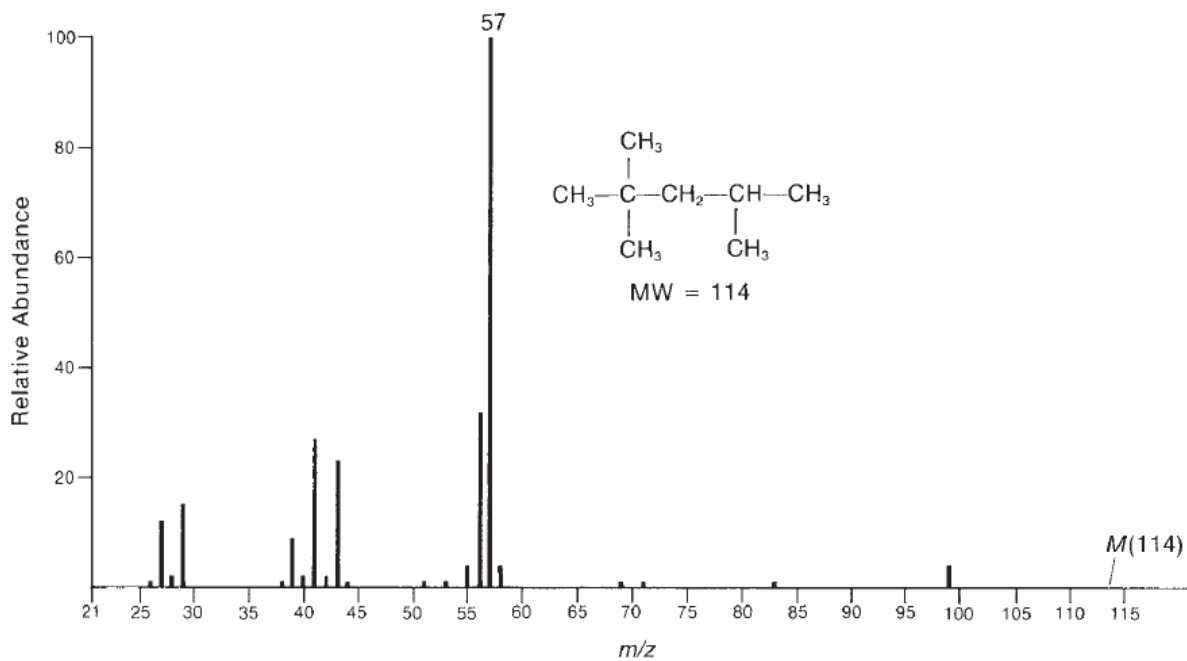


FIGURE 4.9 EI mass spectrum of 2,2,4-trimethylpentane (isooctane).

## B. Cycloalkanes

Cycloalkanes generally form strong molecular ion peaks. Fragmentation via the loss of a molecule of ethene ( $M - 28$ ) is common. The typical mass spectrum for a cycloalkane shows a relatively intense molecular ion peak. Fragmentation of ring compounds requires the cleavage of two carbon-carbon bonds, which is a more difficult process than cleavage of one such bond. Therefore, a larger proportion of cycloalkane molecules than of acyclic alkane molecules survives electron bombardment without undergoing fragmentation. In the mass spectra of cyclopentane (Fig. 4.10) and methylcyclopentane (Fig. 4.11), strong molecular ion peaks can be observed.

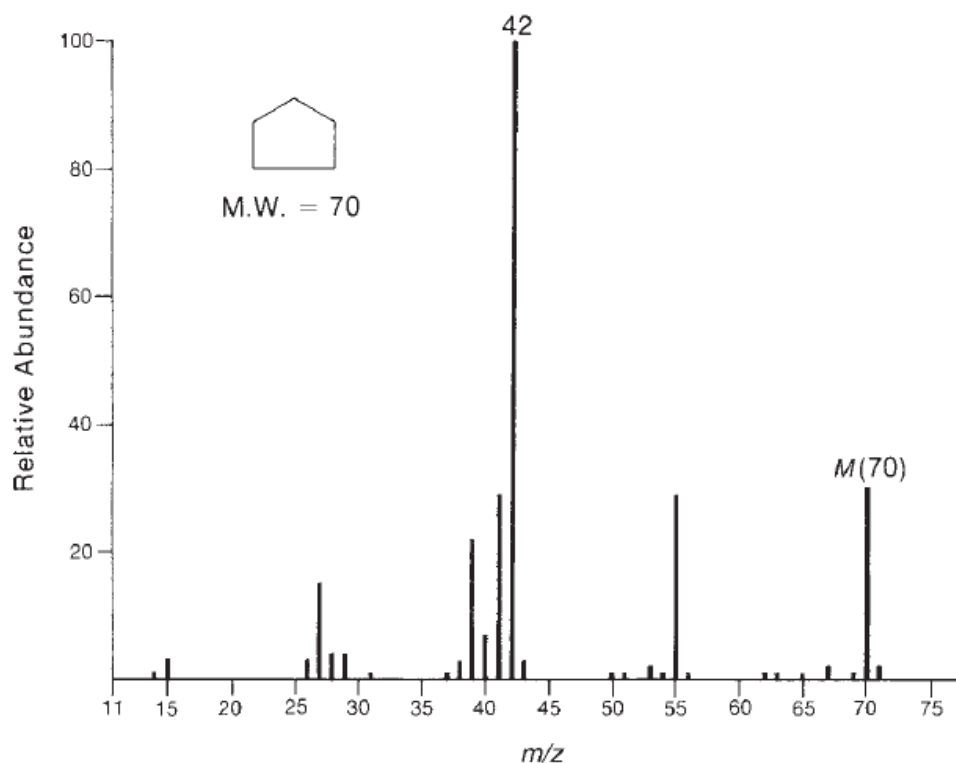
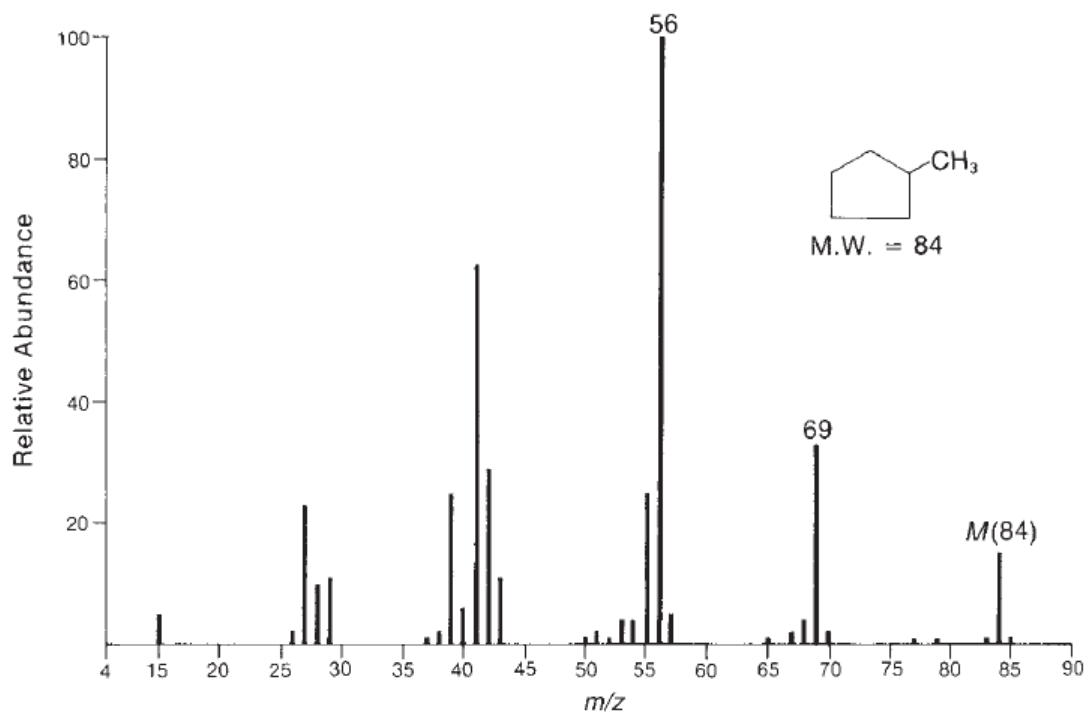


FIGURE 4.10 EI mass spectrum of cyclopentane.





**FIGURE 4.11** EI mass spectrum of methylcyclopentane.

mass spectrum. When the cycloalkane bears a side chain, loss of that side chain is a favorable mode of fragmentation. The fragment peak at  $m/z = 69$  in the mass spectrum of methylcyclopentane is due to the loss of the  $\text{CH}_3$  side chain, which results in a secondary carbocation.

#### SPECTRAL ANALYSIS BOX — Cycloalkanes

##### MOLECULAR ION

Strong  $M^+$

##### FRAGMENT IONS

$M - 28$

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

Applying these pieces of information to the mass spectrum of bicyclo[2.2.1]heptane (Fig. 4.12), we can identify fragment peaks due to the loss of the side chain (the one-carbon bridge, plus an additional hydrogen atom) at  $m/z = 81$  and the loss of ethene at  $m/z = 68$ . The fragment ion peak at  $m/z = 67$  is due to the loss of ethene plus an additional hydrogen atom.

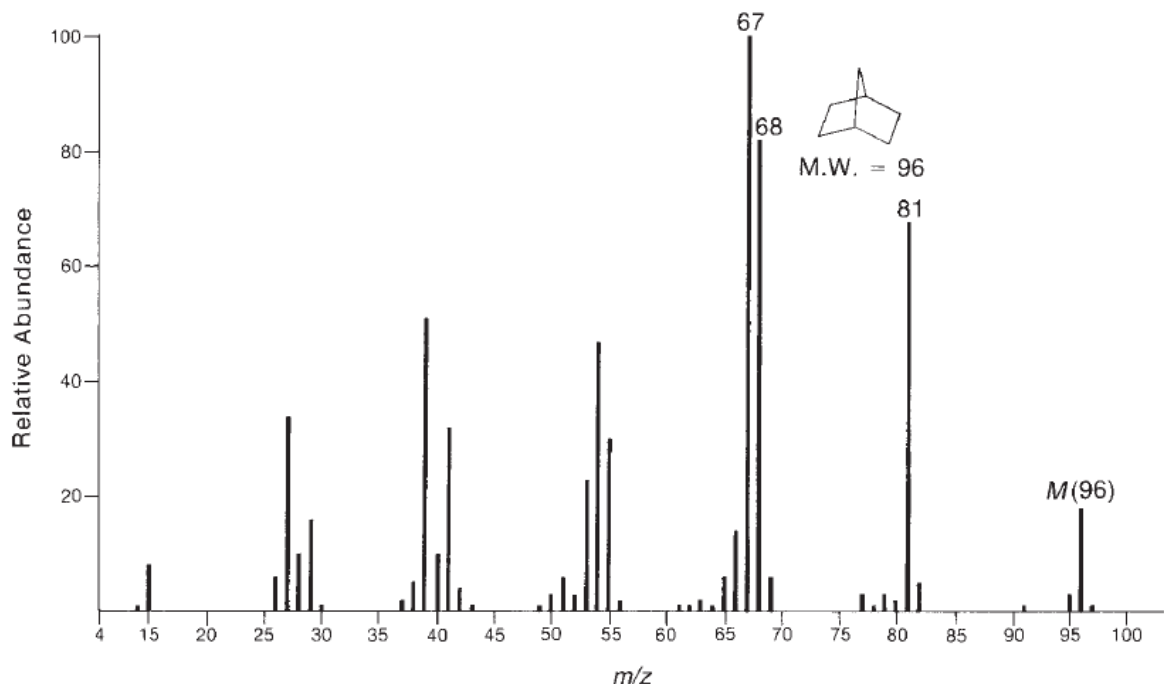


FIGURE 4.12 EI mass spectrum of bicyclo[2.2.1]heptane (norbornane).

## C. Alkenes

The mass spectra of most alkenes show distinct molecular ion peaks. Naturally, the mass of the molecular ion should correspond to a molecular formula with an index of hydrogen deficiency equal to at least *one* (see Chapter 1). Apparently, electron bombardment removes one of the electrons in the  $\pi$  bond, leaving the carbon skeleton relatively undisturbed. When alkenes undergo fragmentation processes, the resulting fragment ions have formulas corresponding to  $C_nH_{2n}^+$  and  $C_nH_{2n-1}^+$ . It is sometimes difficult to locate double bonds in alkenes since they migrate readily. The similarity of

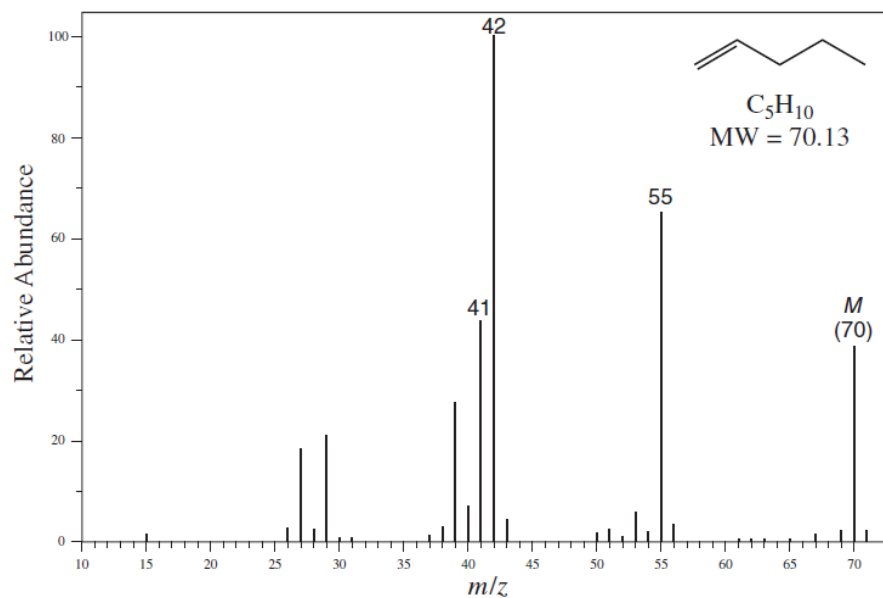


FIGURE 4.13 EI-MS spectrum of 1-pentene.

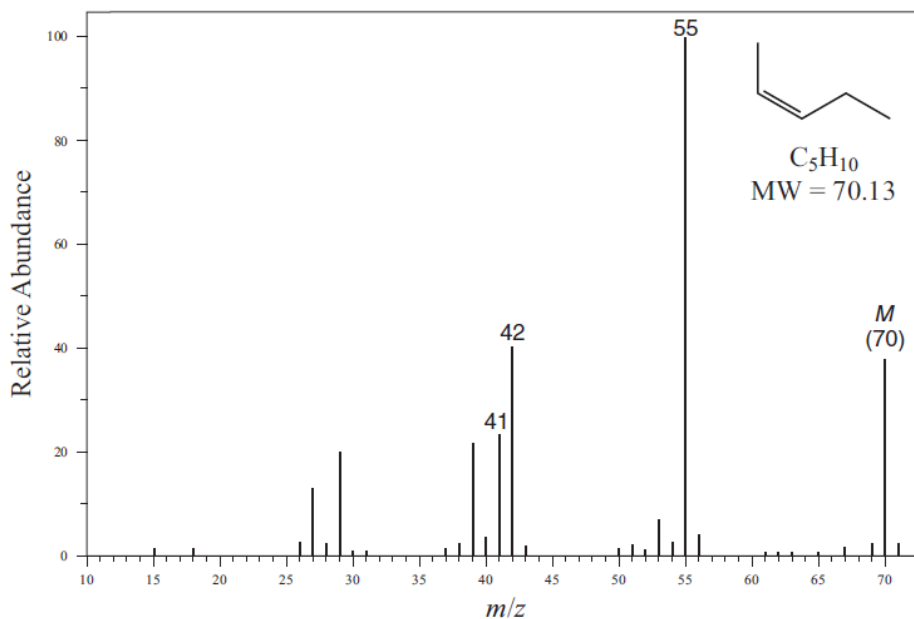


FIGURE 4.14 EI-MS spectrum of Z-2-pentene.

### SPECTRAL ANALYSIS BOX — Alkenes

#### MOLECULAR ION

Strong  $M^+$

#### FRAGMENT IONS

$m/z = 41$

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