

## Lecture #8

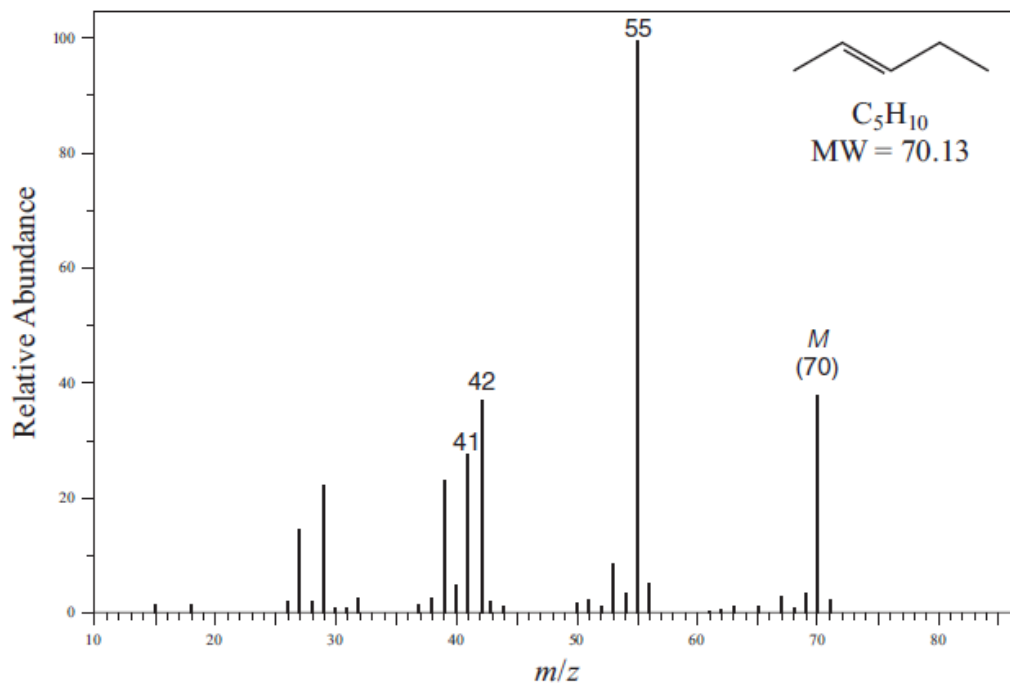


FIGURE 4.15 EI-MS spectrum of *E*-2-pentene.

The mass spectra of cycloalkenes show quite distinct molecular ion peaks. For many cycloalkenes, migration of bonds gives virtually identical mass spectra. Consequently, it may be impossible to locate the position of the double bond in a cycloalkene, particularly a cyclopentene or a cycloheptene. Cyclohexenes do have a characteristic fragmentation pattern that corresponds to a retro Diels–Alder reaction (Fig. 4.4). In the mass spectrum of the monoterpene limonene (Fig. 4.16), the intense peak at  $m/z = 68$  corresponds to the diene fragment arising from the retro Diels–Alder fragmentation.

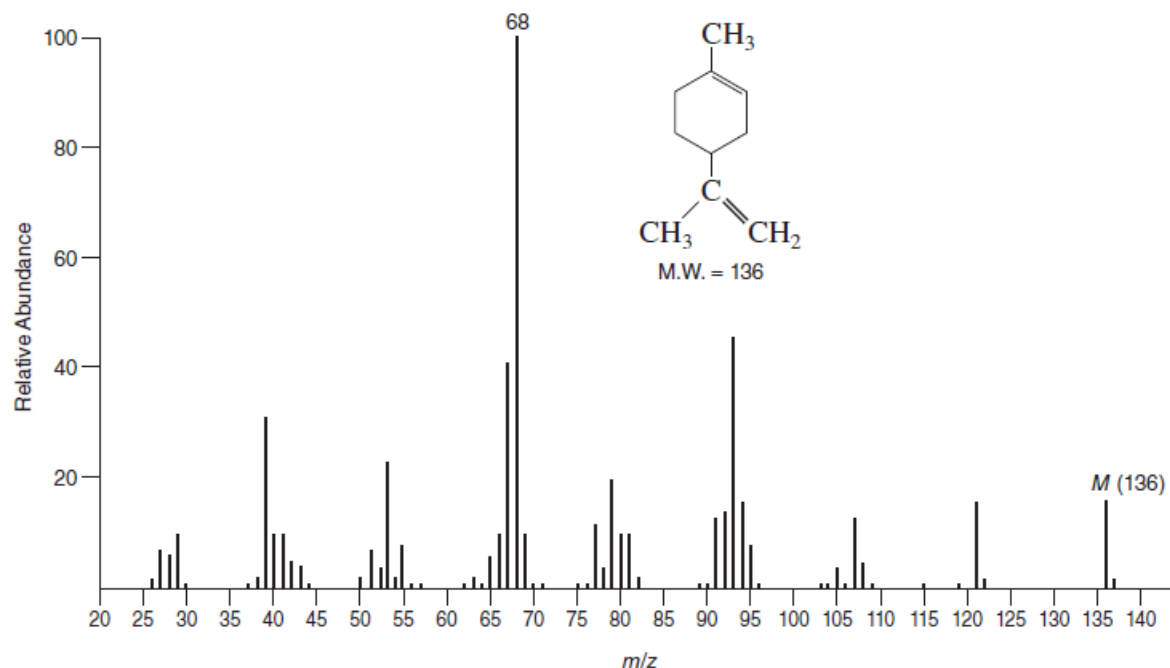


FIGURE 4.16 EI-MS spectrum of limonene.

The mere presence of a cyclohexene moiety does not guarantee that a retro Diels–Alder fragmentation will be observed in the mass spectrum. Consider the mass spectra of  $\alpha$ - and  $\beta$ -ionone (Fig. 4.17). The spectrum of  $\alpha$ -ionone shows much more fragmentation in general and a peak at  $m/z = 136$  in particular that is created by a retro Diels–Alder fragmentation of the cyclohexene ring and loss of isobutene. Retro Diels–Alder fragmentation of  $\beta$ -ionone should give a peak at  $m/z = 164$  from loss of ethene, but the peak at that position is miniscule. In the case of  $\beta$ -ionone, loss of a methyl radical via  $\alpha$ -cleavage adjacent to the ring double bond yields a relatively stable tertiary allylic cation. This fragmentation is not available to  $\alpha$ -ionone.

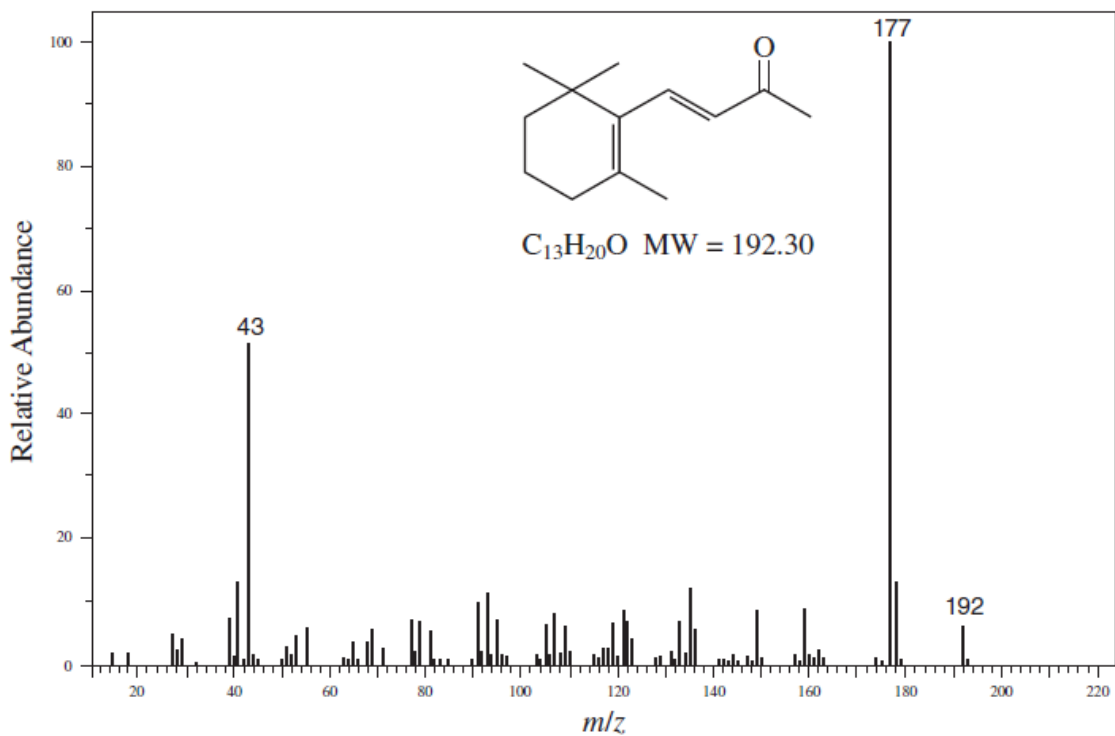
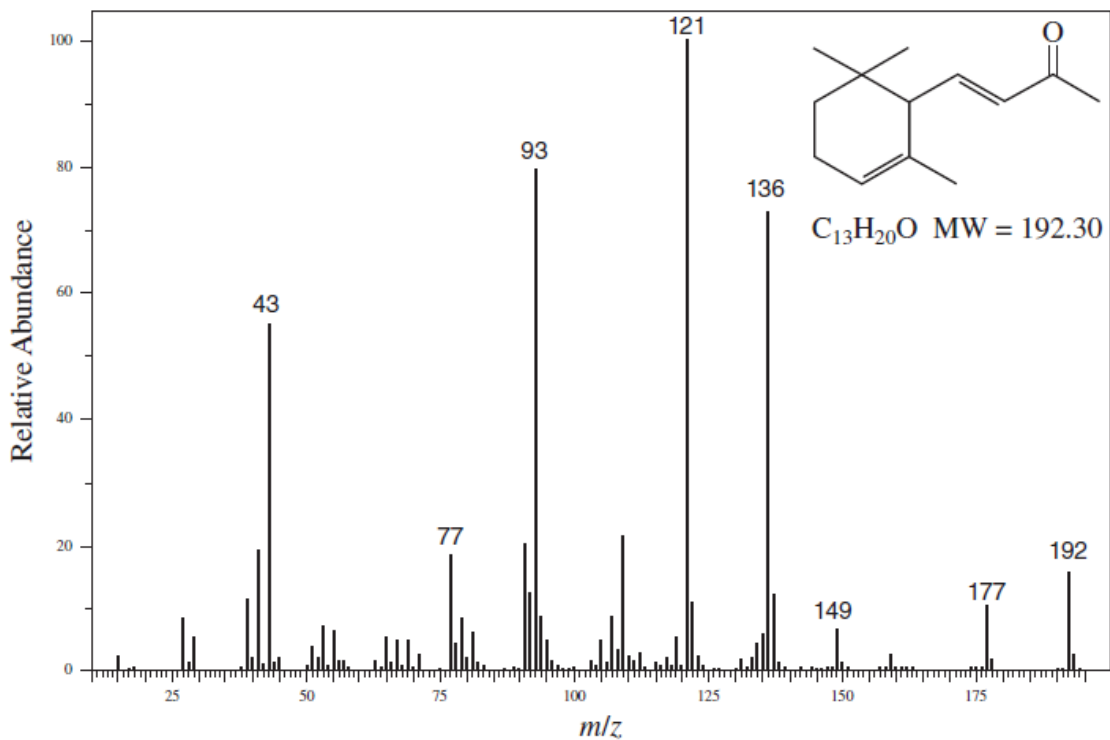


FIGURE 4.17 EI-MS spectra of  $\alpha$ -ionone (top) and  $\beta$ -ionone (bottom).

## D. Alkynes

The mass spectra of alkynes are very similar to those of alkenes. The molecular ion peaks tend to be rather intense, and fragmentation patterns parallel those of the alkenes. As can be seen from the mass spectrum of 1-pentyne (Fig. 4.18), an important fragmentation is the loss of an ethyl radical via an  $\alpha$ -cleavage to produce the propargyl ion ( $m/z = 39$ ). Similarly, loss of methyl radical in an  $\alpha$ -cleavage

of 2-pentyne produces a resonance-stabilized propargylic cation at ( $m/z = 53$ ) (Fig. 4.19). Another important mode of fragmentation for terminal alkynes is the loss of the terminal hydrogen, yielding a strong  $M - 1$  peak. This peak appears as the base peak ( $m/z = 67$ ) in the spectrum of 1-pentyne.

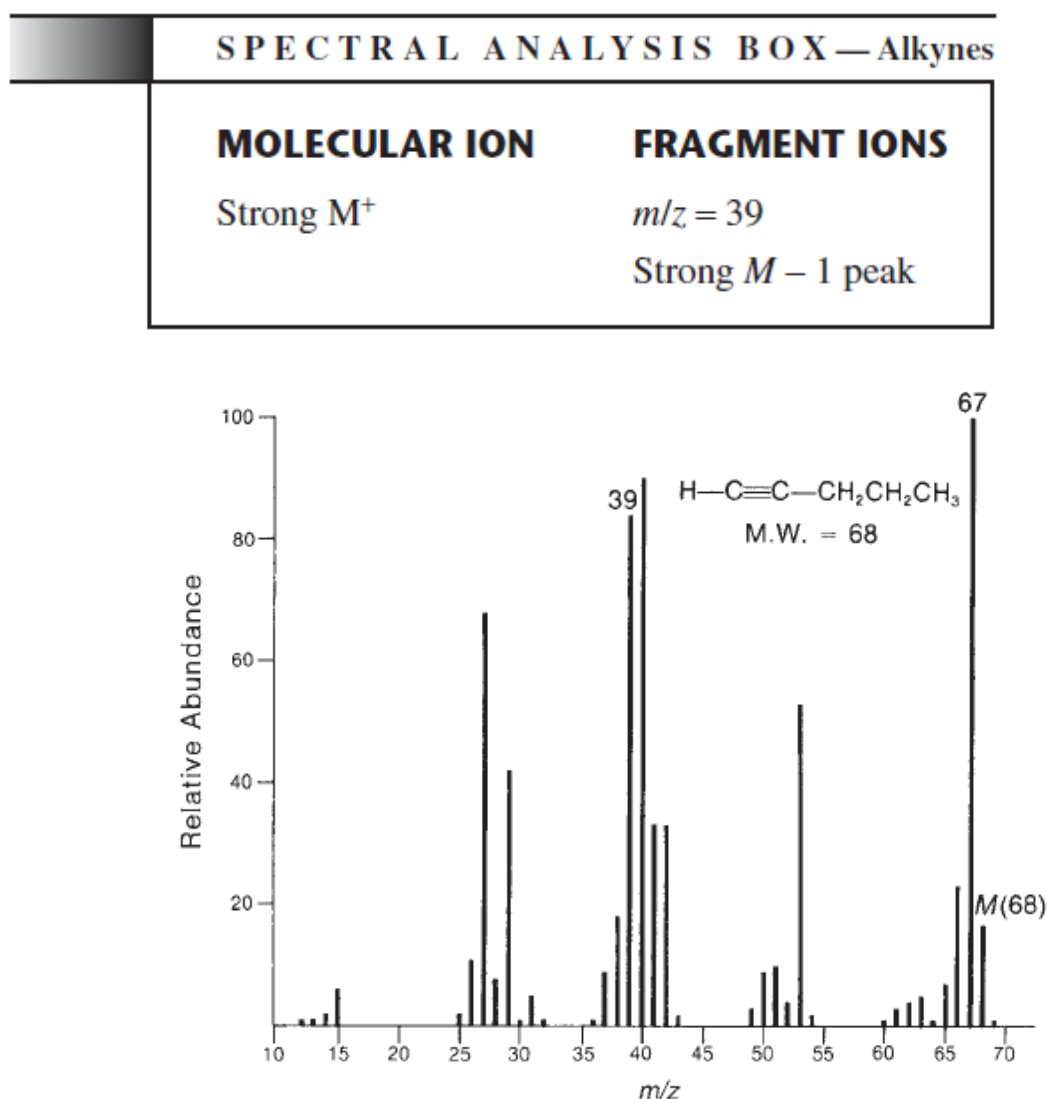


FIGURE 4.18 EI-MS spectrum of 1-pentyne.

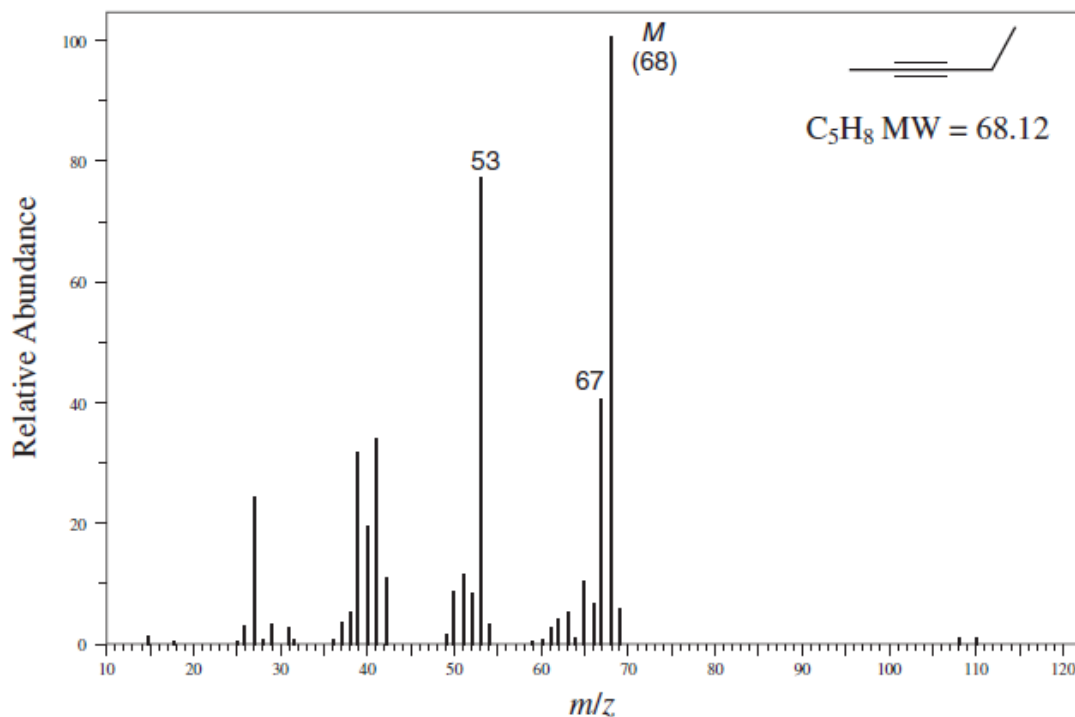


FIGURE 4.19 EI-MS spectrum of 2-pentyne.

### E. Aromatic Hydrocarbons

The mass spectra of most aromatic hydrocarbons show intense molecular ion peaks. As is evident from the mass spectrum of benzene (Fig. 4.20), fragmentation of the benzene ring requires a great deal of energy. Such fragmentation is not observed to any significant extent. In the mass spectrum of toluene (Fig. 4.21), loss of a hydrogen atom from the molecular ion gives a strong peak at  $m/z = 91$ . Although it might be expected that this fragment ion peak is due to the benzyl carbocation ( $C_6H_5CH_2^+$ ), isotope-labeling experiments suggest that the benzyl carbocation actually rearranges to form the aromatic delocalized **tropylium ion** ( $C_7H_7^+$ , Figure 4.25). When a benzene ring contains larger side chains, a favored mode of fragmentation is cleavage of the side chain to form initially a **benzyl cation**, which spontaneously rearranges to the tropylium ion. When the side chain attached to a benzene ring contains three or more carbons, ions formed by a McLafferty rearrangement can be observed.

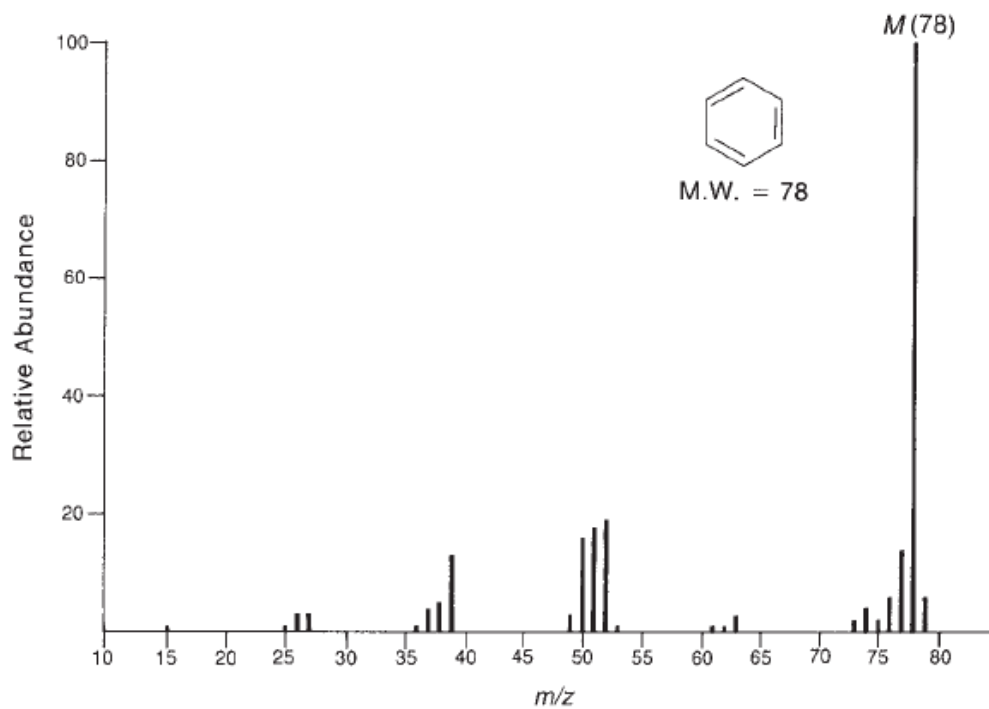


FIGURE 4.20 EI-MS spectrum of benzene.

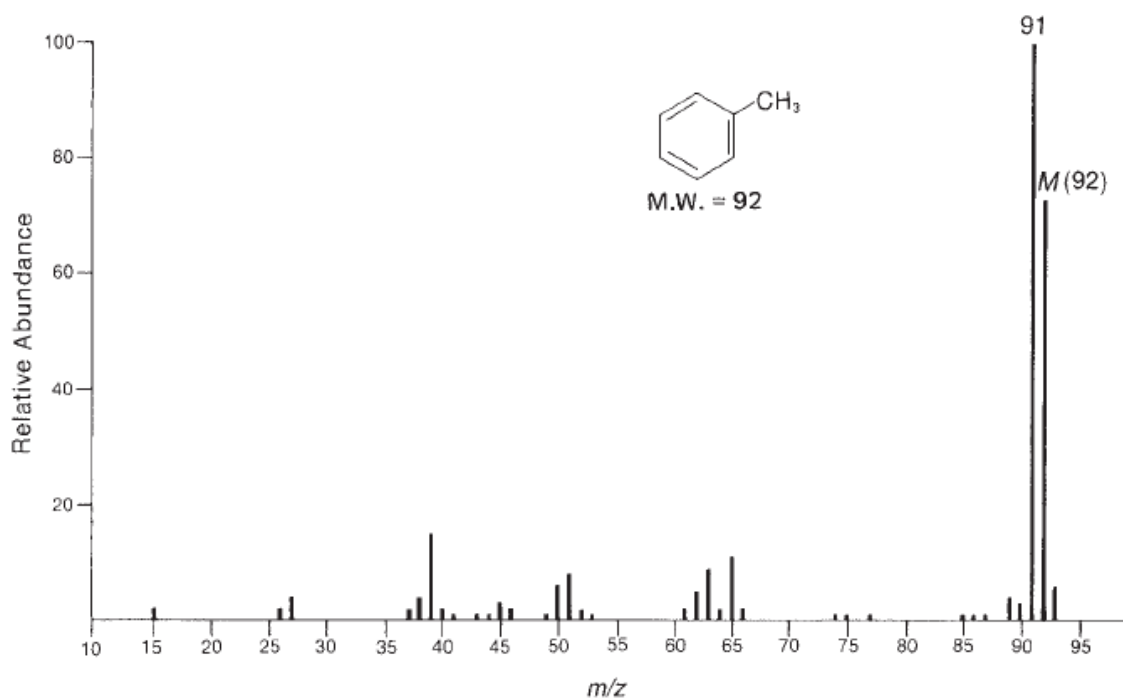


FIGURE 4.21 EI-MS spectrum of toluene.

The mass spectra of the xylene isomers (Figs. 4.22 and 4.23 for example) show a medium peak at  $m/z = 105$ , which is due to the loss of a hydrogen atom and the formation of the methyltropylium ion. More importantly, xylene loses one methyl group to form the tropylium ( $m/z = 91$ ). The mass spectra of *ortho*-, *meta*-, and *para*-disubstituted aromatic rings are essentially identical. As a result, the substitution pattern of polyalkylated benzenes cannot be determined by mass spectrometry.

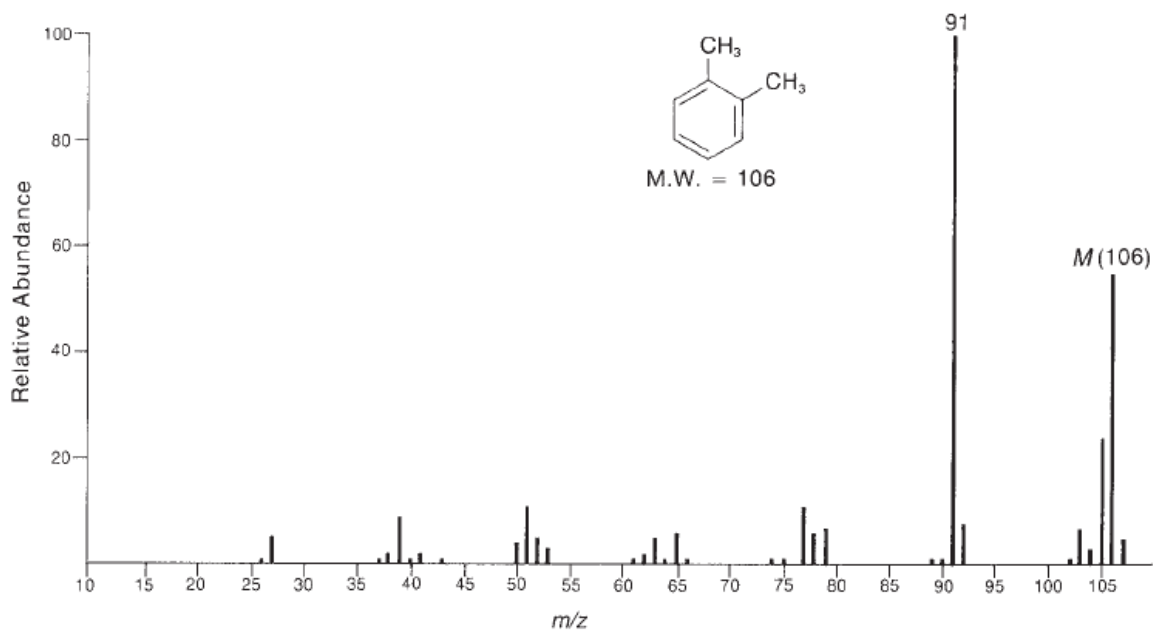


FIGURE 4.22 EI-MS spectrum of *ortho*-xylene.

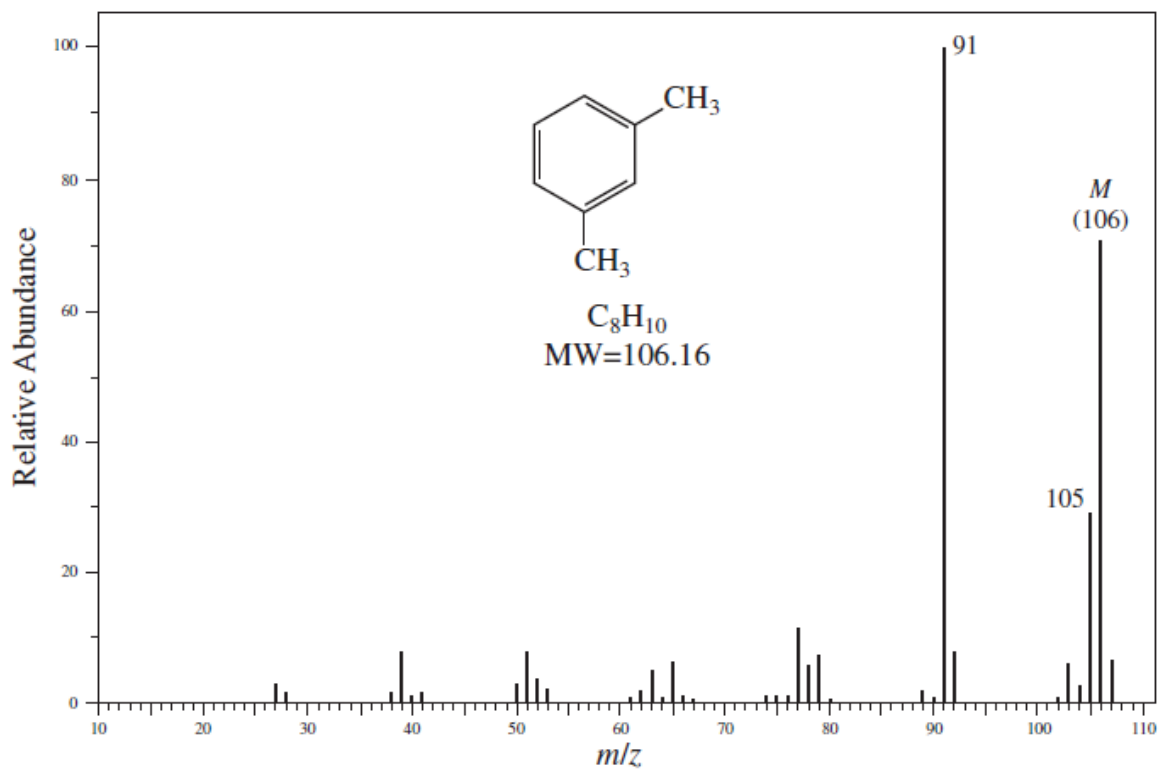


FIGURE 4.23 EI-MS spectrum of *meta*-xylene.

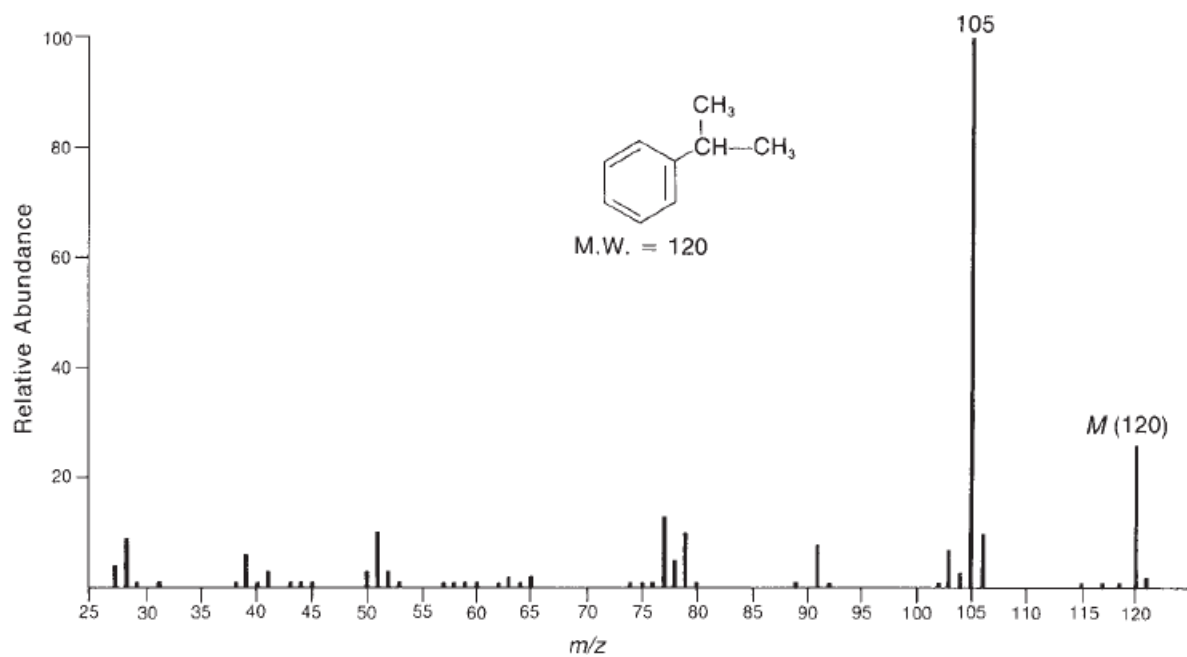


FIGURE 4.24 EI-MS of isopropylbenzene (cumene).



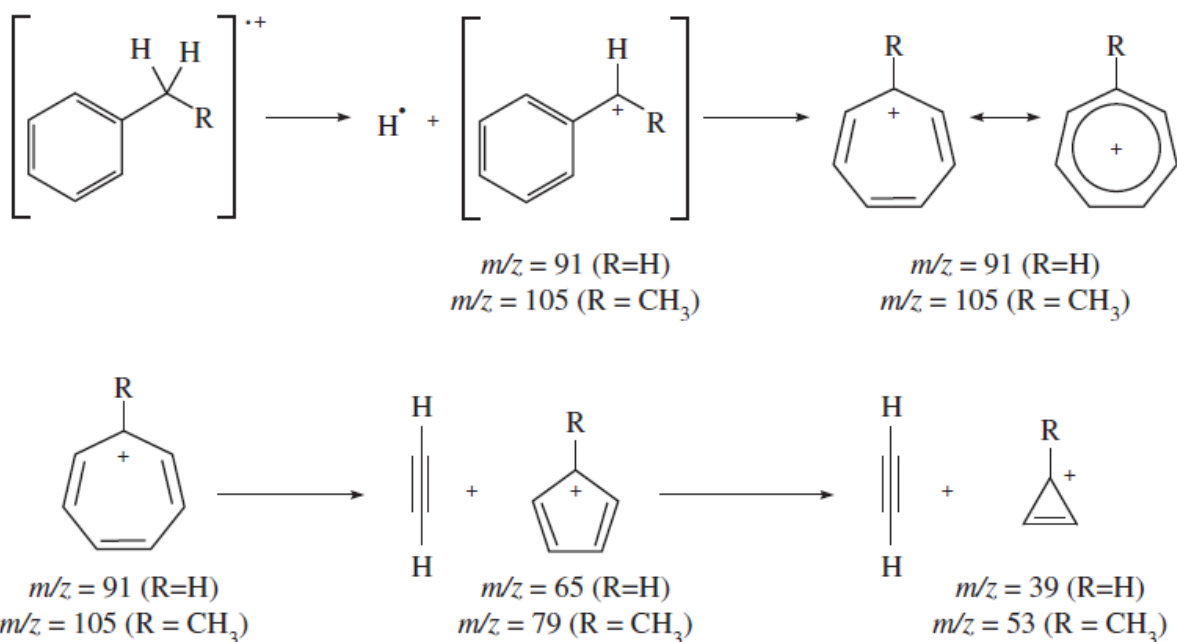


FIGURE 4.25 Formation and fragmentation of the tropylium ion.

#### 4.4 FRAGMENTATION PATTERNS OF ALCOHOLS, PHENOLS, AND THIOLS

The intensity of the molecular ion peak in the mass spectrum of a primary or secondary alcohol is usually rather low, and the molecular ion peak is often entirely absent in the mass spectrum of a tertiary alcohol. Common fragmentations of alcohols are  $\alpha$ -cleavage adjacent to the hydroxyl group and dehydration.

#### SPECTRAL ANALYSIS BOX — Alcohols

##### MOLECULAR ION

$M^+$  weak or absent

##### FRAGMENT IONS

Loss of alkyl group

$M - 18$

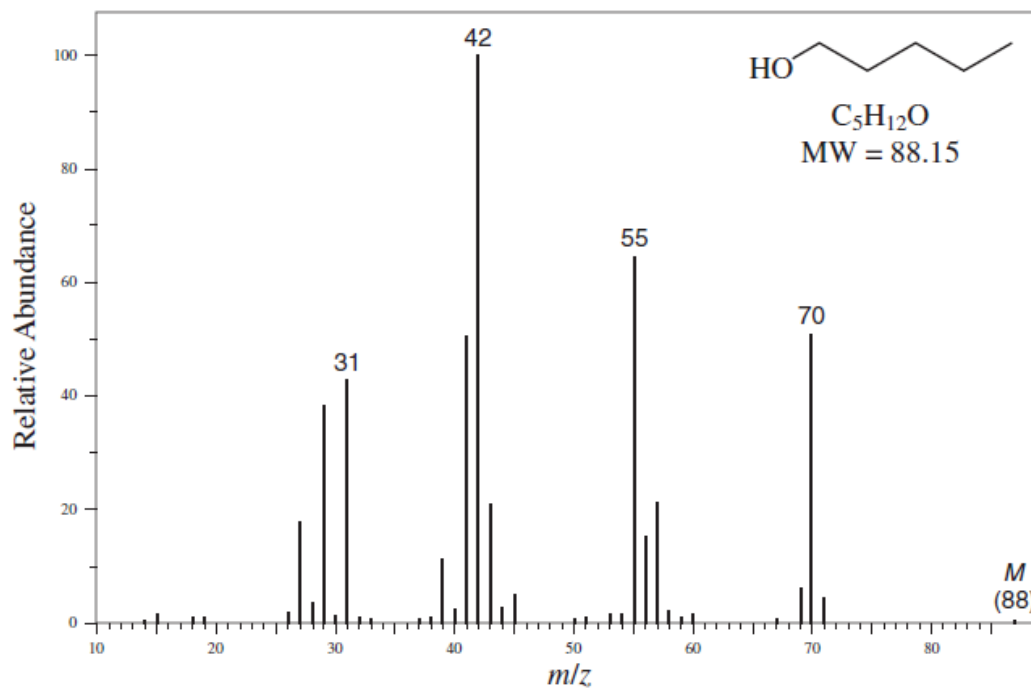


FIGURE 4.27 EI-MS of 1-pentanol.

The mass spectrum of straight-chain pentanol isomers, 1-pentanol (Fig. 4.27), 2-pentanol (Figure 4.28), and 3-pentanol (Fig. 4.29) all exhibit very weak molecular ion peaks at  $m/z = 88$ , while the molecular ion in the mass spectrum of the tertiary alcohol 2-methyl-2-butanol (Fig. 4.30) is entirely absent. The most important fragmentation reaction for alcohols is the loss of an alkyl group via  $\alpha$ -cleavage. As discussed earlier, the largest alkyl group is most readily lost. In the spectrum of 1-pentanol (Fig. 4.27), the peak at  $m/z = 31$  is due to the loss of a butyl group to form an  $\text{H}_2\text{C}=\text{OH}^+$  ion. 2-Pentanol (Fig. 4.28) loses either a propyl group to form the  $\text{CH}_3\text{CH}=\text{OH}^+$  fragment at  $m/z = 45$  or a methyl radical to form the relatively small peak at  $m/z = 73$  corresponding to  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{OH}^+$ .

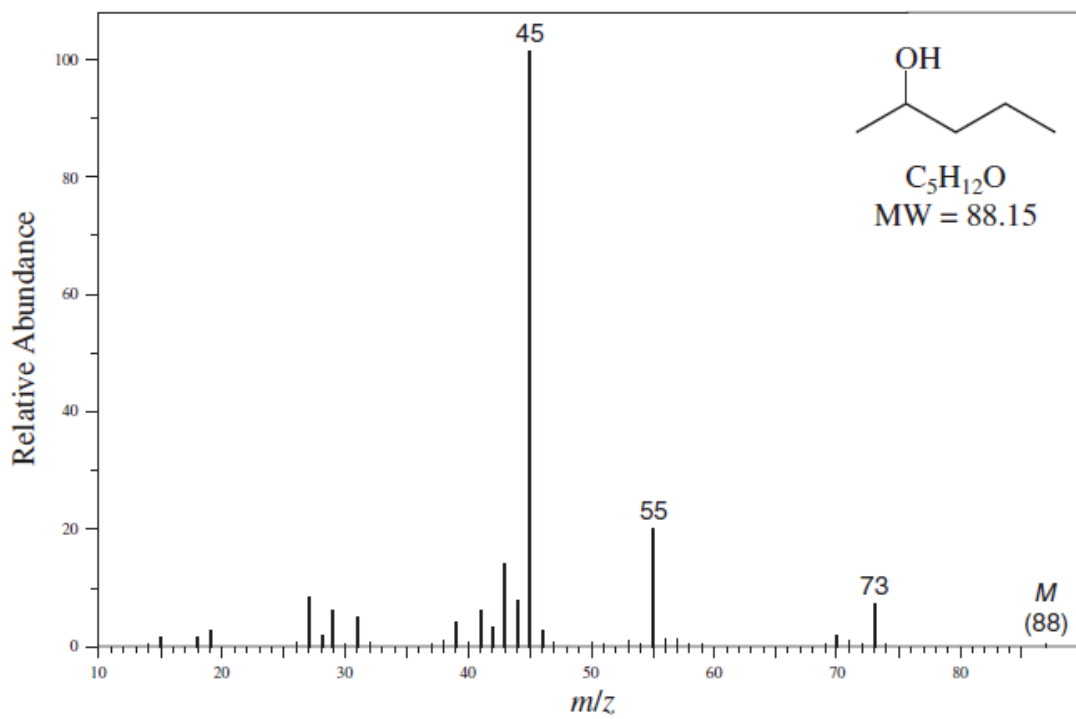


FIGURE 4.28 EI-MS of 2-pentanol.

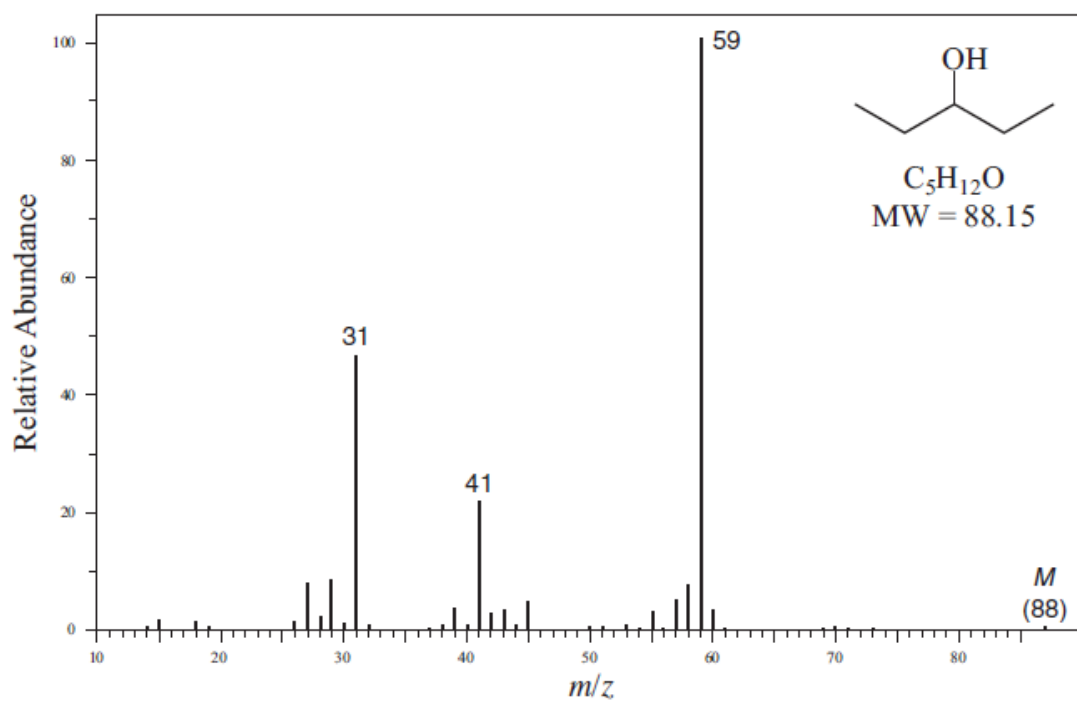


FIGURE 4.29 EI-MS of 3-pentanol.

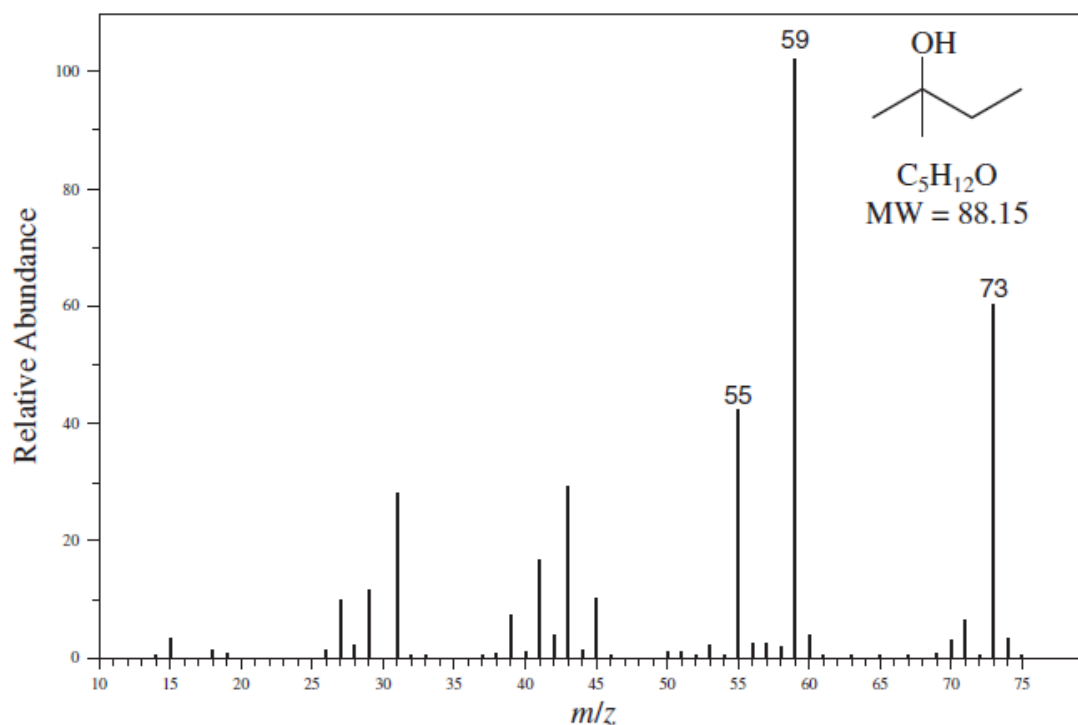
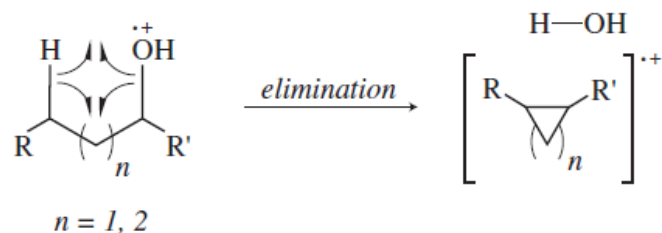


FIGURE 4.30 EI-MS of 2-methyl-2-butanol.

3-Pentanol loses an ethyl radical to form the  $\text{CH}_3\text{CH}_2\text{CH}=\text{OH}^+$  ion at  $m/z = 59$ . The symmetry of 3-pentanol means there are two identical  $\alpha$ -cleavage paths, making the peak corresponding to that ion even more prevalent (Fig. 4.29). 2-Methyl-2-butanol (Fig. 4.30) undergoes  $\alpha$ -cleavage to lose a methyl radical two different ways, creating a considerable size peak at  $m/z = 73$  in addition to the peak at  $m/z = 59$  corresponding to the  $(\text{CH}_3)_2\text{C}=\text{OH}^+$  ion formed by loss of an ethyl radical.

A second common mode of fragmentation involves dehydration. The importance of dehydration increases as the chain length of the alcohol increases. While the fragment ion peak resulting from dehydration ( $m/z = 70$ ) is very intense in the mass spectrum of 1-pentanol, it is quite weak in the other pentanol isomers. Dehydration may occur by either **thermal dehydration** prior to ionization or by fragmentation of the molecular ion. Thermal dehydration is especially troublesome for alcohol samples analyzed by GC-MS. The injection port of the gas chromatograph is usually maintained at more than  $200^\circ\text{C}$ , and many alcohols, especially tertiary or allylic/benzylic, will dehydrate before the sample molecules even reach the GC column and certainly before the molecules reach the ion source of the mass spectrometer. Thermal dehydration is a **1,2-elimination** of water. If the alcohol molecules reach the ion source intact, however, dehydration of the molecular ion can still occur, but in this case it is a **1,4-elimination** of water via a cyclic mechanism:



Alcohols containing four or more carbons may undergo the *simultaneous* loss of both water and ethylene. This type of fragmentation is not prominent for 1-butanol but is responsible for the base peak at  $m/z = 42$  in the mass spectrum of 1-pentanol (Fig. 4.27).

Cyclic alcohols may undergo fragmentation by at least three different pathways, and these are illustrated for the case of cyclohexanol in Figure 4.31. The first fragmentation is simply an

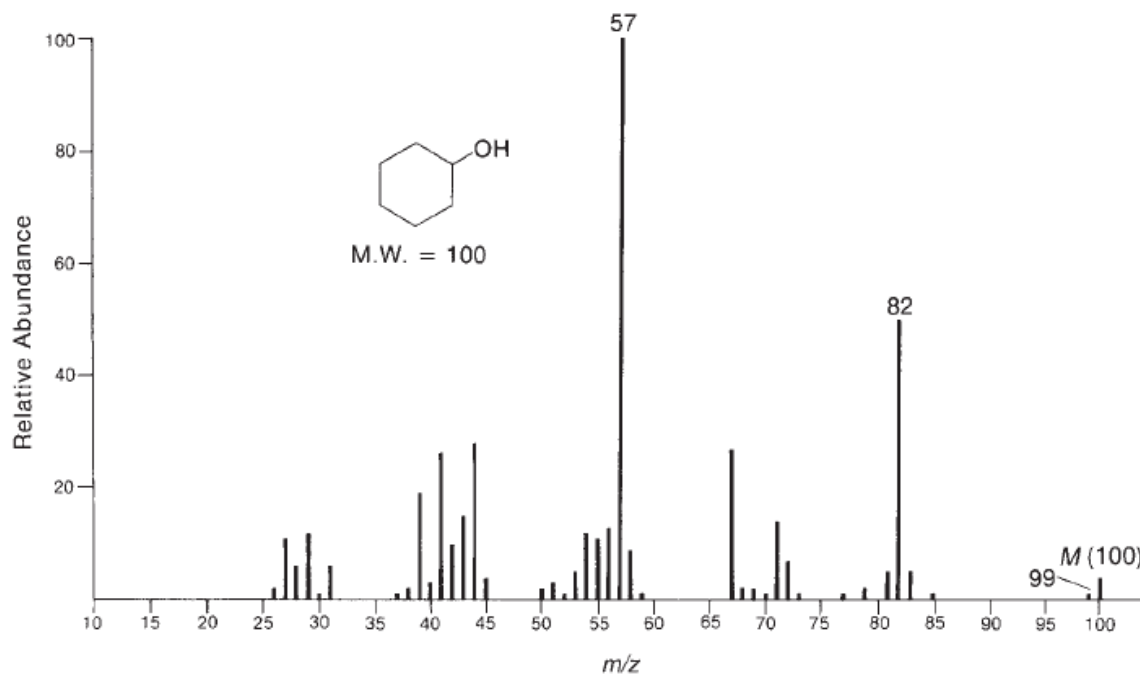


FIGURE 4.32 EI-MS of cyclohexanol.

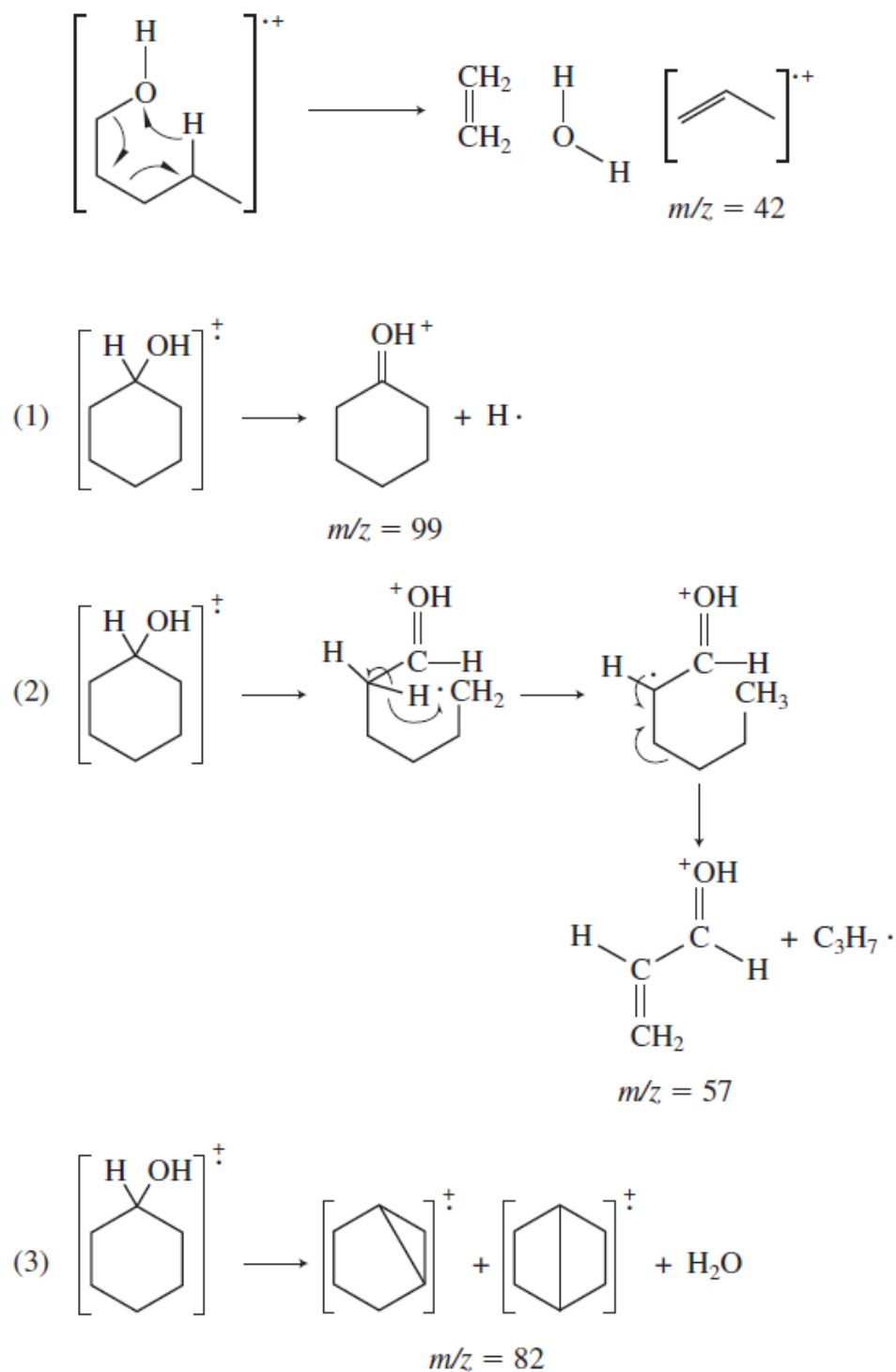


FIGURE 4.31 Fragmentation pathways for cyclohexanol.

Benzylic alcohols usually exhibit strong molecular ion peaks. The following sequence of reactions illustrates their principal modes of fragmentation. Loss of a hydrogen atom from the molecular ion leads to a hydroxytropylium ion ( $m/z = 107$ ). The hydroxytropylium ion can lose carbon monoxide to form a resonance-delocalized cyclohexadienyl cation ( $m/z = 79$ ). This ion can eliminate molecular hydrogen to create a phenyl cation,  $C_6H_5^+$ ,  $m/z = 77$ . Peaks arising from these fragment ions can be observed in the mass spectrum of benzyl alcohol (Fig. 4.33).

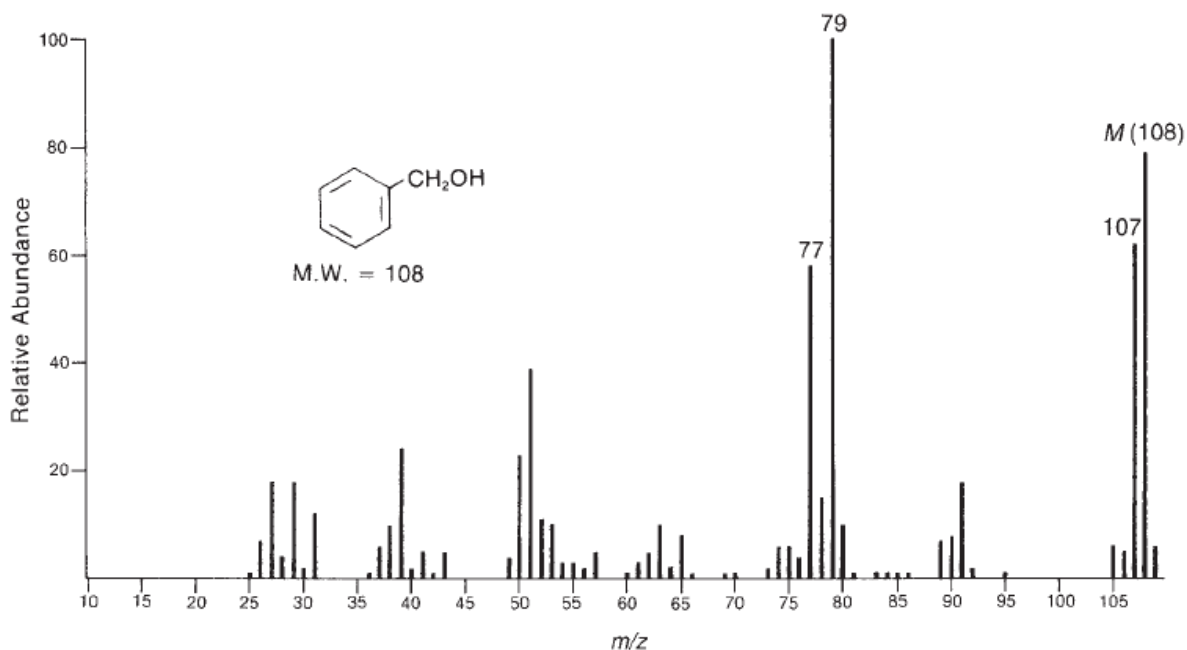


FIGURE 4.33 EI-MS of benzyl alcohol.

### SPECTRAL ANALYSIS BOX — Phenols

#### MOLECULAR ION

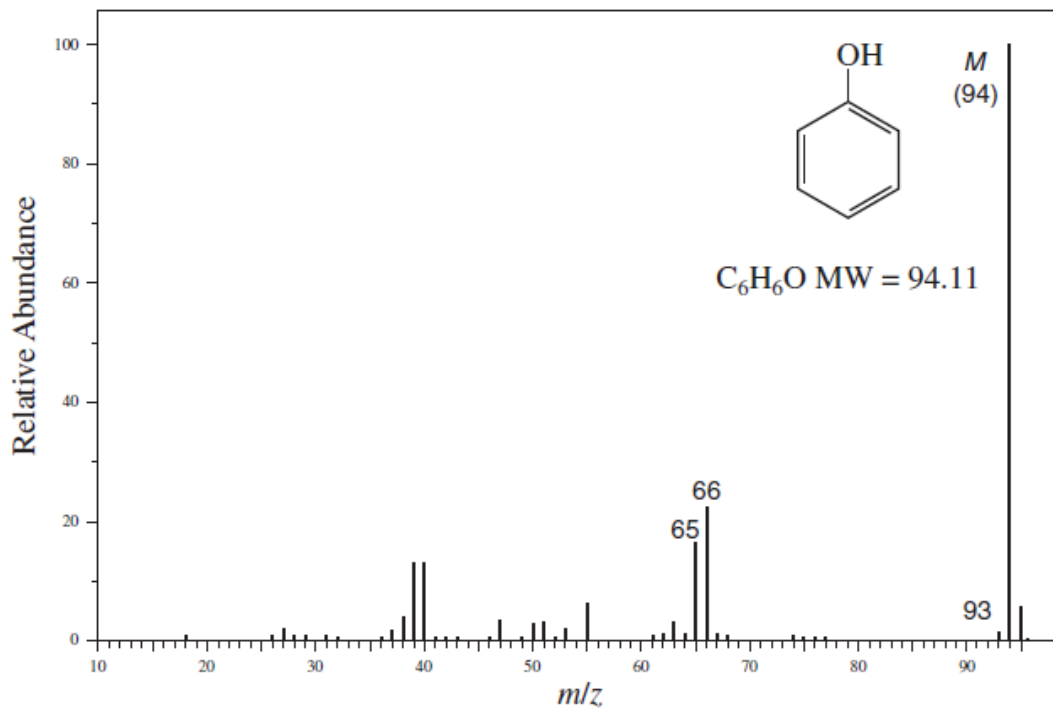
$M^+$  strong

#### FRAGMENT IONS

$M - 1$

$M - 28$

$M - 29$



**FIGURE 4.34** EI-MS of phenol.

Thiols show molecular ion peaks that are more intense than those of the corresponding alcohols. A characteristic feature of the mass spectra of sulfur compounds is the presence of a

significant  $M + 2$  peak. This peak arises from the presence of the heavy isotope,  $^{34}\text{S}$ , which has a natural abundance of 4.4%.

The fragmentation patterns of the thiols are very similar to those of the alcohols. As alcohols tend to undergo dehydration under some conditions, thiols tend to lose the elements of hydrogen sulfide, giving rise to an  $M - 34$  peak.