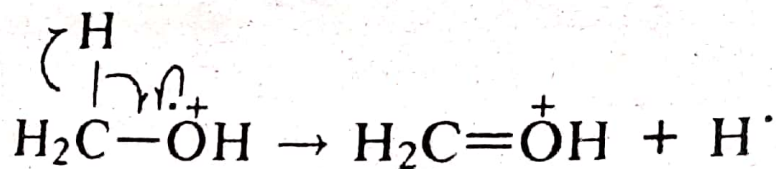


9.2. FRAGMENTATIONS OF ALCOHOLS

The mass spectra of methanol and ethanol were described in Section 1. Recall that the base peak in both is m/z 31, $\text{CH}_2=\overset{+}{\text{O}}\text{H}$. In methanol this is due to the loss of H^\cdot



It is conventional to shorten this mechanism to:

showing the movement of only one of the electrons involved, in order to simplify the picture. We will use this convention where it helps to clarify what might become a rather cluttered formula. In ethanol, Fig. 9.2a, the same process can occur.

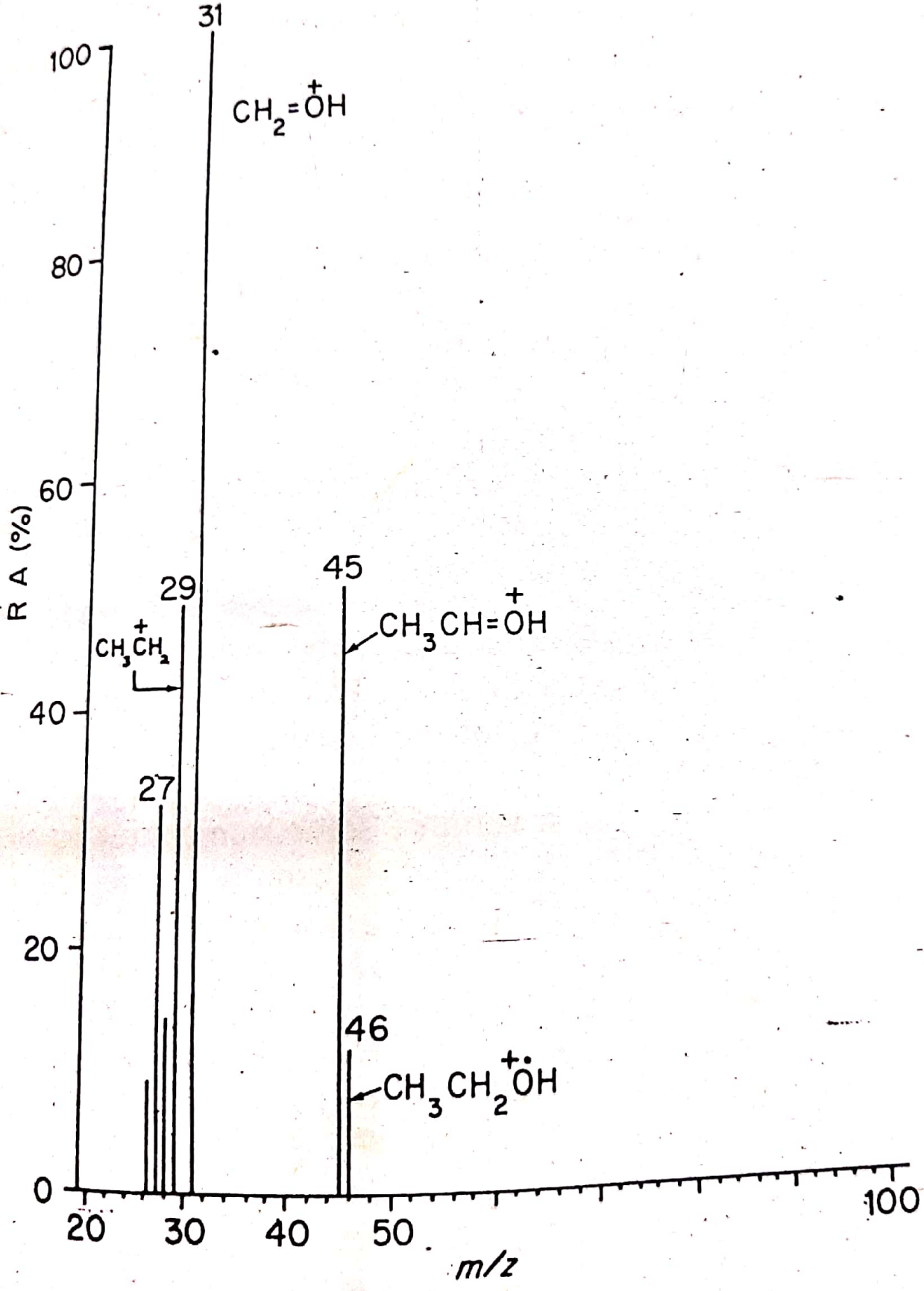
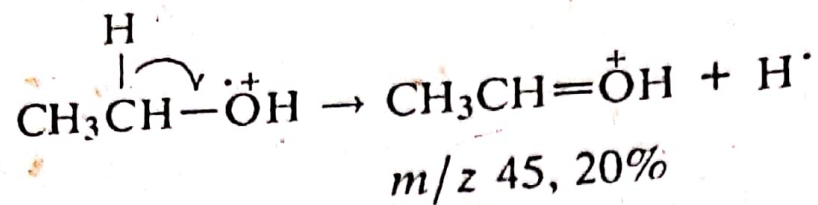
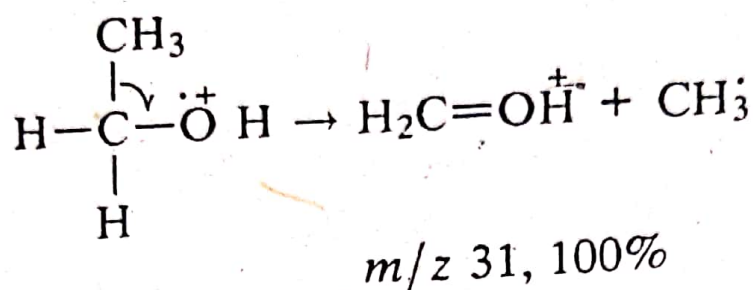


Fig. 9.2a. Mass spectrum of $\text{CH}_3\text{CH}_2\text{OH}$



but the base peak is formed by the alternative loss of CH_3



These processes of homolytic α -cleavage are competitive. In longer chain primary alcohols eg butanol, Fig. 9.2b (i), the amount of $(\text{M} - \text{H})^+$ is much smaller, around 1% and $\text{CH}_2=\overset{+}{\text{O}}\text{H}$ is still the base peak.

II Why should the loss of the alkyl fragment be preferred over the loss of H^\cdot in the α -cleavage of primary alcohol molecular ions?

The radical $\text{CH}_3\text{CH}_2^\cdot$ would be more stable than CH_3^\cdot , just as CH_3CH_2^+ is more stable than CH_3^+ .

This question was explained by Stevenson in the early 1950's. He was the first to notice this tendency for the largest alkyl fragment to be preferentially lost as a radical. The molecular ion is a high energy species trying to get rid of as much energy as quickly as possible. An alkyl radical has several bonds which can be in higher vibrational states, thus absorbing the excess energy of the molecular ion and leaving with it. The hydrogen atom can only depart with kinetic energy. The more bonds the radical species has, the better. Thus we have a very useful empirical rule named after Stevenson:

In a fragmentation, the largest radical is lost preferentially.

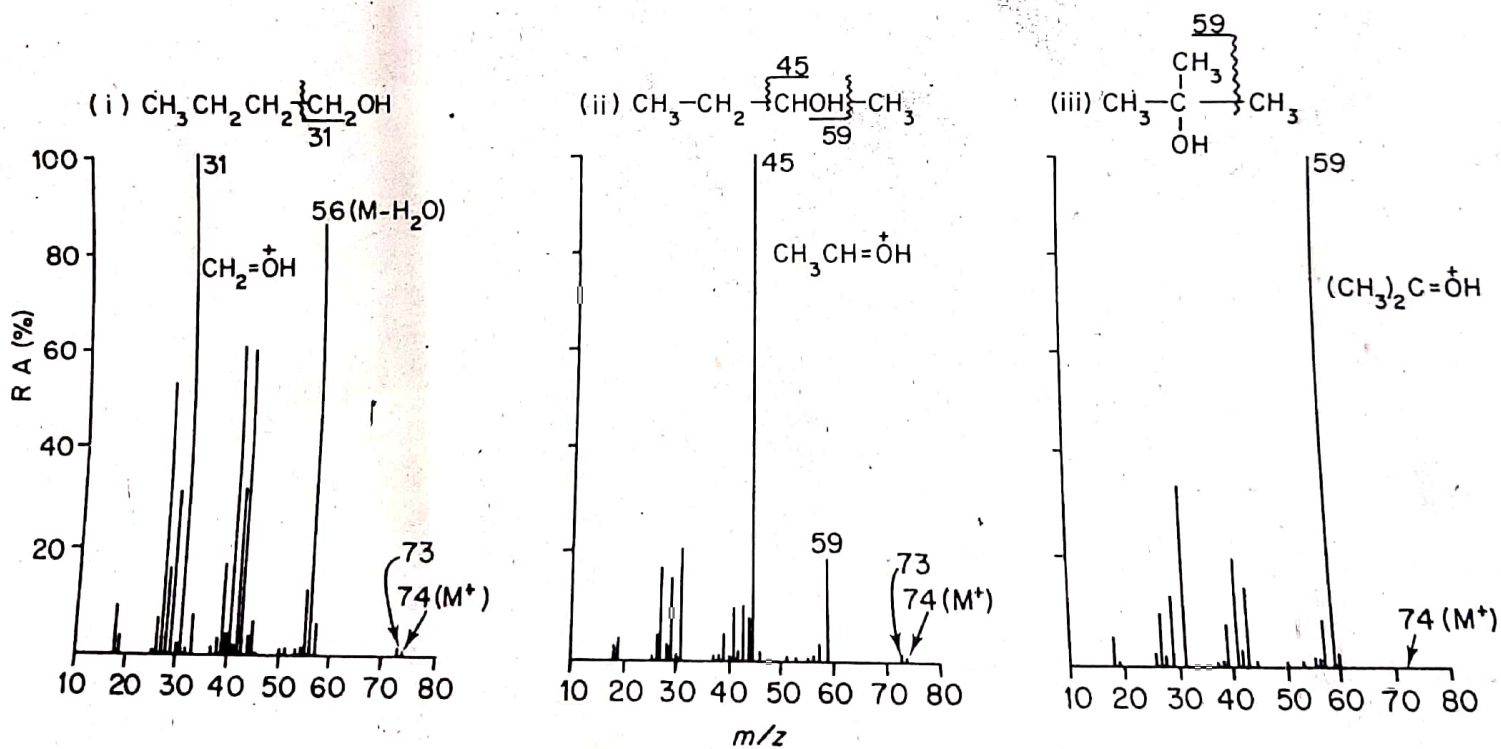
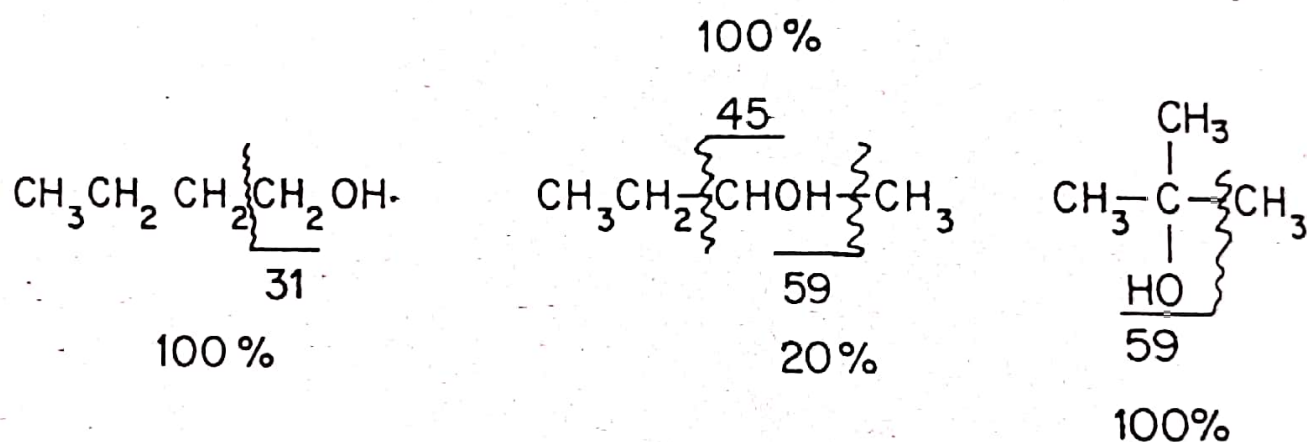


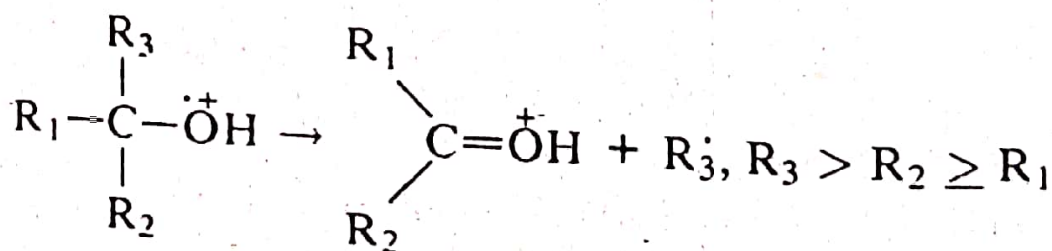
Fig. 9.2b. Mass spectra of the three isomeric butanols

Examine the spectra of the isomeric butanols now and see if this works (Fig. 9.2b (i), (ii) and (iii)). Butan-2-ol (Fig. 9.2b (ii)) cleaves to give 100% $(M-CH_3CH_2)^+$ m/z 45, and 20% $(M-CH_3)$ m/z 59, a ratio of 5:1 in favour of the loss of CH_3CH_2 . In fact the ion $CH_3CH=\overset{+}{O}H$ is typical of 2-ols because in the structure CH_3CHOHR if $R=CH_3$, CH_3 will be lost because $CH_3 > H$. For any other R, it will be larger than CH_3 so R is lost according to Stevenson's Rule. 2-Methylpropan-2-ol (*t*-butyl alcohol), Fig. 9.2b (iii), is really analogous to methanol because it has three identical groups round the α -carbon and can only lose CH_3 to form $(CH_3)_2C=\overset{+}{O}H$ as base peak. These cleavages are summarised below:

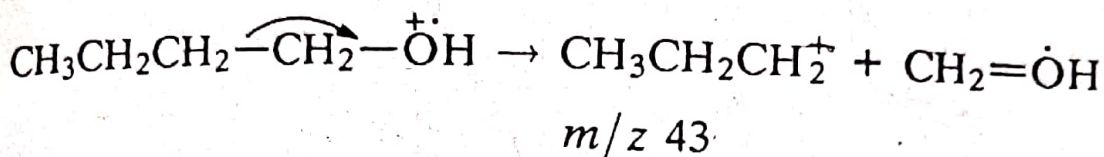
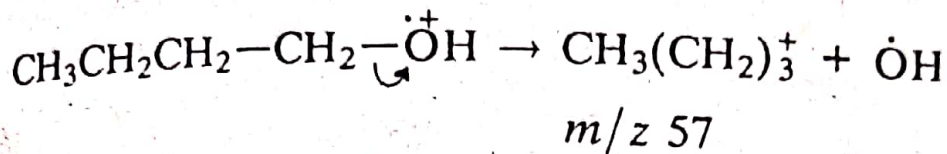
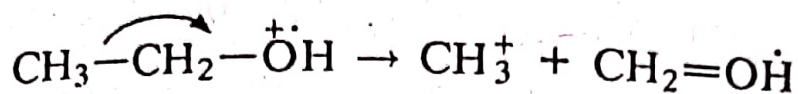
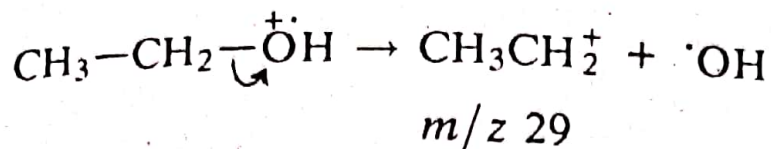


In this shorthand presentation, the bond cleaved is shown broken by a wavy line, and the ion formed and its intensity are shown above or below the horizontal straight line. This is a very useful way of summarising the main features of a spectrum.

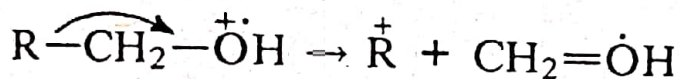
We can summarise the application of Stevenson's Rule to aliphatic alcohols by saying that the base peak is usually formed by the loss of the largest radical attached to the α -carbon:



The α - and β - bonds in alcohols can also break heterolytically to give hydrocarbon ions, which can be seen in the spectra in Fig. 9.2a and 9.2b:



and generally



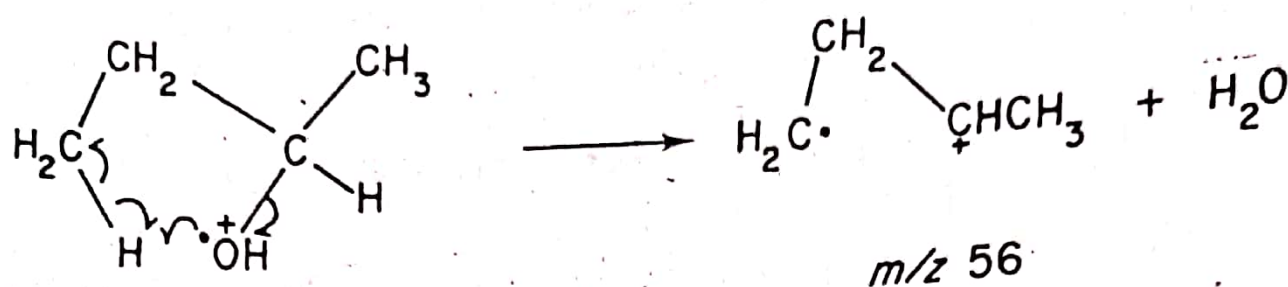
These hydrocarbon ions and daughter ions derived from them are usually of less RA than the $\text{R}_1\text{R}_2\text{C}=\overset{+}{\text{O}}\text{H}$ ions, but increase in importance in long chain, especially branched alcohols, which come to resemble the corresponding hydrocarbons (see Section 9.7).

II In a secondary or tertiary alcohol there might be two or three different R^+ which could be formed. Try to predict what would happen if the R groups were CH_3 , CH_3CH_2 , and $(\text{CH}_3)_2\text{CH}$ in the structure $\text{R}_1\text{R}_2\text{R}_3\text{COH}$.

The ion $(\text{CH}_3)_2\overset{+}{\text{C}}\text{H}$ would have the greatest intensity, followed by CH_3CH_2^+ , then CH_3^+ very much the least. I hope you said this was because the order of stability of carbocations is tertiary > secondary >> primary - if so, well done! If you did not remember the stability order of carbocations, revise Section 8.2. In some alcohol spectra, the R^+ ions are as intense or more intense than the $\text{R}_1\text{R}_2\text{C}=\overset{+}{\text{O}}\text{H}$ ions if R is secondary or tertiary.

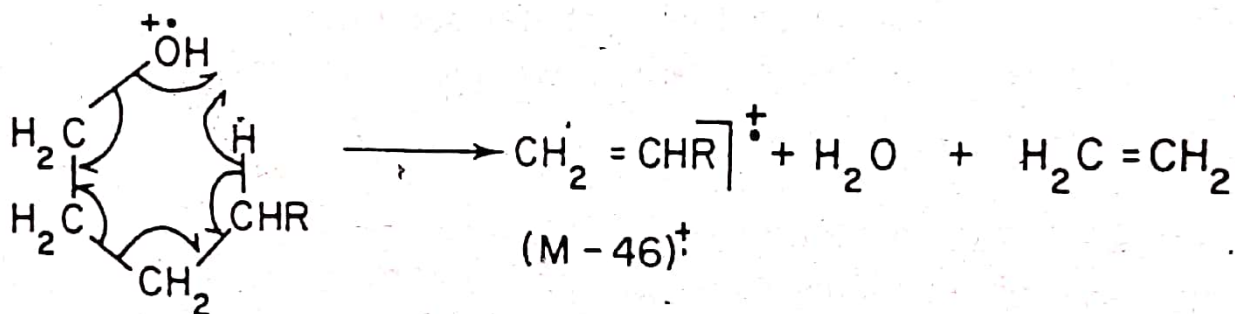
There is one other feature of the alcohol spectra which we have yet to explain - the loss of H_2O . This gives rise to the prominent m/z 56 in butan-1-ol (Fig. 9.b(i)), but only minor peaks in ethanol

1,3-elimination



Since ethanol and 2-methylpropan-2-ol have neither 3 nor 4 carbons let alone hydrogens, they show little loss of H_2O .

Alcohols with 5 carbons or more can lose $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$ in a single concerted step (as shown by a metastable ion for the loss of 46 amu all at once). The mechanism for this is:



Both this and the 1,4- H_2O elimination are typical examples of an electron-impact induced hydrogen transfer process involving a six-centred ring transition state.

A similar six-centred ring process involving the loss of $\text{CH}_2=\text{CH}_2 + \text{CH}_3$ occurs in the fragmentation of cyclopentanols and hexanols, which behave distinctively. The fragmentation starts by α -cleavage next to the $-\text{OH}$ group but further bond reorganisation and cleavages must follow in a cyclic compound before daughter ions can be produced. For cyclohexanol the mass spectrum is shown in Fig. 9.2c and the proposed fragmentation is shown in Fig. 9.2d.

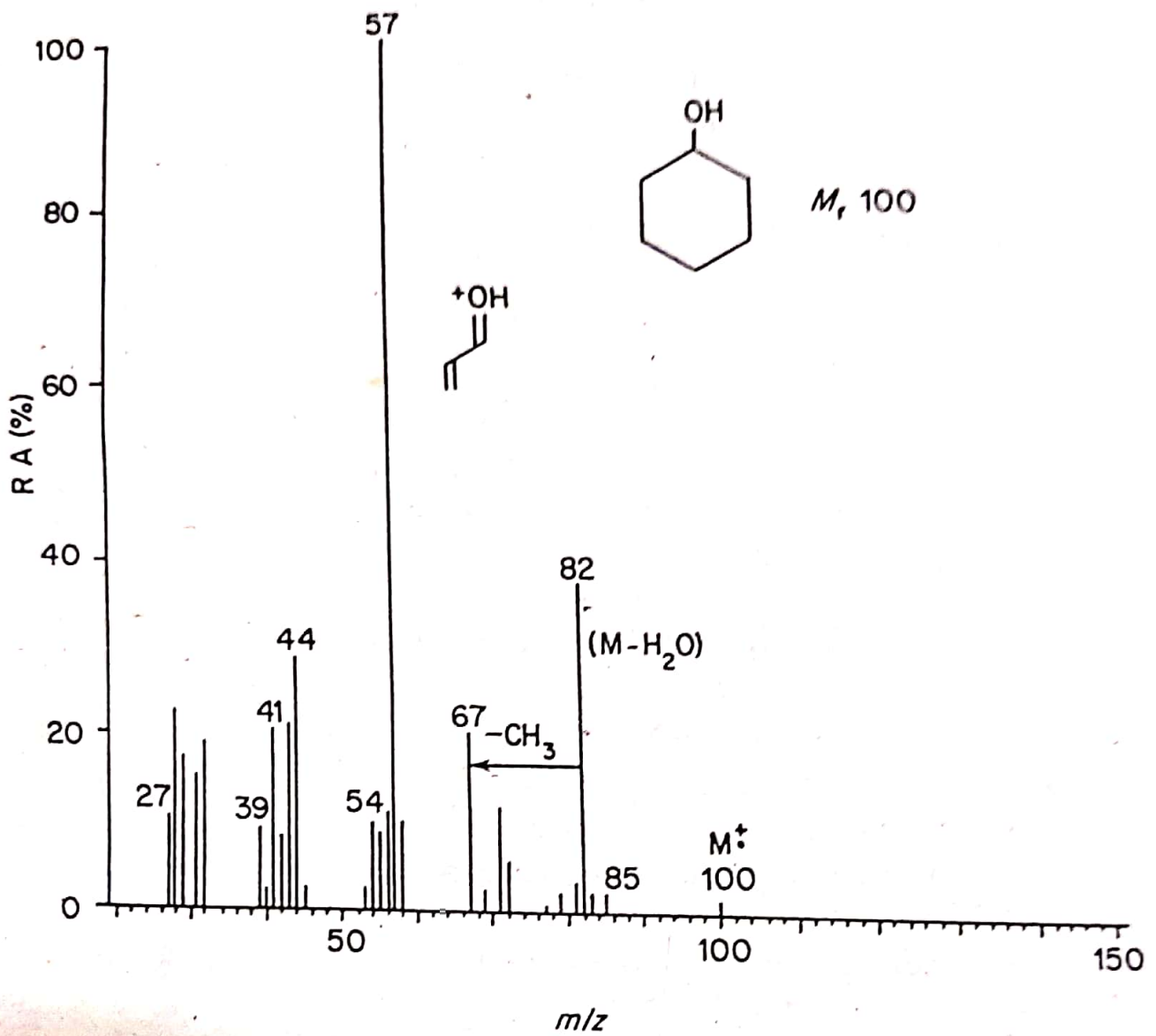


Fig. 9.2c. Mass spectrum of cyclohexanol

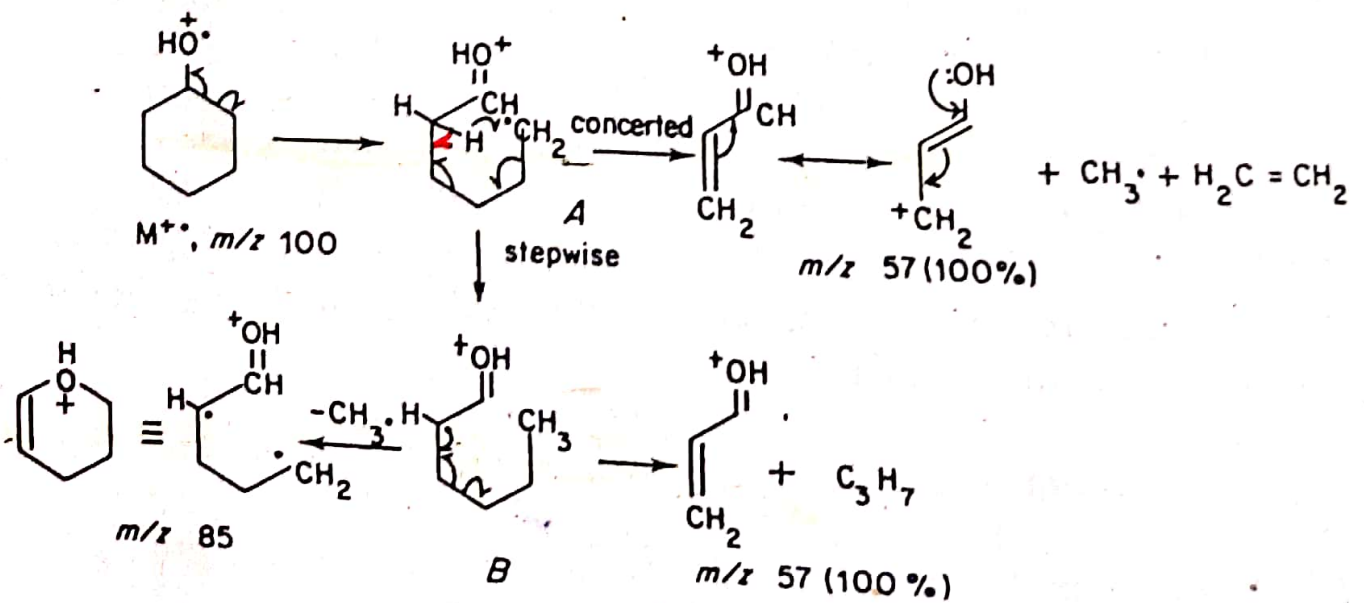


Fig. 9.2d. Fragmentations of cyclohexanol

The fact that m/z 85 ($M-CH_3$)⁺ is present in the spectrum shows that the stepwise mechanism is followed to some extent, though there is no doubt the major route to m/z 57 is concerted. This ion is the major one in most cyclanol spectra ($C_5 \rightarrow C_8$). It is shifted appropriately to higher mass if there are substituents at the 2- and 3- positions of the cyclanols. For example in 3-methylcyclohexanol the homologue of m/z 57 (m/z 71) is 64% while m/z 57 is 35%.

Π Why do you think the m/z 57 is given by such a range of ring sizes in the cyclanols?

The answer is shown in Fig. 9.2d. This ion is conjugated, so the positive charge is *stabilised by resonance*. This is yet another example of the importance of +M groups in determining the direction and mechanisms by which molecular ions fragment.

You will have noticed that the molecular ions are generally of low abundance in the mass spectra of saturated aliphatic alcohols. In many cases they are too low to be seen at all. There is one major exception to this rule that alcohols show weak to non-existent M^+ peaks. This is found in the spectra of aromatic alcohols which show quite intense M^+ peaks. Look at Fig. 9.2e and 9.2f now.

These are the spectra of benzyl alcohol and 2-phenylethanol. You would not mistake these for aliphatic alcohols. In benzyl alcohol M^+ is also the base peak and both show intense typically aromatic ions such as $C_6H_5^+$, $C_7H_7^+$ and $C_7H_7O^+$, m/z 77, 91 and 107. Equally they do not behave like primary aliphatic alcohols, or observe Stevenson's Rule.

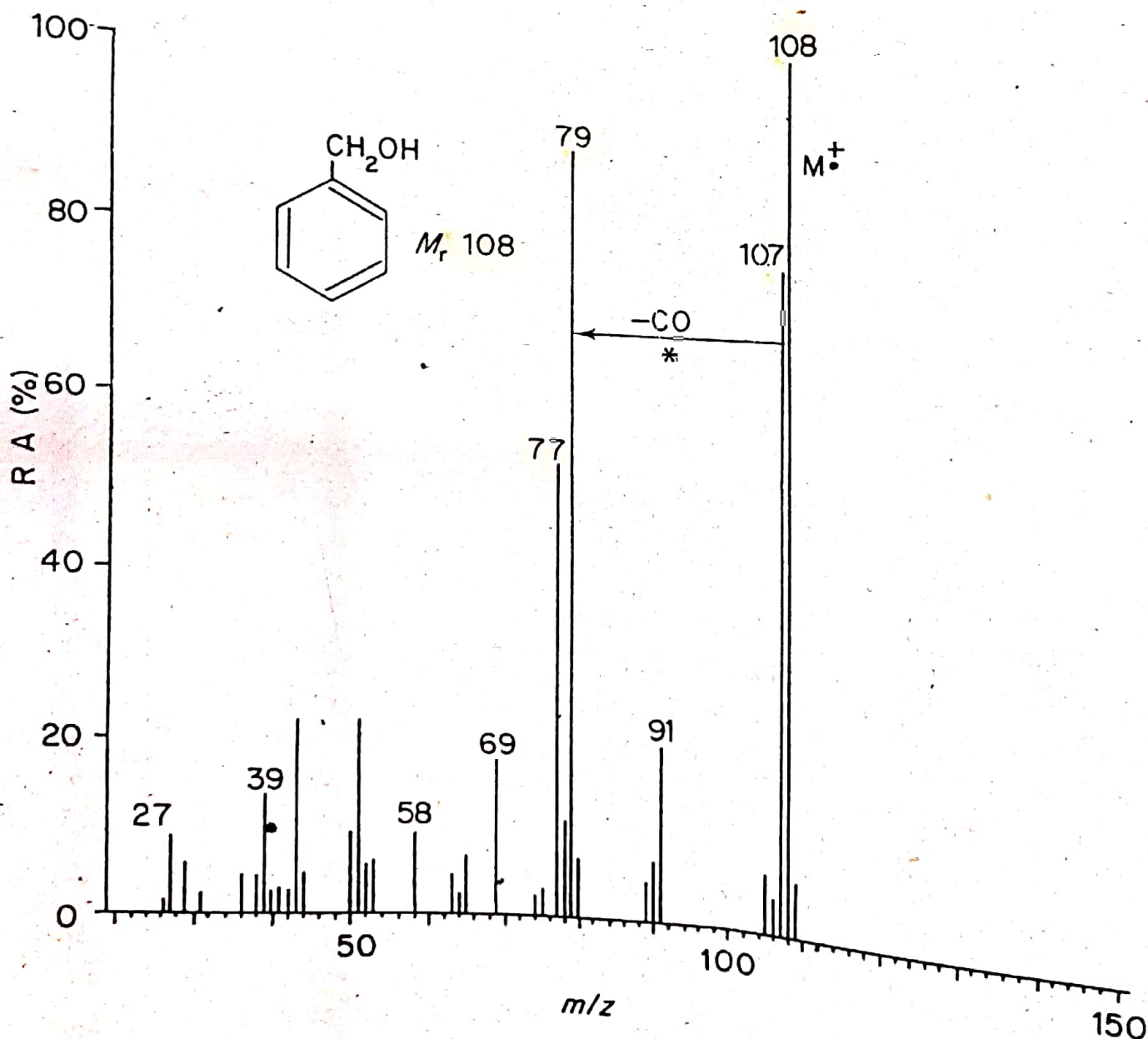


Fig. 9.2e. Mass spectrum of benzyl alcohol
Scanned with CamScanner

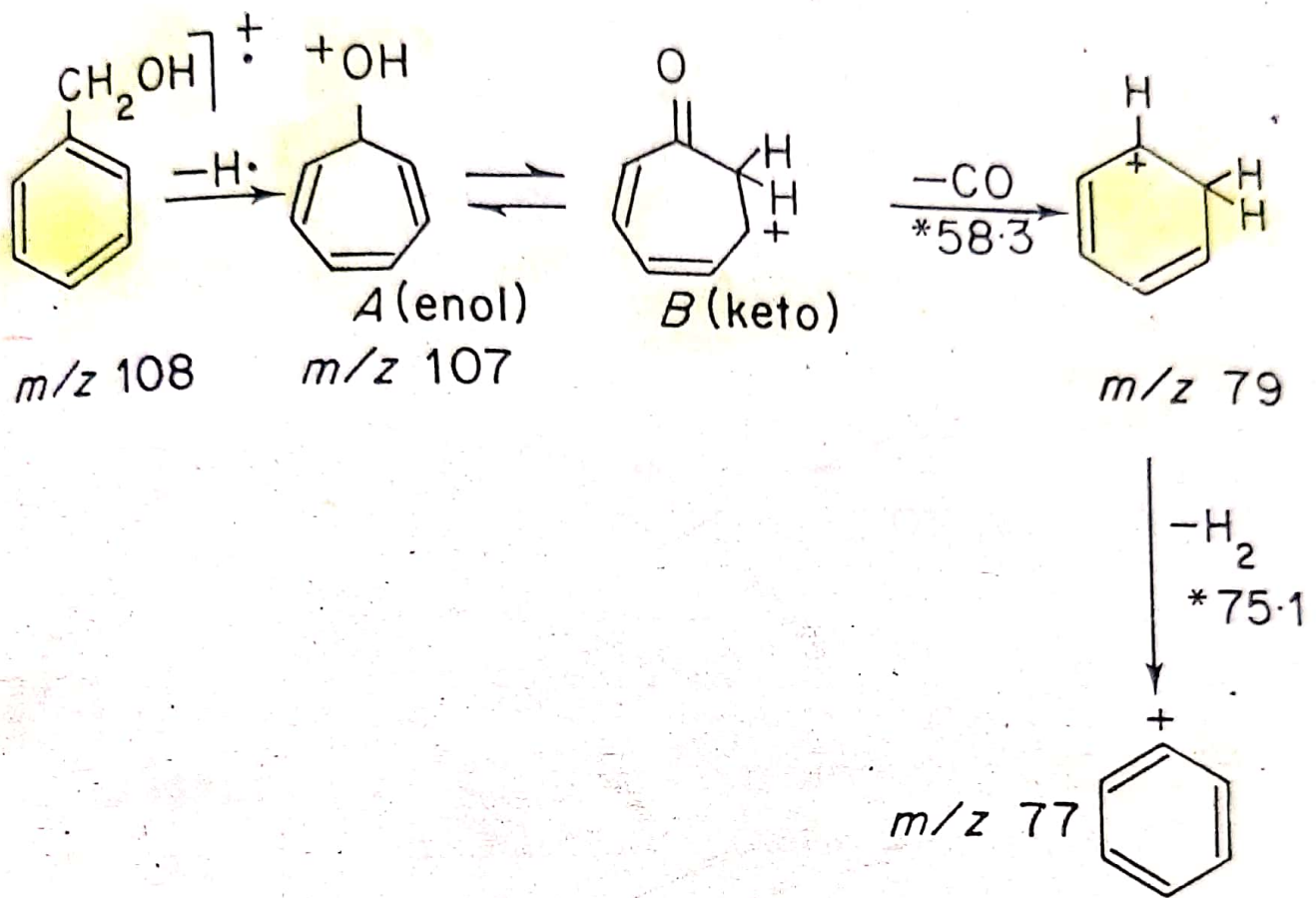


Fig. 9.2g. Fragmentation of benzyl alcohol (* indicates a metastable ion is observed)

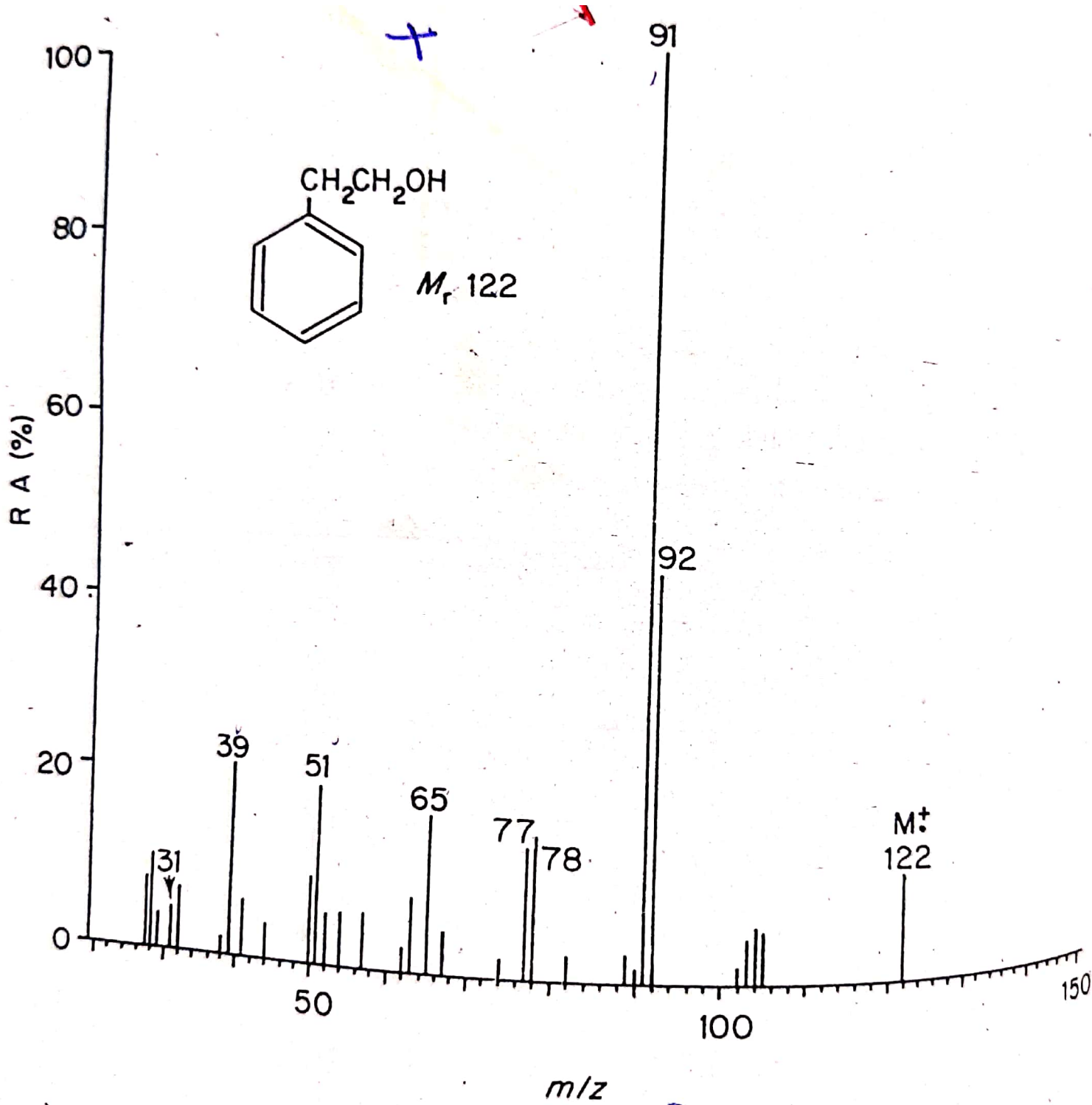


Fig. 9.2f. Mass spectrum of 2-phenylethanol

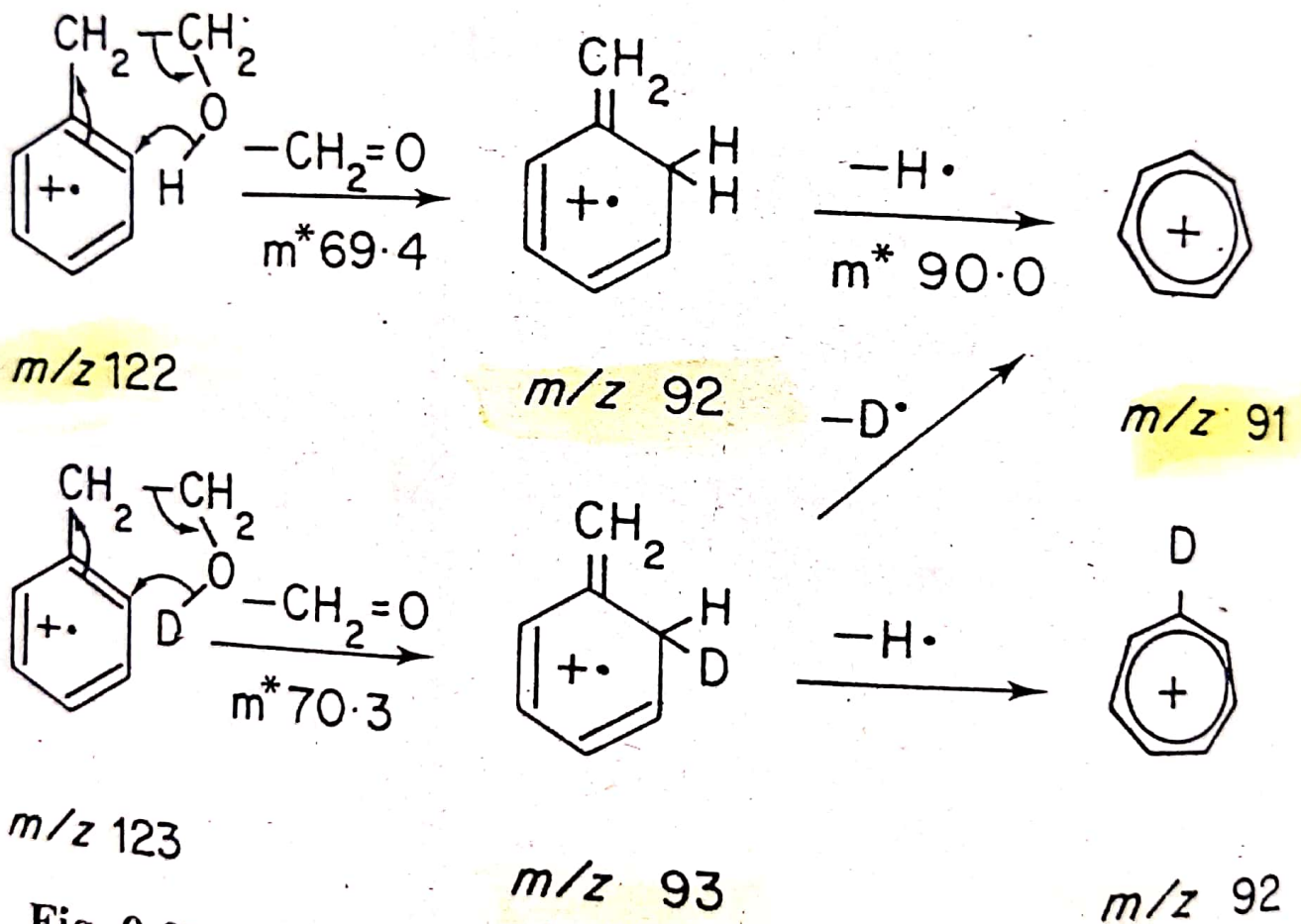
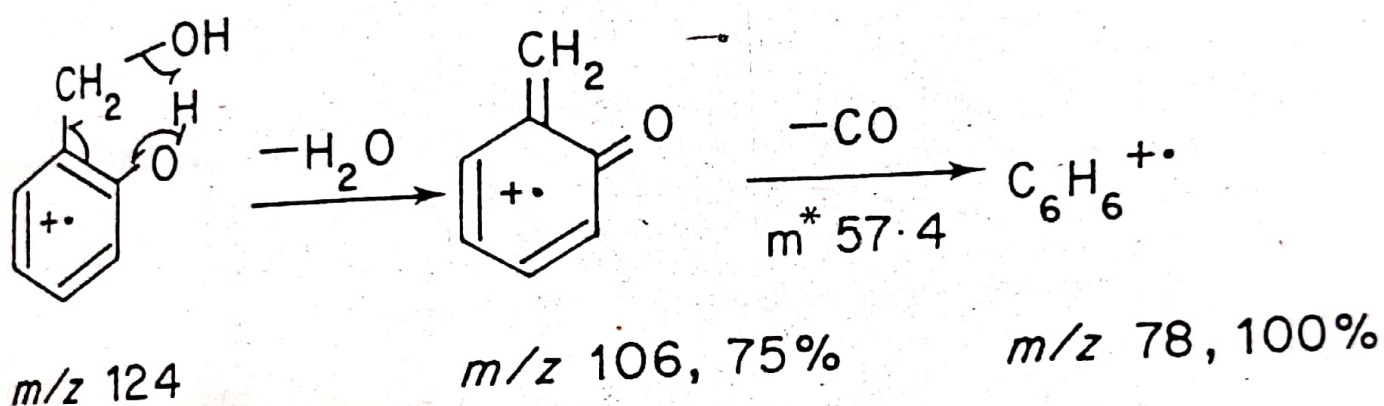
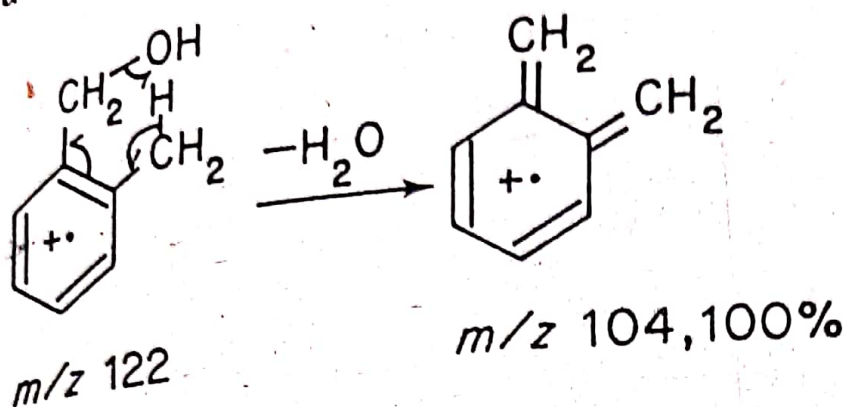
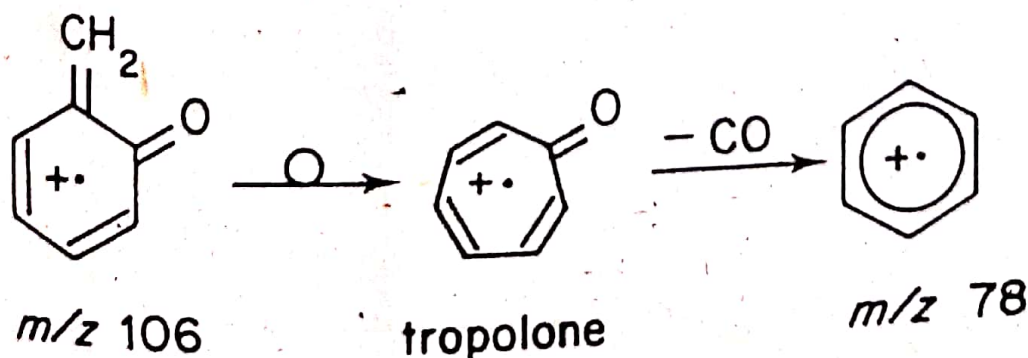


Fig. 9.2h. Fragmentation of 2-phenylethanol and 2-phenylethanol-O-D

What happens is:



The 3- and 4- isomers in each case cannot possibly form such six-membered transition states, so they lose $\cdot OH$, then $\cdot H$ more conventionally to reach m/z 104 and 106 in differing amounts from the 2-isomers. It is interesting that the m/z 106 of the 2-isomer in the second case further fragments to give the M^+ of benzene, $C_6H_6^+$ by loss of $\cdot C=O$. Possibly it has rearranged itself to the M^+ of tropolone in order to facilitate this:



SAQ 9.2c

Fig. 9.2i shows the mass spectrum of an alcohol, *Unknown 6*. Interpret this spectrum and identify the alcohol. Note that m/z 31, not shown in Fig. 9.2i, is actually 45%.

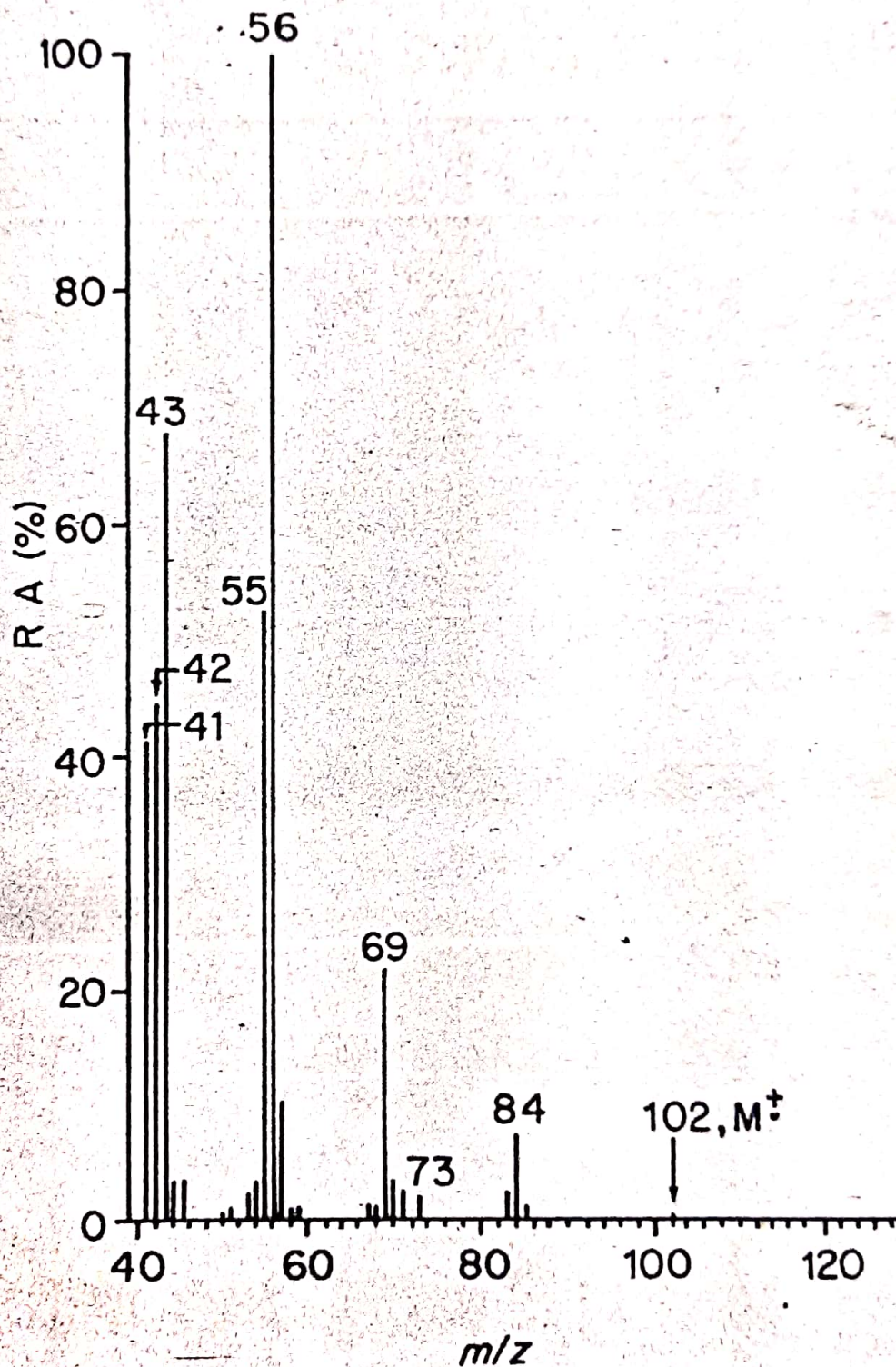


Fig. 9.2i. Mass spectrum of *Unknown 6*

SAQ 9.2d

Fig. 9.2j shows the mass spectrum of an alcohol, *Unknown 7*. Interpret this spectrum and identify the alcohol.

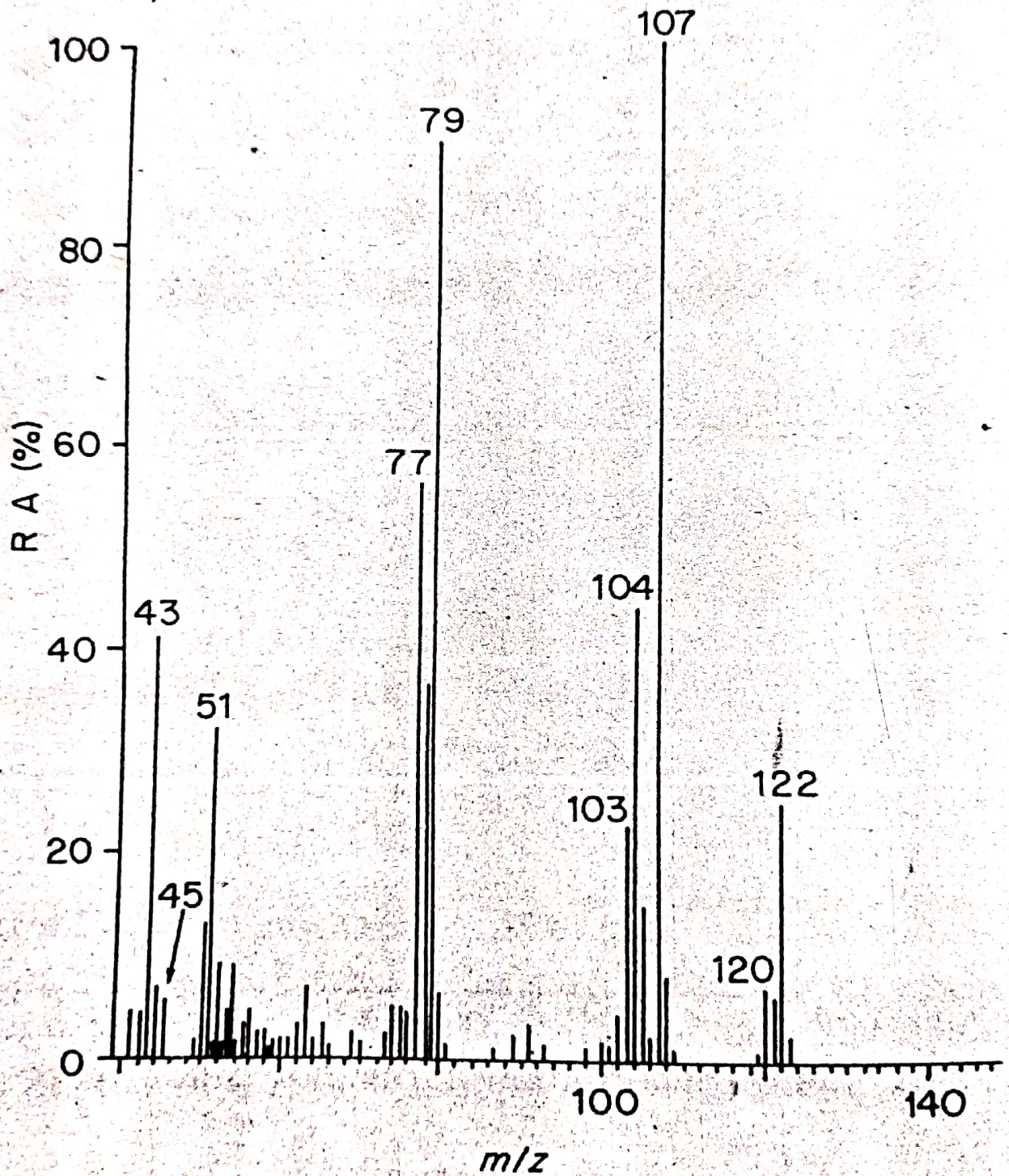


Fig. 9.2j. Mass spectrum of *Unknown 7*