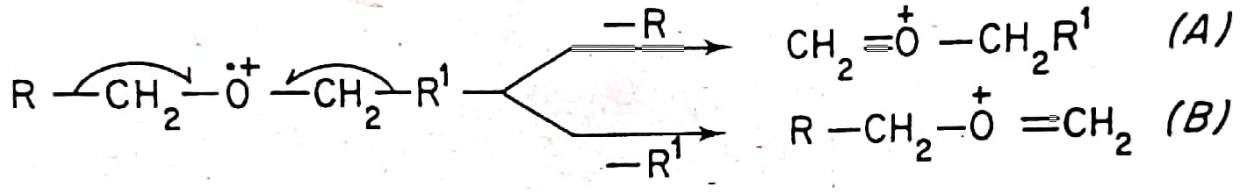
- recognise and write mechanisms for the elimination of H_2O in the mass spectra of 2-substituted benzyl alcohols, and appreciate that such ortho effects generally are useful in distinguishing 1,2-disubstituted aromatic compounds from their 1,3- and 1,4-disubstituted isomers.

9.3. FRAGMENTATIONS OF ETHERS

Ethers and alcohols are isomeric compounds eg diethyl ether, $CH_3CH_2OCH_2CH_3$ and butanol, $CH_3CH_2CH_2CH_2OH$; benzyl alcohol $C_6H_5CH_2OH$ and methoxybenzene $C_6H_5OCH_3$, so it is interesting to ask the question, can mass spectrometry readily distinguish between them?

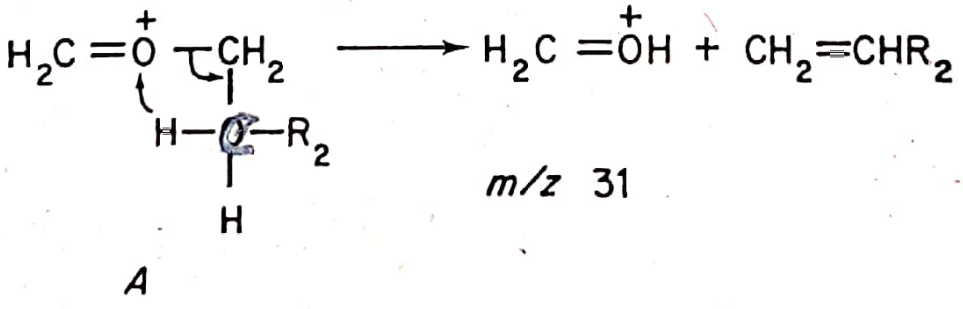
Firstly ethers tend to show more intense M^+ than the isomeric alcohols, though they are still rather weak. They fragment by primary cleavages similar to those occurring in alcohols, ie



(A) (B)

to give oxonium ions *A* or *B* of m/z 45, 59, 73, 87 ... , which are isomeric with the $R_1R_2C{=}\overset{+}{O}H$ ions found in alcohol spectra.

However, ethers show a further easy fragmentation which is *not* found in most isomeric alcohols. This is the loss of a neutral alkene derived from the remaining alkyl substituent in *A* or *B*:



A

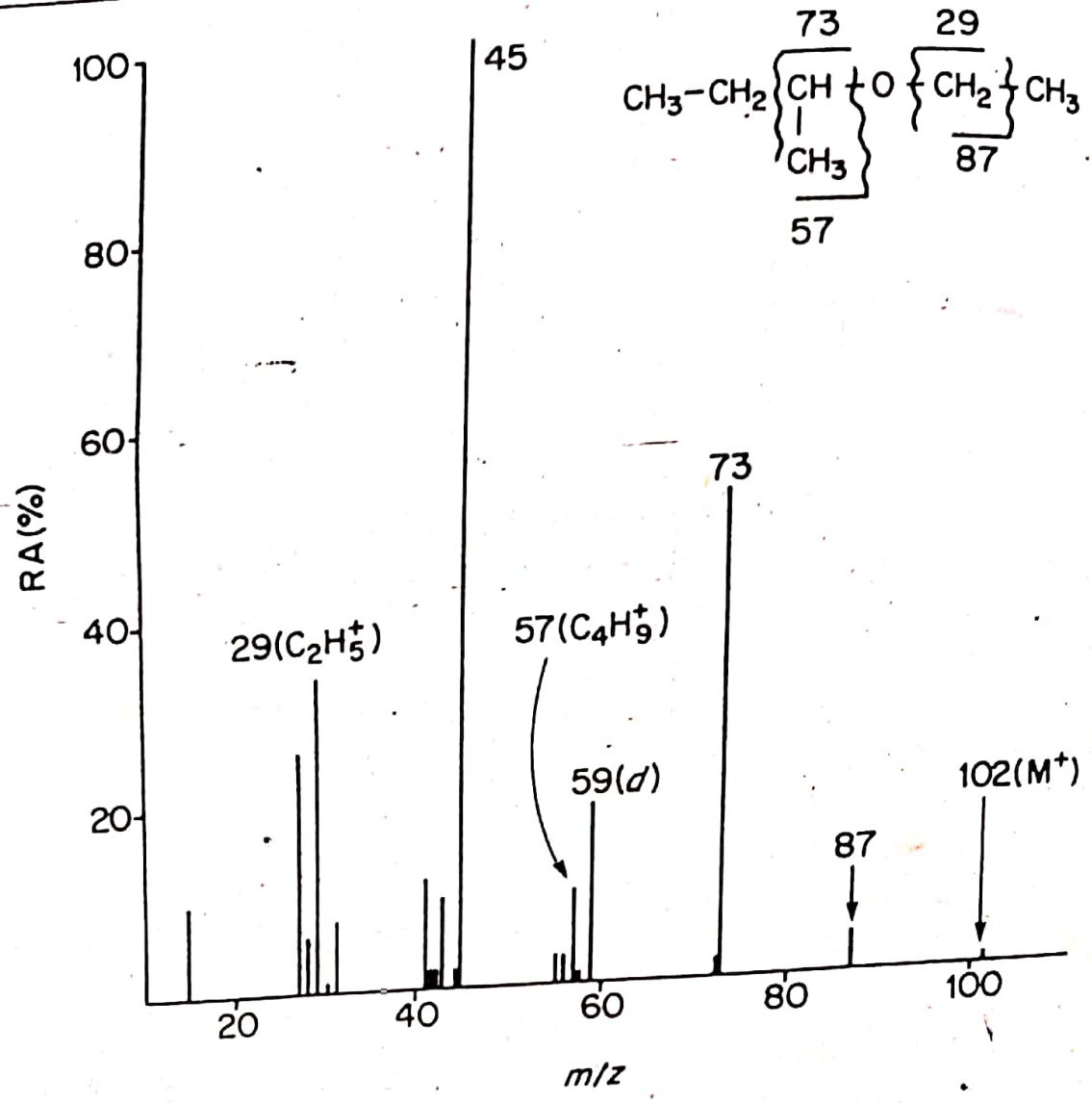


Fig. 9.3a. *Mass spectrum of ethyl 1-methylpropyl ether*

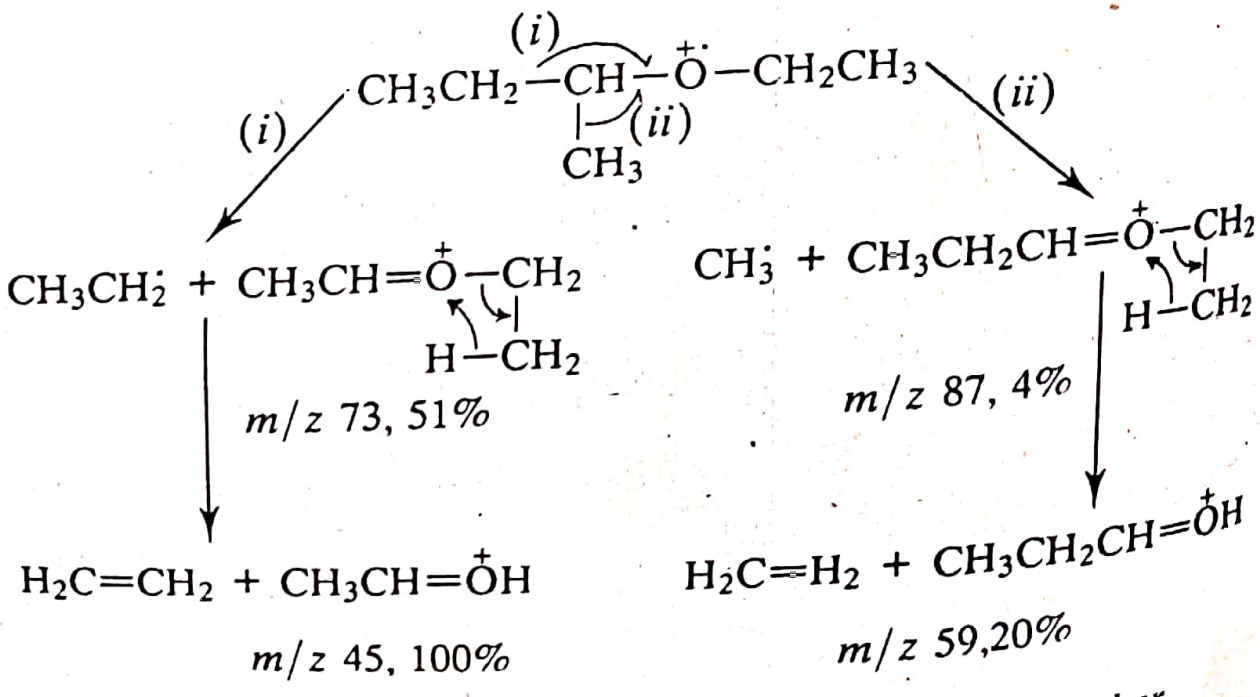


Fig. 9.3b. *Fragmentations of ethyl 1-methylpropyl ether*

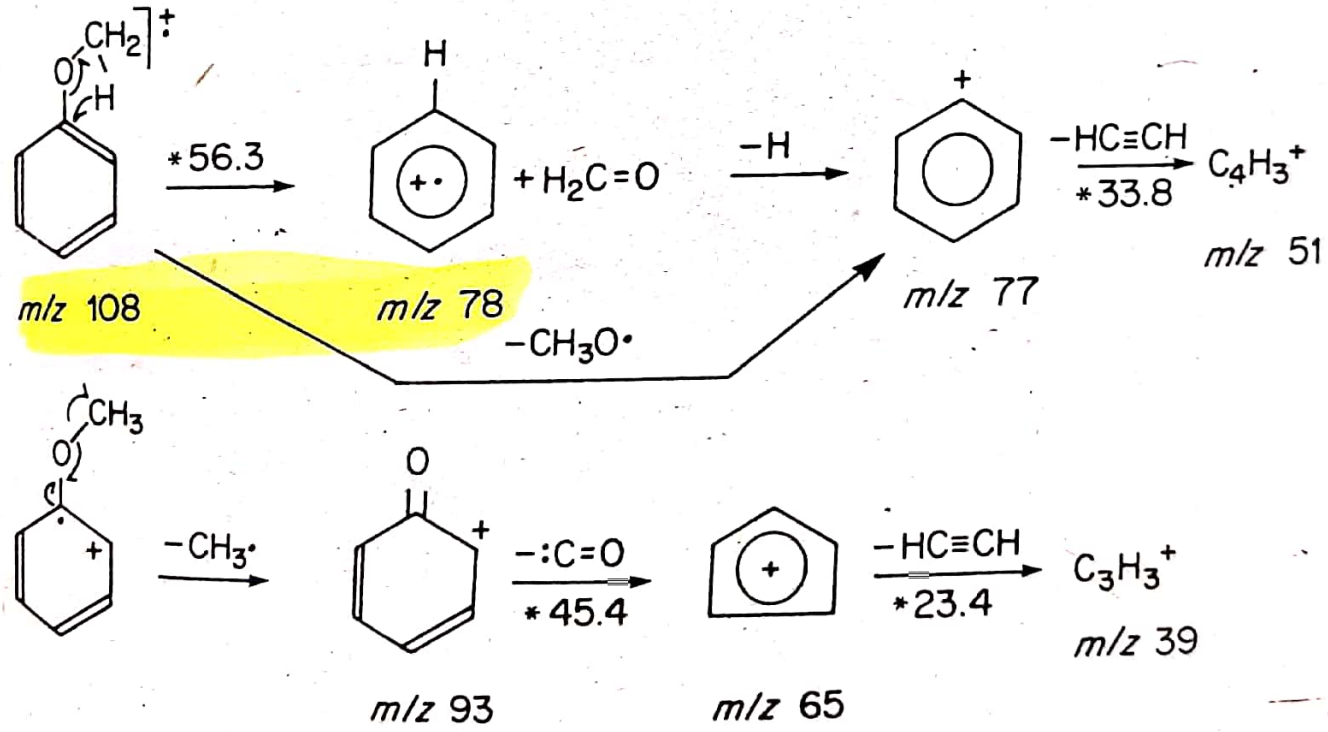


Fig. 9.3c. *Fragmentations of methoxybenzene*

In Fig. 9.3c, the mechanism of the loss of $CH_2{=}O$ has been left rather vague. Can you supply it?

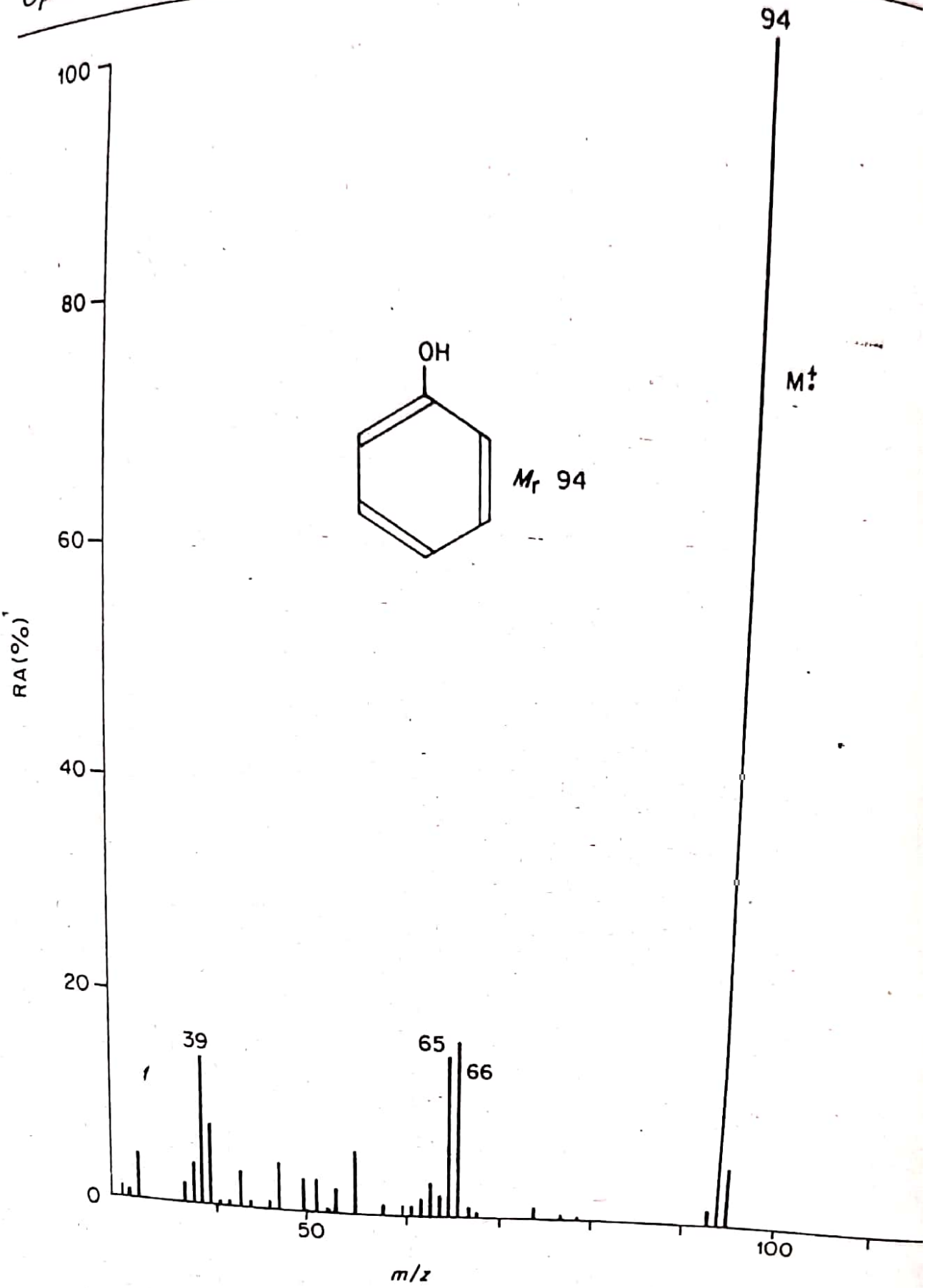


Fig. 9.4a. *Mass spectrum of hydroxybenezene (phenol)*

Π Have a closer look at Fig. 9.4a, the mass spectrum of hydroxybenzene itself. What strikes you as peculiar about it, and what neutral fragments do you think are being released when m/z 66 and 65 are formed?

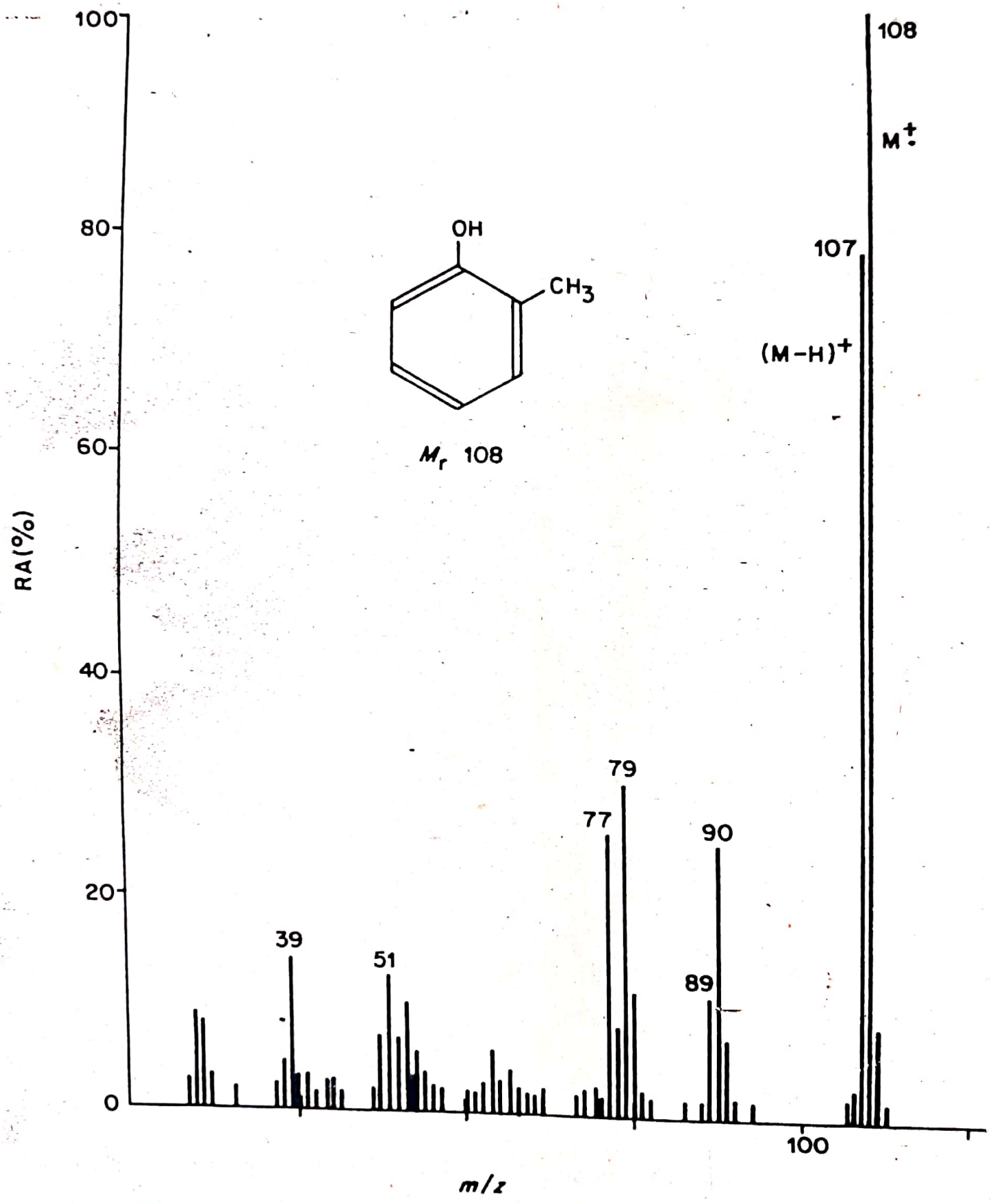


Fig. 9.4b. *2-Methylhydroxybenzene*

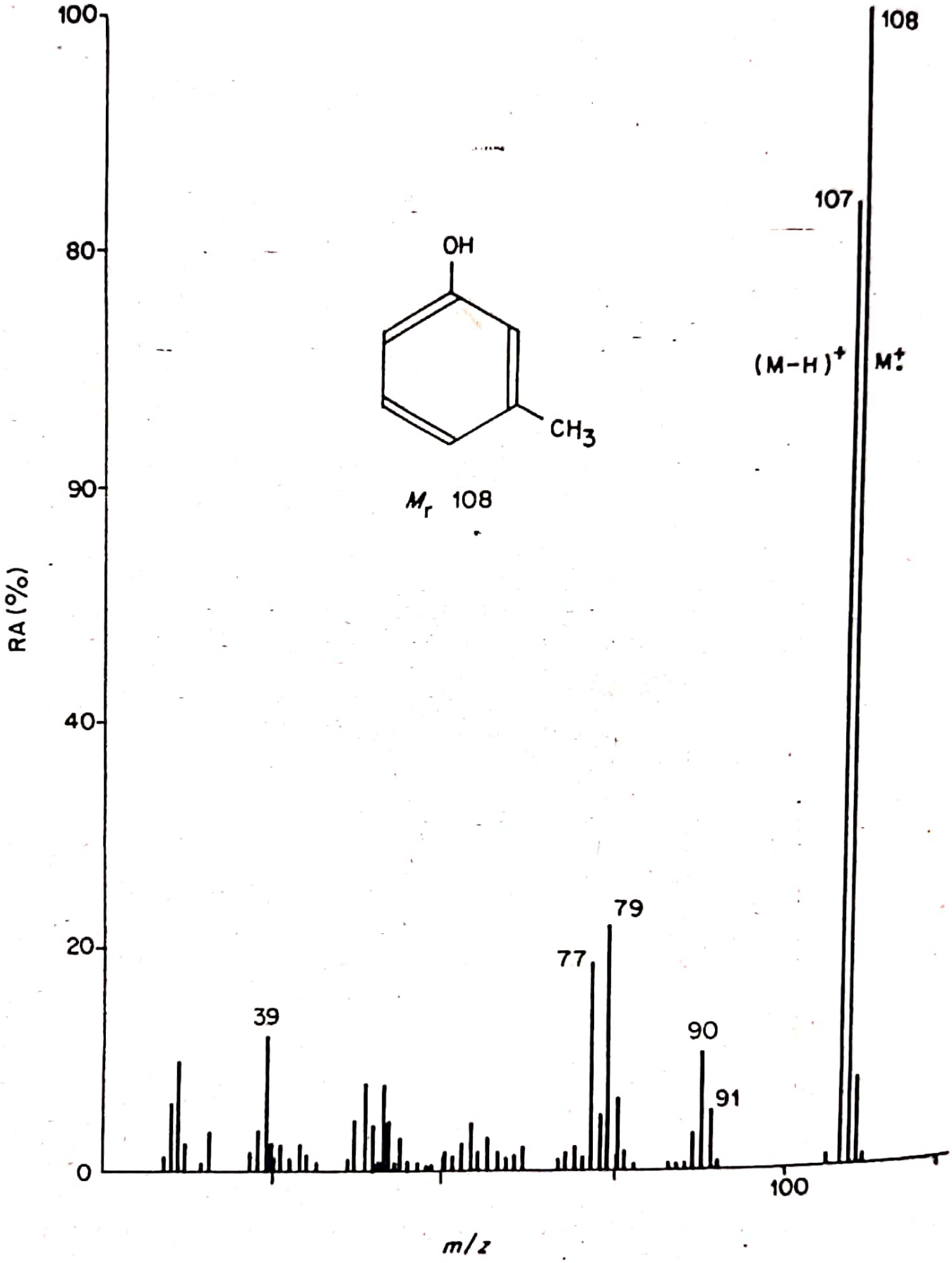


Fig. 9.4c. *3-Methylhydroxybenzene*

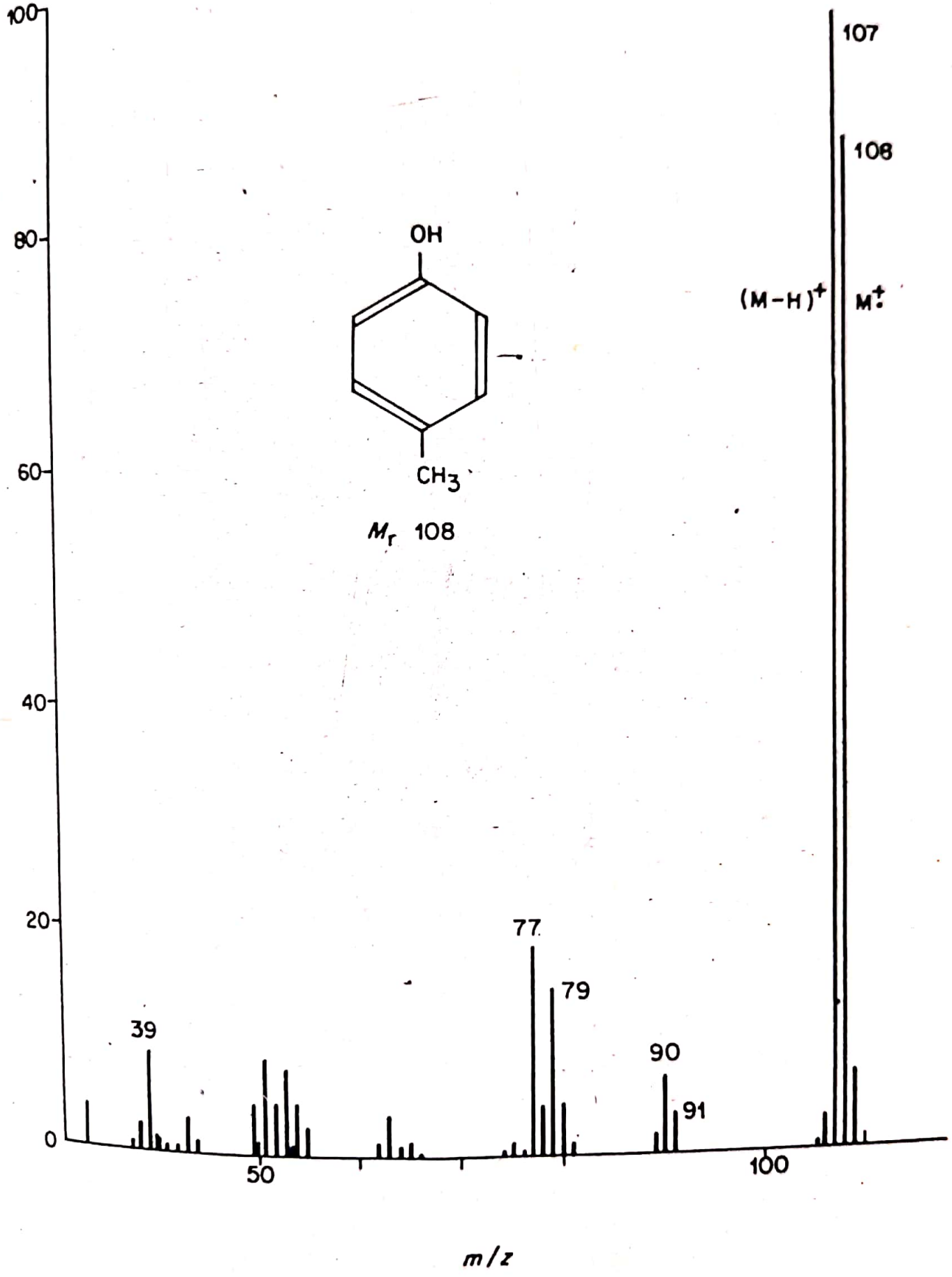
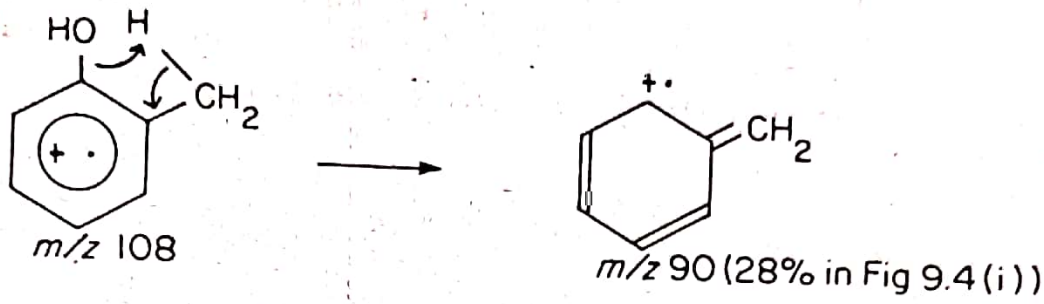
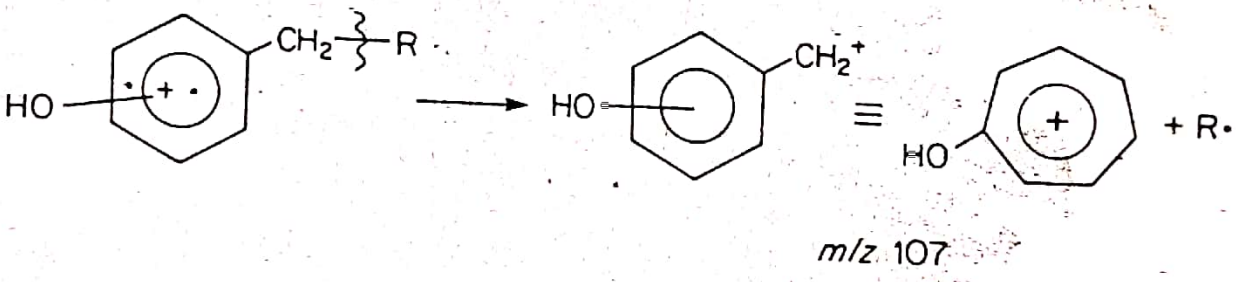


Fig. 9.4d. *4-Methylhydroxybenzene*

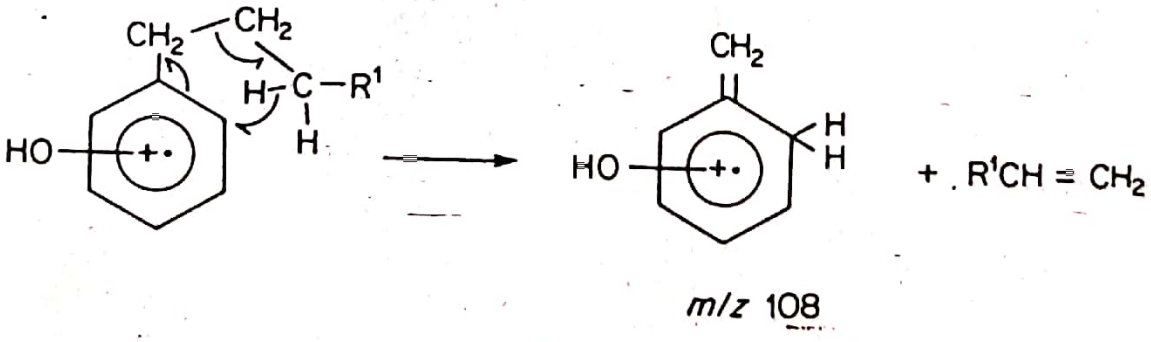
2-Methylhydroxybenzenes show an ortho effect which causes the elimination of H_2O:



while hydroxybenzenes with longer saturated carbon chains undergo both *benzylic cleavage*:



and a *six-centred hydrogen transfer process* involving a γ-hydrogen from the alkyl chain, if it is long enough to have one:



This means that both m/z 107 and 108 may be present in the spectra of such compounds.

Now try SAQ 9.4a to see if you can identify an unknown phenol from its spectrum.

AQ 9.4a

Fig. 9.4e shows the mass spectrum of a phenol, *Unknown 10*. Interpret this spectrum and suggest a structure for *Unknown 10*.

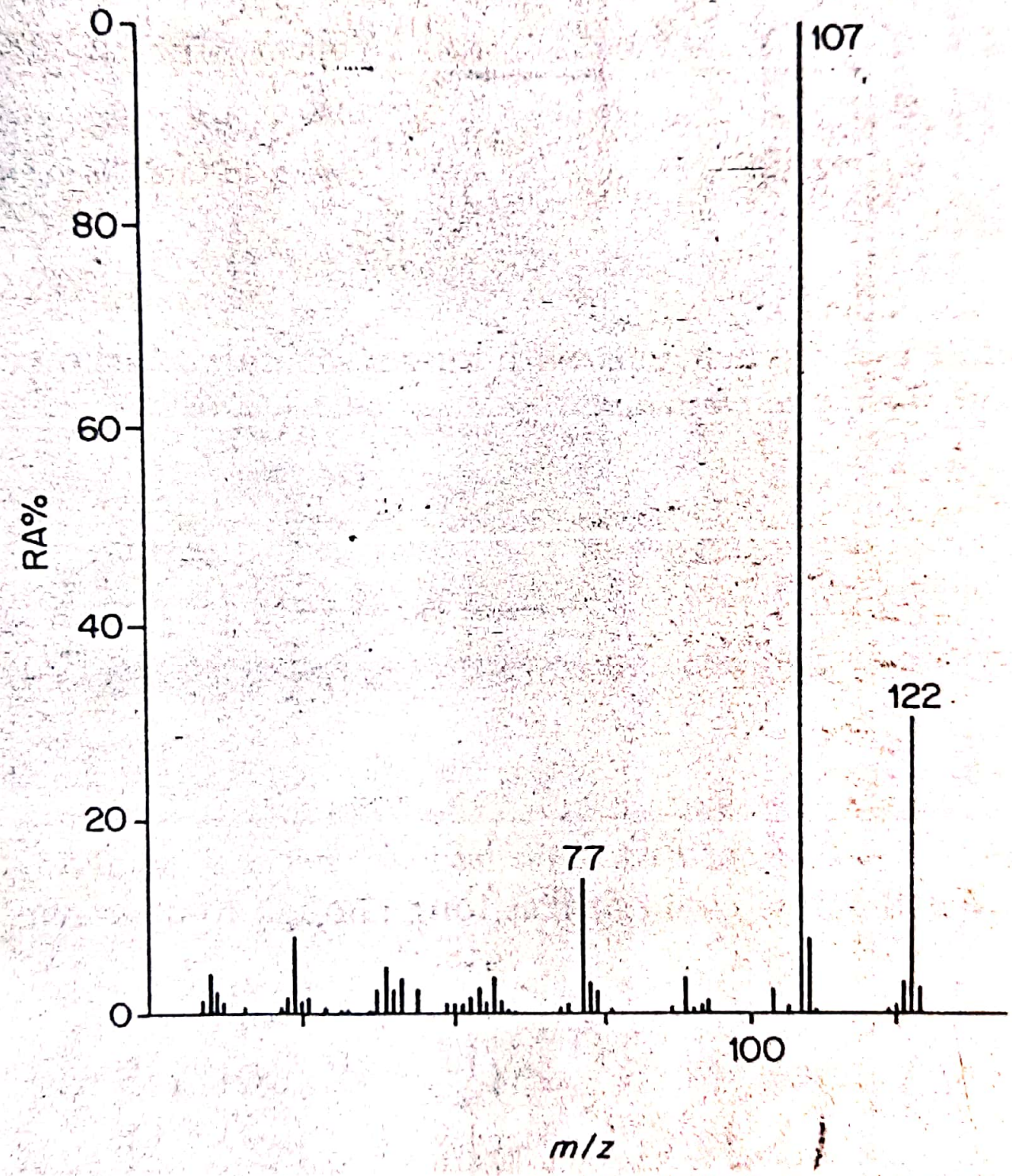


Fig. 9.4e. *Mass spectrum of* Unknown *10*