**SAQ 9.2c (cont.)**

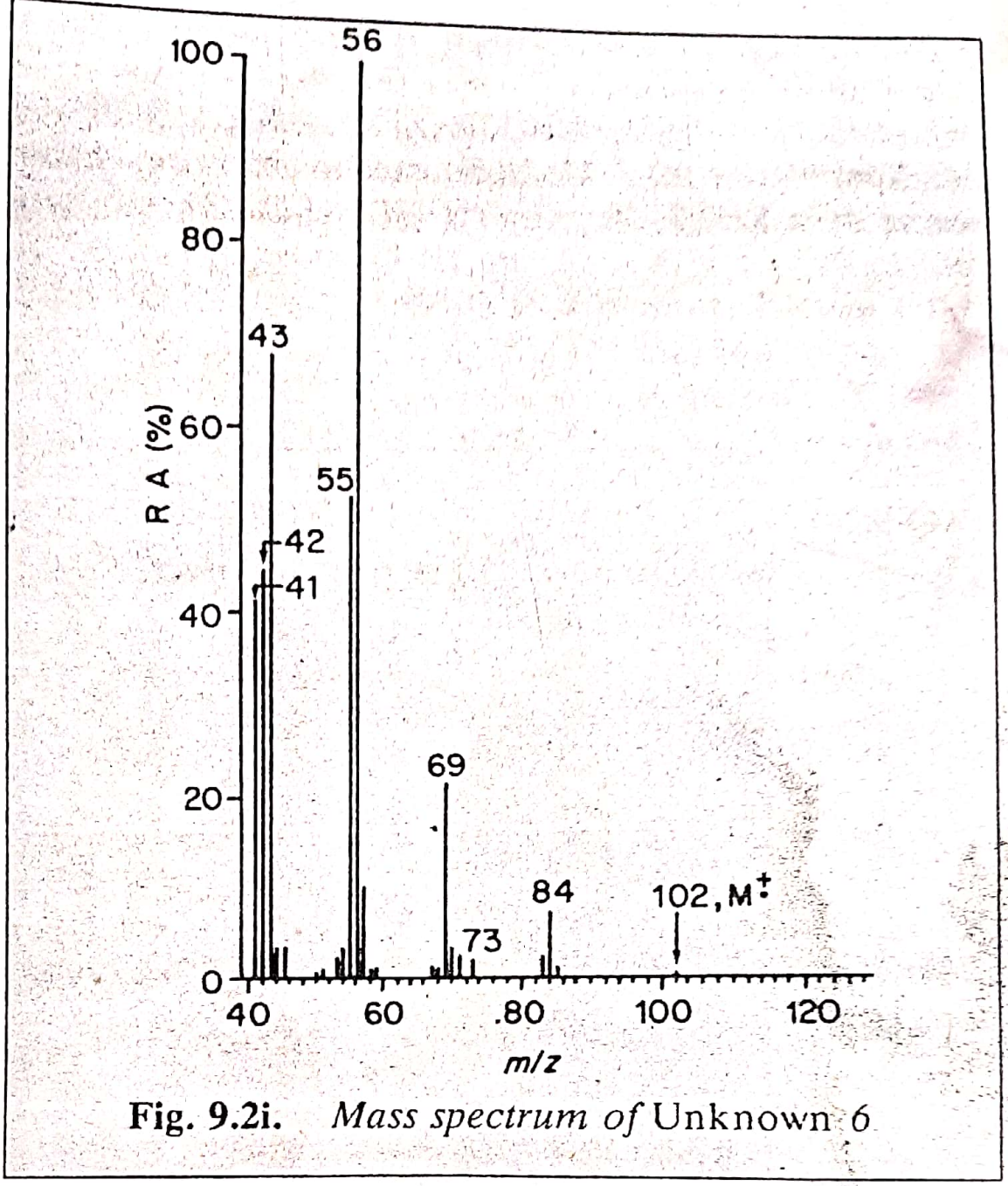
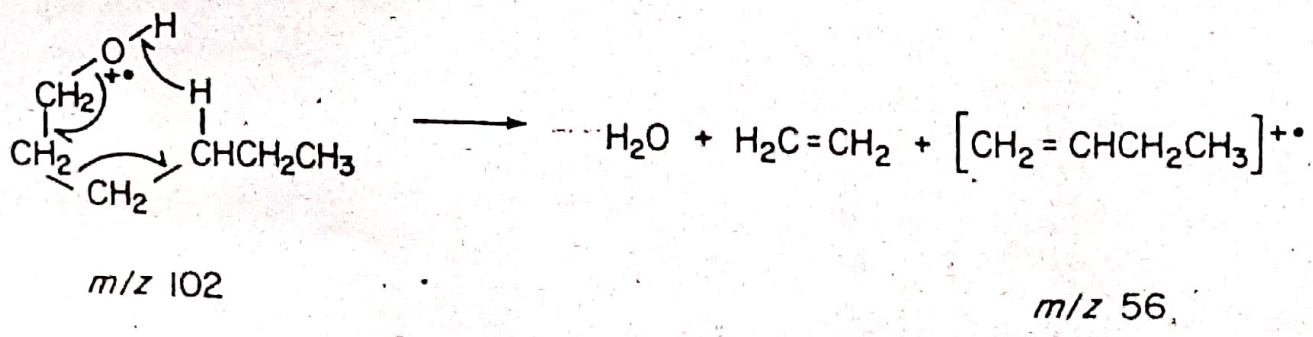



**Fig. 9.2i.** *Mass spectrum of* Unknown 6

**Response**

*Unknown 6* is hexanol, $CH_3(CH_2)OH$. The $M_r$ of 102 indicates a molecular formula of $C_6H_{14}O$, a saturated alcohol, and its low intensity is typical of primary alcohols. The base peak in this spectrum is $m/z$ 56 ie $(M - 46)^+$. This is typical of the concerted loss of $H_2O$ and $H_2C{=}CH_2$ shown by longer chain alcohols.



$m/z$ 31, $CH_2\overset{+}{O}H$, is not shown in Fig. 9.2i but in fact is about 45% RA. Other peaks are $(M - H_2O)$, $m/z$ 84; $(M - H_2O{-}CH_3)^+$ $m/z$ 69; $(M - H_2O{-}CH_2CH_3)^+$ $m/z$ 55; and $CH_3CH_2\overset{+}{C}H_2$ $m/z$ 43. Apart from $m/z$ 43, hydrocarbon ions are of low abundance, see eg $m/z$ 57, 71, 85.

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**SAQ 9.2d**

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

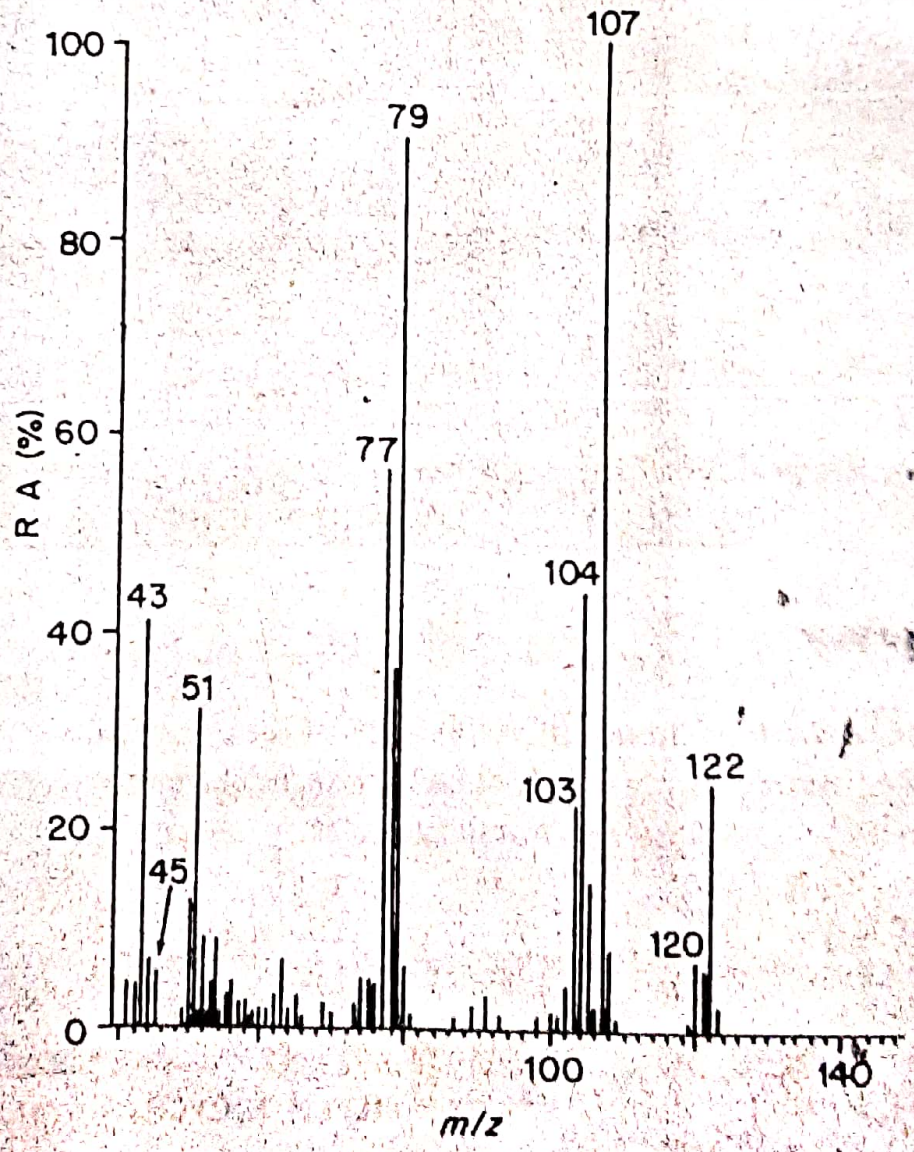
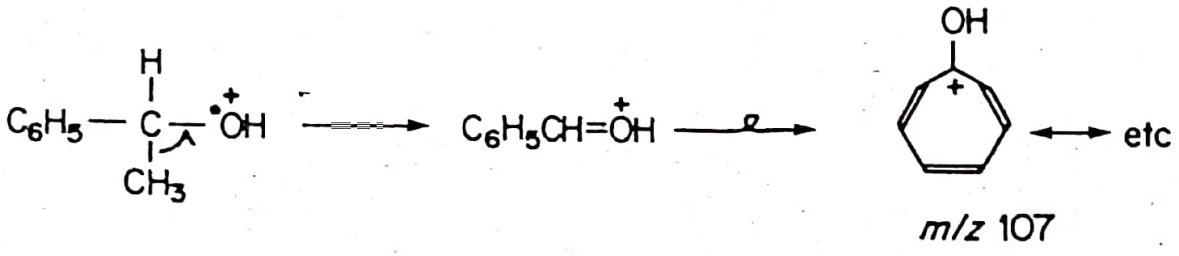



**Fig. 9.2j.** *Mass spectrum of* Unknown 7

**Response**

*Unknown 7* is 1-phenylethanol, $C_6H_5CH(OH)CH_3$. The $M^{+\cdot}$ indicates that this is an isomer of 2-phenylethanol (Fig. 9.2f) but the lack of $m/z$ 91 shows that the $C_6H_5CH_2$ grouping is absent. The presence of $m/z$ 107 combined with 79, 77 and 51 is very typical of the hydroxytropylium ion and its fragments so *Unknown 7* must contain a structural unit capable of forming this ion, but not containing $C_6H_5CH_2O$. The answer has to be a secondary alcohol, which loses $CH_3^{\cdot}$ preferentially against the predictions of Stevenson's Rule, because of the high stability of the hydroxytropylium ion:




$m/z$ 104 results from $(M - H_2O)^+$ and $m/z$ 103 from $[(M - H) - H_2O]^+$. In this spectrum $m/z$ 45 $CH_3CH{=}\overset{+}{O}H$ is replaced by $m/z$ 43, $CH_3CO^+$. It appears that $M^{+\cdot}$ loses two H to give $C_6H_5COCH_3^{+\cdot}$ (common in alcohol mass spectra since the ketone has a more stable $M^{+\cdot}$) and $CH_3CO^+$ is formed by $\alpha$-cleavage of this ion.

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