Response

Unknown 4 is butanal, $CH_3CH_2CH_2CHO$

You should have obtained an analysis table similar to the one opposite:

m/z	Possible Structures	Associated X	Inferences loss (amu)
72			$M^{+\cdot}$
71	C_5H_{11}, C_3H_7CO	1	aldehyde, acetal
57	C_4H_9, (C_3H_5O)	15	CH_3 loss – methyl compound
44	$CH_2{=}CHOH$, CO_2	28	aldehyde with γ-H, anhydride
43	CH_3CO, C_3H_7	29	CHO or C_2H_5 loss from ethyl compound or aldehyde
41	C_3H_5		shows presence of 3-carbon chain
39	C_3H_3		shows presence of 3-carbon chain
29	CHO, C_2H_5	43	aldehyde and/or C_2H_5 compound
27	C_2H_3		confirms hydrocarbon chain

Unknown 4 cannot be aromatic as the M_r is below that of benzene (78). The loss of $H^{\cdot}$ from $M^{+\cdot}$ is typical of aldehydes and acetals. The other compounds mentioned in the (M − X) table are irrelevant as they are aromatic or contain nitrogen. The presence of m/z 29 confirms an aldehyde rather than an acetal. The base peak m/z 44 is especially characteristic of aldehydes having γ-H atoms, which rearrange to give the ion $CH_2{=}CHOH^{+\cdot}$ (Fig. 9.1b). $(M - CH_3)^+$ and $(M - CH_3CH_2)^+$ are both present indicating an alkyl chain, along with other typical hydrocarbon ions at m/z 27, 39 and 41. Putting this together to reach the required M_r of 72 we get

$$\overset{\gamma}{CH_3}-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-CHO$$

As shown, this has three γ-H and therefore would form *m/z* 44, typical of aliphatic aldehydes.

Other structures you might have thought of are $(CH_3)_2CHCHO$ (but this has no γ-H so could not form *m/z* 44) or $CH_3COCH_2CH_3$ (would give *m/z* 57, 43, 29 and 27, but not the all-important base peak *m/z* 44). If you thought *4* was pentane or one of its isomers because of the odd mass ions which could be hydrocarbon cations such as *m/z* 27, 29, 39, 41, 43, 57 this was not a bad guess because some of them *are* hydrocarbon ions, but *m/z* 44 cannot be obtained from pentane. Odd electron ions like *m/z* 44 are always very significant in mass spectra.

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SAQ 9.1b

Analyse the spectrum of *Unknown 5*, Fig. 9.1j, which contains a nitrogen atom. Suggest a possible structure for the compound, using the correlations in Fig. 9.1a and 9.1b.

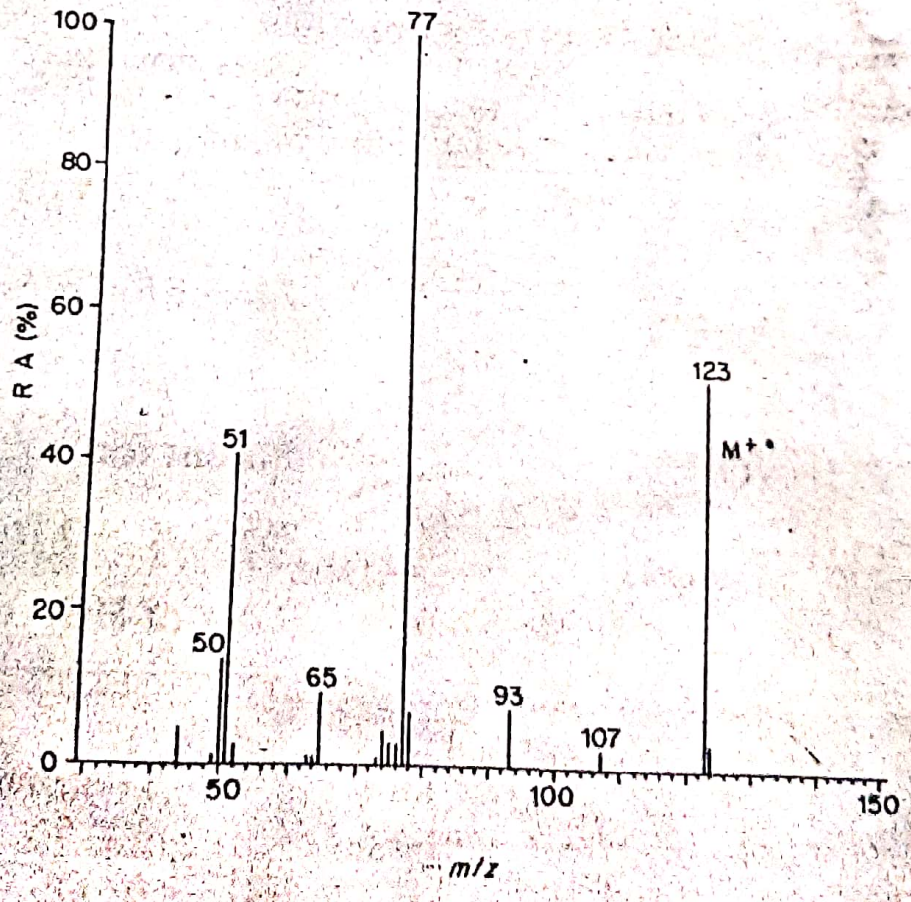

Fig. 9.1j. *Mass spectrum of* Unknown 5

Response

Unknown 5 is nitrobenzene, $C_6H_5NO_2$

You should have obtained an analysis table similar to the one below:

m/z	Possible Structure	Associated X Loss (amu)	Inferences
123	$C_6H_5NO_2$		M^+ – odd mass, so contains odd number of N
107	C_6H_5NO	16	Loss of O – nitrocompound
93	C_6H_5O, C_6H_6N	30	Loss of NO from nitrocompound, or aromatic methyl ether
77	C_6H_5	46	Loss of NO_2 from nitrocompound, aliphatic alcohols?, ethyl *o*-ester?
65	C_5H_5	58	Does not make sense
93	C_6H_5O	–	Parent for m/z 66 and 65?
65	C_5H_5	28	Loss of CO from m/z 93
93	C_6H_6N	–	Parent for m/z 66 and 65?
65	C_5H_5	28	Loss of HCNH?
107	C_6H_5NO	–	Parent for m/z 77?
77	C_6H_5	30	Loss of NO from m/z 107
51	C_4H_3	26	Loss of HC=CH from m/z 77

The intense M^+ and higher ions are very characteristic of an aromatic compound. The losses of O (16 amu), NO (30 amu), and NO_2 (46 amu) are characteristic of nitrocompounds. This accounts for the ions at m/z 107, 93 and 77. The presence of m/z 51 confirms that m/z 77 is $C_6H_5^+$, because this ion always gives some m/z

51 by loss of ethyne. You will not see one without the other. If m/z 77 is $C_6H_5^+$, then 5 must contain a single NO_2 group to get the M_r of 123. The m/z 93 ion could be C_6H_5O or C_6H_6N, but only the former can lose 28 amu easily (CO) to give $C_5H_5^+$ at m/z 65. If you said 5 was $C_6H_5NH{-}NO$ this was consistent with the formation of m/z 93, but this ion would be expected to lose HCN to give m/z 64. Congratulations if you said 5 was $C_6H_5O{-}NO$. This was a very logical structure to deduce, and in fact nitrobenzenes *do* rearrange to nitrites before they lose NO (see Section 9.9)

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