

Mass Spectra of α -Aminonitriles. I.

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GUSTAV SCHROLL

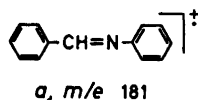
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The mass spectra of a series of α -aminonitriles have been recorded and interpreted. When the amino group is not fully substituted, HCN is easily eliminated from the molecular ion leading to ionized Schiff bases, the fragmentations of which are determining the mass spectrum. When the compound is α,β -unsaturated, the HCN-elimination is negligible, and the fragmentations are triggered by the enamine group. Finally, when the amino group is fully substituted, α -cleavages are the dominant features. Skeletal rearrangements are observed in some cases.

RESULTS AND DISCUSSION

α -Aminonitriles are important intermediates in the Strecker synthesis of α -aminoacids,¹ and we therefore found it worthwhile to investigate this class of compound by mass spectrometry.

The mass spectrum of 2-anilino-2-phenylacetonitrile (I, Fig. 1) displays a small molecular ion peak as well as $M+1$ and $M-1$ peaks indicating the cyano group.² The main fragmentation mode is the elimination of HCN from the molecular ion leading to ionized benzanil (*a*).



The remaining part of the mass spectrum is virtually that of *a*.^{3,4} This corresponds to the facile expulsion of HCN from the molecular ion observed in the mass spectra of various cyanohydrins.⁵

The same features were observed for all 2-anilino-2-arylacetonitriles investigated. Whereas this was also true for 2-anilino-2-styrylacetonitrile,

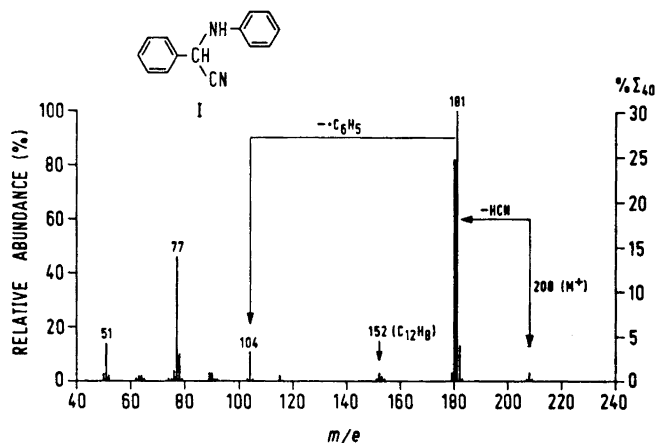


Fig. 1

the isomeric enamine 2-anilino-4-phenylcrotonitrile (II) eliminates HCN to a small extent only. The molecular ion is responsible for the base peak in the mass spectrum of II (Fig. 2). Enamines are known to undergo γ -cleavages upon

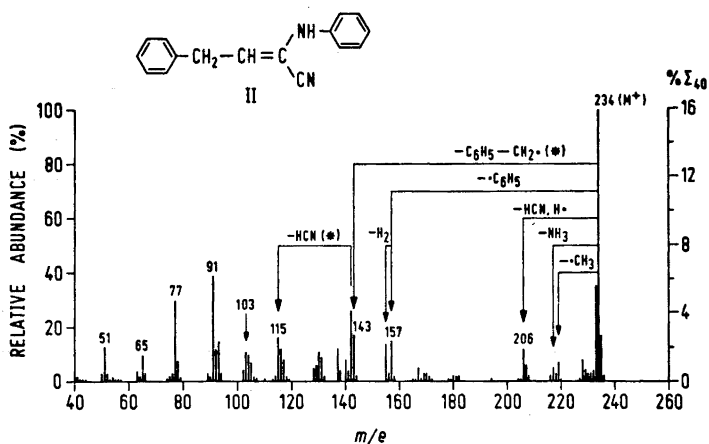
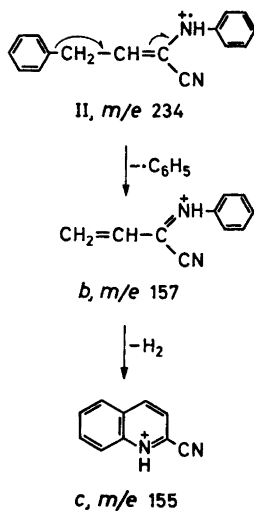


Fig. 2

electron impact,⁶ and the peaks at $M-1$ and $M-77$ in the mass spectrum of II are the results of such processes with the loss of $H\cdot$ and $\cdot C_6H_5$, respectively. The formation of ions with mass 155, corresponding to $M - \cdot C_6H_7$ (H. R.), can be rationalized as the formation of protonated 2-cyanoquinoline (c) by the loss of H_2 from b as depicted in Scheme 1. Exact mass measurements (Table 1) revealed that the peaks at m/e 219 and 217 correspond to the loss



SCHEME 1

of $\cdot\text{CH}_3$ and NH_3 from the molecular ion. Both processes require skeletal rearrangements of the molecular ion prior to fragmentation.

Table 1.

Compound	Observed mass	Composition	Calculated mass
I	153.0697	C ₁₂ H ₉	153.0704
II	219.0929	C ₁₅ H ₁₁ N ₂	219.0922
	217.0889	C ₁₆ H ₁₁ N	217.0891
	155.0601	C ₁₀ H ₇ N ₂	155.0609
	143.0607	C ₉ H ₇ N ₂	143.0609
	142.0638	C ₁₀ H ₈ N	142.0657
IV	171.0910	C ₁₁ H ₁₁ N ₂	171.0922
VI	201.1511	C ₁₄ H ₁₃ N	201.1517
	186.1289	C ₁₃ H ₁₃ N	186.1283
	169.0767	C ₁₁ H ₉ N ₂	169.0766
	110.0970	C ₇ H ₁₂ N	110.0970

The formation of $\text{M} - \cdot\text{C}_7\text{H}_7$ ions (H. R.) from the molecular ion of II is supported by the presence of a metastable peak (indicated in the figure by an asterisk) and so is the loss of HCN from the $\text{M} - \text{C}_6\text{H}_5\text{NH}\cdot$ ions. The unexpected importance of the β -cleavage in the electron impact induced fragmentation of this enamine can only be rationalized by the assumption of a skeletal rearrangement as stressed below in the discussion of the mass spectrum of the enamine VIII. Hydrocarbon fragment ions of mass 115, 91, 77, 65, and

51 are observed. When the α -amino group is fully substituted as in the case of 2-phenyl-2-piperidinoacetonitrile (III), the formation of a Schiff base by HCN-elimination is no longer possible, and the importance of the molecular ion peak increases. Hence, whereas the molecular ion peak in the case of I has an abundance of 0.9% Σ_{40} , the molecular ion of III (Fig. 3) is responsible for about 10% Σ_{40} .

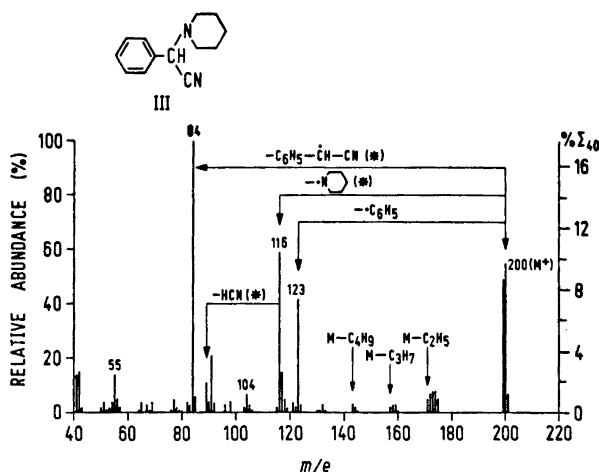
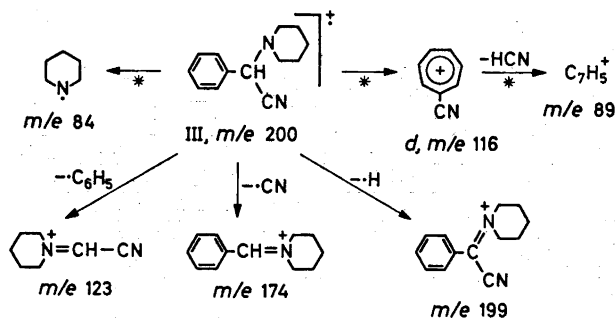


Fig. 3

Cleavage of the bond between the α -carbon and the amino group in the molecular ion of III leads to ions of mass 84 and 116, depending on the charge locus in the molecular ion. Both processes are supported by metastable peaks. The m/e 116 ions can be formulated as the cyanotropylium ion,⁸ *d* (Scheme 2). α -Cleavages in the molecular ion take place with the loss of $H\cdot$, $\cdot CN$, and $\cdot C_6H_5$, respectively, as depicted in Scheme 2. This fragmentation mode is typical for amines.⁹ Fragmentations in the piperidino moiety with loss of



SCHEME 2

C_2 , C_3 , and C_4 hydrocarbon species are indicative for the cyclic amine,¹⁰ but of low abundance.

The mass spectrum of the morpholino analogue IV (Fig. 4) supports the interpretation of the mass spectrum of III, although the abundance of the various ions differ to some extent. Interesting is the abundant $M-31$ peak

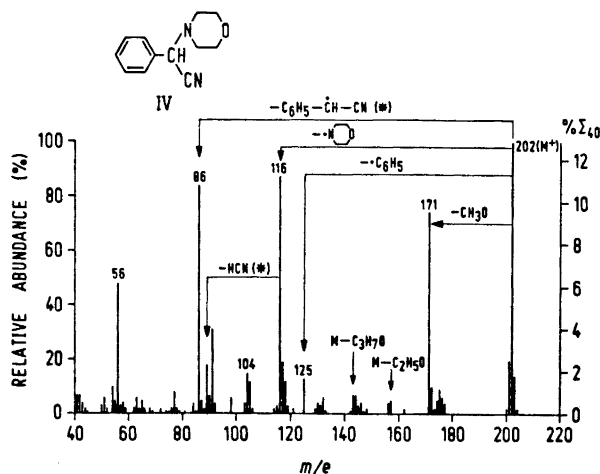


Fig. 4

in the mass spectrum of IV. This is due to the loss of $CH_3O\cdot$ from M^+ . The abundance of this peak relative to that of M^+ decreases with decreasing electron energy, whereas the percentage of the total ion current increases slightly from 70 to 15 eV. The actual figures are:

$$\begin{array}{l} 70 \text{ eV: } 74 \%, 7.83 \%, \sum_{50}; \quad 25 \text{ eV: } 68 \%, 8.40 \%, \sum_{50}; \\ 20 \text{ eV: } 62 \%, 9.18 \%, \sum_{50}; \quad 15 \text{ eV: } 52 \%, 9.25 \%, \sum_{50}; \\ 12 \text{ eV: } 33 \%, 7.76 \%, \sum_{50}. \end{array}$$

Finally, the mass spectrum (Fig. 5) of 2-*p*-chlorophenyl-2-morpholinoacetonitrile (V) displays a fragmentation pattern similar to that of IV.

2-Styryl-2-piperidinoacetonitrile (VI) and 2-styryl-2-morpholinoacetonitrile (VII) display similar mass spectra (Figs. 6 and 7). In both spectra, the molecular ion peak is the most abundant. The loss of a hydrogen atom from VI leads to the formation of rather abundant $M-1$ ions (65%, 5.8% \sum_{40}). At 20 eV, the abundance is 40% (8.4% \sum_{40}), and at 15 eV, this process is still favourable, giving rise to a 15% peak (6.9% \sum_{40}). If the $M-H\cdot$ ion is the result of a simple cleavage reaction, it is most likely that one of the hydrogens α to the piperidino nitrogen is lost. If, however, the formation of this ion involves bond-making, the loss of one of the *ortho*-hydrogens from the phenyl group is more probable (*e*, Scheme 3). The relative high abundance of the $M-1$ peak in the low energy mass spectra of VI supports the latter formulation.¹¹

Peaks in the mass spectrum of VI at m/e 211, 197, 183, and 169 are due to the loss of $\cdot CH_3$, $\cdot C_2H_5$, $\cdot C_3H_7$, and $\cdot C_4H_9$, respectively. A similar frag-

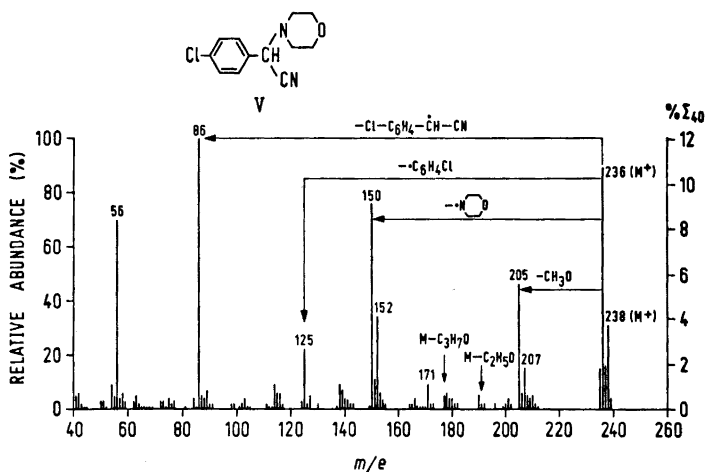


Fig. 5

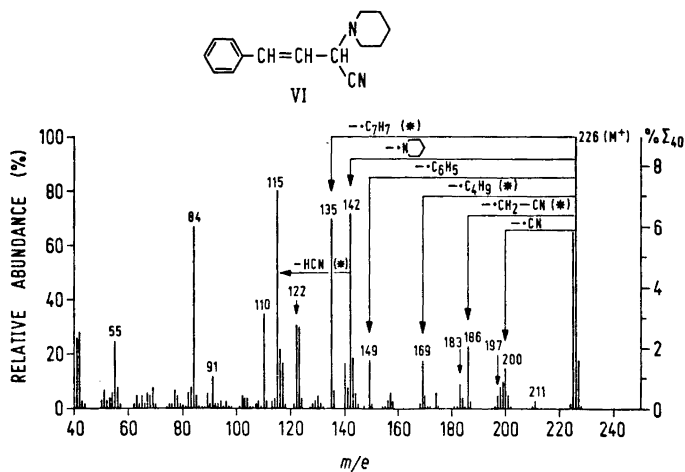


Fig. 6

mentation pattern involving the piperidino group was observed in the mass spectrum of III. The expulsion of the butyl radical from the molecular ion is indicated by a metastable peak. The abundances of the M -alkyl peaks decrease with decreasing electron beam energy, and only the $M-\cdot C_4H_9$ peak remains at 15 eV. By analogy the morpholino compound VII undergoes loss of alkoxy radicals. Whereas the peaks corresponding to $M-\cdot OCH_3$ were very prominent in the mass spectra of IV and V, the $M-\cdot OCH_3$ peak in the mass spectrum of VII is of surprisingly low abundance. It should also be noted that the expulsion of C_3H_6O is more important than the loss of $\cdot OC_3H_7$ (m/e 169).

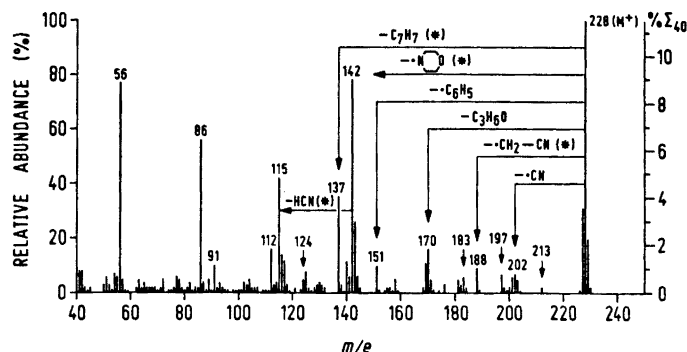
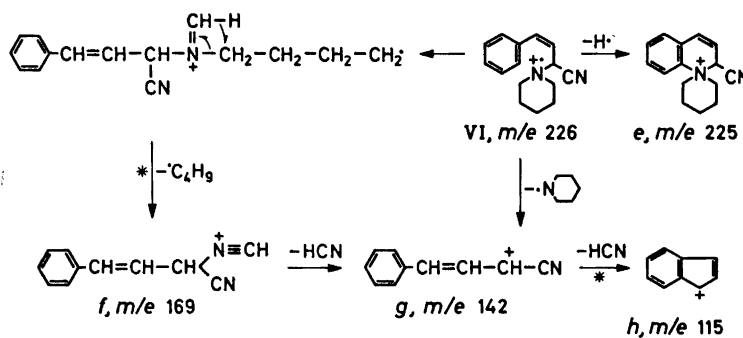


Fig. 7

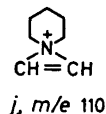
The formation of ions with mass 142 takes place by the cleavage of the bond between the α -carbon and the nitrogen. These ions may also be the result of HCN-elimination from *f*, as depicted in Scheme 3. Further loss of HCN from *g* leads to what is assumed to be *h*.

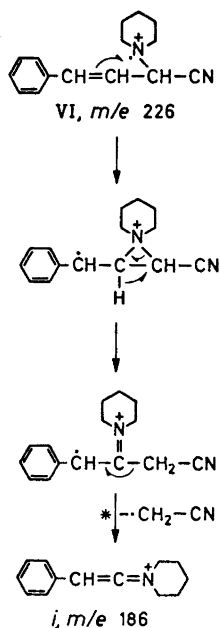


SCHEME 3

A peak in the mass spectrum of VI at m/e 186 corresponds to $\text{M} - \cdot\text{CH}_2\text{-CN}$. This process necessitates a skeletal rearrangement of the molecular ion, as visualized in Scheme 4.

The ions of mass 110 from VI have the composition $\text{C}_7\text{H}_{12}\text{N}$. In the mass spectrum of the morpholino compound VII, a peak at m/e 112 is due to analogue ions, whereas no peak of similar abundance at m/e 112 is found in the mass spectrum (Fig. 8) of the enamine VIII. In the mass spectra of VI, the abundances of these ions are: 3.1% Σ_{40} at 70 eV, 4.5% Σ_{40} at 20 eV, and 2.1% Σ_{40} at 15 eV. These ions may be formulated as *j*:

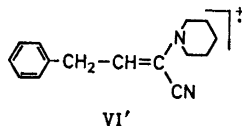




SCHEME 4

Loss of the styryl groups from VI and VII results in the formations of ions with mass 123 and 125, respectively, corresponding to the loss of $\cdot\text{C}_6\text{H}_5$ from III and IV. $\text{M} - \cdot\text{C}_6\text{H}_5$ ions are also found from the mass spectra of VI and VII (m/e 149 and 151, respectively).

These ions probably undergo elimination of HCN, leading to ions of mass 122 and 124. The loss of the phenyl group might be due to an initial isomerization of VI to ionized 2-piperidino-4-phenylcrotonitrile and of VII to VIII from which $\cdot\text{C}_6\text{H}_7$ radicals are lost by α -cleavages as in the case of compound II.



However, as seen from the mass spectrum of VIII (Fig. 8) expulsion of a phenyl radical is even less important here than in the case of VII. The $\text{M} - 77$ ion from VI can be formulated as *k*, and the ions formed by further loss of HCN as *l*:

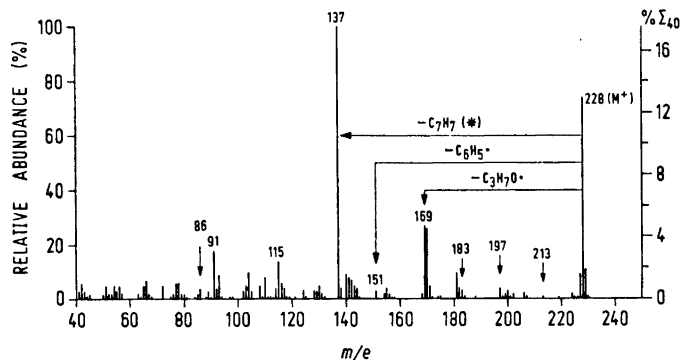
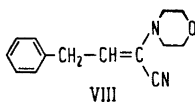
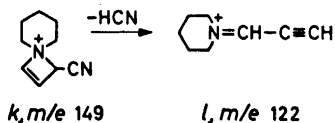


Fig. 8

Whereas the isomerizations of VI to VI' and of VII to VIII were not involved in the elimination of $\cdot\text{C}_6\text{H}_5$, these processes probably occur prior to the expulsions of $\cdot\text{CH}_2\text{-C}_6\text{H}_5$ from VI and VII. In the mass spectrum of the enamine VIII, the $\text{M}-\cdot\text{CH}_2\text{-C}_6\text{H}_5$ ions are responsible for about 17% Σ_{40} . This is more than 30 times the abundance of the $\text{M}-\cdot\text{C}_6\text{H}_5$ α -cleavage ions, expected to be the more prominent.⁸ When VIII was partially deuterated in the 4-position (approximately 40% d_2 , 50% d_1 , and 10% d_0 , from the molecular ion peaks) the m/e 137 peak was partially shifted to m/e 138 (m/e 137: m/e 138 = 46/54), although NMR spectroscopy confirmed that only the benzylic hydrogens were exchanged with deuterium. The m/e 137 and 138 ions contributed together 17.75% Σ_{40} , whereas the abundance of the m/e 137 peak in the mass spectrum of d_0 -VIII has an abundance of 17.68% Σ_{40} . Further, metastable peaks in the mass spectrum of deuterated VIII indicate the formation of 137^+ from d_0 -VIII, d_1 -VIII and d_2 -VIII, as well as the formation of 138^+ from d_1 -VIII and d_2 -VIII.

These findings can only be due to an initial scrambling of the hydrogens with the deuteriums in the molecular ions of d_1 - and d_2 -VIII, prior to the β -cleavage.

The only explanation for the facile formation of the $\text{M}-\cdot\text{C}_7\text{H}_7$ ions from VI, VII, and VIII is the formation of a stable ion, as m .



$m, m/e$ 135

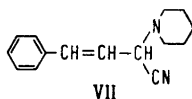
EXPERIMENTAL

The mass spectra were recorded with an A.E.I. MS 902 double focusing mass spectrometer, using the direct inlet with a source temperature of 120°C. Electron beam energies listed are only nominal.

All aldehydes and amines used were freshly distilled. Some of the nitriles employed in this study were prepared as described earlier in the literature,¹² some by a new method.¹³ The nitriles II, VI, VII, and VIII are new compounds. Microanalytic data and melting points are listed in Table 2.

Table 2.

Compound		% C	% H	% N	% O	M.p.
II	Calc.	82.05	5.98	11.96	—	99–100°
	Found	82.00	5.90	11.80	—	
VI	Calc.	79.64	7.96	12.39	—	112°
	Found	79.60	7.90	12.20	—	
VII	Calc.	73.68	7.01	12.28	7.01	85°
	Found	73.20	7.00	12.00	—	
VIII	Calc.	73.68	7.01	12.28	7.01	62°
	Found	73.30	7.00	12.10	—	



VII

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