Mass Spectral Fragmentation Pattern of *trans*-1,2-Di-(3-pyridyl)ethylene and *trans*-1,2-Di(4-pyridyl)ethylene

NEIL G. KEATS and LINDSAY A. SUMMERS

Department of Chemistry, The University of Newcastle, 2308, New South Wales, Australia

(Z. Naturforsch. **32b**, 1152-1155 [1977]; received June 13, 1977)

Mass Spectra, *trans*-1,2-Di(3-pyridyl)ethylene, *trans*-1,2-Di-(4-pyridyl)ethylene

The mass spectral fragmentation patterns of *trans*-1,2-di-(3-pyridyl)ethylene and *trans*-1,2-di-(4-pyridyl)ethylene obtained on electron impact have been elucidated. They are more complex than the disintegration pathway observed with *trans*-1,2-di-(2-pyridyl)ethylene.

The mass spectrum of stilbene (1) has attracted considerable interest¹⁻¹⁴. It is dominated⁶ by the peaks due to the molecular ion at mass 180, which is the base peak and the dehydrogenated species M-1 (85%) and M-2 (50%). The principal initial fragmentation routes involve the unusual loss of CH₃· from the molecular ion to give a peak at mass 165 (40%) and loss of C₂H₂ from the M-2 species to give a peak at mass 152 (10%).

We recently reported¹⁵ the mass spectral fragmentation pattern of *trans*-1,2-di-(2-pyridyl)ethylene (2). In this case the base peak was due to the (M-1)⁺ ion, the M⁺ ion giving rise to a peak of 36% of the intensity of the base peak. The principal fragmentation routes involved loss of HCN from the M-1 ion to afford a C₁₁H₈N⁺ ion at mass 154 (9%) and rupture of one of the pyridyl-CH bonds to afford peaks at mass 104 due to the C₇H₆N⁺ ion (10%) and at mass 78 due to the C₅H₄N⁺ ion (14%). The loss of CH₃· was not a significant disintegration pathway. We have now extended this study to an analysis of the fragmentation pathways of *trans*-

1,2-di-(3-pyridyl)ethylene (3) and *trans*-1,2-di-(4-pyridyl)ethylene (4). The mass spectrum of 4 has been briefly recorded⁶ but no high resolution mass measurements were reported.

The mass spectrum of *trans*-1,2-di-(3-pyridyl)ethylene (3) (Fig. 1) is quite different from that

Fig. 1. Mass spectrum of *trans*-1,2-di-(3-pyridyl)ethylene.

of *trans*-1,2-di-(2-pyridyl)ethylene (2)¹⁵ and is more complex. Unlike 2, the base peak in the spectrum of 3 is due to the molecular ion at mass 182. The M-1 ion at mass 181 gives rise to a peak of 52% of the intensity of the base peak. Like 2, however, and in contrast to the fragmentation of stilbene, the loss of CH₃· from the molecular ion of 3 is a very minor fragmentation pathway. It produces a small peak (1%) at mass 167 due to a C₁₁H₇N₂⁺ ion.

Another minor fragmentation route (Scheme 1) from the molecular ion of 3 involves loss of the elements C₂H₃ to afford a species of formula

Requests for reprints should be sent to Professor L. A. SUMMERS, Department of Chemistry, The University of Newcastle, 2308, New South Wales, Australia.

Scheme 1

$C_{10}H_7N_2^+$ at mass 155 (4%) presumably a bipyridyl molecular ion less one hydrogen. This species is also formed by the loss of C_2H_2 from the $M-1$ ion of **3** at mass 181. Metastable transitions for the fragmentations $182 \rightarrow 155$ and $181 \rightarrow 155$ were present. The analogous losses of C_2H_3 and C_2H_2 were not observed to any significant extent in the disintegration of 1,2-di-(2-pyridyl)ethylene (**2**)¹⁵. The subsequent fragmentation of the $C_{10}H_7N_2^+$ ion at mass 155 involves loss of HCN . This accounts in part for the peak at mass 128 (4%) due to a $C_9H_6N^+$ ion considered to be the isoquinoline molecular ion less one hydrogen. A metastable peak for the transition $155 \rightarrow 128$ was observed. The $C_{10}H_7N_2^+$ ion may also lose $C_4H_3^*$ and this fragmentation route might account for the major component of the peak at mass 104 (2%) due to a $C_6H_4N_2^+$ species. No metastable corresponding to the transition $155 \rightarrow 104$ was however observed.

The principal fragmentation route from the molecular ion of **3** involves loss of HCN from the $M-1$ ion at mass 181. This gives rise to a strong peak (40%) at mass 154 due to a $C_{11}H_8N^+$ ion probably the 3-phenylpyridine molecular ion less one hydrogen. Loss of hydrogen from the $C_{11}H_8N^+$ ion accounts

for the small peaks at mass 153 (3%; $C_{11}H_7N^+$), and 152 (1%; $C_{11}H_6N^+$). A strong metastable peak is present corresponding to the $181 \rightarrow 154$ transition. The loss of HCN from the $C_{11}H_8N^+$ ion, for which a metastable is observed, accounts for the major component of the peak at mass 127 (5%; $C_{10}H_7^+$) and further loss of H^+ for the peak at mass 126 (3%; $C_{10}H_6^+$). The $C_{11}H_8N^+$ ion also loses C_2H_2 and this disintegration provides another source of the $C_9H_6N^+$ ion at mass 128.

The small peak at mass 130 (2%) is due to a $C_9H_8N^+$ ion probably formed from the molecular ion of **3** by loss of $\cdot CH=CH-CN$ although no metastable for the transition $182 \rightarrow 130$ was observed. The $C_9H_8N^+$ ion is depicted as the isoquinolinium ion. Likewise the $C_9H_7N^+$ species at mass 129 (4%), considered to be the isoquinoline molecular ion, may be formed by loss of the same elements (C_3H_2N) from the $M-1$ ion of **3** at mass 181.

The minor component of the peak at mass 104, due to a $C_7H_6N^+$ ion (1%), is presumably formed by rupture of one of the CH -pyridyl bonds of **3**. This fragmentation route from **3** is very much less pronounced than the similar bond rupture observed

with *trans*-1,2-di-(2-pyridyl)ethylene (**2**)¹⁵. The other component of the central bond rupture of **3**, the C₅H₄N⁺ ion at mass 78, is also present only in small amounts (2%). In contrast the C₅H₄N⁺ ion gave rise to a prominent peak in the spectrum of **2**¹⁵.

The peaks at mass 103 (2%; C₇H₅N⁺), 102 (5%; C₈H₆⁺), 102 (2%; C₇H₄N⁺) and 101 (3%; C₈H₅⁺) in the spectrum of **3** are typical of those observed from the fragmentation of isoquinoline derivatives¹⁶. Likewise the peaks below a mass of 100 are largely those to be expected from pyridine and benzene derivatives and require no comment.

The empirical formulae of the ions obtained by high resolution mass measurements are given in Table I. Fragmentation pathways where the ap-

Table I. Empirical formula of fragment ions*.

Compound	Mass (formula)
3	167 (C ₁₁ H ₇ N ₂); 155 (C ₁₀ H ₇ N ₂);
	154 (C ₁₁ H ₈ N); 153 (C ₁₁ H ₇ N);
	152 (C ₁₁ H ₆ N); 130 (C ₉ H ₈ N);
	129 (C ₉ H ₇ N); 128 (C ₉ H ₆ N);
	127 (5%; C ₁₀ H ₇); 127 (1%; C ₉ H ₅ N);
	126 (C ₁₀ H ₆); 104 (1%; C ₇ H ₆ N);
	104 (2%; C ₆ H ₄ N ₂); 103 (C ₇ H ₅ N);
	102 (5%; C ₈ H ₆); 102 (2%; C ₇ H ₄ N);
	101 (C ₈ H ₅); 91 (M [⊕]); 90 (C ₆ H ₄ N);
	89 (C ₇ H ₅); 88 (C ₇ H ₄); 87 (C ₇ H ₃).
4	155 (12%; C ₁₁ H ₉ N); 155 (3%; C ₁₀ H ₇ N ₂);
	154 (C ₁₁ H ₈ N); 153 (C ₁₁ H ₇ N);
	152 (C ₁₁ H ₆ N); 142 (C ₁₀ H ₈ N);
	141 (C ₁₀ H ₇ N); 140 (C ₁₀ H ₆ N);
	129 (C ₉ H ₇ N); 128 (7%; C ₉ H ₆ N);
	128 (4%; C ₁₀ H ₈); 127 (11%; C ₁₀ H ₇);
	127 (1%; C ₉ H ₅ N); 126 (C ₁₀ H ₆);
	104 (2%; C ₇ H ₆ N); 104 (2%; C ₆ H ₄ N ₂);
	103 (C ₇ H ₅ N); 102 (4%; C ₈ H ₆);
	102 (1%; C ₇ H ₄ N); 101 (C ₈ H ₅);
	100 (1%; C ₈ H ₄); 100 (1%; C ₇ H ₂ N);
	99 (1%; C ₈ H ₃); 99 (1%; C ₇ HN);
	91 (M [⊕]); 90 (C ₆ H ₄ N); 89 (C ₇ H ₅);
	88 (C ₇ H ₄); 87 (C ₇ H ₃).

* Only peaks above mass 80 and ≥ 1% of base peak in intensity are recorded.

propriate metastable transitions were observed are denoted in the Schemes by an asterisk.

The spectrum of *trans*-1,2-di-(4-pyridyl)ethylene (**4**) (Fig. 2) is very similar to that of *trans*-1,2-di-(3-pyridyl)ethylene (**3**) but is quite different from that of *trans*-1,2-di-(2-pyridyl)ethylene (**2**). There

Fig. 2. Mass spectrum of *trans*-1,2-di-(4-pyridyl)ethylene.

are, however, a few differences between the fragmentation patterns of **3** and **4** (Scheme 2). The most striking difference is that the base peak in the spectrum of **4** is due to the M-1 ion at mass 181. The M⁺ ion at mass 182 gives rise to a peak of 90% of the intensity of the base peak. There is also no significant loss of CH₃· from the molecular ion of **4**. The peak at mass 155 is much more pronounced in **4** than in **3**. In the spectrum of **4** it is made up of contributions from a C₁₁H₉N⁺ ion (12%), presumably the 4-phenylpyridine molecular ion as well as the C₁₀H₇N₂⁺ (3%) ion observed in the spectrum of **3**. There is a cluster of small peaks (1-2%) at mass 142, 141 and 140 in the spectrum of **4**. These arise from the loss of C₂H₂N· from the molecular ion of **4** giving a C₁₀H₈N⁺ ion at mass 142 followed by loss of hydrogen. This disintegration route is known to occur in both pyridine and 4,4'-bipyridine¹⁶ but is scarcely present in the case of **3**. Another minor difference between the spectra of **3** and **4** is in the composition of the peak at mass 128. In **4** a substantial contribution to this peak comes from a C₁₀H₈⁺ species (4%), depicted as the naphthalene molecular ion, formed by loss of HCN from the C₁₁H₉N⁺ species at mass 155. The major component of this peak is, however, due to the C₉H₆N⁺ ion (7%) as in the spectrum of **3**.

Experimental

The spectra were determined with an A. E. I. MS-30 mass spectrometer. The samples were analysed by a direct insertion probe at an ionising current of 70 eV. The ion source temperature was 100 °C. Elemental compositions were obtained by the peak matching method.

trans-1,2-Di-(3-pyridyl)ethylene¹⁷ and *trans*-1,2-di-(4-pyridyl)ethylene were analytically pure.

Scheme 2

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