Mass Spectral Fragmentation Pattern of 2,2'-Bipyridyls. Part X. *trans*-1,2-Di-(2-pyridyl)ethylene

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The base peak in the mass spectrum of *trans*-1,2-di-(2-pyridyl)ethylene is due to the M-1 ion. A major fragmentation route involves loss of HCN from the M-1 ion. Another important pathway involves rupture of one of the bonds linking a pyridine ring with the central CH=CH group.

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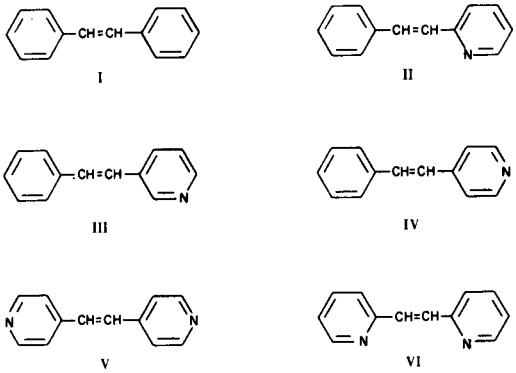
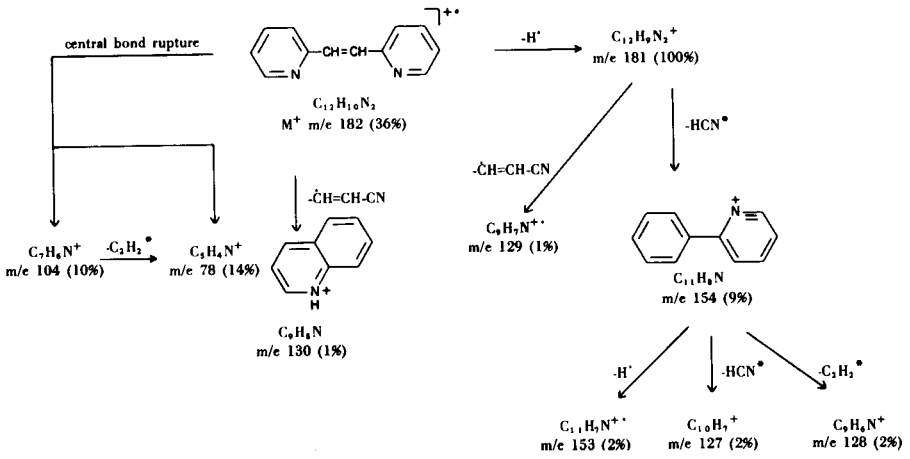
The mass spectrum of stilbene (I) has been the subject of considerable study (1-14). It is dominated (6) by the peaks due to the molecular ion at mass 180, which is the base peak and the dehydrogenated species M-1 (85%) and M-2 (50%). The principal initial fragmentation routes involve the unusual loss of $CH_3^{\bullet}$ from the molecular ion to give a peak at mass 165 (40%) and loss of C_2H_2 from the M-2 species to give a peak at mass 152 (10%). In the related styrylpyridines (II-IV) (6) the base peak is the M-1 ion. The loss of $CH_3^{\bullet}$ from the molecular ions is much less pronounced than with stilbene. With 1,2-di-(4-pyridyl)ethylene (V) the M-1 ion is again the base peak (6) but there is no evidence for a significant loss of $CH_3^{\bullet}$ from the molecular ion. As part of our study of the mass spectra of relatives of 2,2'-bipyridyl containing an atom of group placed between the pyridine rings (15-18) we now report the fragmentation pattern on electron impact or *trans*-1,2-di-(2-pyridyl)ethylene (VI) (2,2'-(1,2-ethenediyl)bispyridine). The spectrum is quite different from that of (V) (6).



The base peak in the mass spectrum of *trans*-1,2-di-(2-pyridyl)ethylene is due to the M-1 ion, $C_{12}H_9N_2^+$, at mass 181 while the molecular ion at mass 182 gives rise to a peak of 36% of the intensity of the base peak. The predominance of the M-1 ion recalls the similar result in the mass spectrum of 2,2'-thiodipyridine (17). The M-2 species at mass 180, and the M-3 species at mass 179 give very small speaks (2%).

One major fragmentation route involves loss of HCN from the M-1 ion at mass 181 to afford a $C_{11}H_8N^+$ ion at mass 154 (9%) probably due to the M-1 ion of 2-phenylpyridine. There is a very strong metastable peak corresponding to the transition 181 → 154. The $C_{11}H_8N^+$ ion may lose $H^{\bullet}$ to afford a $C_{11}H_7N^{+\bullet}$ species at mass 153 (2%). The $C_{11}H_8N^+$ ion at mass 154 disintegrates further by loss of either HCN to afford a $C_{10}H_7^+$ ion at mass 127 (2%) or C_2H_2 to give a $C_9H_6N^+$ ion at mass 128 (2%). Metastable peaks for both these transitions

Scheme



were observed in the spectrum.

A minor fragmentation route involves loss of the elements CH=CH-CN from the molecular ion of *trans*-1,2-di-(2-pyridyl)-ethylene, perhaps by rupture of one of pyridine rings, to afford a $C_9H_8N^+$ ion at mass 130 (1%) depicted as the quinolinium ion. The peak at mass 129, due to a $C_9H_7N^{+\cdot}$ species (1%), may be obtained by loss of the same elements from the M-1 ion of *trans*-1,2-di-(2-pyridyl)ethylene at mass 181.

Table 1

High Resolution Data

m/e	Elemental Composition	Observed Mass	Calculated Mass
154	$C_{11}H_8N$	154.0656	154.0657
153	$C_{11}H_7N$	153.0577	153.0578
130	C_9H_8N	130.0654	130.0657
129	C_9H_7N	129.0575	129.0578
128	C_9H_6N	128.0499	128.0500
127	$C_{10}H_7$	127.0547	127.0548
104	C_7H_6N	104.0499	104.0500

The second major fragmentation route involves rupture of one of the pyridyl-CH bonds of the molecular ion of *trans*-1,2-di-(2-pyridyl)ethylene. This results in the peak at mass 104 due to a $C_7H_6N^+$ ion (10%) and the peak at mass 78 due to a $C_5H_4N^+$ ion (14%). The small peaks below a mass of 78 in the spectrum are typical of those from pyridine derivatives.

Unlike stilbene the loss of $CH_3^{\cdot}$ is not a significant disintegration pathway with *trans*-1,2-di-(2-pyridyl)-ethylene.

The elemental composition of the ions depicted in the Scheme was in accord with high resolution data (Table 1). The metastable transitions are recorded in Table 2.

EXPERIMENTAL

The mass spectrum was determined with an A.E.I. MS-30 mass spectrometer. The sample was analysed by a direct insertion probe at an ionising current of 70 eV. The source temperature was 60°. Elemental compositions were obtained by the peak matching method.

trans-1,2-Di-(2-pyridyl)ethylene was analytically pure.

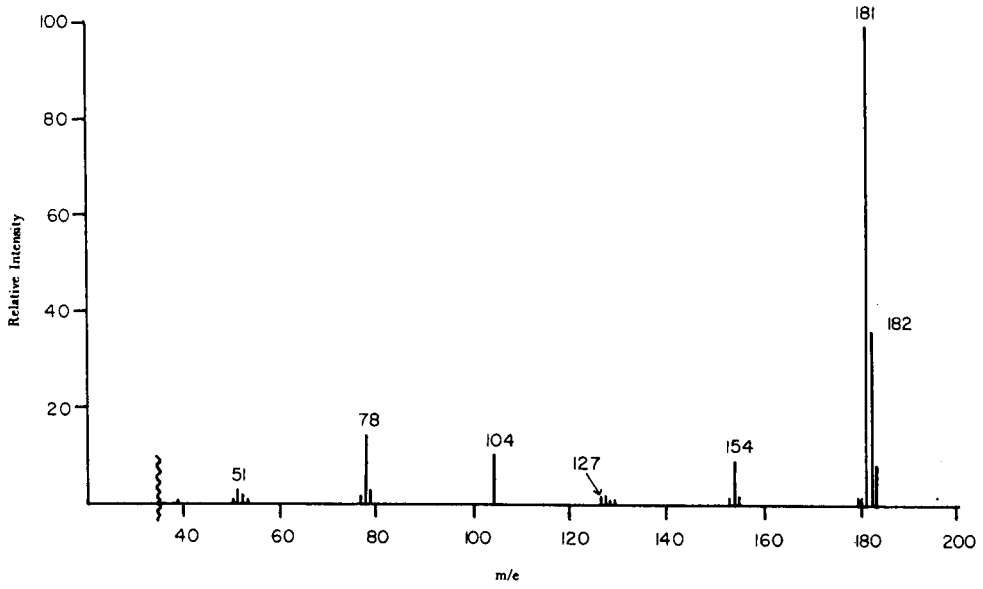


Figure: Mass Spectrum of *trans*-1,2-Di-(2-pyridyl)ethylene

Table 2

Metastable Ions

Initial Ion	Resultant Ion	Transition	Calculated m*	Found m*	Fragment Expelled
$C_{12}H_9N_2$	$C_{11}H_8N$	181 → 154	131.0	131.0	HCN
$C_{11}H_8N$	C_9H_6N	154 → 128	106.4	106.4	C_2H_2
$C_{11}H_8N$	$C_{10}H_7$	154 → 127	104.8	104.9	HCN
C_7H_6N	C_5H_4N	104 → 78	58.5	58.5	C_2H_2

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