The Electron Impact Fragmentation of 3- and 4-Styrylpyridazine

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The electron impact mass spectrometric fragmentation of *trans*-3- and *trans*-4-styrylpyridazine is reported in detail, including a comparison with other aza-stilbenes. With regard to a distinction between the two isomeric styrylpyridazines, the intensity ratio of the $M^{+\cdot}$ and $[M-1]^+$ ions, the general degree of fragmentation and the elimination pathways of nitrogen proved to be most characteristic.

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Introduction.

Compared to stilbene, which has been the subject of numerous investigations (1-14), the reported fragmentation of its monoaza (6) and diaza-analogs (6,15) upon electron impact is governed essentially by two competitive factors: i) the influence of nitrogen incorporation on a stabilizing cyclisation of the molecular structure; and ii) the driving force of nitrogen expulsion *via* elimination of N_1- and/or N_2-containing fragments. A comparison of isomeric styrylpyridines (6), however, shows that the mass spectrometric behaviour resulting from these effects, depends additionally on the position of the nitrogen atom; the *ortho*-isomer, *i.e.*, with -N= in the 2-position, exhibits little and well explicable fragmentation, whereas otherwise rather complex spectra are obtained.

A further group of aza-analogous stilbenes, the styryl pyridazines, from which complementary information could be expected, has now been studied. This report investigates *trans*-3- (16) and *trans*-4-styrylpyridazine (17) with regard to their aza-analogous fragmentation and, in particular, to possible distinction criteria between the two isomers.

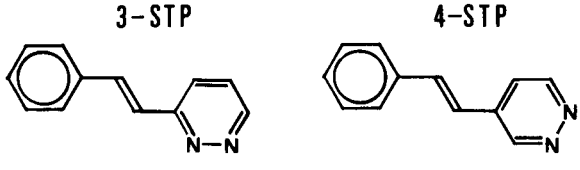

Figure 1. 3- and 4-styrylpyridazine.

Results and Discussion.

3-Styrylpyridazine.

The mass spectrum of 3-styrylpyridazine as given in Figure 2, shows only little fragmentation due to an obviously very stable $[M-1]^+$ ion. The favoured loss of one $H^{\cdot}$ gives evidence for a (conrotatory) cyclisation (1,18) of the molecular ion. From this cyclic intermediate (structure **a**, see Figure 2) a stable cation can be formed by $H^{\cdot}$-elimination. Structure **b** (see Figure 2) was formulated

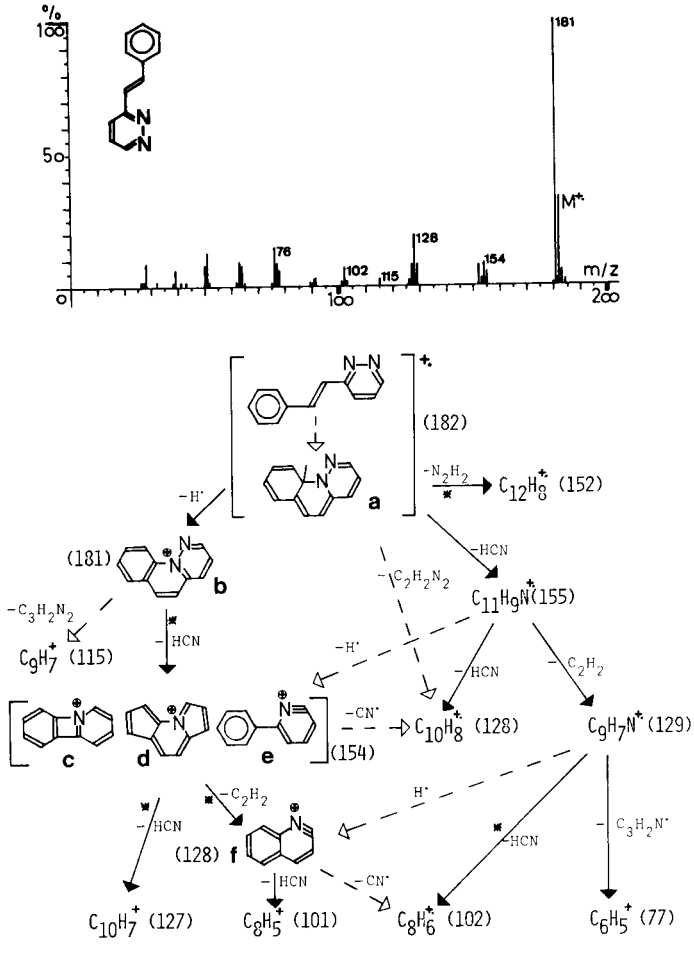

Figure 2. Mass spectrum and nitrogen elimination scheme of 3-styrylpyridazine.

in analogy to the pyridinium cation proposed for 2-styrylpyridine (6). In agreement with the assumed cyclisation, also no indication of a $CH_3^{\cdot}$-elimination, *i.e.*, neither a $[M-15]^+$ ion nor its possible fragmentation products (14), is found, since this process would require migration of two hydrogens (1,19).

The elimination of nitrogen was observed to proceed

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mainly in two steps by loss of HCN. Also a one-step mechanism, however, has to be considered to account for instance for the formation of the $[C_{12}H_8]^{+\cdot}$ ion, which was identified by high resolution measurements (see Experimental). As shown in Figure 2, various probable structures (**c-e** and **f**, respectively) may be assumed for the $[C_{11}H_8N]^+$ and $[C_9H_6N]^+$ ions. They either correspond to analogous fragmentation products of stilbene (**c** and **d**) (14), or (**e** and **f**) to structures proposed for fragments of 1,2-di-(2-pyridyl)ethylene (15) and 2,2'-bipyridyl (20), respectively.

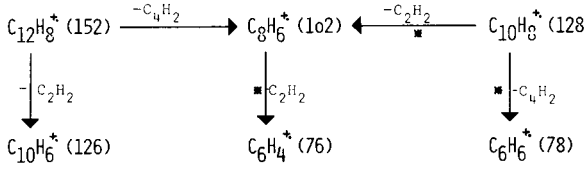

Figure 3. Fragmentation scheme of $[C_{12}H_8]^{+\cdot}$, $[C_{10}H_8]^{+\cdot}$, $[C_8H_6]^{+\cdot}$.

Figure 3 shows the observed fragmentation of hydrocarbon fragments, namely $[C_{12}H_8]^{+\cdot}$, $[C_{10}H_8]^{+\cdot}$ and $[C_8H_6]^{+\cdot}$. It agrees well with that reported for stilbene and naphthalene (21), respectively, which indicates similar ion formation and structures. When referring to the $[C_{12}H_8]^{+\cdot}$ fragment (m/z 152), biphenylene or benzopentalene structures may be discussed as in the case of stilbene (14).

4-Styrylpyridazine.

Figure 4

As expected for 4-styrylpyridazine, there is a considerable degree of fragmentation mainly resulting from an increased tendency for nitrogen elimination. In contrast to 3-styrylpyridazine, loss of N_2-containing fragments is the dominating process. With regard to the type of removed species, a dependence on the precursor ions involved was found, *e.g.*, loss of N_2 exclusively from the $M^{+\cdot}$, while primary loss of HCN from the $[M-1]^+$ ion. In order to explain this, cyclisation (generating a fixed -N=N- element in the $M^{+\cdot}$, but not in the $[M-1]^+$) might again be postulated as shown in Figure 4 (structures **g** and **h**).

In contrast to 3-styrylpyridazine, any cyclic structure of the $M^{+\cdot}$ of 4-styrylpyridazine should, in principle, permit a migration of both *ortho*-hydrogens and thus also the elimination of $CH_3^{\cdot}$. The fact that practically no such $CH_3^{\cdot}$ – loss from the $M^{+\cdot}$ was observable, however, does not necessarily contradict cyclisation, since it might also result from the competition of energetically favoured nitrogen eliminations (6). In agreement with this assumption, a $CH_3^{\cdot}$-elimination seems to occur from the $[M-N_2]^{7+\cdot}$ ion (m/z 154), leading to the $[C_{11}H_7]^+$ fragment at m/z 139 (see Figure 5). Considering the aza-analogy of N_2 and C_2H_2, this fragmentation corresponds, though not in its

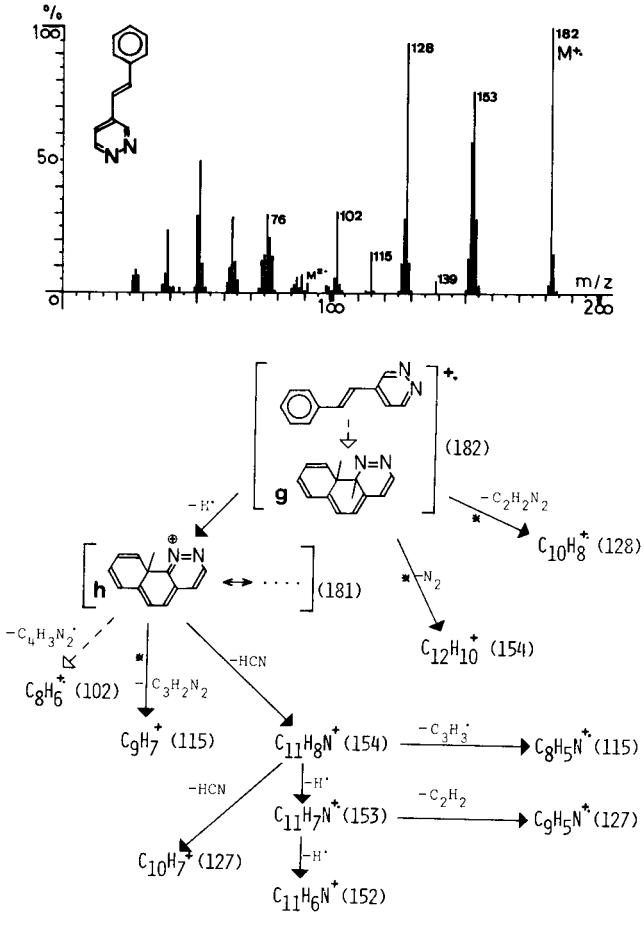

Figure 4. Mass spectrum and nitrogen elimination scheme of 4-styrylpyridazine.

sequence, to the subsequent losses of $CH_3^{\cdot}$ and C_2H_2 observed for stilbene. Final conclusions in this respect, however, can only be drawn from the results of labelling experiments.

All the hydrocarbon fragmentation pathways found for 3-styrylpyridazine were also observed for 4-styrylpyridazine. For the $[C_{12}H_{10}]^{+\cdot}$ fragment which is not formed in the case of 3-styrylpyridazine, additional fragmentation steps must be assumed as shown in Figure 5.

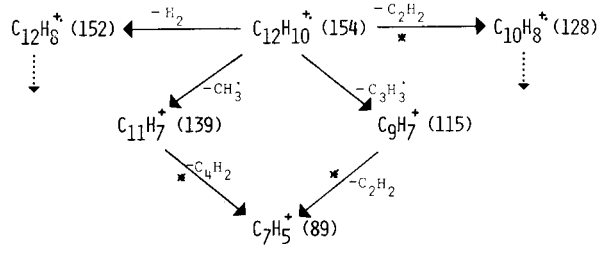

Figure 5. Fragmentation scheme of $[C_{12}H_{10}]^{+\cdot}$.

Table I

Relative Intensities of the $M^{+\cdot}$, $[M-1]^+$, $[M-2]^{+\cdot}$ and $[M-15]^+$ Ions of Stilbene (6,14) and Various Mono- (6) and Diaza-Stilbenes (6,15) with Electron Impact (70 eV) Ionisation

Compound	Relative Intensity (%) of				Abundance of Base Peak (% t.i.i.) (a)
	$M^{+\cdot}$	$[M-1]^+$	$[M-2]^{+\cdot}$	$[M-15]^+$	
Stilbene (6)	100	86	51	40	27
Stilbene (14)	100	57	33	23	30
4-Styrylpyridine	87	100	4	6	37
3-Styrylpyridine	58	100	3	3	30
2-Styrylpyridine	25	100	<2	<2	56
1,2-Di-(4-pyridyl)ethylene	96	100	<2	<2	25
1,2-Di-(2-pyridyl)ethylene	37	100	2	0	50
4-Styrylpyridazine	100	4	0.1	0.2 (4) (b)	10
3-Styrylpyridazine	33	100	1	0 (0.4) (b)	39

(a) % t.i.i. = % of total ion intensity for m/z ≥ 50. (b) Intensity of the $[M-N_2-15]^+$ ion.

Table 2

High Resolution Mass Measurements

Compound	Fragment	Relative Intensity (a)	m/z Calculated	m/z Found
3-Styrylpyridazine	$C_{11}H_8N$	100	154.0657	.066
	$C_{12}H_8$	90	152.0626	.063
	$C_{11}H_6N$	10	.0500	.050
	C_9H_7N	100	129.0578	.058
	$C_{10}H_8$	60	128.0626	.063
	C_9H_6N	40	.0500	.050
	$C_{10}H_7$	95	127.0548	.055
	C_9H_5N	5	.0422	.043
	C_8H_6	100	102.0469	.047
4-Styrylpyridazine	$C_{12}H_{10}$	95	154.0783	.078
	$C_{11}H_8N$	5	.0657	.066
	$C_{12}H_9$	95	153.0704	.070
	$C_{11}H_7N$	5	.0578	.058
	$C_{12}H_8$	95	152.0626	.062
	$C_{11}H_6N$	5	.0500	.050
	$C_{11}H_7$	100	139.0548	.054
	$C_{10}H_8$	100	128.0626	.062
	$C_{10}H_7$	95	127.0548	.055
	C_9H_5N	5	.0422	.042
	C_9H_7	95	115.0548	.055
	C_8H_5N	5	.0422	.041

(a) ^{13}C-isotope peak corrected.

Comparison of Styrylpyridazines and Other Aza-Stilbenes.

As already discussed, the elimination scheme of nitrogen allows to differentiate between the two isomeric styrylpyridazines. The possible loss of N_2-containing fragments can also be used as a distinction criterion between styrylpyridazines and dipyridylethylenes.

A comparative characterisation of all aza-stilbenes and also stilbene itself, however, seems possible only if based on the following two aspects: fragmentation within the molecular region, and general intensity of fragmentation. As demonstrated in Table 1 with styrylpyridines and dipyridylethylenes, azastilbenes containing a single nitrogen (per ring) can be characterized by their intensity ratio of $[M^{+\cdot}/M-1]^+$, which clearly depends on the position of the heteroatom. As can be calculated from the values given in Table 1, the ratio increases from the *ortho*- (0.3) to the *para*-position (≈ 1) and, if extrapolated beyond *para*, consequently leads to the value of stilbene (>1). Similar considerations also apply to the $[M-2]^{+\cdot}$ and $[M-15]^+$ intensities.

A further nitrogen (in one ring) affects this classification as illustrated by a comparison of 3-styrylpyridine *versus*

3-styrylpyridazine and 4-styrylpyridazine. If the second -N= group is located in the 2-position, the intensity ratio of $[M^{+\cdot}/M\text{-}1]^{+}$ (being 0.3) fully corresponds to that of an *ortho*-monoazastilbene, whereas in the case of position 4 it is shifted beyond the typical *para*-value, in this case to a ratio > 10. In addition to this effect on the intensity distribution, the general stability of the molecular structure is found to increase slightly (with position 2) or decrease considerably (with position 4). This is indicated by the absolute abundance of the respective base peaks, *i.e.*, the $M^{+\cdot}$ or $[M\text{-}1]^{+}$ signals (see Table 1).

In conclusion, all these observations can be referred to the already discussed stabilizing effect which is exerted from an aza-group in 2-position, and which seems to be only slightly influenced by incorporation of further nitrogen. Without this stabilisation, *i.e.*, with an -N= in position 3 or 4, the second nitrogen atom, however, drastically intensifies and changes the entire fragmentation.

EXPERIMENTAL

4-Styrylpyridazine.

4-Styrylpyridazine was prepared according to the literature (17,22), m.p. (uncorrected) 64°, lit. (17,22) m.p. 64°.

3-Styrylpyridazine.

3-Styrylpyridazine was prepared following the reported procedure (16), m.p. (uncorrected) 102-102.5°, lit. (16) m.p. 101-102°.

Anal. Calcd. for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.37. Found: C, 78.97; H, 5.41; N, 15.42.

According to uv spectroscopic data (23) both styrylpyridazines were in the *trans*-configuration.

Mass Spectrometry.

A double focusing instrument (MS-902, Kratos-AEI, Manchester, U. K.) was used. Operating conditions were: electron beam 70 eV, 150 μA; accelerating voltage 8 kV; source temperature 160°; resolution 5000 and 18000 (10% valley); direct probe inlet. Elemental compositions were determined via peak matching at high resolving power. The results are given in Table 2. Perfluorotri-*t*-butylamine (Fluka, Zug, Switzerland) served as mass reference. Metastable peaks (2nd FFR) were evaluated from medium resolution ($m/\Delta m$ = 5000) spectra.

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