Mass Spectral Fragmentation Pattern of 2,2'-Bipyridyls. Part IX. 6-Alkoxy-2,2'-bipyridyls

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The mass spectral fragmentation patterns of 6-methoxy-, 6-ethoxy- and 6-propoxy-2,2'-bipyridyls are reported. The base peaks in the spectra of both the 6-methoxy and 6-ethoxy compounds are due to the M-1 ion of 6-methoxy-2,2'-bipyridyl, while the base peak with 6-propoxy-2,2-bipyridyl is due to a species formed by loss of C_3H_6 from the molecular ion.

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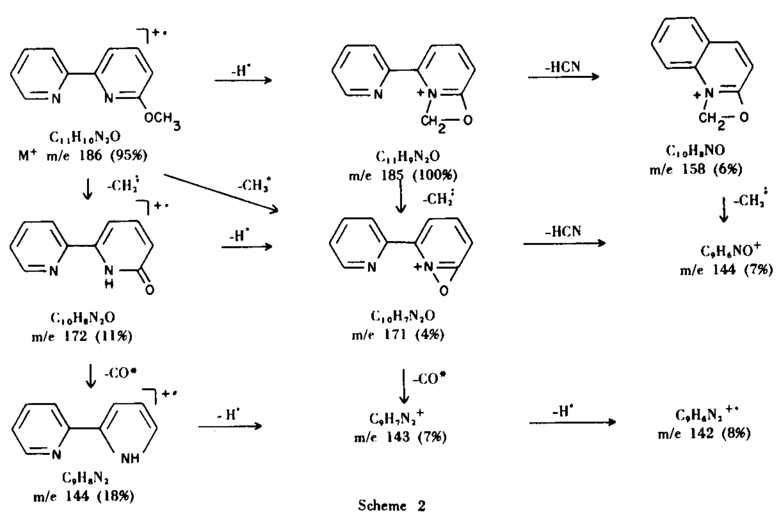
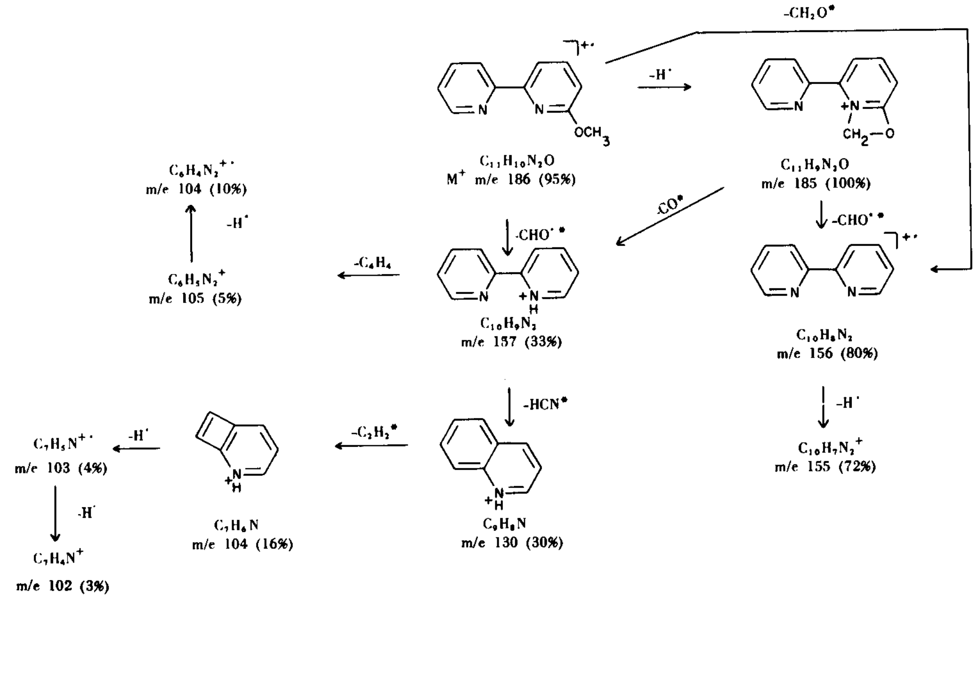
The mass spectra of 2,2'-bipyridyl (1) (2), and its 5-hydroxy (3), 5-alkoxy (3), 5-carboxylic acid (4) and 5-sulphonic acid (4) derivatives have recently been reported as well as the spectra of the polycyclic derivatives 2-(2-pyridyl)quinoline (5) and 2,2'-biquinoline (5). In most of these cases interesting molecular rearrangements occur on electron impact. In continuation of these studies we now report the mass spectra of 6-methoxy-, 6-ethoxy- and 6-propoxy-2,2-bipyridyls which were prepared in connection with our study of the relationship between chemical constitution and biological activity in bipyridylium herbicides (6).

The mass spectrum of 6-methoxy-2,2'-bipyridyl (Figure 1) is quite different from the spectrum of the 5-methoxy analogue (3). With 5-methoxy-2,2'-bipyridyl the base peak in the spectrum is due to the molecular ion at mass

Scheme 1



Scheme 2



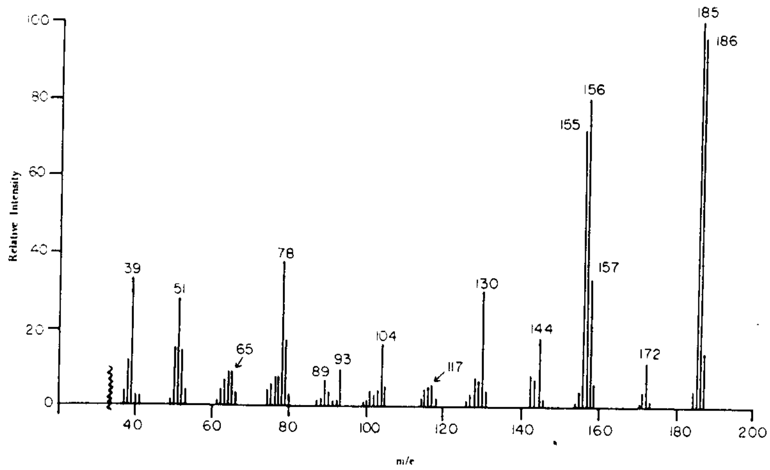


Figure 1. Mass Spectrum of 6-Methoxy-2,2'-bipyridyl.

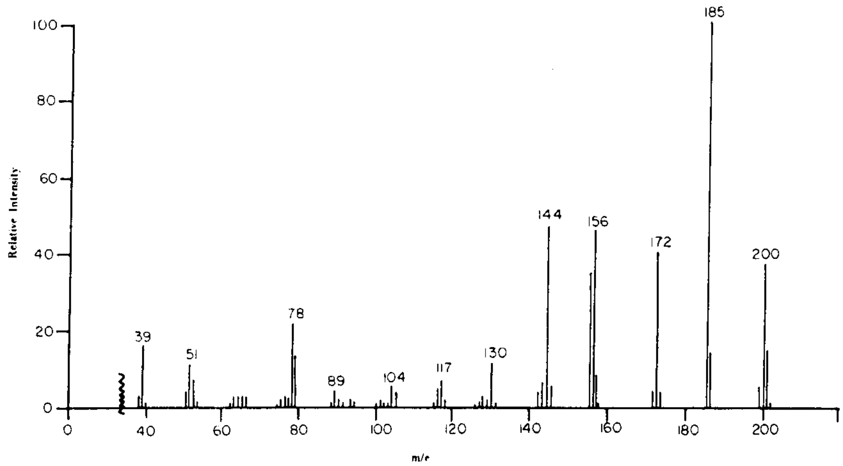


Figure 2. Mass Spectrum of 6-Ethoxy-2,2'-bipyridyl.

186, while the peak due to the M-1 ion amounts to only 4% of the intensity of the base peak. The major fragmentation from the molecular ion of 5-methoxy-2,2'-bipyridyl commences with the loss of $CH_3^{\bullet}$ to form a $C_{10}H_7N_2O^+$ ion at mass 171 due to the M-1 ion of 5-hydroxy-2,2'-bipyridyl. The spectrum of 5-methoxy-2,2'-bipyridyl below a mass of 171 is largely due to the subsequent fragmentation of the M-1 ion of 5-hydroxy-2,2'-bipyridyl. In contrast to the spectrum of 5-methoxy-2,2'-bipyridyl, the base peak in the spectrum of 6-methoxy-2,2'-bipyridyl is due to the M-1 ion at mass 185. The molecular ion at mass 186 gives rise to a peak of 95% of the intensity of the base peak. The predominance of the M-1 ion in the spectrum of 6-methoxy-2,2'-bipyridyl recalls the similar high intensity of the M-1 ion in the spectrum of 2-methoxyquinoline compared with the spectrum, for example, of 3-methoxy-quinoline (7) and may be due to the formation of a fused 1,3-oxazetine type structure as shown in Schemes 1 and 2. Similar behaviour has subsequently been observed with methoxypyridines (8).

One fragmentation route from the molecular ion of 6-methoxy-2,2'-bipyridyl (Scheme 1) results in the formation of a species of empirical formula $C_{10}H_8N_2O$ at mass 172 (11%) almost certainly due to the molecular ion of 6-hydroxy-2,2'-bipyridyl depicted as the pyridone tautomeric form. This species may lose a $H^{\bullet}$ to form a $C_{10}H_7N_2O^+$ ion at mass 171 (4%). It is not certain how these two ions are formed due to the absence of the appropriate metastable transitions but it seems likely they are obtained largely by the loss of CH_2: from the molecular ion of 6-methoxy-2,2'-bipyridyl at mass 186 and its M-1 ion at mass 185 respectively. The $C_{10}H_7N_2O^+$ ion at mass 171 may possibly also be formed by loss of $CH_3^{\bullet}$ from the molecular ion of 6-methoxy-2,2'-bipyridyl. The 6-hydroxy-2,2'-bipyridyl molecular ion at mass 172, as expected, loses CO to form a $C_9H_8N_2^{+\bullet}$ species at mass 144 (18%) depicted as the 2-(2'-pyrrolyl)-pyridine molecular ion. This may lose $H^{\bullet}$ to form a $C_9H_7N_2^+$ ion at mass 143 (7%). The $C_9H_7N_2^+$ ion at mass 143 is also formed from the M-1 ion of 6-hydroxy-2,2'-bipyridyl at mass 171 by loss of CO. Metastable transitions for the loss of CO were observed. The $C_9H_7N_2^+$ ion can lose a further H$^{\bullet}$ to form the $C_9H_6N_2^{+\bullet}$ species at mass 142 (8%). The subsequent fragmentation of the 2-(2′-pyrrolyl)-pyridine molecular ion at mass 144 and its M-1 species at mass 143 is similar to that already reported in the discussion of the mass spectrum of 5-hydroxy-2,2′-bipyridyl (3). This accounts for instance, for the two peaks at mass 117 (6%; $C_8H_7N^{+\bullet}$) thought to be due to the indole or pyrindine molecular ion, and its M-1 ion at mass 116 (5%; $C_8H_6N^+$). These two species are formed by loss of HCN from the 2-(2′-pyrrolyl)-pyridine molecular ion and its M-1 species respectively. The peaks at mass 115 (4%; $C_8H_5N^{+\bullet}$) and 114 (2%; $C_8H_4N^+$) presumably arise by further loss of H$^{\bullet}$.

A major fragmentation pathway from the molecular ion of 6-methoxy-2,2′-bipyridyl involves loss of CHO$^{\bullet}$ to give a species of formula $C_{10}H_9N_2$ at mass 157 (33%) almost certainly due to the 2,2′-bipyridylium ion (Scheme 2). A metastable peak for the transition 186 → 157 was observed. The $C_{10}H_9N_2^+$ ion is also formed from the M-1 ion of 6-methoxy-2,2′-bipyridyl at mass 185 by loss of CO. The fragment CHO$^{\bullet}$ is also lost from the M-1 ion of 6-methoxy-2,2′-bipyridyl to afford a $C_{10}H_8N_2^{+\bullet}$ species at mass 156 (80%) almost certainly due to the 2,2′-bipyridyl molecular ion. The 2,2′-bipyridyl molecular ion is also formed from the molecular ion of 6-methoxy-2,2′-bipyridyl at mass 186 by loss of the elements of formaldehyde, CH_2O. As expected, the 2,2′-bipyridyl molecular ion may lose H$^{\bullet}$ to afford the M-1 ion of 2,2′-bipyridyl at mass 155 (72%). Contributions to the M-1 ion of 2,2′-bipyridyl at mass 155 may also come from the loss of $OCH_3^{\bullet}$ from the molecular ion of 6-methoxy-2,2′-bipyridyl at mass 186 and loss of CH_2O from the M-1 ion of 6-methoxy-2,2′-bipyridyl at mass 185 but no clear metastable peaks corresponding to the transitions 186 → 155 and 185 → 155 were observed.

The subsequent fragmentation of the 2,2′-bipyridylium ion at mass 157 accounts for the high intensity peak (30%) at mass 130. It is formed by loss of HCN and is due to a $C_9H_8N^+$ ion considered to be the quinolinium ion. The $C_9H_8N^+$ ion may lose C_2H_2 to afford the $C_7H_6N^+$ ion at mass 104 (16%). A small metastable peak was present corresponding to the 130 → 104 transition. The $C_7H_6N^+$ ion may subsequently lose hydrogens to afford the peaks at mass 103 (4%; $C_7H_5N^{+\bullet}$) and 102 (3%; $C_7H_4N^+$). Loss of C_4H_4 from the 2,2′-bipyridylium ion ($C_{10}H_9N_2^+$) at mass 157 may also account for the presence of a $C_6H_5N_2^+$ ion at mass 105 (5%) although no metastable peak for this transition was observed. Loss of H$^{\bullet}$ from the $C_6H_5N_2^+$ ion can give a contribution to the $C_6H_4N_2^{+\bullet}$ species at mass 104 (10%).

The fragmentation of the 2,2′-bipyridyl molecular ion ($C_{10}H_8N_2^{+\bullet}$) at mass 156 and its M-1 species at mass 155 is, as expected, very similar to that already reported in the mass spectrum of 2,2′-bipyridyl (1). This accounts for the peaks at mass 129 (7%; $C_9H_7N^{+\bullet}$), 128 (8%; $C_9H_6N^+$) and 127 (3%; $C_9H_5N^{+\bullet}$) and gives rise to a contribution to the $C_9H_8N^+$ ion at mass 130. We were however unable to detect the presence of a $C_8H_6N_2^{+\bullet}$ species at mass 130 in the spectrum of 6-methoxy-2,2′-bipyridyl. This species is present to a small extent (2%) in the fragmentation of

Table 1

High Resolution Data

m/e	Elemental Composition		Observed mass	Calculated mass
	(a) 6-Methoxy-2,2′-bipyridyl			
172	$C_{10}H_8N_2O$		172.0632	172.0637
171	$C_{10}H_7N_2O$		171.0558	171.0558
158	$C_{10}H_8NO$		158.0607	158.0606
157	$C_{10}H_9N_2$		157.0766	157.0766
156	$C_{10}H_8N_2$		156.0688	156.0687
155	$C_{10}H_7N_2$		155.0608	155.0609
144	$C_9H_8N_2$	(18%)	144.0687	144.0687
144	C_9H_6NO	(7%)	144.0448	144.0449
143	$C_9H_7N_2$		143.0609	143.0609
142	$C_9H_6N_2$		142.0530	142.0531
130	C_9H_8N		130.0658	130.0657
129	C_9H_7N		129.0577	129.0578
128	C_9H_6N		128.0498	128.0500
127	C_9H_5N		127.0422	127.0422
117	C_8H_7N		117.0576	117.0578
116	C_8H_6N		116.0500	116.0500
115	C_8H_5N		115.0422	115.0422
114	C_8H_4N		114.0344	114.0344
105	$C_6H_5N_2$		105.0449	105.0453
104	C_7H_6N	(16%)	104.0496	104.0500
104	$C_6H_4N_2$	(10%)	104.0371	104.0374
103	C_7H_5N		103.0421	103.0422
102	C_7H_4N		102.0344	102.0344
101	C_8H_5		101.0390	101.0391
	(b) 6-Ethoxy-2,2′-bipyridyl			
185	$C_{11}H_9N_2O$		185.0715	185.0715
172	$C_{10}H_8N_2O$		172.0636	172.0637
171	$C_{10}H_7N_2O$		171.0557	171.0558
157	$C^{13}C_9{}^{12}H_8N_2$		157.0720	157.0721
156	$C_{10}H_8N_2$		156.0687	156.0687
155	$C_{10}H_7N_2$		155.0608	155.0609
144	$C_9H_8N_2$		144.0688	144.0687
143	$C_9H_7N_2$		143.0607	143.0609
142	$C_9H_6N_2$		142.0531	142.0531
	(c) 6-Propoxy-2,2′-bipyridyl			
199	$C_{12}H_{11}N_2O$		199.0872	199.0871
185	$C_{11}H_9N_2O$		185.0715	185.0715
184	$C_{12}H_{12}N_2$	(6%)	184.0998	184.1000
184	$C_{11}H_8N_2O$	(1%)	184.0636	184.0637
172	$C_{10}H_8N_2O$		172.0636	172.0637
171	$C_{10}H_7N_2O$		171.0558	171.0558
156	$C_{10}H_8N_2$		156.0687	156.0687
155	$C_{10}H_7N_2$		155.0608	155.0609
144	$C_9H_8N_2$		144.0686	144.0687
143	$C_9H_7N_2$		143.0606	143.0609
142	$C_9H_6N_2$		142.0530	142.0531

Table 2

Metastable Ions

Initial Ion	Resultant Ion	Transition	Found m*	Calculated m*	Fragment Expelled
		(a) 6-Methoxy-2,2'-bipyridyl			
$C_{11}H_9N_2O$	$C_{10}H_9N_2$	185 → 157	133.2	133.2	CO
$C_{11}H_{10}N_2O$	$C_{10}H_9N_2$	186 → 157	132.5	132.5	CHO
$C_{11}H_9N_2O$	$C_{10}H_8N_2$	185 → 156	131.5	131.5	CHO
$C_{11}H_{10}N_2O$	$C_{10}H_8N_2$	186 → 156	130.9	130.9	CH_2O
$C_{10}H_8N_2O$	$C_9H_8N_2$	172 → 144	120.5	120.6	CO
$C_{10}H_7N_2O$	$C_9H_7N_2$	171 → 143	119.7	119.6	CO
$C_{10}H_9N_2$	C_9H_8N	157 → 130	107.7	107.6	HCN
$C_9H_8N_2$	C_8H_7N	144 → 117	95.3	95.1	HCN
$C_9H_7N_2$	C_8H_6N	143 → 116	94.2	94.1	HCN
C_9H_8N	C_7H_6N	130 → 104	83.4	83.2	C_2H_2
		(b) 6-Ethoxy-2,2'-bipyridyl			
$C_{12}H_{12}N_2O$	$C_{11}H_9N_2O$	200 → 185	171.2	171.2	CH_3
$C_{12}H_{12}N_2O$	$C_{10}H_8N_2O$	200 → 172	148.1	147.9	C_2H_4
$C_{12}H_{12}N_2O$	$C_{10}H_7N_2$	200 → 155	120.4	120.1	OC_2H_5
		(c) 6-Propoxy-2,2'-bipyridyl			
$C_{13}H_{14}N_2O$	$C_{11}H_9N_2O$	214 → 185	160.0	160.0	C_2H_5
$C_{13}H_{14}N_2O$	$C_{10}H_8N_2O$	214 → 172	138.2	138.2	C_3H_6

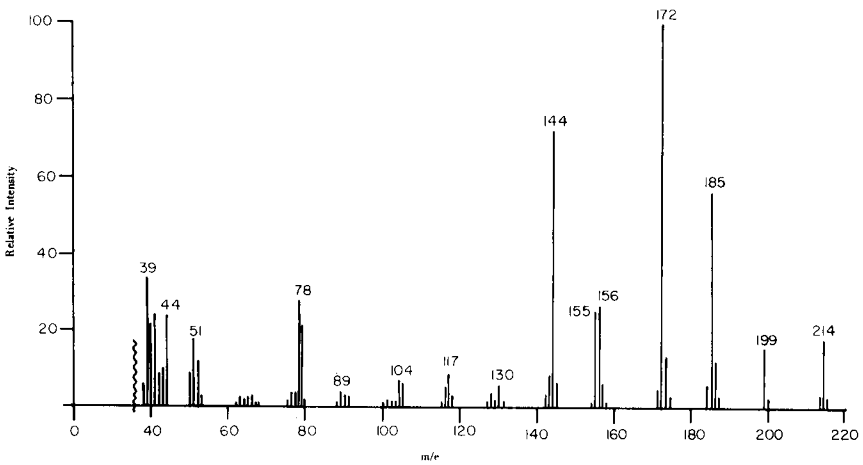


Figure 3. Mass Spectrum of 6-Propoxy-2,2'-bipyridyl.

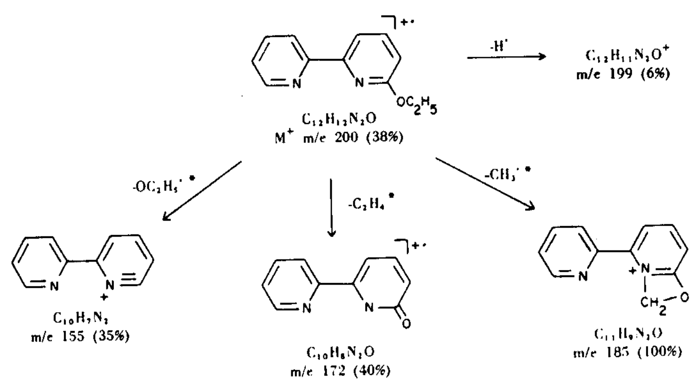
2,2'-bipyridyl (1). The cluster of peaks at mass 101-104 in the spectrum of 6-methoxy-2,2'-bipyridyl is similar to that observed in the spectrum of 2,2'-bipyridyl.

Two peaks above a mass of 100 in the spectrum of 6-methoxy-2,2'-bipyridyl remain unexplained. These two peaks comprise the small intensity peak at mass 158 (6%), due to a species of empirical formula $C_{10}H_8NO$ and the minor component of the peak at mass 144 corresponding to a C_9H_6NO species (7%). The $C_{10}H_8NO^+$ ion probably arises from the M-1 ion of 6-methoxy-2,2'-bipyridyl at mass 185 by loss of HCN while the $C_9H_6NO^+$ ion is obtained by further loss of CH_2: or by loss of HCN from the $C_{10}H_7N_2O^+$ ion at mass 171 but the appropriate metastable peaks for these fragmentations were not observed in the spectrum (Scheme 1).

The peaks in the spectrum of 6-methoxy-2,2'-bipyridyl below a mass of 100 are typical of those obtained from the further disintegration of the 2-(2'-pyrrolyl)-pyridine molecular ion (3) and from pyridine and quinoline derivatives (1) (3). The peak at mass 93 (90%) is due to the M^{++} ion. The high resolution mass measurements are given in Table 1 and the metastable transitions of importance in elucidating the fragmentation pathways in Table 2.

In the mass spectrum of 6-ethoxy-2,2'-bipyridyl (Figure 2) the base peak is also at mass 185 and is due to a species of formula $C_{11}H_9N_2O$. This species is almost certainly the M-1 ion of 6-methoxy-2,2'-bipyridyl, as in the spectrum of 6-methoxy-2,2'-bipyridyl (Figure 1), and is likewise depicted as an oxazetine type structure. It is formed by the loss of $CH_3^{\cdot}$ from the molecular ion of 6-ethoxy-2,2'-bipyridyl at mass 200. A metastable peak for the transition 200 → 185 is present in the spectrum. This result resembles that obtained with 2-ethoxy-pyridine where the base peak in the spectrum is due to a M-15 species (9). The molecular ion of 6-ethoxy-2,2'-bipyridyl at mass 200 gives a peak of 38% of the intensity of the base peak. The M-1 ion of 6-ethoxy-2,2'-bipyridyl at mass 199 gives a small peak (6%).

Scheme 3



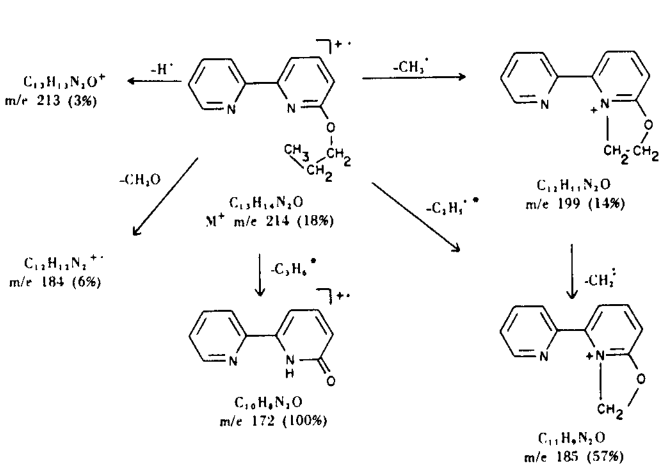
Apart from the loss of $CH_3^{\cdot}$ the molecular ion of 6-ethoxy-2,2'-bipyridyl at mass 200 may lose the elements of ethylene (C_2H_4) to form a $C_{10}H_8N_2O^{+\cdot}$ species at mass 172 (40%) due to the 6-hydroxy-2,2'-bipyridyl molecular ion drawn in its pyridone tautomeric form (Scheme 3). A very strong metastable transition for the loss of ethylene was observed. The loss of ethylene is analogous to that observed in the mass spectrum of phenetole which likewise loses ethylene from the molecular ion to form phenol (10).

One other fragmentation route from the molecular ion of 6-ethoxy-2,2'-bipyridyl involves the loss of $OC_2H_5^{\cdot}$ to give a $C_{10}H_7N_2^+$ species at mass 155 (35%) considered to be the M-1 ion of 2,2'-bipyridyl. A metastable peak for the loss of $OC_2H_5^{\cdot}$ was observed. Contributions to the $C_{10}H_7N_2^+$ ion will also come from the disintegration of the $C_{11}H_9N_2O^+$ ion at mass 185 (see Scheme 2).

As expected, the subsequent fragmentation of the M-1 ion of 6-methoxy-2,2'-bipyridyl ($C_{11}H_9N_2O^+$) at mass 185 and the molecular ion of 6-hydroxy-2,2'-bipyridyl ($C_{10}H_8N_2O^{+\cdot}$) at mass 172 follows closely that already described for the fragmentation of these species in the spectrum of 6-methoxy-2,2'-bipyridyl. Consequently, the spectrum of 6-ethoxy-2,2'-bipyridyl below a mass of 140 is very similar to that of 6-methoxy-2,2'-bipyridyl although the intensity of the peaks is not as great. The peak at mass 157 requires comment. In the spectrum of 6-ethoxy-2,2'-bipyridyl this peak arises almost entirely from the $C^{13}C_9{}^{12}H_8N_2^{+\cdot}$ species, whereas in the spectrum of 6-methoxy-2,2'-bipyridyl it is largely due to the 2,2'-bipyridylium ion ($C_{10}H_9N_2^+$) formed as shown in Scheme 2.

Unlike the spectra of 6-methoxy-2,2'-bipyridyl and 6-ethoxy-2,2'-bipyridyl the base peak in the mass spectrum of 6-propoxy-2,2'-bipyridyl (Figure 3) is due to the 6-hydroxy-2,2'-bipyridyl molecular ion ($C_{10}H_8N_2O^{+\cdot}$), depicted in the pyridone form (Scheme 4), at mass 172. It is formed by the loss of the elements of propylene, C_3H_6, from the molecular ion of 6-propoxy-2,2'-bipyridyl at mass 214. In this respect the spectrum of 6-propoxy-2,2'-bipyridyl resembles that of 5-propoxy-2,2'-bipyridyl (3) and recalls the similar behaviour observed in the spectrum of 2-propoxyquinoline (11).

Scheme 4



The molecular ion of 6-propoxy-2,2'-bipyridyl at mass 214 gives a peak only 18% of the intensity of the base peak. The M-1 ion at mass 213 is also of low abundance (3%). Apart from the loss of C_3H_6 the molecular ion of 6-propoxy-2,2'-bipyridyl loses $CH_3^{\cdot}$ to form a $C_{12}H_{11}N_2O^+$ ion at mass 199 (14%) although no clear metastable peak was observed for this transition. The molecular ion of 6-propoxy-2,2'-bipyridyl may also lose $C_2H_5^{\cdot}$ to afford a $C_{11}H_9N_2O^+$ ion at mass 185 of high abundance (57%). A metastable peak for the transition 214 → 185 is present in the spectrum. The $C_{11}H_9N_2O^+$ ion, as in the spectra of 6-methoxy- and 6-ethoxy-2,2'-bipyridyls, is depicted as an oxazetine ion corresponding to the M-1 ion of 6-methoxy-2,2'-bipyridyl. It may presumably also be formed by the loss of CH_2: from the $C_{12}H_{11}N_2O^+$ ion at mass 199. The subsequent fragmentation of the $C_{11}H_9N_2^+$ ion at mass 185 and the $C_{10}H_8N_2O^{+\cdot}$ species at mass 172 is substantially the same as that already described in the spectra of 6-methoxy- and 6-ethoxy-2,2'-bipyridyls.

One peak in the spectrum of 6-propoxy-2,2'-bipyridyl remains unexplained. It is the peak at mass 184 which is made up of two components. The minor component is due to a $C_{11}H_8N_2O^{+\bullet}$ species (1%) and it probably arises from the $C_{11}H_9N_2O^+$ ion at mass 185 by loss of $H^\bullet$. The major component of the peak at mass 184 is due to a $C_{12}H_{12}N_2^{+\bullet}$ species (6%) which is presumably obtained from the molecular ion of 6-propoxy-2,2'-bipyridyl at mass 214 by loss of the elements of formaldehyde, CH_2O, although no metastable for this transition was observed.

EXPERIMENTAL

The mass spectra were determined with an A.E.I. MS-30 mass spectrometer. The samples were analysed by a direct insertion gas probe (150°) at an ionising current of 70 eV. Elemental compositions were obtained by the peak matching method.

6-Methoxy-, 6-ethoxy- and 6-propoxy-2,2'-bipyridyls were analytically pure (6).

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