Mass Spectral Fragmentation Pattern of 2,2′-Bipyridyls. Part II. 5-Hydroxy- and 5-Alkoxy-2,2′-bipyridyls

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The mass spectra of 5-hydroxy-, 5-methoxy-, 5-ethoxy- and 5-propoxy-2,2′-bipyridyls are reported. The fragmentation proposals are supported by high resolution mass measurements and metastable transitions.

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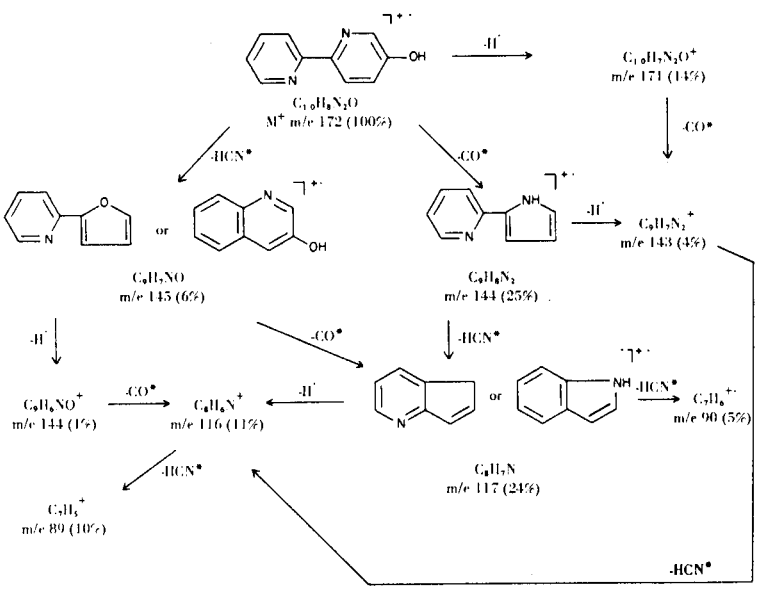
The mass spectrum of 2,2′-bipyridyl has been reported and its fragmentation pattern discussed (1) (2). There has, however, been no report of the results of electron impact on ring substituted 2,2′-bipyridyls apart from two dimethyl substituted derivatives (2). As part of our programme on the relationship between chemical constitution and biological activity in bipyridylium herbicides we prepared 5-hydroxy-, 5-methoxy-, 5-ethoxy- and 5-propoxy-2,2′-bipyridyls (3). We now report on the mass spectra of these four compounds.

The mass spectrum of 5-hydroxy-2,2′-bipyridyl (Figure 1) is dominated by the peak due to the molecular ion $C_{10}H_8N_2O$ at mass 172. Loss of H· gives the peak at mass 171 (14% of molecular ion). The relative intensity of the M-1 peak is much less than the corresponding peak obtained from 2,2′-bipyridyl (1) (2).

The fragmentation of the molecular ion (see Scheme) proceeds along two main pathways apart from the loss of H·. The minor route involves loss of HCN to give the C_9H_7NO species (6% of molecular ion) of mass 145 depicted either as a hydroxyquinoline molecular ion or the 2-(2′-furyl)pyridine molecular ion. This subsequently loses CO to give a C_8H_7N species at mass 117. The C_9H_7NO species may first lose H· to give the $C_9H_6NO^+$ ion of mass 144 before loss of CO to produce the $C_8H_6N^+$ ion of mass 116.

The principal fragmentation from the molecular ion of 5-hydroxy-2,2′-bipyridyl involves loss of CO to give a $C_9H_8N_2$ species of mass 144 (25% of molecular ion) considered to be the 2-(2′-pyrrolyl)pyridine molecular ion. This loses H· to form a $C_9H_7N_2^+$ ion of mass 143 (4% of molecular ion) which is also formed by loss of CO from the

Scheme



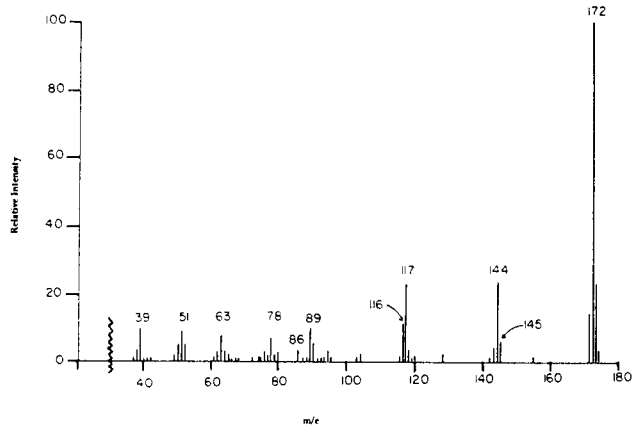


Figure 1: Mass Spectrum of 5-Hydroxy-2,2'-bipyridyl.

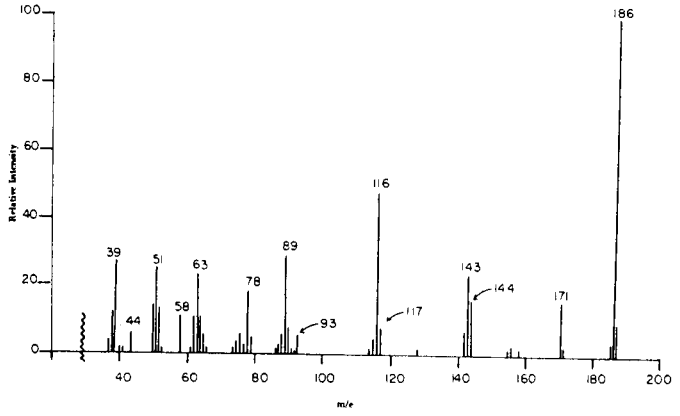


Figure 2: Mass Spectrum of 5-Methoxy-2,2'-bipyridyl.

M-1 ion. The $C_9H_8N_2$ species then loses HCN to form a strong peak of formula C_8H_7N at mass 117 (24% of molecular ion) probably due to the indole or pyrindine molecular ion.

The peak at mass 116 (11% of molecular ion) is due to the $C_8H_6N^+$ ion which is formed in at least three ways, by loss of H· from the C_8H_7N species, by loss of HCN from $C_9H_7N_2^+$ and, as indicated above, by loss of CO from the $C_9H_6NO^+$ ion. The C_8H_7N and C_8H_6N species both lose HCN to form the C_7H_6 species of mass 90 (4% of molecular ion) and the $C_7H_5^+$ ion of mass 89 (10% of molecular ion) respectively. High resolution mass measurements show that the peak at mass 90 is also made up of very small contributions (less than 1% of molecular ion) from C_6H_4N, C_6H_2O and $C_5H_2N_2$ species.

The other peaks below a mass of 116 in the spectrum are typical of those to be expected from pyridine derivatives and require little comment. The peak at mass 86 (3% of molecular ion) is due to the M^{++} species. The peaks at mass 94 (3% of molecular ion), due to the $C_5H_4NO^+$ ion, and at mass 78 (7% of the molecular ion), due to the

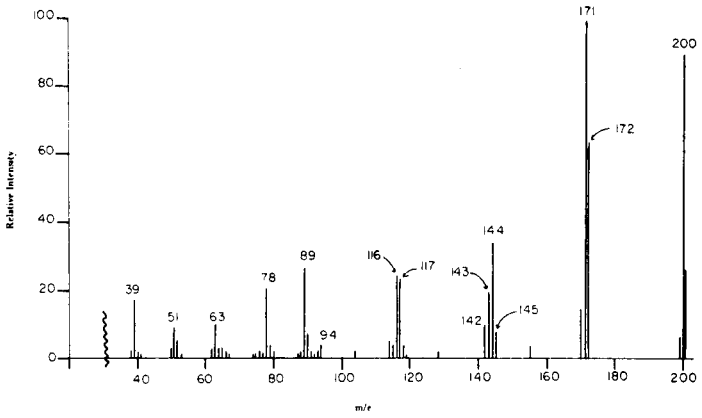


Figure 3: Mass Spectrum of 5-Ethoxy-2,2'-bipyridyl.

Table I

High Resolution Data

m/e	Elemental Composition	Observed Mass	Calculated Mass
	(a) 5-Hydroxy-2,2'-bipyridyl		
145	C_9H_7NO	145.0528	145.0528
144	C_9H_6NO (1%)	144.0452	144.0449
144	$C_9H_8N_2$ (25%)	144.0688	144.0687
143	$C_9H_7N_2$	143.0610	143.0609
117	C_8H_7N	117.0589	117.0578
116	C_8H_6N	116.0501	116.0500
94	C_5H_4NO	94.0292	94.0293
90	C_7H_6	90.0470	90.0469
89	C_7H_5	89.0391	89.0391
78	C_5H_4N	78.0343	78.0344
	(b) 5-Methoxy-2,2'-bipyridyl		
171	$C_{10}H_7N_2O$	171.0559	171.0558
156	$C_{10}H_8N_2$	156.0686	156.0687
144	C_9H_6NO	144.0450	144.0449
143	$C_9H_7N_2$	143.0609	143.0609
142	$C_9H_6N_2$	142.0529	142.0531
116	C_8H_6N	116.0500	116.0500
	(c) 5-Ethoxy-2,2'-bipyridyl		
172	$C_{10}H_8N_2O$	172.0637	172.0637
171	$C_{10}H_7N_2O$	171.0558	171.0558
170	$C_{10}H_6N_2O$	170.0480	170.0480
155	$C_{10}H_7N_2$	155.0611	155.0609
145	C_9H_7NO	145.0528	145.0528
144	C_9H_6NO (6%)	144.0453	144.0449
144	$C_9H_8N_2$ (25%)	144.0687	144.0687
143	$C_9H_7N_2$	143.0608	143.0609
142	$C_9H_6N_2$	142.0530	142.0531
	(d) 5-Propoxy-2,2'-bipyridyl		
172	$C_{10}H_8N_2O$	172.0633	172.0637
171	$C_{10}H_7N_2O$	171.0558	171.0558
144	C_9H_6NO (2%)	144.0449	144.0449
144	$C_9H_8N_2$ (6%)	144.0689	144.0687
117	C_8H_7N	117.0578	117.0578

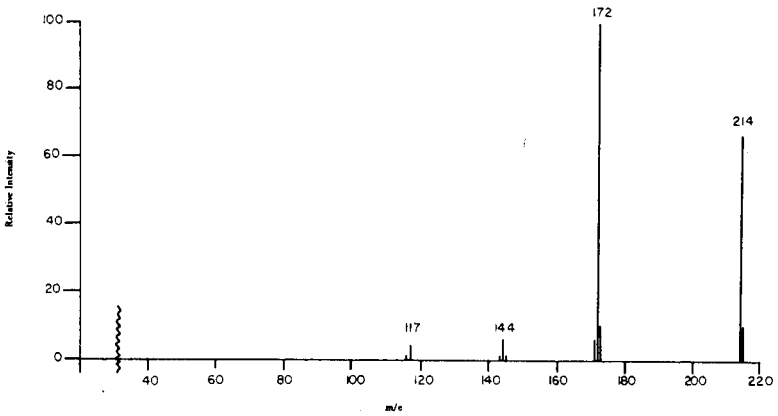


Figure 4: Mass Spectrum of 5-Propoxy-2,2′-bipyridyl.

Table II

Metastable Ions

Initial Ion	Resultant Ion	Transition	Found m*	Calculated m*	Fragment Expelled
		(a) 5-Hydroxy-2,2′-bipyridyl			
$C_{10}H_8N_2O$	C_9H_7NO	172 → 145	122.2	122.3	HCN
$C_{10}H_8N_2O$	$C_9H_8N_2$	172 → 144	120.6	120.6	CO
$C_{10}H_7N_2O$	$C_9H_7N_2$	171 → 143	119.6	119.6	CO
$C_9H_8N_2$	C_8H_7N	144 → 117	95.1	95.1	HCN
C_9H_7NO	C_8H_7N	145 → 117	94.3	94.3	CO
C_9H_6NO	C_8H_6N	144 → 116	93.5	93.5	CO
$C_9H_7N_2$	C_8H_6N	143 → 116	94.1	94.1	HCN
C_8H_7N	C_7H_6	117 → 90	69.2	69.2	HCN
C_8H_6N	C_7H_5	116 → 89	68.3	68.3	HCN
		(b) 5-Methoxy-2,2′-bipyridyl			
$C_{11}H_{10}N_2O$	$C_{10}H_7N_2O$	186 → 171	157.1	157.2	CH_3
$C_{10}H_7N_2O$	$C_9H_7N_2$	171 → 143	119.6	119.6	CO
$C_9H_7N_2$	C_8H_6N	143 → 116	94.1	94.1	HCN
C_9H_6NO	C_8H_6N	144 → 116	93.5	93.5	CO
		(c) 5-Ethoxy-2,2′-bipyridyl			
$C_{12}H_{12}N_2O$	$C_{10}H_8N_2O$	200 → 172	147.9	147.9	C_2H_4
$C_{10}H_8N_2O$	C_9H_7NO	172 → 145	122.2	122.3	HCN
$C_{10}H_8N_2O$	$C_9H_8N_2$	172 → 144	120.6	120.6	CO
$C_{10}H_7N_2O$	$C_9H_7N_2$	171 → 143	119.6	119.6	CO
		(d) 5-Propoxy-2,2′-bipyridyl			
$C_{13}H_{14}N_2O$	$C_{10}H_8N_2O$	214 → 172	138.2	138.2	C_3H_6

$C_5H_4N^+$ ion are presumably obtained by rupture of the central bond of 5-hydroxy-2,2′-bipyridyl.

The spectrum of 5-methoxy-2,2′-bipyridyl (Figure 2) is also dominated by the peak due to the molecular ion at mass 186. Loss of $H^{\cdot}$ to form the M-1 ion at mass 185 results in a peak of small intensity (4% of the molecular ion).

The principal fragmentation route from the molecular ion commences with loss of $CH_3^{\cdot}$ to form the $C_{10}H_7N_2O^+$ ion of mass 171 (14% of molecular ion), presumably equivalent to the M-1 ion of 5-hydroxy-2,2′-bipyridyl. The subsequent fragmentation is similar to that described for 5-hydroxy-2,2′-bipyridyl. The $C_{10}H_7N_2O^+$ ion either loses HCN to give the $C_9H_6NO^+$ ion of mass 144 (14% of

molecular ion) or CO to produce the $C_9H_7N_2^+$ ion of mass 143 (24% of molecular ion). The $C_9H_7N_2^+$ ion loses H· to form the $C_9H_6N_2$ species of mass 142 (7% of molecular ion) or HCN to form the $C_8H_6N^+$ ion of mass 116 (48% of molecular ion). The $C_8H_6N^+$ ion is also formed from the $C_9H_6NO^+$ ion by loss of CO. The spectrum below mass 116 is very similar to that of 5-hydroxy-2,2′-bipyridyl. The peak at mass 93 (6% of molecular ion) is due to the M^{++} species.

A minor fragmentation pathway from the molecular ion of 5-methoxy-2,2′-bipyridyl involves loss of the elements of formaldehyde, CH_2O to form the $C_{10}H_8N_2$ species at mass 156 (3% of molecular ion) presumably due to the 2,2′-bipyridyl molecular ion.

In the mass spectrum of 5-ethoxy-2,2′-bipyridyl (Figure 3) the base peak is not that due to the molecular ion. The molecular ion at mass 200 gives a peak of 90% of the intensity of the base peak while the M-1 ion at mass 199 gives a peak of 7% of the intensity of the base peak. The principal initial fragmentation from the molecular ion involves loss of C_2H_4 to give the peak at mass 172 of empirical formula $C_{10}H_8N_2O$ (64% of base peak) presumably due to the 5-hydroxy-2,2′-bipyridyl molecular ion. 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 (4). The base peak in the spectrum of 5-ethoxy-2,2′-bipyridyl at mass 171 is due to the $C_{10}H_7N_2O^+$ ion and arises from the loss of the elements of ethylene and hydrogen from the molecular ion. There is no metastable transition, however, corresponding to the elimination of C_2H_4 from the M-1 ion and so presumably the base peak arises from the loss of ethylene from the molecular ion, for which a strong metastable transition is observed, followed by loss of hydrogen. There is also a fairly intense peak (15% of base peak) at mass 170 due to the further loss of H· to give the $C_{10}H_6N_2O$ species. As expected, the subsequent disintegration follows closely the fragmentation pattern of 5-hydroxy-2,2′-bipyridyl and requires no comment. A small intensity peak (4% of base peak) at mass 155 is worth noting. It is due to a $C_{10}H_7N_2^+$ ion formed by loss of C_2H_5O from the molecular ion and is presumably the 2,2′-bipyridyl molecular ion less one hydrogen.

The mass spectrum of 5-propoxy-2,2′-bipyridyl (Figure 4) is remarkably simple. The peak due to the molecular ion at mass 214 (66% of the base peak) and the base peak at mass 172 due to the 5-hydroxy-2,2′-bipyridyl molecular ion of formula $C_{10}H_8N_2O$ are the only high intensity peaks in the spectrum. The base peak is clearly obtained by loss of the elements of propylene, $CH_3{\cdot}CH{=}CH_2$, from the molecular ion (*cf.* reference 4). Small intensity peaks (4-6% of base peak) at mass 171, 144 and 117 are analogous to those observed in the spectrum of 5-hydroxy-2,2′-bipyridyl.

The elemental compositions of those ions of importance in elucidating the fragmentation patterns are recorded in Table I and the metastable transitions in Table II.

EXPERIMENTAL

The mass spectra were determined with an A. E. I. MS-30 mass spectrometer. The samples were analyzed by a direct insertion probe at an ionizing current of 70eV. Elemental compositions were obtained by the peak matching method.

5-Hydroxy-2,2′-bipyridyl and the 5-methoxy, 5-ethoxy and 5-propoxy analogues were analytically pure (3).

REFERENCES AND NOTES

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