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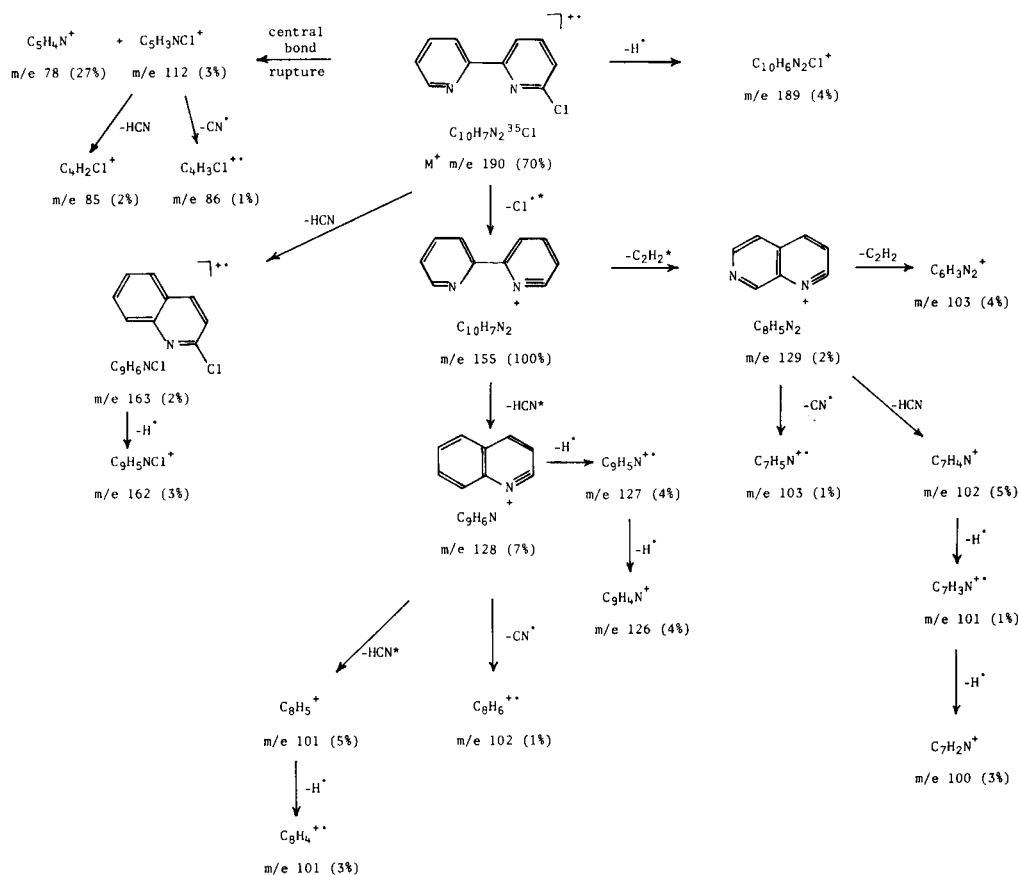
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The mass spectra of 6-chloro- and 6-bromo-2,2'-bipyridyls are reported. The principal fragmentation route from the molecular ions involves loss of the halogen group to give the M-1 ion of 2,2'-bipyridyl which gives rise to the base peak in the spectra. Loss of HCN before loss of Cl<sup>•</sup> occurs to a small extent with 6-chloro-2,2'-bipyridyl.

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In our studies of the electron impact mass spectra of 2,2'-bipyridyls we have so far examined several substituted 2,2'-bipyridyls, namely 5-hydroxy- (1), 5-alkoxy- (1) and 6-alkoxy-2,2'-bipyridyls (2) as well as the 5-carboxylic acid (3) and the 5-sulphonic acid (3). With 5-hydroxy-2,2'-bipyridyl there is a competition in the initial fragmentation from the molecular ion between the loss of HCN, due to rupture of a pyridine ring as in 2,2'-bipyridyl (4), and the loss of CO due to disintegration at the hydroxy substituent (1). With 5-alkoxy-2,2'-bipyridyls (1) disintegration starts almost entirely at the alkoxy

substituent. With 6-methoxy-2,2'-bipyridyl loss of H<sup>•</sup> from the molecular ion is a prominent initial fragmentation but thereafter there is again competition between loss of HCN and disintegration at the substituent (2). With 6-ethoxy and 6-propoxy-2,2'-bipyridyls disintegration commences almost entirely at the substituent (2). Interestingly with both the 5-carboxylic acid and the 5-sulphonic acid the loss of HCN (or CN<sup>•</sup>) competes with fragmentations at the substituents although the latter disintegration routes predominate (3). We have now studied the mass spectra of 6-chloro (5) and 6-bromo-2,2'-bipyridyls (5).



SCHEME

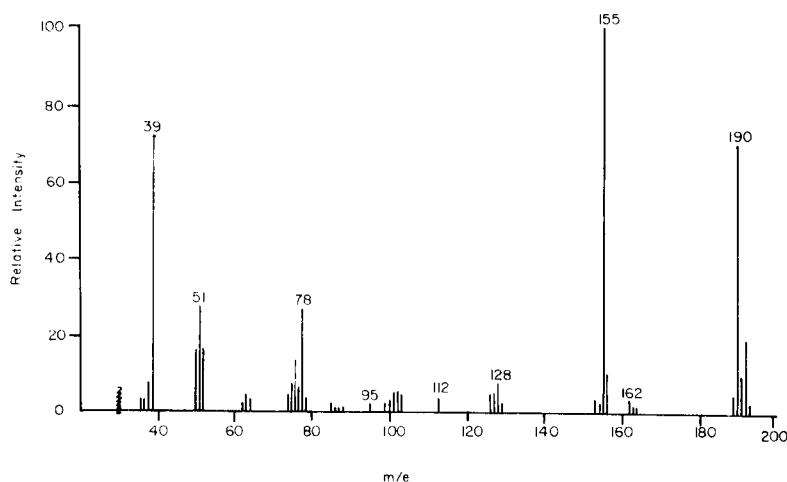


Figure 1: Mass Spectrum of 6-Chloro-2,2'-bipyridyl

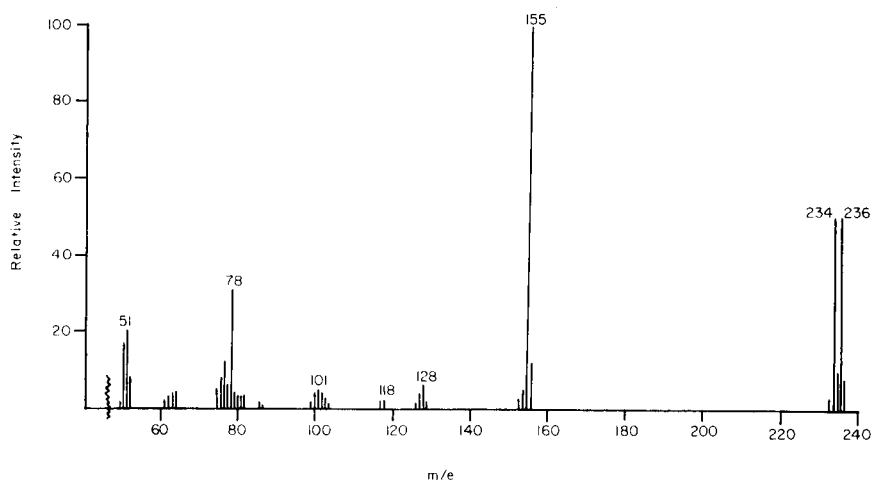


Figure 2: Mass Spectrum of 6-Bromo-2,2'-bipyridyl

The base peak in the mass spectrum of 6-chloro-2,2'-bipyridyl (Figure 1) is at mass 155 and is due to a  $C_{10}H_7N_2^+$  ion, presumably the 2,2'-bipyridyl molecular ion less one hydrogen, formed from the molecular ion by loss of Cl. This result is analogous to that observed in the mass spectrum of 2-chloropyridine (6). The molecular ion of 6-chloro-2,2'-bipyridyl at mass 190 gives rise to a peak of 70% of the intensity of the base peak. Loss of HCN from the molecular ion of 6-chloro-2,2'-bipyridyl with retention of the halogen does occur to a small extent and accounts for the peak at mass 163 (2%;  $C_9H_6N^{35}Cl$ ). Loss of  $H^+$  from this species gives a peak at mass 162 (3%;  $C_9H_5N^{35}Cl$ ).

Most of the remaining peaks in the spectrum can be accounted for by the subsequent disintegration of the 2,2'-bipyridyl molecular ion less one hydrogen at mass 155 in a manner very closely analogous to the fragmenta-

tion routes already described for 2,2'-bipyridyl (4). For example, the cluster of peaks at mass 126-129 of low intensity arise either by loss of  $C_2H_2$  to give a  $C_8H_5N_2^+$  ion at mass 129 (2%) or loss of HCN to give a  $C_9H_6N^+$  ion at mass 128 (7%) followed by subsequent loss of  $H^+$  to produce the peaks at mass 127 (4%;  $C_9H_5N^+$ ) and 126 (4%;  $C_9H_4N^+$ ).

Likewise the peaks at mass 100-103 can be accounted for by the subsequent fragmentation of the  $C_8H_5N_2^+$  ion and the  $C_9H_6N^+$  ion by processes (see Scheme and Table I) analogous to those which gave rise to peaks of similar mass numbers in the spectrum of 2,2'-bipyridyl (4).

As with 2,2'-bipyridyl, rupture of the central bond of 6-chloro-2,2'-bipyridyl occurs to some extent. This process takes place mainly after loss of the halogen group and gives rise to the  $C_5H_4N^+$  ion at mass 78 (27%) and the  $C_5H_3N^+$  species at mass 77 (6%). The central bond rup-

Table I  
High Resolution Data for 6-Chloro-2,2'-bipyridyl

m/e	Elemental Composition	Observed Mass	Calculated Mass
163	C <sub>9</sub> H <sub>6</sub> N <sup>35</sup> Cl	163.0189	163.0189
162	C <sub>9</sub> H <sub>5</sub> N <sup>35</sup> Cl	162.0109	162.0111
155	C <sub>10</sub> H <sub>7</sub> N <sub>2</sub>	155.0609	155.0609
129	C <sub>8</sub> H <sub>5</sub> N <sub>2</sub>	129.0450	129.0453
128	C <sub>8</sub> H <sub>6</sub> N	128.0499	128.0500
127	C <sub>8</sub> H <sub>5</sub> N	127.0422	127.0422
126	C <sub>8</sub> H <sub>4</sub> N	126.0344	126.0344
112	C <sub>8</sub> H <sub>5</sub> N <sup>35</sup> Cl	111.9954	111.9954
103	C <sub>8</sub> H <sub>3</sub> N <sub>2</sub> (4%)	103.0296	103.0296
	C <sub>7</sub> H <sub>5</sub> N (1%)	103.0422	103.0422
102	C <sub>7</sub> H <sub>4</sub> N (5%)	102.0344	102.0344
	C <sub>8</sub> H <sub>6</sub> (1%)	102.0465	102.0469
101	C <sub>8</sub> H <sub>5</sub> (5%)	101.0391	101.0391
	C <sub>7</sub> H <sub>3</sub> N (1%)	101.0265	101.0265
100	C <sub>8</sub> H <sub>4</sub> (3%)	100.0313	100.0313
	C <sub>7</sub> H <sub>2</sub> N (3%)	100.0186	100.0187
86	C <sub>4</sub> H <sub>3</sub> <sup>35</sup> Cl	85.9918	85.9924
85	C <sub>4</sub> H <sub>2</sub> <sup>35</sup> Cl	85.9845	84.9845
78	C <sub>3</sub> H <sub>4</sub> N	78.0345	78.0344

ture does occur to some extent, however, before loss of chlorine as is evident by the presence of the small peak at mass 112 (3%; C<sub>8</sub>H<sub>5</sub>N<sup>35</sup>Cl<sup>+</sup>). This species may subsequently lose CN<sup>•</sup> or HCN to give peaks at mass 86 (1%; C<sub>4</sub>H<sub>3</sub>Cl<sup>+</sup>) and 85 (2%; C<sub>4</sub>H<sub>2</sub>Cl<sup>+</sup>) respectively.

The peak at mass 95 (2%) is due to the M<sup>++</sup> ion of 6-chloro-2,2'-bipyridyl. The high resolution data are presented in Table I and the observed metastable transitions, which are noted in the Scheme by an asterisk, are given in Table II.

In the mass spectrum of 6-bromo-2,2'-bipyridyl (Figure 2) the base peak is again at mass 155 due to the C<sub>10</sub>H<sub>7</sub>N<sub>2</sub><sup>+</sup> ion formed from the molecular ion by loss of Br<sup>•</sup>. The peaks due to the molecular ion at mass 234 and 236 amount to only 50% of the intensity of the base peak thus indicating that the bromine group is more readily lost than the chlorine group from 6-chloro-2,2'-bipyridyl. In keeping with this observation and unlike the spectrum of 6-chloro-2,2'-bipyridyl there were no peaks in the spectrum of 6-bromo-2,2'-bipyridyl corresponding to the loss of HCN from the molecular ion or to rupture of the central bond with retention of the halogen group. The spectrum below mass 155, as expected, is very similar to that obtained with 6-chloro-2,2'-bipyridyl and requires no comment. The peaks at mass 117 and 118 (2%) are due to the M<sup>++</sup> ions.

#### EXPERIMENTAL

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

6-Chloro- and 6-bromo-2,2'-bipyridyls (5) were analytically pure.

#### REFERENCES AND NOTES

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Table II  
Metastable Ions Present in the Mass Spectrum of 6-Chloro-2,2'-bipyridyl

Initial Ion	Resultant Ion	Transition	Calculated m*	Found m*	Fragment Expelled
C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> Cl	C <sub>10</sub> H <sub>7</sub> N <sub>2</sub>	190—155	126.4	126.6	Cl
C <sub>10</sub> H <sub>7</sub> N <sub>2</sub>	C <sub>9</sub> H <sub>6</sub> N	155—128	105.7	105.7	HCN
C <sub>10</sub> H <sub>7</sub> N <sub>2</sub>	C <sub>9</sub> H <sub>5</sub> N <sub>2</sub>	155—129	107.4	107.4	C <sub>2</sub> H <sub>2</sub>
C <sub>9</sub> H <sub>6</sub> N	C <sub>8</sub> H <sub>5</sub>	128—101	79.7	79.8	HCN