Mass Spectral Fragmentation Pattern of 4,4'-Bipyridines. Part II. 4,4'-Oxybispyridine and 4,4'-Thiobispyridine

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The mass spectra of 4,4'-oxybispyridine and 4,4'-thiobispyridine are reported. In the former the base peak is due to the molecular ion and the fragmentation routes involve loss of H, CO, HCN, C_2H_2N and C_2HO from the molecular ion as well as rupture of the central bonds. In the latter the base peak is also due to the molecular ion and the fragmentation routes involve loss of H, CS, S, HCN and C_2HS as well as central bond rupture.

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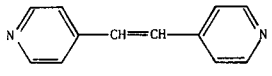
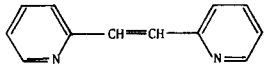
We have recently reported on the mass spectral fragmentation pattern of several derivatives of 2,2'-bipyridine containing an atom or group placed between the pyridine rings (1-7). In studies in the corresponding 4,4'-bipyridine series it has so far been found that there are considerable differences in the mass spectrum of 1,2-di-(4-pyridyl)ethylene (I) (8) compared with that of the 2,2'-bipyridine analogue 1,2-di-(2-pyridyl)ethylene (II) (3). To examine further this difference in behaviour in the 2,2'-bipyridine and 4,4'-bipyridine series we have studied the mass spectra of 4,4'-oxybispyridine (III) and 4,4'-thiobispyridine (IV) to compare them with the mass spectra of 2,2'-oxybispyridine (6) and 2,2'-thiobispyridine (5) respectively.



I



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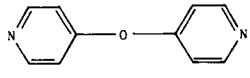

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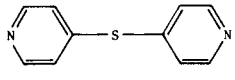
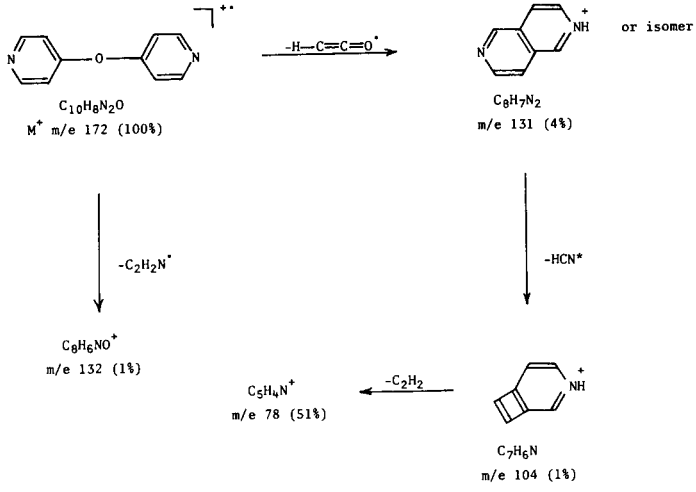


IV

The base peak in the mass spectrum of 4,4'-oxybispyridine (Figure 1), is due to the molecular ion $C_{10}H_8N_2O$ at mass 172. Loss of $H^\cdot$ gives a peak at mass 171 of intensity 24% of that of the base peak. The intensity of the M-1 peak is much less than in the case of 2,2'-oxybispyridine where the M-1 ion gives a peak of 56% of the intensity of the base peak.

Apart from the loss of $H^\cdot$ the fragmentation of the molecular ion of 4,4'-oxybispyridine follows at least five different pathways. One minor route involves loss of the elements C_2HO (Scheme 1) from the molecular ion with the formation of a $C_8H_7N_2^+$ ion at mass 131 (4% of molecular ion) considered to be due to a naphthyridinium ion. A similar fragmentation route was observed in the spectrum

SCHEME 1



of 2,2'-oxybispyridine (6). The $C_8H_7N_2^+$ ion fragments at least by the loss of HCN to give a peak at mass 104 (1%) due to a $C_7H_6N^+$ ion. A metastable for the transition 131 → 104 was observed. The $C_7H_6N^+$ ion may lose C_2H_2 to give a $C_5H_4N^+$ species of mass 78 which is a prominent peak in the spectrum of 4,4'-oxybispyridine (see also Scheme 4).

Another minor fragmentation route from the molecular ion of 4,4'-oxybispyridine involves the loss of $C_2H_2N^\cdot$ to give a peak at mass 132 (1%) due to a $C_8H_6NO^+$ species. This fragmentation route was not observed with 2,2'-oxybispyridine but the loss of $C_2H_2N^\cdot$ is known to occur in the fragmentation of the pyridine molecular ion (9).

A third fragmentation route from the 4,4'-oxybispyridine molecular ion ($C_{10}H_8N_2O$) involves loss of neutral CO. This gives rise to a peak at mass 144 (1%) due to a species of empirical formula $C_9H_8N_2$ depicted as a pyridoazepine molecular ion. The 4,4'-oxybispyridine molecular ion may lose $H^\cdot$ to form the M-1 ion before loss of CO to form a $C_9H_7N_2^+$ ion of mass 143 (3%). The species at mass 143 can also be formed from the pyridoazepine molecular ion

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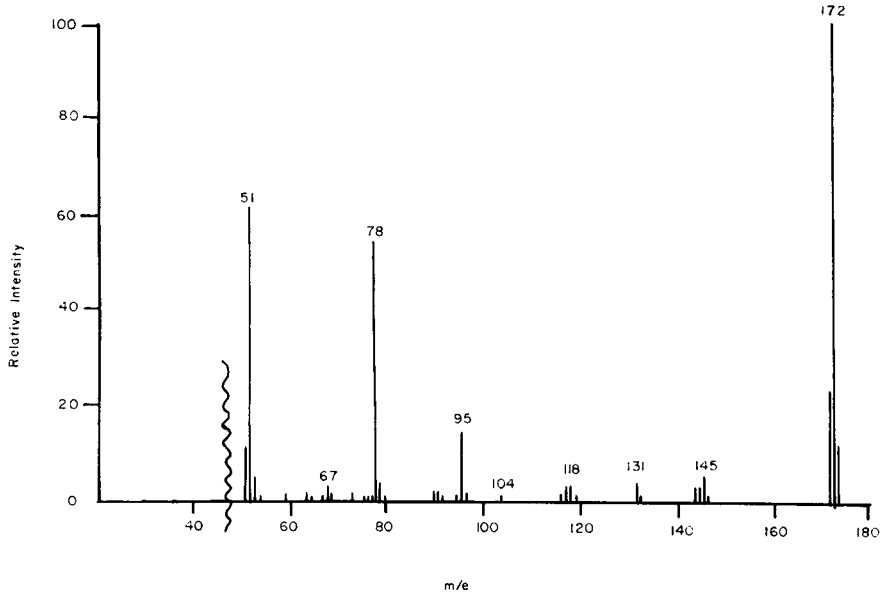


Figure 1: Mass Spectrum of 4,4'-Oxybispyridine

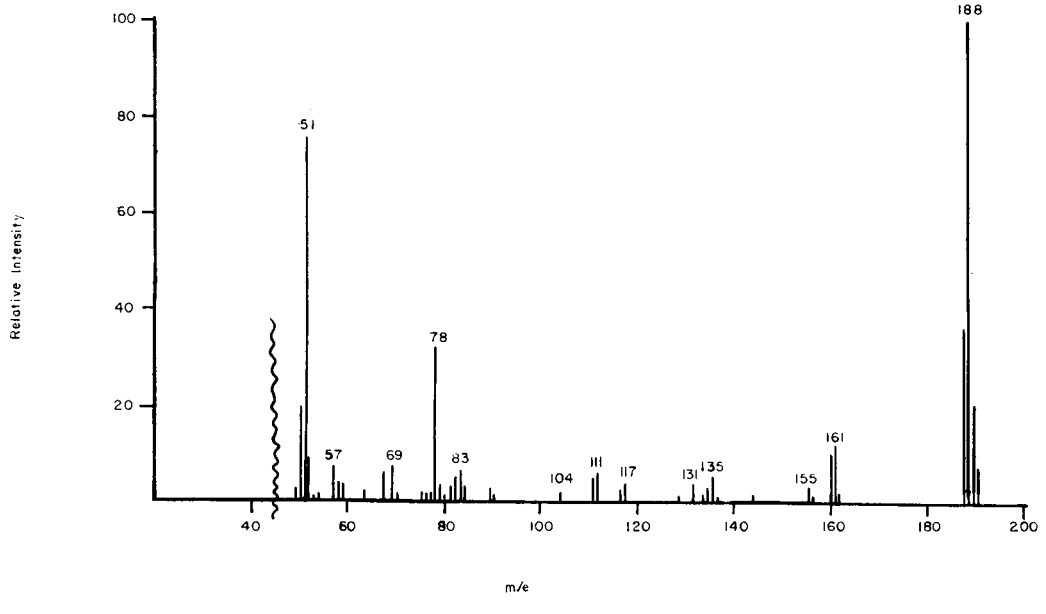
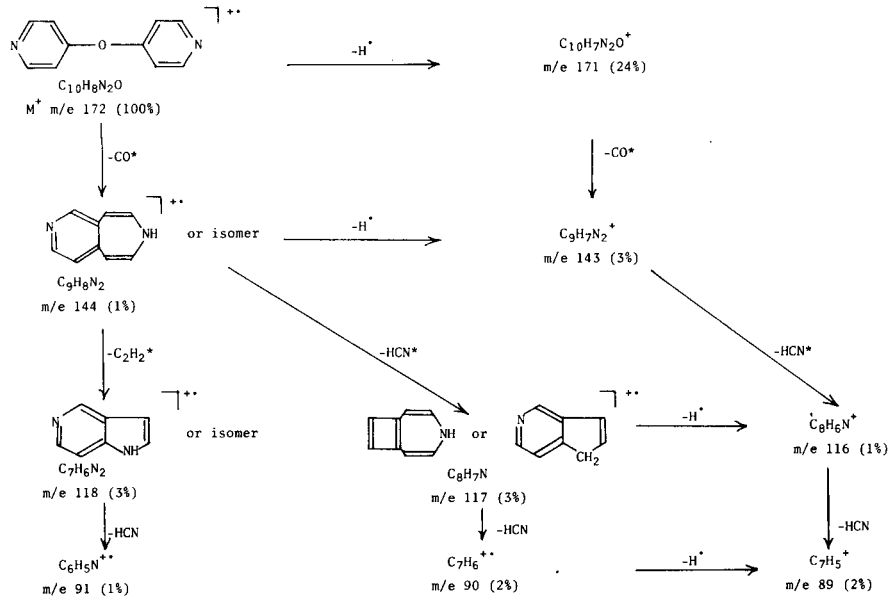


Figure 2: Mass Spectrum of 4,4'-Thiobispyridine

(mass 144) by loss of $H^{\cdot}$. The loss of neutral CO from the $M^{+\cdot}$ and M-1^{+} ions is much less pronounced with 4,4'-oxybispyridine than was observed in the spectrum of 2,2'-oxybispyridine. The subsequent fragmentation of the pyridoazepine molecular ion at mass 144 involves either loss of C_2H_2 to give a peak at mass 118 (3%) of empirical formula $C_7H_6N_2$ depicted as a pyrrolopyridine molecular ion or loss of HCN to give a peak at mass 117 (3%) of formula C_8H_7N considered to be due to a pyrindine or related species (see Scheme 2). Metastable peaks for these two transitions were observed. The species at mass 117 (C_8H_7N) may lose $H^{\cdot}$ to form the ion $C_8H_6N^{+}$ at mass 116 (1%). The $C_8H_6N^{+}$ ion is also formed from the pyridoazepine molecular ion less one hydrogen ($C_9H_7N_2^{+}$) at mass 143 by loss of HCN. The pyrrolopyridine molecular ion (mass 118) and the pyrindine or related species (mass 117) and its M-1 species (mass 116)

SCHEME 2



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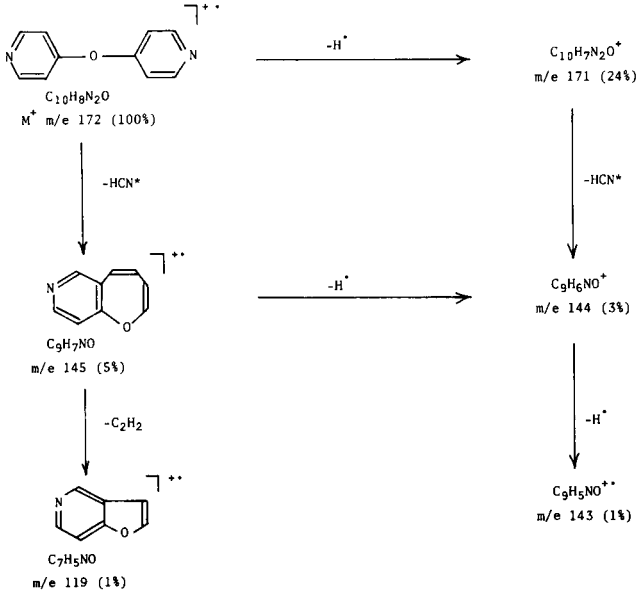


disintegrate further by loss of neutral HCN to give small peaks (1-2%) at mass 91 ($C_6H_5N^{+\cdot}$), 90 ($C_7H_6^{+\cdot}$) and 89 ($C_7H_5^+$) respectively.

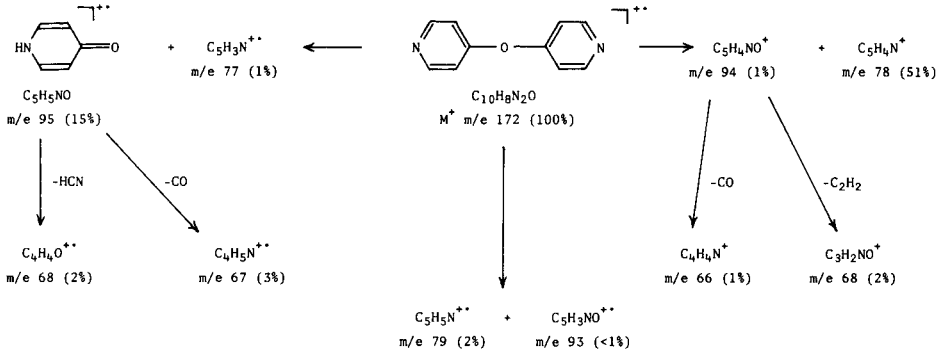
A fourth fragmentation route from the 4,4'-oxybispyridine molecular ion ($C_{10}H_8N_2O$) involves loss of HCN (see Scheme 3). This gives rise to a peak at mass 145 (5%) due to a species of empirical formula C_9H_7NO depicted as a pyridooxepin molecular ion. The 4,4'-oxybispyridine molecular ion may lose $H^\cdot$ to form the M-1 ion before loss of HCN to form a $C_9H_6NO^+$ ion of mass 144 (3%). The species at mass 144 can also be formed from the pyridooxepin molecular ion (mass 145) by loss of $H^\cdot$. The loss of HCN from the $M^{+\cdot}$ and M-1 ions was not observed to any significant extent in the spectrum of 2,2'-oxybispyridine.

Table I

High Resolution Data for 4,4'-Oxybispyridine

m/e	Elemental Composition	Observed Mass	Calculated Mass
145	C_9H_7NO	145.0525	145.0528
144	$C_9H_8N_2$ (1%)	144.0684	144.0687
	C_9H_6NO (3%)	144.0451	144.0449
143	$C_9H_7N_2$ (3%)	143.0608	143.0609
	C_9H_5NO (1%)	143.0373	143.0371
132	C_8H_6NO	132.0448	132.0449
131	$C_8H_7N_2$	131.0609	131.0609
119	C_7H_5NO	119.0370	119.0371
118	$C_7H_6N_2$	118.0531	118.0531
117	C_8H_7N	117.0578	117.0578
116	C_8H_6N	116.0500	116.0500
104	C_7H_6N	104.0500	104.0500
95	C_5H_5NO	95.0371	95.0371
94	C_5H_4NO	94.0292	94.0293
91	C_6H_5N	91.0422	91.0422
90	C_7H_6	90.0469	90.0469
89	C_7H_5	89.0388	89.0391
79	C_5H_5N	79.0422	79.0422
78	C_5H_4N	78.0344	78.0344
77	C_5H_3N	77.0266	77.0265
76	C_5H_2N	76.0187	76.0187
75	C_5HN	75.0109	75.0109
68	C_4H_4O (2%)	68.0262	68.0262
	C_3H_2NO (2%)	68.0137	68.0136
67	C_4H_5N	67.0422	67.0422
66	C_4H_4N	66.0344	66.0344

SCHEME 4



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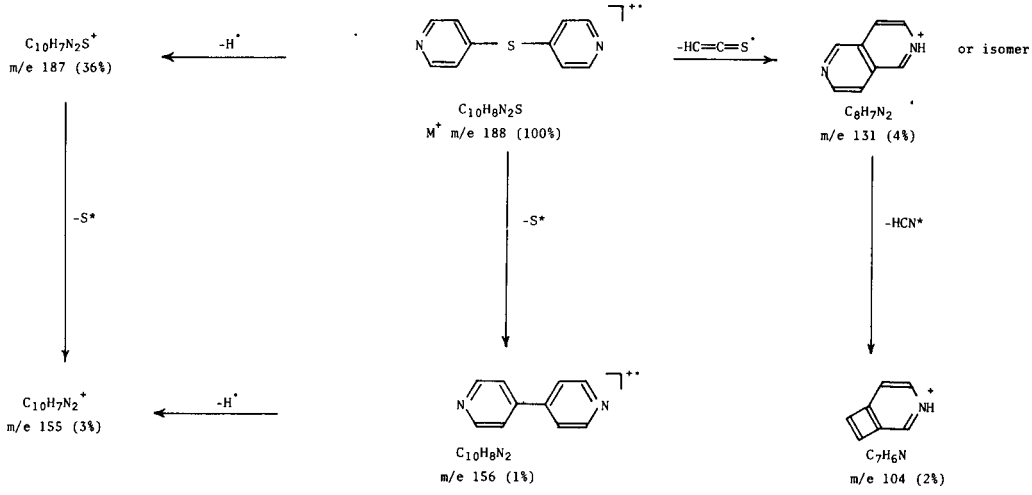

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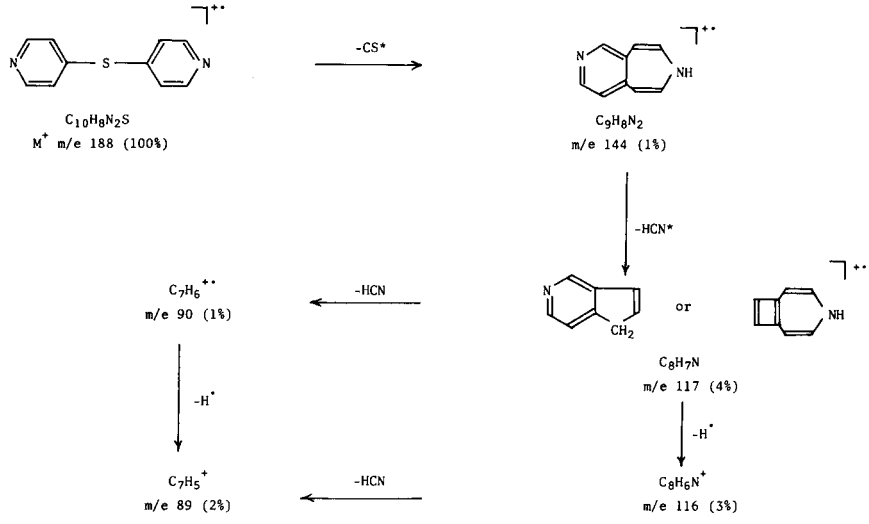
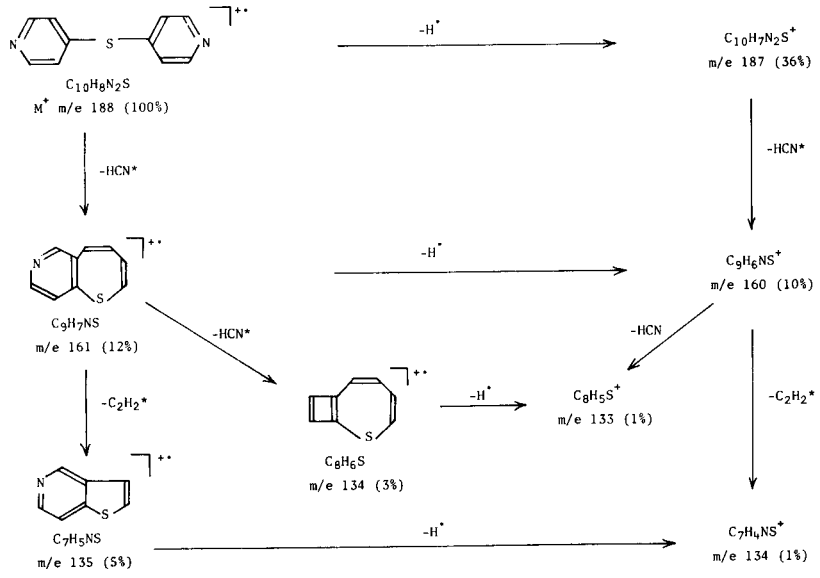
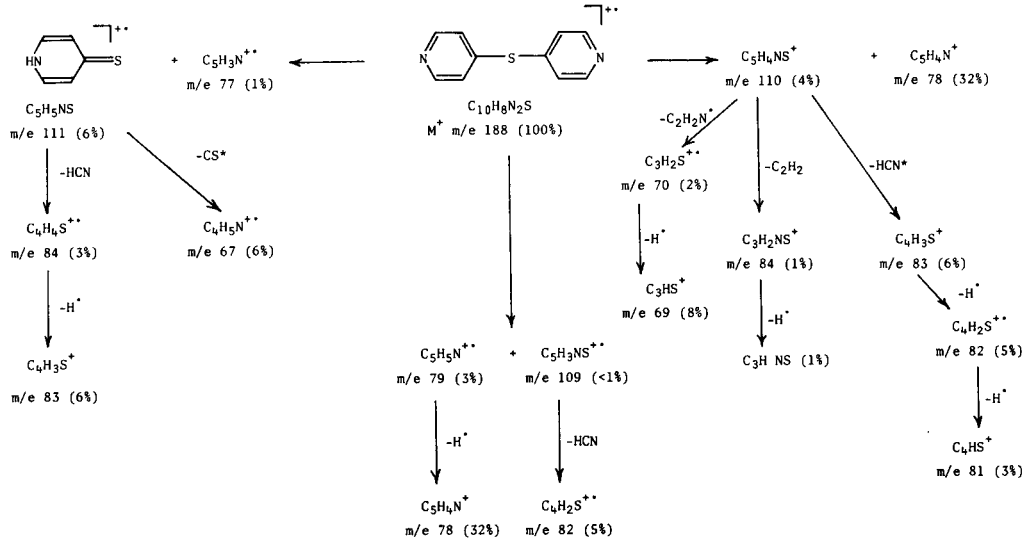


SCHEME 7



SCHEME 8



The pyridooxepin molecular ion at mass 145 loses C_2H_2 to give a species of mass 119 ($C_7H_5NO^{+\bullet}$) depicted as a pyridofuran molecular ion.

The fifth fragmentation route from the molecular ion of 4,4'-oxybispyridine is the major one and involves rupture of the central bonds (Scheme 4). It gives rise, as in the case of 2,2'-oxybispyridine, to some interesting ions, the formation of which must involve hydrogen migrations. For instance, the peak at mass 95 (15%) is due to a species of empirical formula C_5H_5NO considered to be due to the 4-pyridone molecular ion and must be formed by a hydrogen migration. The accompanying fragment at mass 77 and empirical formula C_5H_3N is present in small amounts (1%). In keeping with the assignment of the peak at mass 95 as the 4-pyridone molecular ion the $C_5H_5NO^{+\bullet}$ species disintegrates by loss of HCN to give a peak at mass 68 ($C_4H_4O^{+\bullet}$; 2%) or by loss of CO to give a peak at mass 67 ($C_4H_5N^{+\bullet}$; 3%) in a way typical of 4-pyridone (9). Another central bond rupture with concomitant hydrogen migration gives rise to the small peak at mass 79 (2%) due to the $C_5H_5N^{+\bullet}$ species presumably the pyridine molecular ion. The accompanying fragment $C_5H_3NO^{+\bullet}$ at mass 93 is present in only very small amounts. The $C_5H_5N^{+\bullet}$ species was much more prominent (34%) in the spectrum of 2,2'-oxybispyridine.

Table II

Metastable Ions in the Spectrum of 4,4'-Oxybispyridine

Initial Ion	Resultant Ion	Transition	Found m*	Calculated m*	Fragment Expelled
$C_{10}H_8N_2O$	C_9H_7NO	172 → 145	122.4	122.3	HCN
$C_{10}H_7N_2O$	C_9H_6NO	171 → 144	121.3	121.3	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	119.4	119.5	CO
$C_9H_8N_2$	$C_7H_6N_2$	144 → 118	96.7	96.7	C_2H_2
$C_9H_8N_2$	C_8H_7N	144 → 117	95.2	95.1	HCN
$C_9H_7N_2$	C_8H_6N	143 → 116	94.1	94.1	HCN
$C_8H_7N_2$	C_7H_6N	131 → 104	82.5	82.5	HCN

Table III

High Resolution Data for 4,4'-Thiobispyridine

m/e	Elemental Composition	Observed Mass	Calculated Mass
161	C_9H_7NS	161.0299	161.0299
160	C_9H_6NS	160.0221	160.0221
156	$C_{10}H_8N_2$	156.0678	156.0687
155	$C_{10}H_7N_2$	155.0609	155.0609
144	$C_9H_8N_2$	144.0687	144.0687
135	C_7H_5NS	135.0141	135.0143
134	C_8H_6S (3%)	134.0190	134.0190
	C_7H_4NS (1%)	134.0064	134.0064
133	C_8H_5S	133.0112	133.0112
131	$C_8H_7N_2$	131.0609	131.0609
117	C_8H_7N	117.0578	117.0578
116	C_8H_6N	116.0500	116.0500
111	C_5H_5NS	111.0143	111.0143
110	C_5H_4NS	110.0065	110.0065
104	C_7H_6N	104.0500	104.0500
90	C_7H_6	90.0469	90.0469
89	C_7H_5	89.0390	89.0391
84	C_4H_4S (3%)	84.0032	84.0034
	C_3H_2NS (1%)	83.9908	83.9908
83	C_4H_3S (6%)	82.9951	82.9955
	C_3HNS (1%)	82.9830	82.9830
82	C_4H_2S	81.9877	81.9877
81	C_4HS	80.9799	80.9799
79	C_5H_5N	79.0425	79.0422
78	C_5H_4N	78.0344	78.0344
77	C_5H_3N	77.0265	77.0265
70	C_3H_2S	69.9876	69.9877
69	C_3HS	68.9799	68.9799
67	C_4H_5N	67.0422	67.0422

The straightforward central bond rupture with no hydrogen migration also occurs and is largely responsible for the very strong peak at mass 78 (51%) due to a species of formula C_5H_4N presumably the pyridine molecular ion less one hydrogen. The accompanying pyridyloxy ion $C_5H_4NO^+$ at mass 94 is present in small amounts (1%).

The peak at mass 72.5 (2%) is due to the M^{++} ion of the pyridooxepin species at mass 145.

The elemental compositions of the ions are recorded in Table I. Peaks due to ^{13}C species are omitted from the table. The metastable transitions are recorded in Table II.

The mass spectrum of 4,4'-thiobispyridine shows considerable differences from the spectrum of the corresponding 2,2'-bipyridine analogue 2,2'-thiobispyridine (5). The base peak in the spectrum of 4,4'-thiobispyridine (Figure 2) is due to the molecular ion $C_{10}H_8N_2S$ at mass 188. Loss of $H^\cdot$ gives a peak at mass 187 of intensity 36% of that of the base peak. This behaviour contrasts with that observed in the spectrum of 2,2'-thiobispyridine where the base peak is due to the M-1 ion at mass 187. The molecular ion at mass 188 in this case gives a peak of 36% of the intensity of the M-1 ion (5).

Apart from the loss of $H^\cdot$ the fragmentation of the molecular ion of 4,4'-thiobispyridine follows at least five different pathways. One minor route involves loss of the elements C_2HS (Scheme 5) from the molecular ion analogous to the loss of C_2HO from the molecular ion of 4,4'-oxybispyridine. This fragmentation route results in the formation of a $C_8H_7N_2^+$ ion at mass 131 (4%) depicted as a naphthyridinium ion. The $C_8H_7N_2^+$ ion fragments at least by the loss of HCN to give a peak at mass 104 (2%) due to a $C_7H_6N^+$ ion. A metastable for the transition 131 → 104 was observed in the spectrum.

Another minor fragmentation route from the molecular ion of 4,4'-thiobispyridine involves the loss of S to give a species of formula $C_{10}H_8N_2^{++}$ at mass 156 (1%) almost certainly due to the 4,4'-bipyridine molecular ion (Scheme 5). A metastable for the transition 188 → 156 was observed in the spectrum. The loss of S was also observed to occur from the M-1 ion of 4,4'-thiobispyridine at mass 187 to give the 4,4'-bipyridine molecular ion less one hydrogen at mass 155 (3%). A metastable for the transition 187 → 155 was observed in the spectrum.

A third fragmentation route from the 4,4'-thiobispyridine molecular ion ($C_{10}H_8N_2S$) involves loss of CS analogous to the loss of CO from the molecular ion of 4,4'-oxybispyridine. This gives rise to a peak at mass 144 (1%) due

Table IV

Metastable Ions in the Spectrum of 4,4'-Thiobispyridine

Initial Ion	Resultant Ion	Transition	Found m*	Calculated m*	Fragment Expelled
$C_{10}H_8N_2S$	C_9H_7NS	188 → 161	137.9	137.8	HCN
$C_{10}H_7N_2S$	C_9H_6NS	187 → 160	137.0	136.9	HCN
$C_{10}H_8N_2S$	$C_{10}H_8N_2$	188 → 156	129.4	129.4	S
$C_{10}H_7N_2S$	$C_{10}H_7N_2$	187 → 155	128.5	128.5	S
C_9H_7NS	C_7H_5NS	161 → 135	113.2	113.2	C_2H_2
C_9H_6NS	C_7H_4NS	160 → 134	112.2	112.2	C_2H_2
C_9H_7NS	C_8H_6S	161 → 134	111.5	111.5	HCN
$C_{10}H_8N_2S$	$C_9H_8N_2$	188 → 144	110.3	110.3	CS
$C_9H_8N_2$	C_8H_7N	144 → 117	95.1	95.1	HCN
$C_8H_7N_2$	C_7H_6N	131 → 104	82.5	82.5	HCN
C_5H_4NS	C_4H_3S	110 → 83	62.6	62.6	HCN
C_5H_5NS	C_4H_5N	111 → 67	40.5	40.4	CS

to a species of empirical formula $C_9H_8N_2$ again depicted as a pyridoazepine molecular ion (Scheme 6). Unlike the corresponding situation with 4,4'-oxybispyridine (see Scheme 2) the loss of CS was not observed from the M-1 ion of 4,4'-thiobispyridine. The subsequent fragmentation of the pyridoazepine molecular ion at mass 144 involves loss of HCN to give a peak at mass 117 (4%) of formula C_8H_7N again depicted as a pyrindine or related species. A metastable peak for the transition 144 → 117 was observed in the spectrum. The loss of C_2H_2 from the pyridoazepine molecular ion (*cf.* Scheme 2) was not observed. The subsequent fragmentation of the species C_8H_7N at mass 117 was similar to that already noted in Scheme 2.

A fourth fragmentation route from the 4,4'-thiobispyridine molecular ion ($C_{10}H_8N_2S$) involves loss of HCN (see Scheme 7). This gives rise to a peak at mass 161 (12%) due to a species of empirical formula C_9H_7NS depicted as a pyridothiepin molecular ion. This fragmentation route is much more pronounced than in the spectrum of 2,2'-thiobispyridine. The 4,4'-thiobispyridine molecular ion may lose H$^\cdot$ to form the M-1 ion before loss of HCN to form a $C_9H_6NS^+$ ion at mass 160 (10%). The species at mass 160 can also be formed from the pyridothiepin molecular ion (mass 161) by loss of H$^\cdot$. The pyridothiepin molecular ion at mass 161 and its M-1 ion at mass 160 each lose either C_2H_2 or HCN to give the species depicted as a pyridothiophene molecular ion at mass 135 (C_7H_5NS; 5%) or a cyclobutadiene fused thiepin derivative at mass 134 (C_8H_6S; 3%) and the corresponding M-1 ions at mass 134 ($C_7H_4NS^+$; 1%) or mass 133 ($C_8H_5S^+$; 1%) as depicted in Scheme 7. Metastable peaks for most of these transitions were observed.

The fifth fragmentation route from the molecular ion of 4,4'-thiobispyridine is the major one and involves rupture of the central bonds (Scheme 8). As in the case of the spectrum of 4,4'-oxybispyridine hydrogen migrations sometimes accompany the bond rupture. The species formed by this fragmentation route are summarized in Scheme 8.

The elemental compositions of the ions are recorded in Table III. Peaks due to ^{13}C and ^{34}S species are omitted from the table. The metastable transitions are recorded in Table IV.

EXPERIMENTAL

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

4,4'-Oxybispyridine (10) and 4,4'-thiobispyridine were analytically pure.

Acknowledgements.

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