Mass Spectral Fragmentation Pattern of 2,2′-Bipyridyls. Part XII. 2,2′-Selenodipyridine

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The mass spectrum of 2,2′-selenodipyridine obtained by electron impact is reported. The base peak in the spectrum is due to the $C_5H_4N^+$ ion formed principally by rupture of the central bonds. The molecular ion gives rise to a peak of 50% of the intensity of the base peak. Other fragmentations include loss of H, Se and CSe from the molecular ion and HCN from the M-1 ion.

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Over the past few years we have reported on the mass spectra of several derivatives of 2,2′-bipyridyl containing an atom or group placed between the pyridine rings and have compared the spectra with those of the corresponding diphenyl analogues. We have so far studied the spectra of di-2-pyridyl ketone (1), 2,2′-oxydipyridine (2), 2,2′-thiodipyridine (3), 2,2′-dithiodipyridine (4), 1,2-di-(2-pyridyl)ethylene (5) and 2,2′-iminodipyridine (6). We now report the fragmentation pattern of 2,2′-selenodipyridine which was recently synthesised for the first time (7). The disintegration pattern of 2,2′-selenodipyridine is quantitatively quite different from that of diphenyl selenides.

In the mass spectra of diphenyl selenide and substituted diphenyl selenides the base peak is usually due to species obtained from the molecular ion by loss of selenium (8-10). In the mass spectrum of 2,2′-selenodipyridine (Figure), however, the base peak is at mass 78 and is due to species of empirical formula C_5H_4N.

The molecular ion at mass 236 ($C_{10}H_8N_2{}^{80}Se$) gives rise to a peak of about 50% of the intensity of the base peak. As in the spectrum of 2,2′-thiodipyridine (3) the peak due to the M-1 ion at mass 235 ($C_{10}H_7N_2{}^{80}Se$) is more prominant (80%) than that due to the molecular ion.

Unlike diphenyl selenide the loss of ^{80}Se from the molecular ion or the M-1 ion of 2,2′-selenodipyridine is not a prominant disintegration pathway. This fragmentation route gives rise to peaks at mass 156 ($C_{10}H_8N_2^{+\cdot}$) and 155 ($C_{10}H_7N_2^+$) of only 3% and 7% of the intensity of the base peak respectively presumably due to the 2,2′-bipyridyl molecular ion and its M-1 ion.

The loss of $C^{80}Se$ from the molecular ion of 2,2′-selenodipyridine is another minor fragmentation pathway giving rise to a small peak (1%) at mass 144 ($C_9H_8N_2^{+\cdot}$) probably due to a pyridoazepine molecular ion (see Scheme). This resembles the behaviour of 2,2′-thiodipyridine (3) where the loss of CS from the molecular ion occurs to a small extent. The loss of CO from the 2,2′-oxydipyridine (2) molecular ion is much more pronounced. Subsequent loss of C_2H_2 from the pyridoazepine molecular ion gives rise to a peak at mass 118 (5%; $C_7H_6N_2^{+\cdot}$) while loss of HCN gives a peak at mass 117 (3%; C_8H_7N). These peaks are analogous to those present in the mass spectra of 2,2′-oxydipyridine (2) and 2,2′-thiodipyridine (3).

Loss of HCN from the M-1 ion at mass 235 gives rise to a small peak (1%) at mass 208 due to a $C_9H_6N^{80}Se^+$ ion. The loss of HCN also occurred to a small extent from the M-1 ion of 2,2′-thiodipyridine (3).

The main disintegration route from 2,2′-selenodipyridine involves rupture of the central bonds to produce the species $C_5H_4N^+$ at mass 78 which gives rise to the base peak in the spectrum and the species $C_5H_4N^{80}Se^+$ at mass 158 (3%). The latter ion may lose ^{80}Se to form more of the $C_5H_4N^+$ ion. Contributions to the base peak also come from the rupture of the central bond of the 2,2′-bipyridine

Table I

High Resolution Data

m/e	Elemental Composition	Observed Mass	Calculated Mass
208	$C_{10}H_8N_2{}^{80}Se$	207.9665	207.9665
159	$C_5H_5N^{80}Se$	158.9587	158.9587
158	$C_5H_4N^{80}Se$	157.9508	157.9509
157	$C_5H_5N^{78}Se$	156.9595	156.9595
156	$C_{10}H_8N_2$	156.0687	156.0687
155	$C_{10}H_7N_2$	155.0609	155.0609
144	$C_9H_8N_2$	144.0688	144.0687
132	$C_4H_4{}^{80}Se$	131.9479	131.9478
131	$C_4H_3{}^{80}Se$	130.9396	130.9400
130	C_9H_8N (2%)	130.0654	130.0657
	$C_4H_2{}^{80}Se$ (2%)	129.9318	129.9321
129	C_9H_7N (2%)	129.0578	129.0578
	$C_4H_3{}^{78}Se$ (2%)	128.9409	128.9408
	$C_4H^{80}Se$ (1%)	128.9239	128.9243
128	C_9H_6N	128.0500	128.0500
118	$C_7H_6N_2$ (5%)	118.0533	118.0531
	M^{++} (2%)	117.9928	117.9926
117	C_8H_7N (3%)	117.0579	117.0578
	M^{++} (2%)	116.9934	116.9930
93	$CH^{80}Se$	92.9246	92.9243
80	^{80}Se	79.9166	79.9165
79	C_5H_5N	79.0422	79.0422
78	C_5H_4N (100%)	78.0344	78.0344
	^{78}Se (< 5%)	77.9176	77.9173

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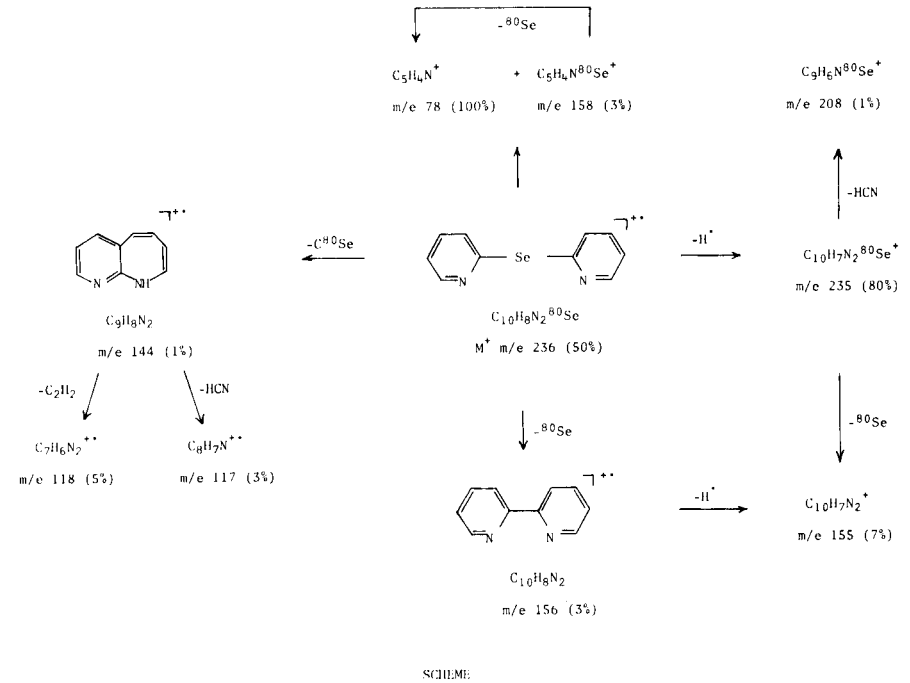

SCHEME

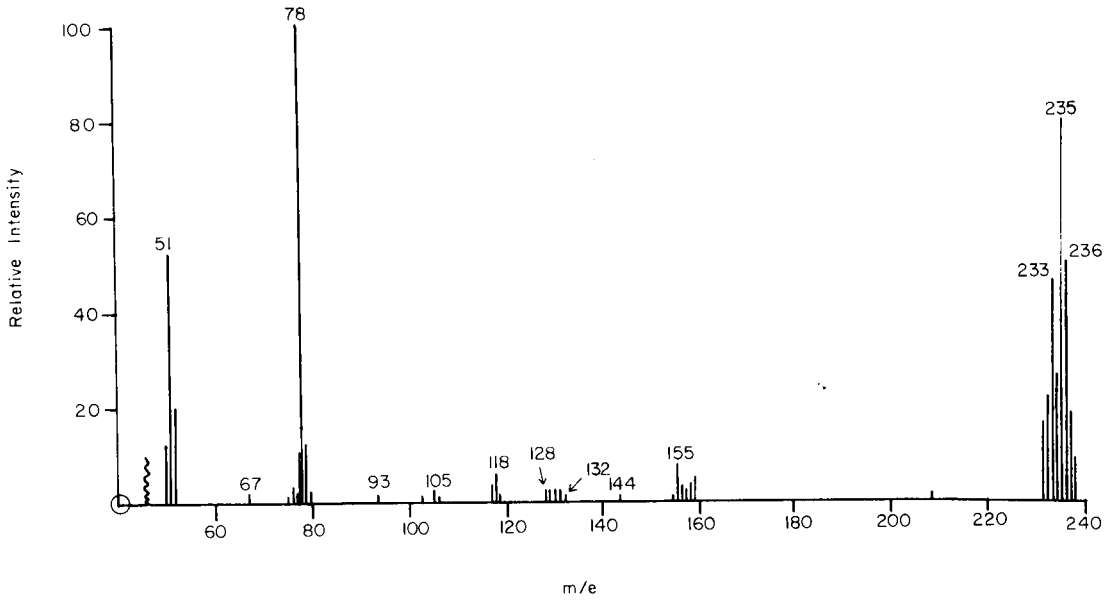

Figure: Mass Spectrum of 2,2′-Selenodipyridine

molecular ion at mass 156 (*cf* reference 11).

The peaks at mass 159 (4%; $C_5H_5N^{80}Se$) and 157 (2%; $C_5H_5N^{78}Se$) indicate that hydrogen migration may accompany the splitting of the central bonds. Such migrations have been noted already in the spectra of 2,2′-oxydipyridine (2), 2,2′-thiodipyridine (3) and 2,2′-iminodipyridine (6).

The cluster of small peaks (1-2%) at 128 (2%, C_9H_6N), 129 (2%, C_9H_7N; 2%, $C_4H_3{}^{78}Se$; 1%, $C_4H^{80}Se$), 130 (2%, C_9H_8N; 2%, $C_4H_2{}^{80}Se$), 131 (2%, $C_4H_3{}^{80}Se$) and 132 (1%; $C_4H_4{}^{80}Se$) arise from the disintegration of the 2,2′-bipyridine molecular ion ($C_{10}H_8N_2$) or its M-1 ion by loss of HCN or CN· (*cf* ref. 11) or by the loss of the same elements from the $C_5H_4N^{80}Se$ ion and related species

followed by loss of H.

The peaks at mass 118 and 117 are in fact doublets due to the presence of the M^{++} species (~ 2%), 236^{++} and 234^{++} respectively.

The spectrum below mass 78 requires no comment. There were no clear metastable transitions above a mass of 40 in the spectrum.

The high resolution data are given in Table I.

EXPERIMENTAL

The mass spectrum was determined with an A.E.I. MS-30 mass spectrometer. The sample was analysed by direct insertion probe at an ionizing current of 70eV. The ion source temperature was 110°. Elemental compositions were obtained by the peak matching method.

2,2′-Selenodipyridine (7) was analytically pure.

REFERENCES AND NOTES

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