

Mass Spectral Fragmentation Pattern of 2,2'-Bipyridyls. Part VI. 2,2'-Thiodipyridine

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The mass spectral fragmentation of 2,2'-thiodipyridine is reported. The base peak is due to the M-1 ion. The principal fragmentation routes involve loss of H, CS, CHCS and HCN from the molecular ion and CS, HCN and S from the M-1 species. Rupture of the central bonds is also an important disintegration pathway.

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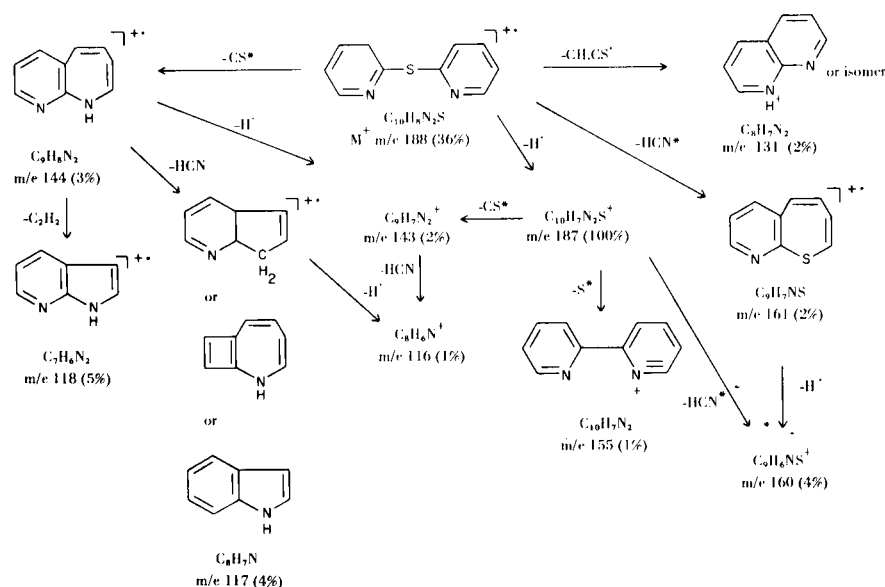
We have recently reported the mass spectral fragmentation patterns of di-2-pyridyl ketone (1) and 2,2'-oxydipyridine (2). In continuation of our study of relatives of 2,2'-bipyridyl containing an atom or group placed between the pyridine rings we now report the mass spectrum of 2,2'-thiodipyridine (I).

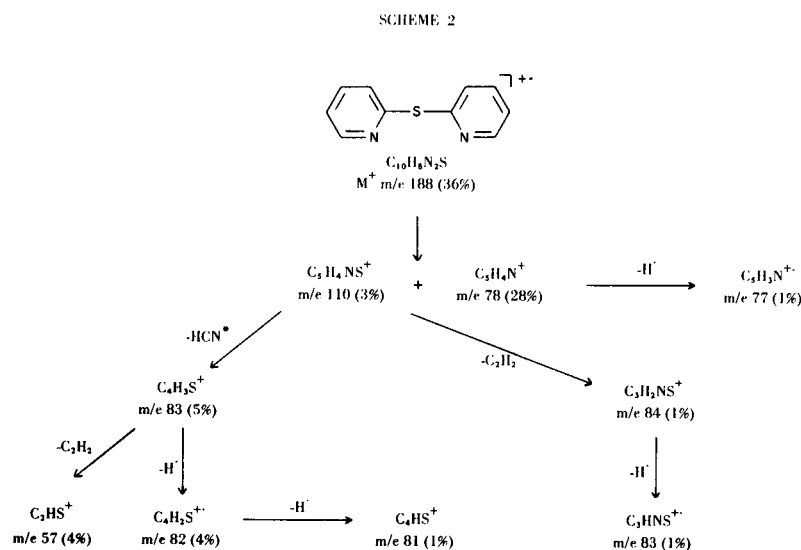
The mass spectrum of diphenyl sulphide (II) has been the subject of some study (3-7). The spectrum (5,7) is dominated by the peak due to the molecular ion at mass 186, which is the base peak, and the M-1 ion (~55%). Small peaks (~2-8%) at mass 171, 153, 152, 142 and 141 are due to the loss of the elements CH₃, SH, SH₂, CS and HCS respectively from the molecular ion, while peaks below a mass of 110 arise principally from the two fragments formed by rupture of the central bonds.



Unlike diphenyl sulphide, the base peak in the spectrum of 2,2'-thiodipyridine (I) is not due to the molecular ion but is due to the M-1 ion at mass 187. The molecular ion at mass 188 gives rise to a peak of 36% of the intensity of the base peak. There are at least four different fragmentation routes from the molecular ion and the M-1 ion of 2,2'-thiodipyridine apart from fragments arising from the rupture of the central bonds. These pathways which give rise to small intensity peaks (below 10% of base peak) are shown in Scheme 1.

SCHEME 1





The first route involves loss of CS from the molecular ion to form a species of empirical formula $C_9H_8N_2$ at mass 144 (3%). This species is presumably formed in a manner analogous to the loss of CO from 2,2'-oxydipyridine (2) and CS from diphenyl sulphide (7). It is depicted as being due to a pyridoazepine molecular ion. The pyridoazepine molecular ion at mass 144 may lose a H⁺ to form the $C_9H_7N_2^+$ ion at mass 143 (2%) which is also formed from the M-1 ion at mass 187 by loss of CS.

The subsequent fragmentation of the pyridoazepine molecular ion ($C_9H_8N_2$) at mass 144 is the same as that already described for the same species formed by the fragmentation of 2,2'-oxydipyridine (2). The fragmentation of the pyridoazepine species involves either loss of C_2H_2 to give a peak at mass 118 (5%) of empirical formula $C_7H_6N_2$ depicted as a pyrrolopyridine molecular ion or loss of HCN to give a peak at mass 117 (4%) of formula C_8H_7N considered to be due to the pyridine or indole molecular ion or related species (see Scheme 1). The species at mass 117 (C_8H_7N) may lose H⁺ to form the ion $C_8H_6N^+$ at mass 116 (1%). The $C_8H_6N^+$ ion may presumably also be formed from the pyridoazepine molecular ion less one hydrogen ($C_9H_7N_2^+$) at mass 143 by loss of HCN.

The second fragmentation route from the molecular ion of 2,2'-thiodipyridine (mass 188) involves loss of the elements CH₂CS to give a species of formula $C_8H_7N_2$ at mass 131 (2%). It is interesting to note that the 2,2'-oxydipyridine molecular ion also disintegrates (2) to a small extent in a similar way by loss of CH₂CO. The species at mass 131 is depicted as a naphthyridinium ion. No metastable for the transition 188→133 was, however, observed.

TABLE I

High Resolution Data

m/e	Elemental Composition	Observed Mass	Calculated Mass
161	C_9H_7NS	161.0297	161.0299
160	C_9H_6NS	160.0220	160.0221
155	$C_{10}H_7N_2$	155.0609	155.0609
144	$C_9H_8N_2$	144.0687	144.0687
143	$C_9H_7N_2$	143.0609	143.0609
131	$C_8H_7N_2$	131.0609	131.0609
118	$C_7H_6N_2$	118.0531	118.0531
117	C_8H_7N	117.0580	117.0578
116	C_8H_6N	116.0498	116.0500
111	C_5H_5NS	111.0141	111.0142
110	C_5H_4NS	110.0064	110.0064
84	C_4H_4S	84.0033	84.0034
84	C_3H_2NS	83.9908	83.9908
83	C_4H_3S	82.9955	82.9956
83	C_3HNS	82.9830	82.9830
82	C_4H_2S	81.9876	81.9877
81	C_4HS	80.9799	80.9799
79	C_5H_5N	79.0422	79.0422
78	C_5H_4N	78.0344	78.0344
67	C_4H_5N	67.0422	67.0422
58	C_2H_2S	57.9877	57.9877
57	C_2HS	56.9799	56.9799

The third fragmentation route from the molecular ion of 2,2'-thiodipyridine involves loss of neutral HCN to give a species of formula C_9H_7NS at mass 161 (2%) depicted as a pyridothiepine molecular ion. The species of mass 161 may lose H⁺ to give a $C_9H_6NS^+$ ion at mass

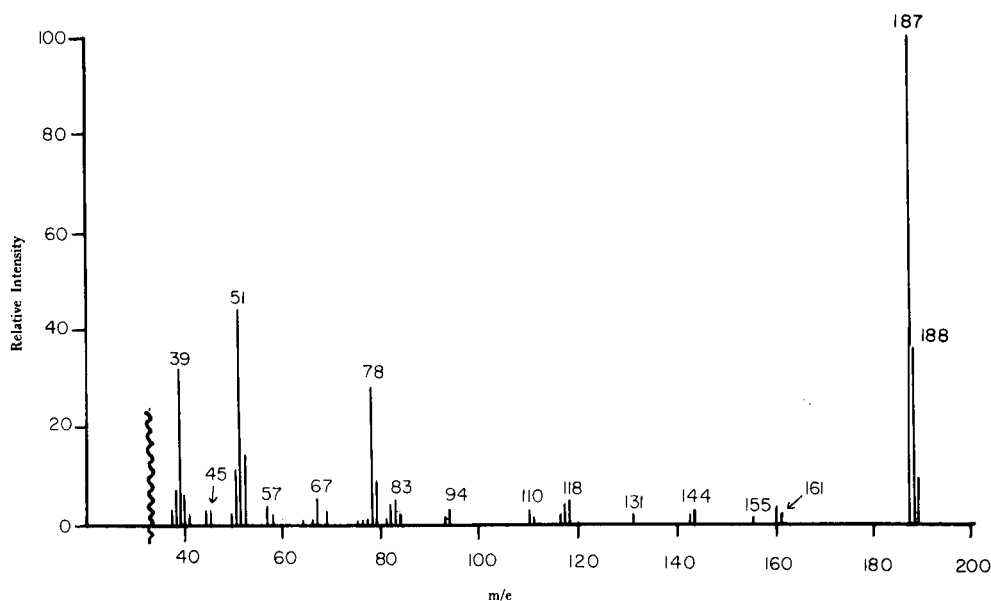
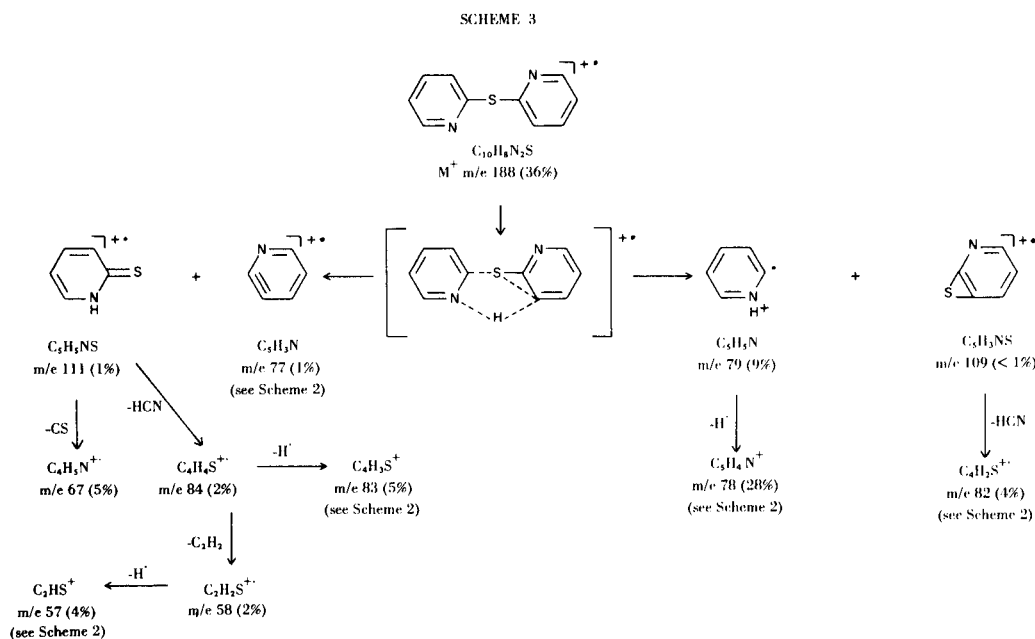


Figure: Mass Spectrum of 2,2'-Thiodipyridine

160 (4%) which is also formed from the M-1 ion of 2,2'-thiodipyridine at mass 187 by loss of HCN. Metastable transitions for the loss of HCN were observed. The similar loss of HCN was not detected to any appreciable extent in the disintegration of the 2,2'-oxydipyridine molecular ion or its M-1 ion (2).

The fourth route of disintegration from the molecular ion of 2,2'-thiodipyridine involves loss of S from the M-1 ion (mass 187) to give a species of formula $C_{10}H_7N_2$ at

mass 155 (1%) considered to be due to the 2,2'-bipyridyl molecular ion less one hydrogen. No metastable transition was observed for the loss of S from the molecular ion of 2,2'-thiodipyridine but a strong metastable corresponding to the transition $187 \rightarrow 155$ was present thus indicating that the molecular ion first loses H^+ before loss of S.

As expected, rupture of the central bonds of 2,2'-thiodipyridine is an important initial fragmentation route (Scheme 2). The straightforward central bond rupture is

TABLE II
Metastable Ions

Initial Ion	Resultant Ion	Transition	Calculated m*	Found m*	Fragment Expelled
C ₁₀ H ₈ N ₂ S	C ₉ H ₇ NS	188 → 161	137.8	137.8	HCN
C ₁₀ H ₇ N ₂ S	C ₉ H ₆ NS	187 → 160	136.9	137.0	HCN
C ₁₀ H ₇ N ₂ S	C ₁₀ H ₇ N ₂	187 → 155	128.5	128.6	S
C ₁₀ H ₈ N ₂ S	C ₉ H ₈ N ₂	188 → 144	110.3	110.5	CS
C ₁₀ H ₇ N ₂ S	C ₉ H ₇ N ₂	187 → 143	109.3	109.4	CS
C ₅ H ₄ NS	C ₄ H ₃ S	110 → 83	62.7	62.7	HCN

largely responsible for the strong peak at mass 78 (28%) due to a species of formula C₅H₄N presumably the pyridine molecular ion less one hydrogen. The accompanying pyridylthio ion, C₅H₄NS⁺, at mass 110 is present in small amounts (3%). Its subsequent disintegration (see Scheme 2) is largely responsible for the peaks (1-5%) at mass 84 (C₃H₂NS⁺), 83 (C₄H₃S⁺ and C₃HNS⁺), 82 (C₄H₂S⁺) and 81 (C₄HS⁺) by loss of C₂H₂, HCN and H.

As in the spectrum of 2,2'-oxydipyridine (2) rupture of the central bonds of 2,2'-thiodipyridine may be accompanied by a hydrogen migration possibly by way of the transition state shown in Scheme 3. This accounts for the peak at mass 79 due to the C₅H₅N⁺ species (9%), presumably the pyridine molecular ion or its equivalent. It may lose H⁺ to form the C₅H₄N⁺ ion at mass 78 (see Scheme 2). The accompanying fragment, C₅H₃NS⁺ at mass 109 is present only in very small amounts (<1%).

Likewise a hydrogen migration is involved in the formation of the C₅H₅NS⁺ species at mass 111 (1%), depicted as the pyridine-2-thione molecular ion. The accompanying fragment, the C₅H₃N⁺ species, at mass 77 (1%) may also be obtained by loss of H⁺ from the C₅H₄N⁺ ion (see Scheme 2). Loss of CS from the C₅H₅NS⁺ species gives rise to a C₄H₅N⁺ species at mass 67 (5%) while loss of HCN accounts for the peak at mass 81 due to a C₄H₄S⁺ species (2%). This latter ion can disintegrate by loss of C₂H₂ and then H⁺ to give the peaks (2-4%) at mass 58 (C₂H₂S⁺) and 57 (C₂HS⁺).

The peak at mass 94 (3%) is due to the M⁺ ion. Peaks below a mass of 56 do not require comment.

The elemental composition of the ions from the fragmentation of 2,2'-thiodipyridine are given in Table I and the observed metastable transitions in Table II.

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.

2,2'-Thiodipyridine was analytically pure.

REFERENCES AND NOTES

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