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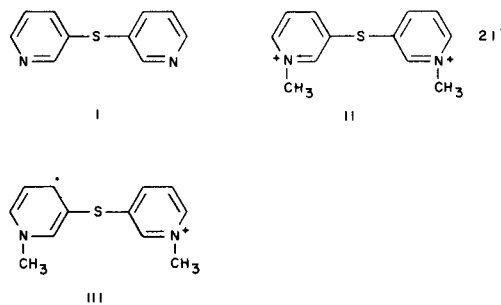
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3,3'-Thiobispyridine is prepared by reaction of pyridine-3-thiol with 3-bromopyridine. The base peak in the mass spectrum of 3,3'-thiobispyridine is due to the molecular ion which fragments by loss of H, HCN and CS as well as by central bond rupture. The 1,1'-dimethyl diquaternary salt of 3,3'-thiobispyridine is reduced polarographically by a one electron transfer not involving hydrogen to an unstable radical cation at a potential ( $E_0$ ) of  $-0.72$  V in the pH range 7.4-11.2.

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The only synthesis of 3,3'-thiobispyridine (I) so far reported [1] involves the conversion of 3-bromopyridine to its *N*-oxide followed by reaction of the *N*-oxide with potassium hydrogen sulfide to afford 3,3'-thiobispyridine 1,1'-dioxide. This last compound was then deoxygenated with phosphorus trichloride to afford 3,3'-thiobispyridine. We recently reported [2] the facile synthesis of 3,3'-oxybispyridine by reaction of 3-hydroxypyridine with 3-bromopyridine. By adaptation of this route we have now found that 3,3'-thiobispyridine is likewise readily obtained in over 60% yield by reaction of 3-bromopyridine with pyridine-3-thiol at  $180^\circ$  in the presence of potassium carbonate and cuprous oxide and this method thus constitutes a simpler route to 3,3'-thiobispyridine than has hitherto been available.

As expected the base peak in the electron impact mass spectrum of 3,3'-thiobispyridine (Figure 1) is due to the molecular ion at mass 188 ( $C_{10}H_8N_2S$ ). The M-1 ion accounts for a peak of 19% of the intensity of the base peak.



There is relatively little fragmentation of the molecule. There are only eight peaks of intensity greater than 4% of the base peak above mass 70. The peaks at mass 161 (7%,  $C_9H_7NS$ ) and 160 (4%,  $C_9H_6NS$ ) are due to the loss of HCN from the molecular ion and the M-1 ion respectively, whereas the peak at mass 144 (4%,  $C_9H_8N_2$ ) results from loss of CS from the molecular ion. The peak at mass 117 (4%,  $C_8H_7N$ ) results from loss of HCN from the  $C_9H_8N_2$  ion at mass 144. The remaining four peaks at mass 110 (7%,

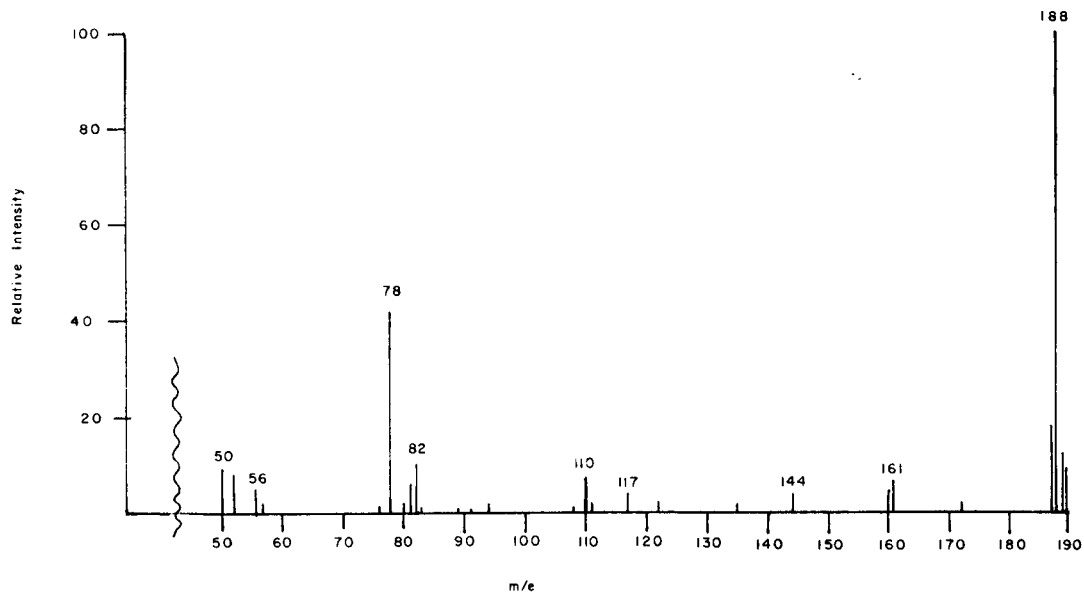


Figure 1. Mass spectrum of 3,3'-thiobispyridine.

$C_5H_4NS$ ), 83 (10%,  $C_4H_3S$ ), 82 (6%,  $C_4H_2S$ ) and 78 (41%,  $C_5H_4N$ ) are due to ions obtained by rupture of the central bond of 3,3'-thiobispyridine followed by subsequent fragmentation. All these fragmentation routes are very similar to those already reported in the mass spectra of 2,2'-thiobispyridine [3] and 4,4'-thiobispyridine [4].

3,3'-Thiobispyridine was further characterised by conversion to the 1,1'-dimethyldiquaternary salt (II) by reaction with excess methyl iodide in ethanol solution. The salt (II) was stable in aqueous solution up to a pH value of about 11.5 (uv evidence) but in strong alkaline solution it decomposed. It was examined by polarography in the pH range 7.4-11.2. In this pH range it gave a typical symmetrical reduction wave which corresponded to the uptake of one electron with a half-wave potential ( $E_{1/2}$ ) of  $-0.72$  V independent of pH and concentration attributed to the formation of the radical cation of which (III) is one canonical form. This behaviour is analogous to the reduction of many bipyridinium diquaternary salts [5] and to the reduction of 1,1'-dimethyl diquaternary salts of 2,2'-thiobispyridine [6,7] and 4,4'-thiobispyridine [8] which are reduced similarly at potentials of  $-0.42$  V and  $-0.57$  V respectively. Interestingly in the oxybispyridine series the 1,1'-dimethyl diquaternary salt of 2,2'-oxybispyridine [9] is reduced likewise to a radical cation at a potential of  $-0.71$  V, whereas diquaternary salts of 3,3'-oxybispyridine [2] and 4,4'-oxybispyridine [10] are reduced at  $-0.81$  V and  $-0.80$  V respectively. In both the thiobispyridine and oxybispyridine series, therefore, the diquaternary salts from the 2,2' isomers are the most easily reduced followed by the salts from the 4,4' isomers with the salts from the 3,3' isomers being the least easily reduced. On nmr evidence it was clear that the salt (II) was slowly reduced in aqueous solution by zinc dust to products as yet unidentified presumably by way of the unstable radical cation (III).

As expected in view of its low reduction potential compared with the bipyridinium herbicides [5] diquat and paraquat the salt (II) was inactive as a post-emergent herbicide at 8 kg/hectare.

#### EXPERIMENTAL

Britton and Robinson buffer solutions were used in the polarography experiments which were conducted at  $20^\circ$  with a standard calomel electrode and 0.001 M and 0.0015 M solutions. The half-wave potentials are given as  $E_{1/2}$  values and were calculated by adding 0.25 V to the  $E_{1/2}$

values. The mass spectrum was determined with an A.E.I. MS-30 spectrometer. The sample was analysed by a direct insertion probe at an ionizing current of 70 eV. The ion source temperature was  $200^\circ$ .

#### 3,3'-Thiobispyridine (I).

3-Bromopyridine (15.0 g), pyridine-3-thiol [11] (13.3 g), potassium carbonate (12.1 g) and cuprous oxide (1.43 g) were heated in a sealed vessel at  $180^\circ$  for six hours. The black solid was extracted with hot benzene ( $\sim 300$  ml). The solution was dried (sodium sulfate) and evaporated to dryness. The residue which was liquid was added to the top of a chromatographic column packed with potassium carbonate. On elution with benzene the yellow fraction which came off first was collected. The solvent was removed and the residue distilled to afford 3,3'-thiobispyridine as a pale yellow liquid, bp  $140^\circ/0.5$  mm which solidified on standing, mp  $36^\circ$  (yield 63%). The bp and mp were similar to literature values [1]. The uv spectrum (water) showed  $\lambda$  max 195, 211 sh, 249, 278 sh ( $\log \epsilon$  4.21, 4.04, 3.94, 3.76). The nmr spectrum (deuteriochloroform) consisted of a multiplet at  $\delta$  7.12-7.35 (2H, 5,5' protons), a doublet at 7.5-7.75 (2H, 4,4' protons) and a multiplet at 8.45-8.65 ppm (4H, 2,2', 6,6' protons).

#### 1,1'-Dimethyl 3,3'-thiobispyridinium Diiodide (II).

A solution of 3,3'-thiobispyridine (3 g) and methyl iodide (11.5 ml) in ethanol (60 ml) was refluxed for three hours. The pale yellow solid was recrystallised from ethanol to give the product, mp  $228^\circ$  (yield 62%). The nmr spectrum (deuterium oxide) consisted of a singlet at  $\delta$  4.45 (6H,  $CH_3$ ), a multiplet at 7.95-8.25 (2H, 5,5' protons), a multiplet at 8.58-8.95 (4H, 4,6,4',6' protons) and a singlet at 9.09 ppm (2H, 2,2' protons). The uv spectrum (water) showed  $\lambda$  max 195, 226, 257 sh, 298 sh ( $\log \epsilon$  4.65, 4.53, 3.88, 3.67).

*Anal.* Calcd. for  $C_{12}H_{14}I_2N_2S$ : C, 30.5; H, 3.0; N, 5.9. Found: C, 30.6; H, 2.8; N, 5.6.

#### Acknowledgements.

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