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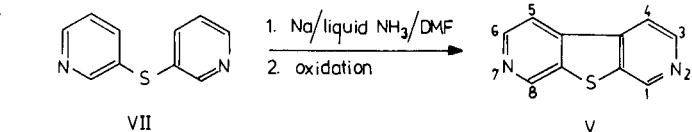
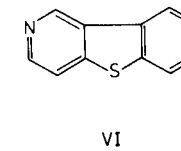
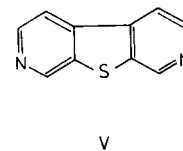
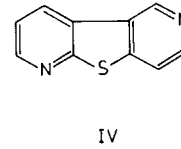
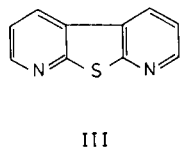
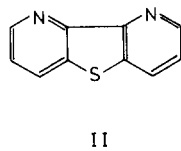
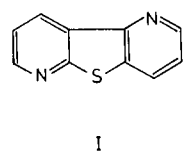
Thieno[2,3-c:5,4-c']dipyridine is synthesised by reaction of 3,3'-thiobispyridine with sodium and liquid ammonia in dimethylformamide. It forms a diquaternary salt with excess methyl iodide. The salt is reversibly reduced to a stable blue-green radical cation in aqueous solution at a potential (E_0) of -0.38V.

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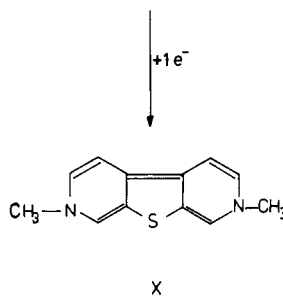
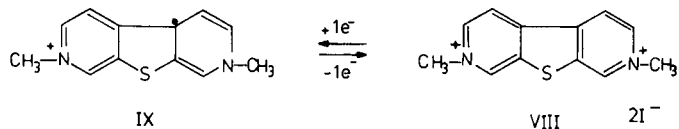
The chemistry of thienodipyridines has received relatively little attention. Of the ten possible thienodipyridines six have so far been reported. Thieno[2,3-*b*:4,5-*b'*]dipyridine (I) was obtained by reacting 3-aminothieno[2,3-*b*]pyridine with malondialdehyde tetraethylacetal [1] and thieno[3,2-*b*:4,5-*b'*]dipyridine (II), thieno[2,3-*b*:5,4-*b'*]dipyridine (III), thieno[2,3-*b*:4,5-*c'*]dipyridine (IV) and thieno[2,3-*c*:5,4-*c'*]dipyridine (V) were synthesised from the appropriate symmetrical bipyridine by reaction with hydrogen sulfide at high temperature in the presence of alumina catalyst [2]. Compound V was obtained in 1% yield and was not analysed but was characterised as the methiodide [2]. Thieno[3,2-*c*:4,5-*c'*]dipyridine (VI) has been obtained by irradiation of 4,4'-thiobispyridine [3]. Further work on the synthesis of II [4], the thin layer chromatography and ionisation constants of I-IV [5,6] and the mass spectra of I-III [7] have been reported. Some sulfone, sulfoxide and *N*-oxide derivatives of I and II have also received attention

[8-10] as well as polychloro derivatives of IV-VI [11-15]. We now report a facile synthesis of thieno[2,3-*c*:5,4-*c'*]dipyridine (V) albeit in 10% yield. By adaptation of the well-known coupling of pyridine to 4,4'-bipyridine [16] we have found that intramolecular ring closure of 3,3'-thiobispyridine (VII) [17] with sodium and liquid ammonia in dimethylformamide, followed by aerial oxidation affords thieno[2,3-*c*:5,4-*c'*]dipyridine (V) in about 10% yield. Unreacted VII (42%) recovered in the process can be recycled.

The structure V was confirmed by elemental analyses, nuclear magnetic resonance spectrum and mass spectrum. As expected the base peak in the electron impact mass spectrum of thieno[2,3-*c*:5,4-*c'*]dipyridine (V) is due to the molecular ion at mass 186 ($C_{10}H_6N_2S$). The M-1 ion ac-



excess MeI/DMF



counts for a peak of 8% of the intensity of the base peak. There is relatively little fragmentation of the molecule. The only peaks above 5% and above mass 70 occur at mass 159 (20%, C_7H_5NS) due to loss of HCN from the molecular ion and at mass 114 (8%, C_6H_4N), 87 (6%, C_7H_3) and 82 (6%, C_4H_2S).

Thieno[2,3-*c*:5,4-*c'*]dipyridine was further characterised by conversion to the deep red diquatery salt 2,7-dimethylthieno[2,3-*c*:5,4-*c'*]dipyridinediium diiodide (VIII) by reaction with excess methyl iodide in dimethylformamide. As a close relative of paraquat (methyl viologen) [18] the salt VIII was reversibly reduced in aqueous solution by a one-electron transfer not involving hydrogen to the blue-green stable radical cation of which IX is one canonical form at a potential (E_o) of -0.38V as determined by polarography in the pH range 3.0-9.0. The potential was independent of pH. The polarographic curves showed a second one-electron reduction wave at lower potential, $\sim -0.75V$, presumably due to the formation of X. The reversibility of the one electron transfer between VIII and IX was confirmed by cyclic voltammetry at pH 5.0 and pH 7.0.

As expected, the salt VIII showed some activity as a post-emergent herbicide when applied at a rate of 4 kg/hectare on mixed grass flora but it was not as active as paraquat [18].

EXPERIMENTAL

Britton and Robinson buffers were used in the polarography experiments which were conducted at 20° with a standard calomel electrode and 0.001M and 0.0015M solutions. The solutions contained 0.2% Triton X-100 to suppress wave maxima. The half-wave potentials are given as $E_{1/2}$ values and were calculated by adding 0.25V to the $E_{1/2}$ values. Cyclic voltammetry experiments were conducted at 19° using a single mercury drop electrode and Ag/AgCl as the reference electrode in aqueous buffer solutions of pH 5.0 and 7.0. The scan was carried out between -0.3V and -0.85V. The mass spectrum was determined with an A.E.I MS-30 Spectrometer.

Thieno[2,3-*c*:5,4-*c'*]dipyridine (V).

Finely cut sodium (1.25 g) was added to liquid ammonia (50 ml) and the deep blue solution stirred for 5 minutes, 3,3'-Thiobispyridine (5 g) [17] was added dropwise over 30 minutes and the mixture stirred for a further 5 minutes. Dimethylformamide (15 ml) was slowly dropped into the mixture over 30 minutes and stirring continued for a further 30 minutes. The oxidation was carried out by adding the reaction mixture in small increments over 1.5 hours to chilled dimethylformamide (25 ml) as a stream of air passed through the solvent. During this time the mixture reached ambient temperature. The oxidation was continued for a further 3 hours. The solution was filtered and the precipitate washed with dimethylformamide. The solvent was removed from the filtrate and the residue extracted with hot chloroform (2 × 50 ml) and filtered. The solvent was removed leaving a brown liquid from which crystalline material formed after 6 days. The solid was removed from the liquid which was found to be largely unreacted 3,3'-thiobispyridine (2.1 g). The solid was crystallised from a mixture of ethanol and petroleum (bp 60-80°) to af-

ford the product as straw colored needles, mp 182-183° (yield 0.5 g). Literature mp is 177-178° [2]. The nmr spectrum (deuteriochloroform) consisted of a doublet at δ 8.05-8.15 (2H, 4,5 protons), a doublet at 8.70-8.80 (2H, 3,6 protons) and a singlet at 9.30 ppm (2H, 1,8 protons). The uv spectrum (ethanol) showed λ max 231, 335 and 348 nm (log ϵ 4.58, 3.67, 3.75).

Anal. Calcd. for $C_{10}H_6N_2S$: C, 64.5; H, 3.2; N, 15.0. Found: C, 64.3; H, 3.1; N, 15.0.

2,7-Dimethylthieno[2,3-*c*:5,4-*c'*]dipyridinediium Diiodide (VIII).

Thieno[2,3-*c*:5,4-*c'*]dipyridine (0.2 g) was dissolved in dimethylformamide (10 ml) containing methyl iodide (2 ml) and the mixture was refluxed for 3 hours, by which time a red precipitate had formed. This was collected and crystallised from aqueous ethanol to give the product as fine red needles, mp > 300° dec (yield 0.25 g). The nmr spectrum (deuterium oxide) consisted of a singlet at δ 4.68 (6H, CH_3), a multiplet at 9.0-9.3 (4H, 3,4,5,6 protons) and a singlet at 10.0 ppm (2H, 1,8 protons). The uv spectrum (water) showed λ max 245, 285, 370 and 389 nm (log ϵ 4.66, 4.08, 3.62, 3.76).

Anal. Calcd. for $C_{12}H_{12}I_2N_2S$: C, 30.6; H, 2.6; N, 6.0. Found: C, 30.25; H, 2.7; N, 6.0.

The diiodide was readily converted to the yellow bisperchlorate salt by reaction with lithium perchlorate in aqueous solution.

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