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3,3'-Oxybispyridine is prepared by reaction of 3-hydroxypyridine with 3-bromopyridine and converted to the 1,1'-dimethyl diquatery salt with methyl iodide. The salt is reduced polarographically by a one electron transfer not involving hydrogen to an unstable radical cation at a potential ( $E_0$ ) of  $-0.81$  V in the pH range 6.3-12.0.

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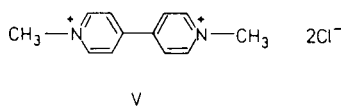
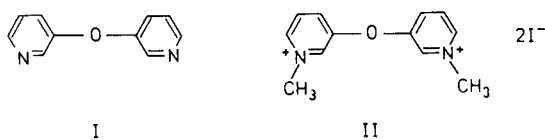
There are six oxybispyridines. The 2,2'- [1-4], 2,3'-[1,5-8], 2,4'- [9], 3,4'- [10] and 4,4'-isomers [10-12] have all been prepared. Very recently the synthesis of the remaining isomer 3,3'-oxybispyridine (I) was reported involving a three step synthesis from 3-bromopyridine [13] in about 15% overall yield. In connection with our research on oxybispyridines [9,12,14-16] as part of our study of compounds related to the bipyridinium herbicides [17] we have found that 3,3'-oxybispyridine is obtained in similar yield in only one step by reacting 3-bromopyridine with 3-hydroxypyridine at  $190^\circ$  in the presence of potassium carbonate and cuprous oxide.

As expected the base peak in the electron impact mass spectrum of 3,3'-oxybispyridine (Figure 1) is due to the molecular ion at mass 172 ( $C_{10}H_8N_2O$ ). The M-1 ion accounts for a peak of only 4% 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 117 (9%;  $C_8H_7N$ ), due to the loss of CO + HCN from the molecular ion, and at mass 95 (28%;  $C_5H_5NO$ ) and mass 78 (84%;  $C_5H_4N$ ) due to rupture of the central

bond with accompanying hydrogen migrations as noted previously in the mass spectra of 2,2'- [15] and 4,4'-oxybispyridines [16]. 3,3'-Oxybispyridine was further characterized by conversion to the 1,1'-dimethyl (II) and 1,1'-diethyl diquatery salts by reaction with excess methyl iodide and ethyl iodide respectively.

The salt II was stable in aqueous solution up to a pH of about 12.0 (uv evidence). It was examined by polarography in the pH range 6.3-12.1. In this range it gave a typical symmetrical one electron reduction wave which corresponded to the uptake of one electron with a half-wave potential ( $E_0$ ) of  $-0.81$  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 that of many bipyridinium diquatery salts [17] and to the reduction of a diquatery salt of 2,2'-oxybispyridine [14]. In the latter case the reduction potential was  $-0.71$  V. The polarography of the salt II revealed the presence of a second reduction wave at lower potential at about  $-0.97$  V but the wave was not symmetrical. 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 very low reduction potential compared with the bipyridinium herbicides [17] diquat IV and paraquat V, which are reduced to stable radical cations at a potential ( $E_0$ ) of  $-0.35$  V and  $-0.45$  V respectively, the salt III was inactive as a post-emergent herbicide at 8 kg/hectare.



## EXPERIMENTAL

Britton and Robinson buffers were used in the polarography experiments which were conducted at  $20^\circ$  with a standard calomel electrode and 0.001M and 0.0015M solutions. The solutions contained 0.1% Triton X-100 to suppress wave maxima. The half-wave potentials are given as  $E_0$  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 samples were analysed by a direct insertion probe at an ionising current of 70 eV. The ion source temperature was  $200^\circ$ .

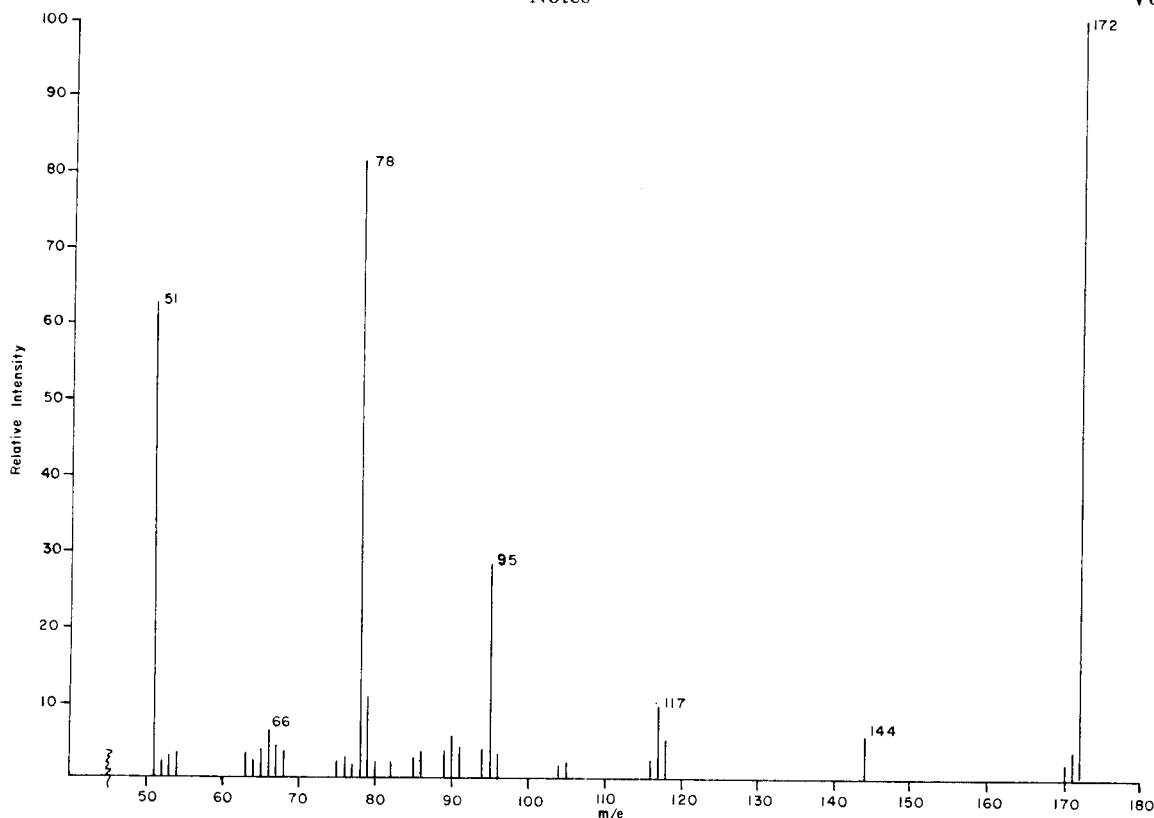


Figure 1. Mass Spectrum of 3,3'-Oxybispyridine.

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

3-Bromopyridine (15.0 g), 3-hydroxypyridine (10.9 g), potassium carbonate (12.1 g) and cuprous oxide (1.43 g) were heated in a sealed vessel at 180-190° for six hours. The black solid was extracted with hot benzene and the solvent removed. The residue was chromatographed on a column packed with potassium carbonate. On elution with benzene 3,3'-oxybispyridine came off first. It was distilled several times to give a colorless liquid, bp 140-141°/0.1 mm (yield 1.70 g). This bp is similar to that recorded in the literature [13]. The nmr spectrum (deuteriochloroform) consisted of a multiplet at  $\delta$  7.3-7.4 (4H, 4,4', 5,5' protons) and a multiplet at 8.4-8.5 ppm (4H, 2,2', 6,6' protons). The uv spectrum (ethanol) showed  $\lambda$  max 216, 268 and 274 nm (log  $\epsilon$  4.30, 4.07, 4.02).

*Anal.* Calcd. for  $C_{10}H_8N_2O \cdot 0.25H_2O$ : C, 68.0; H, 4.9; N, 15.9. Found: C, 67.8; H, 5.0; N, 16.0.

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

A solution of 3,3'-oxybispyridine (1.2 g) and methyl iodide (2.84 g) in ethanol (10 ml) was refluxed for three hours. The pale yellow solid was recrystallised from aqueous ethanol to give the product, mp 264° dec (yield 1.61 g). The nmr spectrum (deuterium oxide) consisted of a singlet at  $\delta$  4.4 (6H,  $CH_3$ ), a multiplet at 7.9-8.4 (4H, 4,4', 5,5' protons), a doublet at 8.75-8.85 (2H, 6,6' protons) and a singlet at 8.9 ppm (2H, 2,2' protons). The uv spectrum (water) showed  $\lambda$  max 226 and 272 nm (log  $\epsilon$  4.53 and 3.93).

*Anal.* Calcd. for  $C_{12}H_{11}I_2N_2O$ : C, 31.6; H, 3.1; I, 55.7; N, 6.1. Found: C, 31.9; H, 3.1; I, 55.5; N, 5.8.

#### 1,1'-Diethyl 3,3'-Oxybispyridinium Diiodide.

A solution of 3,3'-oxybispyridine (0.5 g) and ethyl iodide (1.09 g) in ethanol (5 ml) was refluxed for three hours. The cream solid was recrystallised from aqueous ethanol to give the product mp 192°. The nmr spectrum (deuterium oxide) consisted of a triplet at 1.5-1.8 (6H,  $CH_3$ ), a quartet at 4.5-4.9 (4H,  $CH_2$ ), a multiplet at 7.9-8.4 (4H, 4,4', 5,5' protons), a doublet at 8.8-8.9 (2H, 6,6' protons) and a singlet at 9.0 ppm (2H, 2,2'

protons). The uv spectrum (water) showed  $\lambda$  max 225 and 271 nm (log  $\epsilon$  4.55 and 3.93).

*Anal.* Calcd. for  $C_{14}H_{18}I_2N_2O$ : C, 34.7; H, 3.8; I, 52.4; N, 5.8. Found: C, 34.7; H, 3.9; I, 52.0; N, 5.8.

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