Chemical Constitution and Activity of Bipyridylum Herbicides, XI¹

A Diquaternary Salt of 2,2'-Oxydipyridine

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A diquaternary salt of 2,2'-oxydipyridine has been prepared using methyl fluorosulphonate as quaternising agent. It is unstable at physiological pH values and is reduced at a much lower potential than the bipyridylum herbicides, diquat and paraquat.

The mode of action of the bipyridylum herbicides diquat (1) and paraquat (2) is connected with their ability to be rapidly reduced in aqueous solution to stable radical cations (*e.g.* 3) at a potential (E_0) of about -0.35 to -0.45 volts by a one electron transfer which is rapidly and quantitatively reversed by oxygen². The effect on herbicidal activity of the introduction between the pyridine rings of an atom or group which is capable of acting as an electron transfer bridge has so far been investigated with diquaternary salts of thiodipyridines³⁻⁷, iminodipyridines⁷, 1,2-di-4-pyridylethylene⁸, di-2-pyridyl ketone⁹ and 2,2'-vinylidenedipyridine¹⁰. There has been no study, however, of diquaternary salts of oxydipyridines. This communication reports results obtained with a diquaternary salt of 2,2'-oxy-dipyridine (4).

The chemistry of 2,2'-oxydipyridine (4) has received little study. Although the di-*p*-toluenesulphonate of 4 was obtained as a reaction by-product by MATSUMURA¹¹, the original preparation of 4 is due to DE VILLIERS and DEN HERTOOG who obtained it from the reaction of the silver salt of 2-hydroxypyridine with 2-iodopyridine¹². No other report of 2,2'-oxydipyridine or its derivatives has appeared. We prepared 4 by adopting DE VILLIERS and DEN HERTOOG's method. It reacted with excess methyl iodide to give the monomethiodide salt. The diquaternary salt (5) was obtained by use of methyl fluorosulphonate, "magic methyl," as quaternizing agent. Unlike 2,2'-thiodipyridine which readily

gives diquaternary salts with dibromomethane^{4,6} and 1,2-dibromoethane^{3,6}, 2,2'-oxydipyridine decomposed on heating with these reagents.

The salt 5 was stable in aqueous solution up to a pH of about 5.0 (UV evidence). Just above this pH the salt gradually deteriorated and it rapidly broke down as the solution became more alkaline. On treatment with zinc dust an aqueous solution of 5 showed no colour change. Inspection of the NMR spectrum of the zinc treated solution indicated, however, that the diquaternary salt had been reduced, presumably by way of the intermediate unstable radical cation 6, to a stable product the structure of which is at present being investigated. This result contrasts with the behaviour of aqueous solutions of diquaternary salts of 2,2'-thiodipyridine^{5,6} which slowly give a yellow-green colouration on treatment with zinc dust due to the corresponding radical cation and of diquat and paraquat solutions which immediately give green and violet solutions respectively due to their radical cations. The oxydipyridine salt (5) was examined by polarography in the pH range 3.0-7.0 at two concentrations. In the pH range 3.0-5.0 it gave a reduction wave which corresponded approximately to the uptake of one electron with a half-wave potential (E_0) of -0.71 V independent of pH and concentration presumably due to the formation of the radical cation 6. The corresponding salt from 2,2'-thiodipyridine is much more easily reduced ($E_0 -0.42$ V)^{5,6}. There was no evidence of a second reduction wave. At pH 6.0 the wave height was smaller while at pH 7.0 it was no longer present due to the instability of the salt.

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It is evident, therefore, that the salt **5** is unstable at physiological pH values and is reduced at a much lower potential than diquat and paraquat. In keeping with these results the salt **5** was inactive as a post-emergent herbicide on mixed grass flora at an application rate of 8 kg/hectare.

Experimental

Microanalyses, UV measurements, NMR spectra and polarography experiments were carried out as described previously¹. The solutions used in the polarography experiments contained gelatine (1%) to suppress wave maxima.

2,2'-Oxydipyrindine (4)

This compound was prepared as described by DE VILLIERS and DEN HERTO¹². Our m.p. agreed with that recorded previously.

NMR spectrum (CDCl₃): δ 6.95–7.13 (m, 4H), 7.56–7.88 (m, 2H), 8.20–8.32 (m, 2H), [ppm].

Mass spectrum: $M^+ = 172$.

UV spectrum (C₂H₅OH): $\lambda_{\max}$. 262 (log ϵ 3.85) [nm].

1-Methyl 2,2'-oxydipyrindinium iodide

2,2'-Oxydipyrindine (1 g) and methyl iodide 10 ml were refluxed for 1 hour. The white solid was crystallised from methanol to give the product, m.p. 135–137 °C. (Yield 57%).

C₁₁H₁₁IN₂O

Calcd C 42.0 H 3.5 N 8.9 I 40.4,

Found C 41.9 H 3.5 N 9.2 I 40.1.

NMR spectrum (CDCl₃): $\delta = 4.53$ (s, 3H, CH₃), 7.36–8.90 (m, 7H, 3,4,5,3',4',5',6'-aromatic protons), 9.39–9.51 (d, 1H, 6-aromatic proton) [ppm].

UV spectrum (H₂O): $\lambda_{\max}$. 278 (log ϵ 4.10) [nm].

1,1'-Dimethyl 2,2'-oxydipyrindinium bisfluorosulphonate (5)

2,2'-Oxydipyrindine (1 g) and methyl fluorosulphonate (8 ml) were refluxed for 1½ hr. The white solid was crystallised from water to give the product, m.p. 220 °C (dec.). (Yield 95%).

C₁₂H₁₄F₂N₂O₇S₂

Calcd C 36.0 H 3.5 N 7.0,

Found C 35.9 H 3.6 N 6.7.

NMR spectrum (D₂O): $\delta = 4.45$ (s, 6H, CH₃), 7.89–8.15 (m, 4H), 8.60–9.00 (m, 4H) [ppm].

UV spectrum (H₂O, pH 5.0): $\lambda_{\max}$. 281 (log ϵ 4.25) [nm].

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