

Chemical Constitution and Activity of Bipyridylium Herbicides. Part VI.
Diquaternary Salts of 4,4'-Iminodipyridine and 4,4'-Thiodipyridine.

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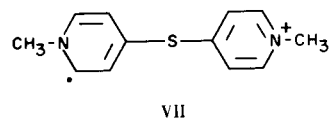
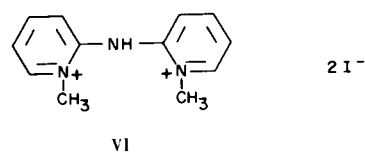
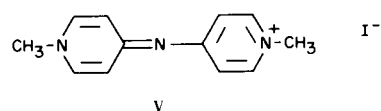
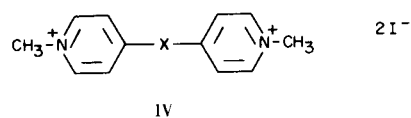
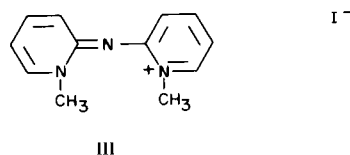
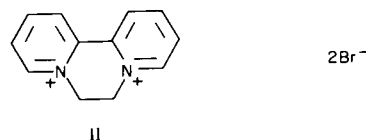
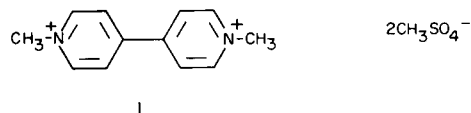
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In work reported in earlier papers of this series (1-5) much evidence has been obtained to support the view that the mode of action of the bipyridylium herbicides, paraquat (I) and diquat (II), is connected with their ability to be reduced in aqueous solution to stable radical cations by a one electron transfer which is reversed by air. The effect on herbicidal activity of the introduction between the pyridine rings of paraquat of a group which is capable of acting as an electron transfer bridge has so far been studied only with diquaternary salts of *trans*-1,2-di-(4-pyridyl)-ethylene (5). We now report our results with diquaternary salts of 4,4'-iminodipyridine and 4,4'-thiodipyridine.

Unlike 2,2'-iminodipyridine, from which only the derivative (III) was isolated from reaction with excess methyl iodide (6), 4,4'-iminodipyridine afforded the diquaternary salt (IV; X = NH) with this reagent. The salt (IV; X = NH) in aqueous solution is in reversible equilibrium, dependent on pH, with another species, which is considered to be the monoquaternary derivative (V) analogous to III. At pH values lower than about 6.8, the predominant form is (IV; X = NH). At pH 11.3, the UV maxima are due to the more conjugated system (V) formed by loss of hydrogen iodide from IV (X = NH). The long wavelength absorption maxima of V is similar to that reported (6) for the analogous derivative (III) obtained from 2,2'-iminodipyridine. In the 2,2'-iminodipyridine series, compound III reverts to the diquaternary salt (VI) only in strong acid solution (6). This difference in the ease with which hydrogen iodide is lost from VI and IV (X = NH) presumably reflects the difference in the proximity of the two positively charged nitrogens in the two series.

Aqueous solutions of diquat, paraquat and several related bipyridylium salts on treatment with zinc dust give intense green or violet solutions due to the corresponding radical cations (7). When IV (X = NH) was treated with zinc powder in aqueous solution, there was no apparent change and this was confirmed by NMR and UV spectroscopy. On polarographic examination there was no evidence of reduction above -1.2 volts. It is clear that the diquaternary salt (IV; X = NH) is not reduced to a radical cation at potentials attainable in aqueous solution. In accord with the theory of the mode of action of bipyri-

dylum herbicides, the salt (IV; X = NH) was inactive against six plant species when tested as a post-emergent herbicide at 8 lbs/acre.



The corresponding diquatery salt from 4,4'-thiodipyridine (IV; X = S), originally prepared by Jerchel and his colleagues (8), was stable in aqueous solution below about pH 10 but was decomposed by strong base. Its behaviour in aqueous solution on reduction with zinc dust and on exposure to sunlight was similar to that reported for diquatery salts of 2,2'-thiodipyridine (I). The yellow-green coloration is attributed, at least in part, to the radical cation of which VII is one canonical form. Polarography experiments in the pH range 4.4 to 8.6 confirmed that the reduction involved the uptake of one electron but not hydrogen. The salt (IV; X = S) gave an almost symmetrical one electron reduction wave with a half-wave potential (E_0) of -0.57 volts, independent of pH. When an aqueous solution (0.00002 M) of IV (X = S) was shaken with zinc dust and the reducing agent removed, the UV spectrum, λ max 265, 330 and 385 m μ , remained unchanged for one week, thus confirming that the final products of the reduction are stable and are not reversibly oxidized by air. On exposure to sunlight an aqueous solution of IV (X = S) showed similar changes in the UV spectrum. These results are consistent with the view that the salt (IV; X = S) is reduced by a one electron transfer to give a radical cation which rapidly decays to products as yet unidentified. The NMR spectrum of IV (X = S) in deuterium oxide, taken 20 minutes after the addition of zinc powder, showed no evidence of the presence of a high concentration of a paramagnetic species (*cf.* refs. 2,5).

As expected, in view of the instability of the radical cation (VII), the salt (IV; X = S) was inactive as a post-emergent herbicide when tested at 8 lbs/acre. These results further support the theory (7) that for herbicidal activity of the type associated with bipyridylum salts, the compounds, *inter alia*, must be capable of being reduced in aqueous solution to stable radical cations which are reversibly oxidized by air.

EXPERIMENTAL

Sorenson or Britton and Robinson buffers were used in the polarography experiments, which were conducted at 20° with a standard calomel electrode and 0.001 M solutions. The half-wave potential is assumed to be an E_0 value and was calculated by

adding 0.25 volts to the $E_{1/2}$ value. NMR spectra were determined at 60Mc/sec. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

Dimethiodide of 4,4'-Iminodipyridine (IV; X = NH).

4,4'-Iminodipyridine (0.5 g.) was refluxed in methanol (15 ml.) and methyl iodide (20 ml.) for 2 hours. The lemon solid which precipitated was crystallized from aqueous methanol to give the diquatery salt, m.p. 310-312° dec., (yield 60%).

Anal. Calcd. for $C_{12}H_{15}I_2N_3$: C, 31.6; H, 3.3; N, 9.2; I, 55.8. Found: C, 31.55; H, 3.3; N, 9.0; I, 55.5.

The NMR spectrum (trifluoroacetic acid) showed a singlet at δ 4.35 (6-N-methyl H), a doublet at 8.02-8.14 (4 aromatic protons at 2,2', 6,6'), a doublet at 8.58-8.70 (4 aromatic protons at 3,3', 5,5') and a singlet at 10.08 p.p.m. (NH proton). The UV spectrum in water, pH 1.8, showed λ max 226 m μ (log ϵ 4.56) and 328 (4.71). At pH 11.3 the spectrum showed λ max 226 (4.56) and 385 (4.72).

Dimethiodide of 4,4'-Thiodipyridine (IV; X = S).

4,4'-Thiodipyridine (0.5 g.) was refluxed with methyl iodide (15 ml.) for 6 hours. The yellow solid which precipitated was washed with boiling ethanol to remove a small amount of the monomethiodide. The diquatery salt which remained was crystallized from aqueous ethanol, m.p. 232° dec., (yield 65%). Jerchel, Fischer and Thomas (8) give m.p. 232-233°.

Anal. Calcd. for $C_{12}H_{14}I_2N_2S$: C, 30.5; H, 3.0; N, 5.9; I, 53.8; S, 6.8. Found: C, 30.7; H, 2.9; N, 5.6; I, 53.9; S, 7.0.

The NMR spectrum (deuterium oxide), with sodium 3-trimethylsilyl-1-propanesulphonate as internal reference, showed a singlet at δ 4.38 (6-N-methyl H), a doublet at 8.10-8.20 (4 aromatic protons at 2,2', 6,6') and a doublet at 8.72-8.83 p.p.m. (4 aromatic protons at 3,3', 5,5'). The UV spectrum in water showed λ max 279 m μ (log ϵ 4.18) and 326 (4.26). Polarographic examination showed a one electron wave with $E_0 = -0.57$ volts.

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