Bipyridylium Quaternary Salts and Related Compounds.   Part IV.[1]   Pyridones derived from Paraquat and Diquat

By **A. Calderbank, D. F. Charlton, J. A. Farrington,*** and **R. James,** Imperial Chemical Industries Limited, Jealott's Hill Research Station, Bracknell, Berkshire

The 1',2'-dihydro-1,1'-dimethyl-2'-oxo-4,4'-bipyridylium cation (IV) and 1,1'-dimethyl-4,4'-bipyridyl-2,2'-dione (V), thought to be possible products of the action of alkali on paraquat, have been synthesised by treatment of paraquat with alkaline ferricyanide. The action of other alkaline oxidising agents was also investigated. 6,7-Dihydro-4-oxodipyrido[1,2-a:2',1'-c]pyrazinium ion (VII) and 6,7-dihydrodipyrido[1,2-a:2',1'-c]pyrazine-4,9-dione (VIII) have been prepared and the former was confirmed as a photochemical decomposition product of diquat.

SALTS of paraquat (1,1'-dimethyl-4,4'-bipyridyldi-ium) have been known since 1882 to react with aqueous alkali to produce an intense blue or purple colour.[2] This colour is due to the one-electron reduction product of paraquat, the radical cation (III). It is now known[3] that the major reducing agent involved in this reaction is
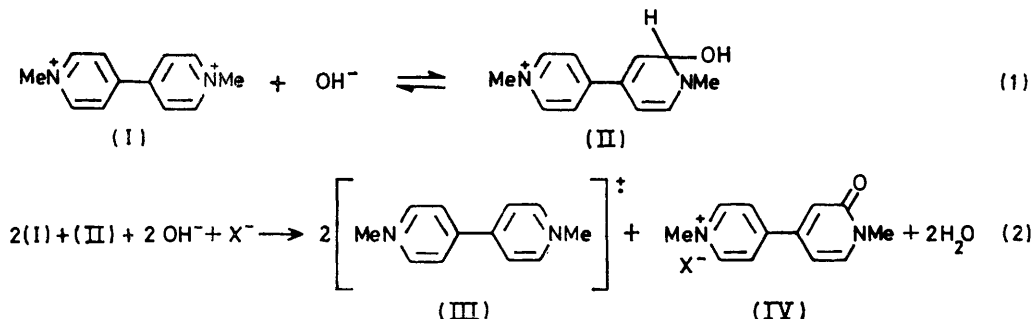
[1] Part III, B. G. White, *Trans. Faraday Soc.*, 1969, **65**, 2000.
[2] H. Weidel and M. Russo, *Monatsh.*, 1882, **3**, 850; *cf.* T. Anderson, *Annalen*, 1870, **154**, 270.

[3] J. A. Farrington, A. Ledwith, and M. F. Stam *Chem. Comm.*, 1969, 259.

methoxide ion, which results from alkaline demethylation of paraquat. However, the scheme suggested initially to explain the formation of the radical was based on the expected ready formation of a pseudo-base (II). This, being a dihydrobipyridyl, was suggested as the reducing agent which attacked unchanged paraquat to give the radical (III) [reactions (1) and (2)].

formed by hydroxylation reactions caused by superoxide ion or hydroxyl radical, which could have been generated by reduction of oxygen by paraquat radical.[5] The experiment was therefore repeated under conditions where this attack could not take place, by adding paraquat solution continuously but very slowly to a stirred solution of alkali containing a one-electron oxidising

$$\text{(1)}$$

$$2(I) + (II) + 2\,OH^- + X^- \longrightarrow 2 \left[\ldots \right]^{\ddagger} + \ldots + 2H_2O \quad (2)$$

This scheme requires that the pyridine (IV) is the other product of the reaction. Alternatively, if hydroxide ion attacked the 4-position, the 1,4-dihydrobipyridyl formed could give N-methyl-4-pyridone on oxidation by paraquat (cf. ref. 4). This paper describes the preparation of the pyridone (IV; X = I) and the corresponding bipyridone (V), and also of the analogous pyridones (VII) and (VIII) from diquat dibromide (6,7-dihydrodipyrido[1,2,-a:2′,1′-c]pyrazinedi-ium dibromide) (VI; X = Br).
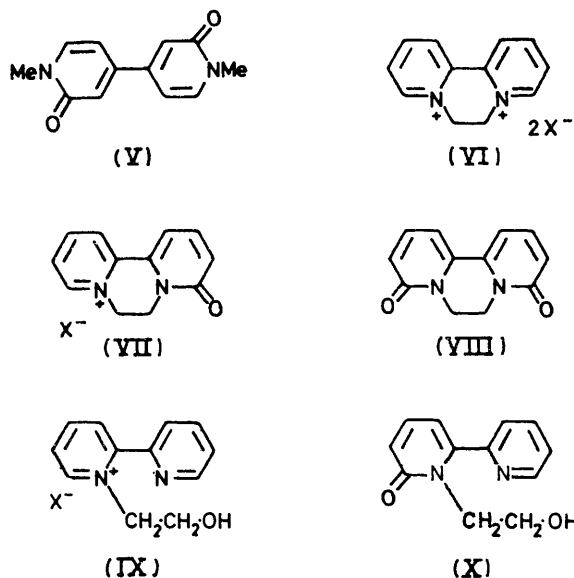
When an aqueous solution of paraquat dichloride was treated in air with 2N-sodium hydroxide and then neutralised and chromatographed, a complex mixture of u.v.-absorbing and fluorescing products was obtained. It was thought that some of these might have been

agent to convert the radical back into paraquat as it was formed. Under these conditions, with ferricyanide as the oxidising agent, only two products were formed, as detected by examination of paper chromatograms in u.v. light. This simplification of the mixture allowed the major, blue-fluorescing product to be isolated and identified as the bipyridone (V). Subsequently, it was found that it was not essential to prevent the formation of radicals in order to obtain the bipyridone, but the yield could not be increased above 40% despite many attempts involving use of a variety of conditions, ratios of reactants, and addition procedures. Demethylation to N-methyl-4,4′-bipyridylium was a competing reaction, but no N-methyl-4-pyridone was detected. This is consistent with the known failure of the Decker reaction to produce 4-pyridones, despite the susceptibility of pyridinium salts to nucleophilic attack by alkoxide ions at the 4- as well as the 2-position.[6] The fact that a one-electron oxidising agent, ferricyanide, is the preferred reagent for pyridone synthesis suggests that the difference in the ability of the 2-hydroxy- and 4-hydroxy-dihydrobipyridyls to give pyridones may lie in the relative stabilities of the intermediate radical oxidation products. If it is assumed, since the Decker reaction is carried out under strongly alkaline conditions, that the pseudo-base is first ionised by loss of the hydroxy-proton before being oxidised, the structures of the intermediate radicals formed from the isomeric-pseudo bases may be represented as in the Scheme. The overall charge separation in the radical corresponding to the 2-pyridone is less than that in the 4-isomer. The 2-isomer should therefore be formed more easily, resulting in the predominant production of 2-pyridone by loss of a second-electron and proton.

The second, yellow-fluorescing product, subsequently shown to be the monopyridone (IV), was present in too

[4] S. F. Mason and R. D. Roberts, Chem. Comm., 1967, 476.

[5] M. Ebert, J. A. Farrington, K. Fletcher, and E. J. Land, Biochim. Biophys. Acta, in the press.

[6] K. Schofield, 'Hetero-aromatic Nitrogen Compounds. Pyrroles and Pyridines,' Butterworths, London, 1967, p. 245.
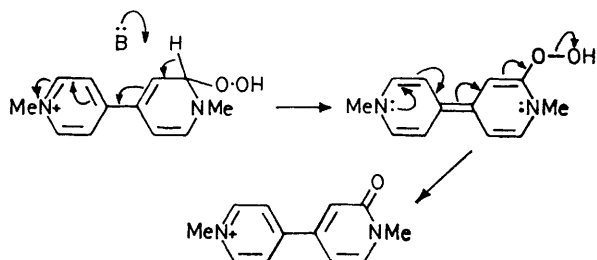
small a proportion to be isolated. It was also formed by treating paraquat with other alkaline oxidising agents,

SCHEME
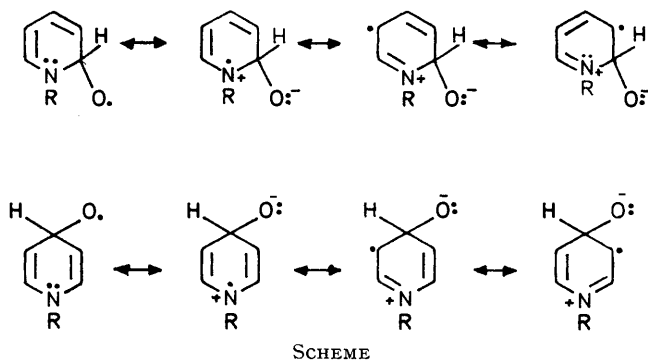
e.g. silver oxide, sodium hypochlorite, or alkaline hydrogen peroxide, or by treating a solution of paraquat radical (III) in dilute acetic acid with nitric oxide.
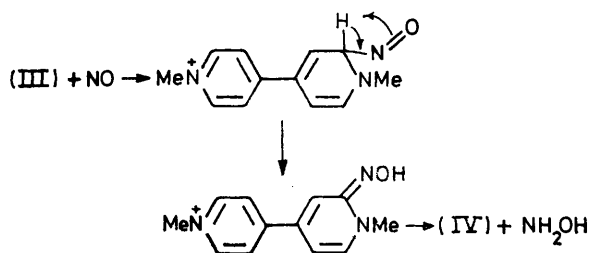
In the case of alkaline hydrogen peroxide, the reaction proceeded at a much lower pH (ca. 11) than when only sodium hydroxide was used (ca. 14), consistent with the greater reactivity of hydroperoxide ion relative to hydroxide ion towards addition to trigonal carbon.[7] Removal of a ring proton followed by heterolysis of the

peroxide bond would convert the initially formed addition product into pyridone. With an excess of alkaline hydrogen peroxide, reaction proceeded beyond

the monopyridone stage, giving N-methylisonicotinate and ultimately oxalic acid as major products.

None of the above reactions gave sufficient monopyridone to allow isolation. It was eventually prepared, as its iodide, by first oxidising N-methyl-4,4'-bipyridylium methosulphate to its pyridone with alkaline ferricyanide, and then quaternising with methyl iodide. Its chromatographic behaviour was identical with that of the yellow-fluorescing product previously obtained. The yield of pyridone formed by direct action of alkali on paraquat was too small to be measured, but its detection on chromatograms confirmed the plausibility of the scheme first suggested.

Analysis of the n.m.r. spectrum of the monopyridone (IV; X = I) allowed the relative effects of pyridinium ring and pyridone on the positions of the ring protons to be deduced. At low resolution the pyridone ring protons showed an AB quartet (J 7 Hz) and a signal which at higher resolution was seen to be a doublet (J 2 Hz). At the same time, the higher-field pair of the AB quartet became split by the same amount. This suggests J 7 Hz for the ortho-coupling between the 5- and 6-protons, and J 2 Hz for the meta-coupling between the 3- and 5-protons. The 5-proton therefore gives the higher-field signals of the AB quartet, as would be expected from its greater separation from the nitrogen atom. Similarly, in the pyridinium ring, the higher-field signals of the A_2B_2 quartet are assumed to be due to the 3- and 5-protons.* On the basis of these assignments, it appears that conversion of the N-methylpyridinium ring into N-methyl-2-pyridone shifts all signals upfield, by the following amounts: N–CH$_3$, 0.44: 3-H, 0.40; 5-H, 0.74; and 6-H, 0.56 p.p.m.

Oxidation of diquat dibromide (VI; X = Br) under conditions similar to those used for preparing paraquat bipyridone gave a complex mixture from which only a very small yield of the bipyridone (VIII) could be isolated. The monopyridone (VII; X = Cl) was therefore synthesised by a procedure analogous to that used for paraquat monopyridone (IV; X = I). 2,2'-Bipyridyl was monoquaternised with 2-bromoethanol, oxidised to the monopyridone (IX; X = Br) with alkaline ferricyanide, and cyclised to the monopyridone (VII; X = Cl) by refluxing with 10N-hydrochloric acid. The intermediate monoquaternary salt (IX; X = Br) gave salts of diquat when refluxed with mineral acids. The monopyridone (VII; X = Cl) gave a small yield of the bipyridone (VIII) when treated with alkaline ferricyanide.

The photochemical degradation of bipyridylium herbicides has been reviewed.[9] Diquat dibromide gives a complex mixture of products amongst which 1,2,3,4-tetrahydro-1-oxopyrido[1,2-a]pyrazin-5-ium bromide, picolinamide, and picolinic acid have been

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* Haque et al.[8] assign the higher-field signals of paraquat to the 2- and 6-protons on the basis of greater broadening, allegedly due to proximity to the N-methyl group. This assignment is in conflict with the normal situation in N-heterocycles, and especially quaternary salts, where the protons closest to the nitrogen atom are most highly deshielded. It would also imply a reversal in chemical shift order for the 2- and 3-protons on going from paraquat to the bipyridone (V), where the signals can be assigned unambiguously on the assumption that the coupling constants are in the order $o > m > p$. Finally, it is inconsistent with our observations that in a series of diquaternary salts of 4,4'-bipyridyl, the lower-field signal varies in position much more than the higher when the quaternising group is varied. We ascribe the broadening of the higher-field, 3-proton signals to restricted rotation about the inter-ring bond.

[7] W. P. Jencks and J. Carriuolo, J. Amer. Chem. Soc., 1960, **82**, 1778; J. O. Edwards and R. G. Pearson, ibid., 1962, **84**, 16; M. D. Johnson, J. Chem. Soc., 1962, 283.

[8] R. Haque, W. R. Coshow, and L. F. Johnson, J. Amer. Chem. Soc., 1969, **91**, 3822.

[9] A. Calderbank, Adv. Pest Control Res., 1968, **8**, 127.

characterised.[10] In addition, an intensely green-fluorescing product has been isolated [9] and tentatively assigned the structure of the monopyridone (VII). The synthetic monopyridone (VII; X = I) had very similar u.v. absorption and fluorescence spectra to this photochemical degradation product, which is therefore assigned the monopyridone structure.

EXPERIMENTAL

M.p.s are corrected. [1]H N.m.r. spectra were recorded at 60 MHz; δ values (in p.p.m.) are measured downfield from internal tetramethylsilane. Paper chromatograms (Whatman no. 1 paper) were eluted with butanol–acetic acid–water (4 : 1 : 2) (solvent A) or (4 : 1 : 5) upper phase, (solvent B). R_F Values measured on circular chromatograms are denoted by c-R_F. Spots were located by examination in u.v. light or by spraying with iodoplatinate reagent.[11]

Reaction of Paraquat with Alkali in the Presence of Air.—Equal volumes of air-saturated aqueous M-paraquat dichloride and 2N-sodium hydroxide were mixed in a glass hypodermic syringe and kept until no further increase in the purple colour occurred (2 h). The solution was then decolourised with air, neutralised with dihydroxytartaric acid (to remove most of the sodium ions from the solution), and filtered. The filtrate was chromatographed on circular papers in solvent A, examined in u.v. light, and then sprayed with iodoplatinate reagent. The products in the Table were observed.

c-R_F	Appearance in u.v. light	Colour with iodoplatinate	Assignment
0—0·2 (brown streak)	Yellow-fluorescing	Purple	Polymer from ring-opened intermediates
0·35	Absorbing * (s)	Blue-black	Paraquat regenerated from radical
0·43	Yellow-fluorescing (vf)		Unassigned
0·51	Absorbing (f)	Purple	N-Methyl isonicotinate
0·59	Yellow-fluorescing (vf)		Unassigned
0·64	Yellow-fluorescing (b)	Blue-black (w)	Monopyridone (IV)
0·70	Absorbing (w)	Blue-black	N-Methyl-4,4′-bipyridylium
0·78	Blue-fluorescing (b)		Bipyridone (V)
0·81	Yellow-fluorescing (vf)		Unassigned

* Absorbing = natural fluorescence of paper quenched.

s = Strong, (v) f = (very) faint, b = bright, w = weak.

When paraquat dichloride, N-methylisonicotinate, monopyridone (IV; X = I), N-methyl-4,4′-bipyridylium methosulphate, and bipyridone (V) were added to the solution and the mixture was re-chromatographed, no new spots appeared.

The brown solution obtained when air was blown through a mixture of equal volumes of M-paraquat dichloride and 2N-sodium hydroxide for 2 h gave a chromatogram which was not significantly different from the above.

1,1′-Dimethyl-4,4′-bipyridyl-2,2′-dione (V).—Paraquat dichloride (2·57 g, 10 mmol) dissolved in water (10 ml) was added dropwise over 5 min to a stirred suspension of

[10] A. E. Smith and J. Grove, *J. Agric. Food Chem.*, 1969, **17**, 609.

powdered potassium ferricyanide (17 g, 50 mmol) in 5N-sodium hydroxide (200 ml), initially at 20°. The potassium ferricyanide dissolved during the addition and colourless needles were precipitated. The mixture was stirred for a further 15 min and the solid was filtered off and washed with water. On paper chromatography (solvent A), the solid gave a single blue-fluorescing spot, c-R_F 0·79, and the filtrate showed a mixture of this and a yellow-fluorescing material (IV), c-R_F 0·63. The filtrate was extracted with chloroform, the extract was evaporated to dryness, and the residue was combined with the solid filtered off and crystallised from ethyl acetate, giving needles of the *bipyridone* (0·72 g, 33%), m.p. 260—262° (Found: C, 66·2; H, 5·9; N, 13·2. $C_{12}H_{12}N_2O_2$ requires C, 66·6; H, 5·6; N, 13·0%), δ (CDCl$_3$) 7·40 (2H, d, *J* 7 Hz, 6-H), 6·35 (2H, q, *J* 7 and 2 Hz, 5-H), 6·75 (2H, d, *J* 2 Hz, 3-H), and 3·60 (6H, s, Me), $\lambda_{max.}$ (H$_2$O) 224 (ε 20,000) and 320 nm (6100).

Reaction of Paraquat with Alkali in the Presence of Other Oxidising Agents.—(a) *Silver oxide.* Freshly prepared silver oxide was stirred with aqueous 0·1M-paraquat dichloride for 30 min. Paper chromatography of the solution showed the presence of paraquat, the monopyridone (IV), and the bipyridone (V).

(b) *Hydrogen peroxide.* Hydrogen peroxide was added to aqueous paraquat dichloride solution to give a solution 10^{-3}M in paraquat and 0·1M in H_2O_2. No change occurred in the u.v. spectrum. Similarly, no change occurred in the spectrum of 10^{-3}M-paraquat in 0·1M-sodium hydroxide. On adding N-sodium hydroxide to the first solution to give a concentration of 10^{-2}N, a broad absorption appeared rapidly at 380 nm, and, when chromatographed, the solution showed spots corresponding to the pyridones (IV) and (V). 5N-Sodium hydroxide (10 ml) was added to a mixture of M-paraquat dichloride (4 ml) and hydrogen peroxide (190 vol; 6 ml). The mixture became warm and a smell of methylamine was detected. A chromatogram of a neutralised portion of the reaction mixture showed bipyridone (V), several yellow-fluorescing spots, and a spot with the same R_F and reaction towards iodoplatinate as N-methylisonicotinate. The solution was left at room temperature for 5 days, by which time crystals (125 mg) had been deposited. The i.r. spectrum of these was identical to that of sodium oxalate.

A solution of [Me-^{14}C]paraquat dichloride (4 × 10^{-3}M, 6 Ci mol^{−1}) was mixed with an equal volume of alkaline hydrogen peroxide (0·5N-NaOH; 0·05M-H_2O_2) and kept at 25°. Samples were taken after 0, 5, 15, 30, 80, and 120 min and spotted on a paper chromatogram kept in an atmosphere of acetic acid. The chromatogram was developed in solvent A and an autoradiograph was taken. The 5-min sample showed the presence of five new products, in addition to some unchanged paraquat, with R_F values 0, 0·49, 0·59, 0·68, and 0·79. The intensities, relative to unchanged paraquat, were estimated visually as 0·1, 1·0, 0·2, 0·9, and 0·3, respectively. After 50 min all the paraquat had disappeared, but the other products were still visible, with intensities 0·02, 1·5, 0·1, 0·8, and 0·5. After 120 min, almost all of the radioactivity was concentrated in the spot of R_F 0·49. After 1 week the reaction was chromatographed side-by-side with N-methylisonicotinate, which ran indistinguishably from the major product (R_F 0·49).

[11] I. Smith, ' Chromatographic and Electrophoretic Techniques,' Heinemann, London, 1960, p. 396.

Reaction of Paraquat Radical with Nitric Oxide.—A solution of paraquat radical was prepared by adding granulated zinc to paraquat dichloride (10^{-4}M) in aqueous sodium acetate buffer, pH 4·9, previously deoxygenated by stirring under vacuum. When the intensity of the blue colour reached that corresponding to *ca.* 5×10^{-5}M-paraquat radical, the solution was decanted, under vacuum, from the zinc into a spectrophotometer cell closed with a serum cap. The u.v. spectrum was recorded, and then nitric oxide was bubbled through a hypodermic needle into the solution. The blue colour disappeared immediately, and the u.v. spectrum of the solution was indistinguishable from that of the original paraquat solution, but paper chromatography showed the presence of a yellow-fluorescing material corresponding in R_F to the monopyridone (IV).

1-Methyl-4,4'-bipyridylium Methosulphate.—A solution of 4,4'-bipyridyl dihydrate (96 g, 500 mmol) in chloroform (500 ml) was refluxed with removal of condensed water until no more appeared in the condensate. Chloroform (100 ml) was then distilled off and replaced by dry chloroform (100 ml). The solution was cooled to 7° in ice–water and a solution of dimethyl sulphate (48·5 g) in dry chloroform (500 ml) was added over 15 min with stirring. After further 45 min stirring the solid was filtered off, washed with chloroform, and dried at room temperature, giving the *monoquaternary salt* (102 g, 72%), m.p. 189° (Found: C, 50·7; H, 5·2; N, 9·8. $C_{12}H_{14}N_2O_4S$ requires C, 51·0; H, 5·0; N, 9·9%), c-R_F 0·73 (paper chromatography in solvent A).

1-Methyl-4,4'-bipyridyl-2-one.— 1-Methyl-4,4'-bipyridylium methosulphate (5·64 g, 20 mmol) in water (20 ml) was added dropwise to a stirred suspension of powdered potassium ferricyanide (17 g, 50 mmol) in 5N-sodium hydroxide at 25—30° over 5 min. The mixture was stirred for a further 15 min and the solid was filtered off, washed with water, dried, and crystallised from benzene, giving the *pyridone* (1·2 g, 32%), m.p. 113—114° (Found: C, 70·9; H, 5·4; N, 15·0. $C_{11}H_{10}N_2O$ requires C, 70·9; H, 5·4; N, 14·7%).

1',2'-Dihydro-1,1'-dimethyl-2'-oxo-4,4'-bipyridylium Iodide (IV; X = I).—The foregoing pyridone (1·0 g, 8 mmol) and methyl iodide (30 ml) in methanol (10 ml) were heated under reflux for 30 min. The mixture was cooled and the yellow *quaternary salt* (1·5 g, 57%), m.p. 280—290° (decomp.), was filtered off and washed with methanol. Crystallisation from aqueous ethanol gave a pure sample (1·0 g), m.p. 280—290° (decomp.) (Found: C, 43·6; H, 3·9; N, 8·4. $C_{12}H_{13}IN_2O$ requires C, 43·9; H, 3·7; N, 8·5%), c-R_F (solvent A) 0·63, δ ($CF_3 \cdot CO_2H$) 4·17 (3H, s, 1-Me), 8·54 (2H, d, *J* 7 Hz, 2- and 6-H), 8·03 (2H, d, *J* 7 Hz, 3- and 5-H), 3·73 (3 H, s, 1'-Me), 7·60 (1 H, d, *J* 2 Hz, 3'-H), 7·27 (1 H, q, *J* 7 and 2 Hz, 5'-H), and 7·96 (1 H, d, *J* 7 Hz, 6'-H), $\lambda_{max.}$ (H_2O) 225 (ε 22,000), 257 (21,000), and 345 nm (2700).

6,7-Dihydrodipyrido[1,2-a:2',1'-c]pyrazine-4,9-dione (VIII).—Diquat dibromide (34·4 g, 100 mmol) dissolved in water (125 ml) was added over 30 min to a vigorously stirred solution of potassium ferricyanide (140 g) in 5N-sodium hydroxide (2 l) at 25°. The resulting dark brown solution was neutralised with 10N-hydrochloric acid and extracted continuously for 5 days with methylene dichloride. The extract was evaporated to dryness and the brown residue recrystallised from water and methanol to give the yellow *bipyridone* (0·92 g, 4·3%), m.p. 313—315° (Found: C, 67·8; H, 4·8; N, 13·3. $C_{12}H_{10}N_2O_2$ requires

C, 67·4; H, 4·7; N, 13·1%), $\lambda_{max.}$ (H_2O) 358 nm, fluorescence maximum at 430 nm. The bipyridone (VIII) was also prepared in 31% yield by oxidising the monopyridone (VII; X = Br) under the conditions used for preparing the hydroxyethylpyridone (X).

1-(2-Hydroxyethyl)-2,2'-bipyridylium Iodide (IX; X = I).—2,2'-Bipyridyl (140 g, 0·9 mol) was refluxed with 2-bromoethanol (24 ml, 0·4 mol) in absolute ethanol (40 ml) for 3 h. The resulting dark solution was diluted with water (200 ml) and extracted with ether (3 × 200 ml) to remove unchanged bipyridyl (80 g). The product was washed with water (200 ml.) through a column (20 cm × 2·5 cm) of Deacidite FF ion-exchange resin in the iodide form. The eluate was concentrated to 50 ml, giving an orange-yellow solution, which was poured into hot acetone (2 l). The acetone solution was cooled to −50°; the *quaternary iodide* (41·6 g, 32%), m.p. 58—60° crystallised and was filtered off, R_F (solvent B) 0·5, $\lambda_{max.}$ (H_2O) 277 nm (ε 9900). It was characterised by conversion into authentic diquat dichloride by treatment with boiling 10N-hydrochloric acid. When the salt (IX; X = I) was refluxed for 4 h in 1 equiv. of methyl iodide in ethanol it gave orange crystals of *1-(2-hydroxyethyl)-1'-methyl-2,2'-bipyridyldi-ium di-iodide* (Found: C, 32·9; H, 3·5; N, 6·0. $C_{13}H_{16}I_2N_2O$ requires: C, 33·2; H, 3·4; N, 6·0%), R_F 0·17 (solvent B), $\lambda_{max.}$ 272 nm (ε 14,000), δ_{max} 3280, 1620, 1592, and 1505 cm^{-1}.

1-(2-Hydroxyethyl)-2,2'-bipyridyl-6-one (X).—A solution of the salt (IX; X = I) (65·6 g) in water (40 ml) was added dropwise to a stirred saturated aqueous solution of potassium ferricyanide (132 g) while the solution was maintained at pH 14 by the addition of 10N-sodium hydroxide. After 3·5 h the pH was brought to 7 by adding 10N-hydrochloric acid, and the solution was extracted continuously with chloroform for 2 h. The extract was dried ($MgSO_4$) and evaporated to give a brown solid (14·7 g). Two crystallisations from benzene gave crystals of the *pyridone*, m.p. 90—91° (Found: C, 66·9; H, 5·5; N, 12·9. $C_{12}H_{12}N_2O_2$ requires C, 66·7; H, 5·6; N, 13·0%), single spot R_F 0·79 (solvent B), $\lambda_{max.}$ (H_2O) 311 nm (ε 9700). It was further characterised by conversion by heating under reflux with methyl iodide into *1',2'-dihydro-1'-(2-hydroxy-ethyl)-1-methyl-2'-oxo-2,6'-bipyridylium iodide*, yellow platelets, m.p. 220—221° (from ethanol) (Found: C, 43·4; H, 4·3; N, 7·3. $C_{13}H_{15}IN_2O_2$ requires C, 43·6; H, 4·2; N, 7·8%), R_F 0·41 (solvent B), $\lambda_{max.}$ (H_2O) 308 (ε 6900) and 265 nm (8700).

6,7-Dihydro-4-oxodipyrido[1,2-a:2',1'-c]pyrazinium Iodide (VII; X = I).—The monopyridone (X) (3·22 g) was heated under reflux with 10N-hydrochloric acid (15 ml) for 4 h. The resulting solution was washed with water (100 ml) through a Deacidite FF ion-exchange column (20 × 2 cm) in the iodide form. The eluate was evaporated to dryness under vacuum, giving the *quaternary iodide* as bright yellow crystals (4·26 g, 88%), m.p. 306—310° (decomp.) (from ethanol) (Found: C, 43·9; H, 3·6; N, 8·2. $C_{12}H_{11}IN_2O$ requires C, 44·2; H, 3·4; N, 8·6%), R_F 0·39 (solvent B), $\lambda_{max.}$ (H_2O) 357 (ε 14,900) and 262 nm (6700). The solution showed an intense green fluorescence with maximum emission at 465—470 nm. The green-fluorescing material isolated from photochemical degradation of diquat [10] had absorption peaks at 260 and 362 nm and had a fluorescence emission maximum at 474 nm.