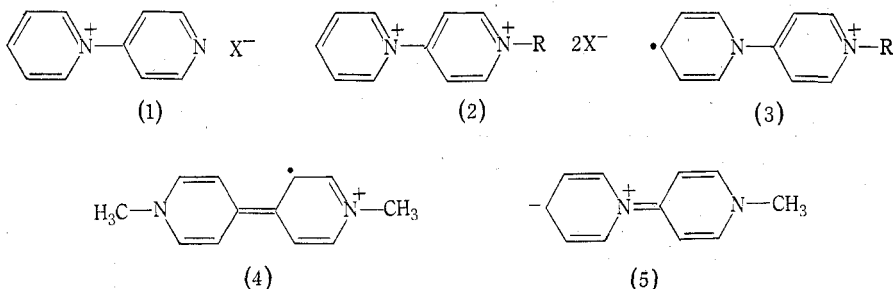


1-(4'-ALKYL-4'-PYRIDINIO)PYRIDINIUM SALTS

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1-(4'-Pyridyl)pyridinium salts (1) and their hydrohalides are well known^{1,2} but there has been no report of the preparation of diquaternary salts of the type (2; R = alkyl) although related polymeric cations have been referred to in patent specifications³ and elsewhere.⁴ Jerchel and his colleagues¹ treated (1; X = Cl) with methyl iodide but the product isolated was the corresponding iodide (1; X = I).



We became interested in the system (2) as a possible precursor of radical cations (e.g. (3)) related to those obtained (e.g. (4)) by the one-electron reduction of diquaternary salts of certain bipyridyls.⁵ Some of the bipyridylium salts are of particular interest as one-electron transfer agents and herbicides.^{6,7} This paper reports the synthesis of salts of type (2; R = alkyl).

The preparation of the salt (2; R = Me, X = Br) was accomplished by treating 1-(4'-pyridyl)pyridinium chloride hydrochloride (2; R = H, X = Cl) with dimethyl sulphate followed by replacement of the methosulphate and chloride anions by bromide. The structure of the salt was confirmed by its n.m.r. spectrum. It was stable in aqueous solution below about pH 7.0 but was rapidly decomposed by alkali.

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¹ Jerchel, D., Fischer, H., and Thomas, K., *Chem. Ber.*, 1956, **89**, 2921.

² Shaw, E. N., in "The Chemistry of Heterocyclic Compounds. Pyridine and Its Derivatives." (Ed. E. Klingsberg.) Part 2, p. 11. (Interscience: New York 1961.)

³ N. V. Philips Gloeilampenfabrieken, Neth. Pat. Appln 6,601,803 (1967) (*Chem. Abstr.*, 1968, **68**, 68894); Neth. Pat. Appln 6,602,233 (1967) (*Chem. Abstr.*, 1968, **68**, 87162).

⁴ Mosher, H. S., in "Heterocyclic Compounds." (Ed. R. C. Elderfield.) Vol. 1, p. 516. (John Wiley: New York 1950.)

⁵ Homer, R. F., Mees, G. C., and Tomlinson, T. E., *J. Sci. Fd Agric.*, 1960, **11**, 309.

⁶ Black, A. L., and Summers, L. A., *J. chem. Soc. (C)*, 1969, 610.

⁷ Dickeson, J. E., and Summers, L. A., *J. Sci. Fd Agric.*, 1969, **20**, 74 and references cited therein.

An aqueous solution of (2; R = Me, X = Br) on treatment with zinc dust developed immediately a yellow-green coloration which is attributed partly to the radical cation (3) and largely to products obtained by decay of the radical species. Polarographic examination, using diquat dibromide as reference,⁸ confirmed that the reduction of (2; R = Me, X = Br) involved one electron but not hydrogen. It gave a symmetrical one-electron reduction wave in the pH range 1.9–7.0 with a half-wave potential (E_0) of -0.28 V independent of pH and concentration. A second one-electron reduction wave was also present with a half-wave potential (E_0) of -0.65 V, also independent of pH and concentration. It is presumably due to the formation of betaine-like structures such as (5). The n.m.r. spectrum of the yellow-green solution taken 5 min after the addition of the zinc powder showed no evidence of the presence of a high concentration of a stable free-radical species (cf.⁶) but indicated that (2; R = Me, X = Br) had been converted into a complex mixture of products. The formation of paramagnetic species on reduction of the diquatery salt was confirmed by the observation that an aqueous solution of (2; R = Me, X = Br) after treatment with zinc dust gave an e.s.r. signal consisting of more than 25 lines with a total width of about 30 G. The spectrum was poorly resolved and rapidly decayed. These results indicate that the salt (2; R = Me, X = Br) is reduced in aqueous solution by a one-electron transfer to give a relatively unstable radical cation. This result contrasts with the behaviour of diquatery salts of 4,4'-bipyridyl⁵ which are reduced to radical cations (e.g. (4)) stable in aqueous solution. This difference in stability is consistent with the fact that in the latter case canonical forms of the radical cation can be written so that the odd electron is delocalized over all of the nuclear positions, whereas in (3) four nuclear positions cannot be occupied by the odd electron unless charge separation forms are invoked.

It was ascertained that the corresponding ethyl derivative (2; R = Et, X = Br), obtained from 1-(4'-pyridyl)pyridinium chloride hydrochloride and diethyl sulphate, behaved similarly.

The salts (2; R = Me, X = Br) and (2; R = Et, X = Br) were inactive in post-emergent herbicidal tests when applied at 8 lb/acre on mixed grass flora, probably because of the instability of the radical cations of type (3) in aqueous solution (cf.⁷).

Experimental

U.v. absorption measurements, n.m.r. spectra, and polarography experiments were carried out as previously reported.⁶ Microanalyses were performed by the Australian Microanalytical Service, Melbourne. The electron spin resonance spectra were taken at room temperature on a Varian V4501 instrument with 6-in. magnet and 100 kHz modulation. The concentration of the salt was approximately 5×10^{-3} M.

1-(4'-Methyl-4'-pyridinio)pyridinium Dibromide (2; R = Me, X = Br)

1-(4'-Pyridyl)pyridinium chloride hydrochloride (1 g) was heated in freshly distilled dimethyl sulphate (5 ml) for 1 hr at 120° . On cooling, the solution was diluted with dry ether (20 ml). The oil which formed was washed with ether and acetone. It was then dissolved in ethanol (20 ml), acidified with concentrated hydrobromic acid, boiled for 2 min (charcoal), and filtered. The filtrate was passed through a column loaded with De-acidite FF in the bromide form. The eluate was concentrated under reduced pressure to one-quarter of its original volume,

⁸ Summers, L. A., *Nature*, 1967, **214**, 381.

and diluted with dry ethanol until crystals began to form. The product was recrystallized from ethanol-aqueous hydrobromic acid to give lemon flakes, m.p. 251° (dec.) (yield 40%) (Found: C, 39.8; H, 3.6; Br (total), 48.4; Br (ionic), 47.9; N, 8.2. Calc. for $C_{11}H_{12}Br_2N_2$: C, 39.8; H, 3.6; Br, 48.2; N, 8.4%). The n.m.r. spectrum (CF_3COOH and D_2O) showed a singlet at δ 4.72 p.p.m. (3 *N*-methyl protons) and a complex multiplet at 8.35–9.45 (9 aromatic protons). The u.v. spectrum showed λ_{max} (water) 237 nm ($\log \epsilon$ 4.10) and 266 (3.96). Polarography experiments showed the presence of two one-electron waves with E_0 –0.28 and –0.65 V.

1-(4'-Ethyl-4'-pyridinio)pyridinium Dibromide (2; R = Et, X = Br)

This was prepared similarly using diethyl sulphate. It crystallized from ethanol-aqueous hydrobromic acid as buff flakes, m.p. 265° (dec.) (Found: C, 41.6; H, 4.3; Br, 45.9; N, 7.9. Calc. for $C_{12}H_{14}Br_2N_2$: C, 41.6; H, 4.0; Br, 46.2; N, 8.1%). The n.m.r. spectrum (D_2O) showed a triplet at δ 1.7–1.95 p.p.m. (3 methyl protons), a quartet at 4.8–5.15 (2 methylene protons), and a complex multiplet at 8.4–9.5 (9 aromatic protons). The u.v. spectrum showed λ_{max} (water) 238 nm ($\log \epsilon$ 4.09) and 268 (3.96). Polarography experiments showed the presence of two one-electron waves with E_0 –0.29 and –0.62 V.

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