6*H*-Dipyrido[2,1-*b*:1′,2′-*e*]-1,3,5-thiadiazinium Dibromide

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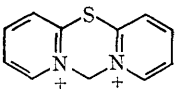
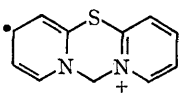
BY continuing our study[1] of diquaternary salts related to bipyridylium herbicides[2] we have now found that 2,2′-dipyridyl sulphide in boiling dibromomethane (3 hours) gives a 50% yield of the novel diquaternary salt (I), m.p. 298° (dec.) (from aqueous ethanol) which represents the first authenticated example of a polycyclic system containing a methylene group flanked by two quaternary pyridine nitrogen atoms (*cf.* ref. 3). The structure was confirmed by elemental analyses (all bromine ionic) and by the n.m.r. spectrum[4] (in water) which consisted of a multiplet at $\delta = 8{\cdot}2$—$9{\cdot}5$ p.p.m. (8 aromatic protons) and a singlet at $\delta = 7{\cdot}3$ (2 methylene protons) with an area ratio of 4 : 1. In deuterium oxide the methylene hydrogen atoms were exchanged for deuterium. The salt was stable,[5] though not, as expected, in the presence of alkali, the u.v. spectrum in water (λ_{max} 235, 290, and 313 mμ; ϵ 9000, 13,500, and 13,000) being unchanged after standing for 24 hr. Like the related dipyridothiadiazepine derivative[1] obtained from 2,2′-dipyridyl sulphide and ethylene bromide an aqueous solution of (I) gave a yellow–green solution on treatment with zinc dust, presumably due to the radical cation of which (II) is one canonical form.

The formation of (I) contrasts with unsuccessful attempts to prepare the corresponding diquaternary salt from 2,2′-bipyridyl which gives instead a dipyrido-oxadiazepine derivative on treatment with methylene sulphate[6] and an aromatic dipyrido-imidazole salt, *inter alia*, with methylene iodide.[3]



$2Br^-$ (I)



(II)

(*Received, July* 11*th*, 1966; *Com.* 477.)

[1] L. A. Summers, *Angew. Chem. Internat. Edn.*, 1966, in the press.
[2] Review by W. R. Boon, *Chem. and Ind.*, 1965, 782.
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[4] Sodium 3-trimethylsilyl-1-propanesulphonate was the internal reference.
[5] *Cf.* F. Krohnke, *Ber.*, 1933, **66**, 1386.
[6] I. C. Calder, W. H. F. Sasse, and T. M. Spotswood, *Austral. J. Chem.*, 1963, **16**, 289; R. F. Homer and T. E. Tomlinson, *J. Chem. Soc.*, 1960, 2498.