Reduction of 1,1′-Dimethyl-4,4′-bipyridylium Dichloride to 1,1′-Dimethyl-1,1′-dihydro-4,4′-bipyridyl

By J. G. CAREY, J. F. CAIRNS, and J. E. COLCHESTER*

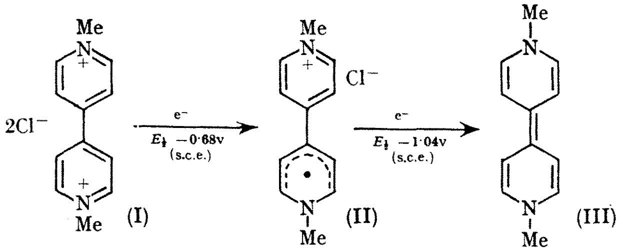
(*Imperial Chemical Industries Limited, Mond Division, Research Department, P.O. Box 8, The Heath, Runcorn, Cheshire*)

Summary 1,1′-Dimethyl-1,1′-dihydro-4,4′-bipyridyl, previously postulated as the product of two-electron reduction of 1,1′-dimethyl-4,4′-bipyridylium dichloride, has been isolated and identified.

THE two electron reduction of 1,1′-dibenzyl- and 1,1′-diphenyl-4,4′-bipyridylium di-iodide to the corresponding 1,1′-disubstituted-1,1′-dihydro-4,4′-bipyridyl has been achieved with sodium amalgam, sodium in ethanol, and with zinc or magnesium in aqueous solution.[1] The yields obtained are poor and the product is frequently contaminated with the cation radical, the product of a one-electron reduction.

We have investigated the reduction of 1,1′-dimethyl-4,4′-bipyridylium dichloride (I) to 1,1′-dimethyl-4,4′-dihydrobipyridyl. It has been inferred[2] from the polarographic behaviour of 1,1′-dimethyl-4,4′-bipyridylium dichloride that the second reduction wave is due to the dihydrobipyridyl. However, this compound has never been isolated or characterised and very little is known about its chemistry.

We now report that 1,1′-dimethyl-1,1′-dihydro-4,4′-bipyridyl can be synthesised quantitatively by reduction of (I) using sodium dithionite in alkaline solution† at room temperature, according to the following reaction sequence:



The addition of a slight excess of dithionite to an aqueous solution of (I) at pH 9—10 in an oxygen-free system leads to immediate and quantitative formation of the intensely coloured cation radical (II). Further reduction to (III) is slow but the reaction is complete in 2 hr. Further addition of base may be necessary in order to maintain a pH 9—10. The dihydrobipyridyl was extracted with toluene and re-crystallised from the same solvent as red–orange needles, m.p. 183°. From ethanol the compound crystallised as irregular flakes: ^{1}H n.m.r. (C_6D_6) δ 5·4 (d, 4H, *J* 7·1 c./sec.) 5·18 (d, 4H, *J* 7·1 c./sec.), and 2·02 p.p.m. (5, 6H): mass

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† Typical conditions are paraquat ion 1·0—3·0 × 10^{-1}M pH 9—10 buffer and $Na_2S_2O_4$ (3—5 equiv.) and NaOH(2N) added in portions during 2—3 hr. to maintain the pH at 9—10.

spectrum *m/e* 186 (M^+, $C_{12}H_{14}N_2$), fragmentation pattern consistent with structure (III); u.v. (cyclohexane) 400 and 376 sh nm.: i.r. (toluene) 1665s, 1575w, 1355m, 1225s, 1195s, 1010s, 775m, and 2890w, (wave numbers).

1,1′-Dimethyl-1,1′-dihydro-4,4′-bipyridyl is a powerful reducing agent and can be oxidised quantitatively to the 1,1′-dimethyl-4,4′-bipyridylium salt.

A recent communication[3] described the reduction of (I) to the cation radical (II) by methoxide ion in methanol and aqueous methanol. The suggested mechanism involved the loss of two electrons and a proton, from the methoxide ion to give formaldehyde according to the following scheme:—

$$\text{(I)} + CH_3O^- \rightarrow \text{(II)} + \overset{-}{C\dot{H}_2O} + H^+$$

$$\text{(I)} + \overset{-}{C\dot{H}_2O} \rightarrow \text{(II)} + CH_2O$$

We have found that under forcing conditions, in methanol with high concentrations of base, further reduction of the radical cation (II) to the dihydrobipyridyl (III) can occur in over a 50%‡ yield. The redox potential[4] of methoxide is not sufficient to reduce the bipyridylium cation radical to the dihydrobipyridyl, however, although methoxide is a more powerful reducing agent in strong sodium hydroxide solution it is possible that formate ion derived from methoxide is the reductant for the second step to (III). The dihydrobipyridyl can be extracted from aqueous methanol by toluene and identified as indicated above.

Under similar reaction conditions but using dimethyl sulphoxide instead of methanol, the dihydrobipyridyl was obtained in a 20% yield. In water as solvent a yield of 2% was obtained.

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‡ (1) Paraquat ion 5×10^{-2}M, MeOH–H_2O (1 : 1), Me_2SO–H_2O (1 : 1) or H_2O 0·4M-NaOH 4×10^{-1}, 70—80°. NaOH (solid or saturated aqueous solution) 40—50 equivalents then added in portions during 1 hr. The dihydrobipyridyl was extracted into toluene and oxidised to paraquat ion which was estimated colorimetrically (S. H. Yuen, J. E. Bagness, and D. Myles, *Analyst*, 1967, **92**, 375).

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[2] R. M. Elofson and R. L. Edsberg, *Canad. J. Chem.*, 1957, **35**, 646.
[3] J. A. Farrington, A. Ledwith, and M. F. Stam, *Chem. Comm.*, 1969, 259.
[4] "An Introduction to Fuel Cells," ed. K. R. Williams, Elsevier, Amsterdam, 1966, p. 119.