Dimerization of Pyridinium Salts by Cyanide

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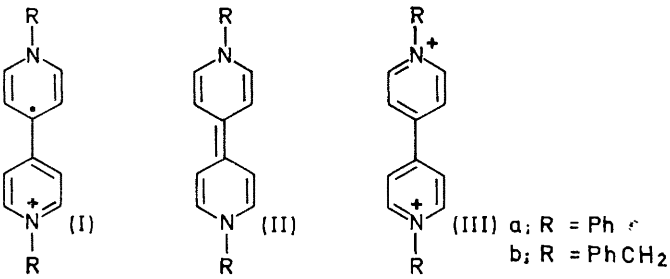
Summary 1,1′-Dihydro-4,4′-bipyridyls (II) are formed from certain pyridinium or 2-methylpyridinium salts and sodium cyanide.

THE reaction of cyanide with pyridinium salts has been shown to produce 1,2-, 1,4-, and 1,6-cyano-adducts.[1] We have observed the reaction of 1-n-dodecylpyridinium bromide with aqueous sodium cyanide yields a dimeric product, the cation radical (I; R = n-$C_{12}H_{25}$).[2]

We now report that cyanide reacts with other pyridinium salts to form products other than the 1,2-, 1,4-, or 1,6-adducts, and the cation radical (I): we have isolated 1,1′-dihydro-4,4′-bipyridyls (II)[3] in excellent yields. Dimerization of pyridinium salts by cyanide apparently has broad applicability.

A benzoin-type mechanism with (II) as an intermediate could be involved in the formation of (I). Since the phenyl- and benzyl-1,1′-dihydro-4,4′-bipyridyls (II; R = Ph and $PhCH_2$) are known and are relatively stable, we attempted to isolate these compounds.

Thus we reacted 1-phenylpyridinium chloride with cyanide in 50% v/v Me_2CO–H_2O under anaerobic conditions. The solution immediately became turbid followed by the appearance of a dark red solid in about five minutes. The solid was collected after 10 days, and although it did contain some free radical (e.s.r.), it was demonstrated to be mainly 1,1′-diphenyl-1,1′-dihydro-4,4′-bipyridyl (95%



(I) (II) (III) a; R = Ph
b; R = $PhCH_2$

yield) by oxidation with a standard iodine solution to 1,1′-diphenyl-4,4′-bipyridinium salt (IIIa)† [equivalent weight 155 (theor. 156)], mass spectrum (70 ev) m/e 310 (M^+: correct for $C_{22}H_{18}N_2$), analysis, and i.r. [identical with that of an authentic sample of (II; $R = Ph$)[6]].

The benzylpyridinium salt was treated with cyanide in the same manner. The initial yellow solution gradually turned dark blue. After 3 days, a solid was collected and was established to be primarily 1,1′-dibenzyl-1,1′-dihydro-4,4′-bipyridyl (80%) as follows. Titration with a standard iodine solution in chloroform[5] gave an equivalent weight of 203, 195, 224, and 182 (theor. 169). These results and the elemental analysis suggested that the solid product contains about 10—20% of the cation radical. Oxidation with an alcoholic iodine solution yielded 1,1′-dibenzyl-4,4′-bipyridinium dibromide (IIIb) (by analysis) after ion exchange. The i.r. spectrum of (II; $R = PhCH_2$) was identical to an authentic sample prepared[6] by heating 1,1′-dibenzyl-1,1′,4,4′-tetrahydro-4,4′-bipyridyl[7] in EtOH.

1,2-Dimethylpyridinium iodide similarly (the solution gradually turned yellow, became green, and after heating in a sealed flask on a steam bath for 3 days, became dark blue) gave a green crystalline solid, which was shown to be 1,1′,2,2′-tetramethyl-1,1′-dihydro-4,4′-bipyridyl (51% yield) by similar evidence (M^+ 214, analysis) and oxidized to 1,1′,2,2′-tetramethyl-4,4′-bipyridinium di-iodide, m.p. 320° (lit. 318,[8] 320[9]), by passing air through an aqueous HBr solution containing the solid, followed by ion exchange.

Since both cation radicals (I) and the 1,1′-dihydro-4,4′-bipyridyls (II) have been isolated from the reaction of cyanide with pyridinium salts, the relative amounts of each formed, the factors which influence this ratio, and the order in which they are formed are of interest. A basic solution of methanol has been shown to reduce 1,1′-dimethyl-4,4′-bipyridinium dichloride to 1,1′-dimethyl-1,1′-dihydro-4,4′-bipyridyl (II; $R = Me$).[10]

Thus far, there has been no evidence for any other dimeric product other than 4,4′-dimers resulting from the reaction of pyridinium salts with cyanide.

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† I.r. identical to that of (IIIa) prepared by the quaternization of bipyridyl: (B. Emmert and N. Roh, *Ber.*, 1925, **58B**, 503); analysis correct.

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