An Adduct of a 2,3-Pyridyne with Furan

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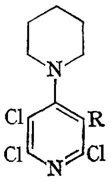
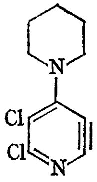
ALTHOUGH they have on many occasions been suggested as reaction intermediates,[1,2] 2,3-pyridynes have proved to be elusive species. The reported examples of *cine*-substitution reactions of 2- and 3-substituted pyridines could proceed by mechanisms other than those involving 2,3-pyridynes,[1,2] and attempts to trap the 2,3-pyridyne intermediates have been almost entirely unsuccessful. In only one instance has any evidence been obtained for the formation of an adduct of a 2,3-pyridyne: the reaction of lithium amalgam with 3-bromo-2-chloropyridine in the presence of furan led to a low yield of quinoline.[3]

We have now succeeded in obtaining a substantial yield of an adduct of a 2,3-pyridyne. The reaction of n-butyl-lithium with 2,3,5,6-tetrachloro-4-(1-piperidyl)pyridine (Ia)[4] in diethyl ether at −75° led to a solution containing 2,5,6-trichloro-4-(1-piperidyl)-3-pyridyl-lithium (Ib) (*cf.* ref. 5); subsequent hydrolysis gave 2,3,6-trichloro-4-(1-piperidyl)pyridine (Ic).

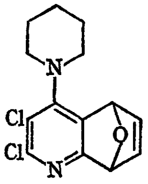
When a solution of the lithium compound (Ib) was allowed to stand at room temperature in the presence of furan, the adduct (III) of furan and 5,6-dichloro-4-(1-piperidyl)-2,3-pyridyne (II) was formed, and isolated in 45% yield. The adduct (III) was characterised by elemental analysis, determination of its molecular weight, and n.m.r. spectroscopy. The proton n.m.r. spectrum showed signals at τ 2·95 (singlet, 2, protons), 4·05 (singlet, 1 proton), 4·65 (singlet, 1 proton), *ca.* 6·9 (broad multiplet, 4 protons) and 8·3 (broad singlet, 6 protons). (The signals described as singlets show signs of unresolved splitting.)



(I) a; R=Cl
b; R=Li
c; R=H



(II)



(III)

Our experiments thus show clearly that a 2,3-pyridyne can be formed, and can react normally, as a dienophile. We are now studying the reactions of this 2,3-pyridyne, and investigating the possibility of generating other arynes by analogous routes.

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[4] S. M. Roberts and H. Suschitzky, *Chem. Comm.*, 1967, 893.

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