Photolysis of Pentachloropyridine and Pentachloropyridine 1-Oxide

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Summary Pentachloropyridine gives 2,3,4,6-tetrachloropyridine in practicable yield on photolysis while pentachloropyridine 1-oxide ring opens and rearranges to pentachlorobutadienyl 1-isocyanate.

PHOTOLYSIS of pentachloropyridine in dioxan or diethyl ether (*cf.* Table 1) constitutes to date the best preparative method for 2,3,4,6-tetrachloropyridine. Previous routes have involved either unsuitable laboratory techniques or lengthy multi-stage syntheses.[1] The results are analogous to those obtained from irradiation of various substituted chlorobenzenes which in benzene give the corresponding biphenyls and in other solvents dechlorinated products.

Metallation of 2,3,4,6-tetrachloropyridine with n-butyllithium to give tetrachloro-3-pyridyl-lithium occurred readily (33%) and provides a potential synthetic route to the rather inaccessible 3-substituted tetrachloropyridines. Some nucleophilic substitution reactions of 2,3,4,6-tetrachloropyridine are given in Table 2.

Substitution *para* to hydrogen in 2,3,4,6-tetrachloropyridine would be expected by analogy with pentachlorobenzene[3] because of the stability of a *para*-quinonoid intermediate in which the I_{π} effect is absent. This is particularly marked when the aprotic benzene is the solvent (*cf.* Table 2).

Photolysis of pentachloropyridine 1-oxide[4] in dry carbon tetrachloride resulted in a complex mixture, inseparable on a column. Distillation at 0·2 mm, however, gave pentachlorobutadienyl 1-isocyanate (**1**; b.p. 55°/0·2 mm) together with pentachloropyridine. An authentic sample of the isocyanate (**1**) was prepared from pentachloro-2,5-pentadienoyl chloride[5] and sodium azide in aqueous acetone to give first the corresponding acid azide [(**1**; NCO replaced by CON$_3$) bands at 2130, 2160 cm^{-1}: $-N_3$, and at 1695 cm^{-1}, $>$C=O] which was made to rearrange in boiling benzene to the product (b.p. 55°/0·2 mm; band at 2260 cm^{-1}, NCO). The isocyanate was further characterised with dry methanol to give methyl *N*-pentachlorobutadienyl carbamate (m.p. 71—73°).

TABLE 1

Photolysis of 0·04M *solutions of pentachloropyridine using a medium pressure lamp* (1 *l Hanovia photochemical reactor*)

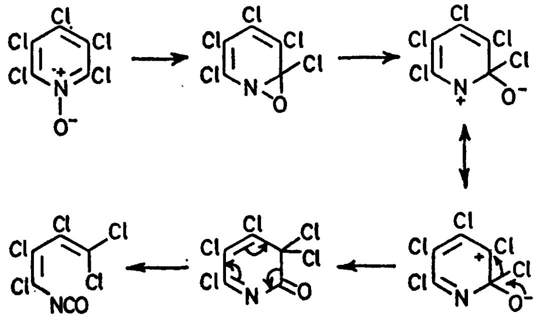
Solvent	Time (h)	Products (%)†
Benzene	18	2,3,4,6-Tetrachloro-5-phenylpyridine (50)
Dioxan	90	2,3,4,6-Tetrachloropyridine (42) 2,3,5,6-Tetrachloropyridine (trace)
Diethyl ether	24	2,3,4,6-Tetrachloropyridine (43) 2,3,5,6-Tetrachloropyridine (trace)
Cyclohexane	120	2,3,4,6-Tetrachloropyridine (10)

TABLE 2

Some reactions of 2,3,4,6-*tetrachloropyridine with nucleophiles* (2 *equiv.*)

Reagent/Solvent	Products (%)†
NaOH/H$_2$O	2,3,4-Trichloro-6-pyridone (34) 2,3,6-Trichloro-4-pyridinol (28) 2,4,5-Trichloro-6-pyridinol (4)
NaOH/MeOH	2,3,6-Trichloro-4-methoxypyridine (61)
MeNH$_2$/EtOH	2,4,5-Trichloro-6-methylaminopyridine (25) 2,3,6-Trichloro-4-methylaminopyridine (50)
C$_5$H$_{11}$N/EtOH	2,3,4-Trichloro-6-piperidinopyridine (2) 2,3,6-Trichloro-4-piperidinopyridine (53) 2,4,5-Trichloro-6-piperidinopyridine (8)
C$_5$H$_{11}$N/C$_6$H$_6$	2,3,4-Trichloro-6-piperidinopyridine (14) 2,3,6-Trichloro-4-piperidinopyridine (23) 2,4,5-Trichloro-6-piperidinopyridine (60)

This photolysis result is noteworthy since it appears to be the first recorded photo-rearrangement of a heteroaromatic *N*-oxide to give an isocyanate. By analogy with the known photolytic behaviour of *N*-oxides[6] we postulate the mechanism shown in the Scheme for the formation of (**1**).



SCHEME

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† All products had the correct analysis and spectra (m.s. and i.r.) in accord with structural assignment.

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