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NOTE

POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS

XVI*. SOME DERIVATIVES OF PENTACHLOROPYRIDINE

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In connection with studies concerned with the preparation of thermally stable polymers, we have been interested in the synthesis of some highly halogenated monomers containing reactive groups such as HMe_2Si-. A typical compound in such a series is 4-(dimethylsilyl)tetrachloropyridine.

$$C_5Cl_5N \rightarrow 4\text{-}MC_5Cl_4N \xrightarrow{HMe_2SiCl} 4\text{-}HMe_2SiC_5Cl_4N$$

Several reports have appeared recently on the chemistry of pentachloropyridine[1-5]. Roeding and co-workers[1] have shown that pentachloropyridine reacts readily with various nucleophiles to give mainly 4-substituted tetrachloropyridines. However, Haszeldine *et al.*[3] observed that displacement of nuclear chlorine can take place at both 2- and 4-positions, depending, in part, on the size of the nucleophilic reagent. Cook, Wakefield and Clayton[4] demonstrated the solvent dependent lithiation of pentachloropyridine; the more polar solvent, like ether, favors halogen–metal exchange at the 4-position, whereas in methylcyclohexane 2-lithiotetrachloropyridine is predominant. A recent communication by Roberts and Suschitzky[5] reports the formation of 2-substituted tetrachloropyridines from pentachloropyridine and various secondary amines.

We are now reporting the preparation of a Grignard reagent from pentachloropyridine and magnesium in THF at −10°. Reaction with chlorotrimethylsilane, chlorodimethylsilane and chlorodimethylphenylsilane gave the corresponding 4-silyl-substituted tetrachloropyridines in satisfactory yields. The position of the silyl substituents was established by alkaline hydrolysis to give 2,3,5,6-tetrachloropyridine. Additionally, the same 4-silylated-tetrachloropyridines were obtained by lithiation using n-butyllithium in THF, followed by treatment of the lithiotetrachloropyridine with the respective chlorosilanes.

It was earlier shown[6] that hexachlorobenzene undergoes a halogen–metal exchange to a small extent; however, at this stage, it appears that the main reaction between pentachloropyridine and benzylmagnesium chloride is coupling.

The reaction of pentachloropyridine with an excess of magnesium uses up more than one equivalent of magnesium, and so indicates poly-Grignard formation.

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* For Part XV see ref. 9.

In this connection 4-(trimethylsilyl)tetrachloropyridine has been found to react with an equivalent of magnesium or n-butyllithium.

EXPERIMENTAL

All melting points are uncorrected. Pentachloropyridine and magnesium turnings were commercial products of reagent grade. Tetrahydrofuran (THF) was ketyl purified. The reactions were carried out in an atmosphere of dry oxygen-free nitrogen. IR and NMR spectra were recorded, employing PE-21 infrared spectrometer and A-60 NMR spectrometer, respectively.

Preparation of the Grignard reagent from pentachloropyridine

Pentachloropyridine (x moles) in THF was added dropwise, with stirring, to magnesium turnings (x g-atoms) in THF, containing 5–6 drops of ethylene bromide, at −10°. After the addition of all pentachloropyridine, the mixture was stirred for about four hours at −10°. The resulting solution assumed a cherry red color and it gave a weakly positive Color Test I[7]. The appropriate chlorosilane (1.2 x moles) in THF was added and stirred for 6–8 hours. The solvent was removed under vacuum and the dark brown residue, after hydrolysis with 10% cold hydrochloric acid, was extracted with ether. The ether-extract was dried ($MgSO_4$) and the solvent was stripped off under reduced pressure. The dark brown residue was taken up in petroleum ether (b.p. 60–70°), filtered and passed through a silica gel column. Removal of petroleum ether gave a white solid which was crystallised from methanol or acetone. The percentage yields, m.p. and NMR data of silyltetrachloropyridines are given in Table 1.

TABLE 1

REACTION OF CHLOROSILANES WITH TETRACHLOROPYRIDYLMAGNESIUM CHLORIDE

Chlorosilane	Silyltetrachloropyridine		
	Yield (%)	M.p. (°C)	NMR data (τ)
Me_3SiCl	79–80	62–63 (methanol)	Si–Me_3 (singlet, 9.45)
HMe_2SiCl	75	115–116 (acetone)	$SiMe_2$ (doublet, 9.45; J = 6–6.5 cps) Si–H (septet, 5.05)
$PhMe_2SiCl$	65	88–89 (methanol)	Si–Ph (multiplet, 2.7) Si–Me (singlet, 9.26)

Alkaline hydrolysis of (trimethylsilyl)tetrachloropyridine

(Trimethylsilyl)tetrachloropyridine (0.5 g, 0.0017 mole) in 10 ml of THF was refluxed with 5 ml of 5% sodium hydroxide solution for 2–3 hours. Usual work up gave a solid (0.26 g, 70%) which was identified as 2,3,5,6-tetrachloropyridine, m.p. 89–90°, after crystallisation from methanol (lit.[8]: m.p. 90°).

A similar hydrolysis reaction with (hydrodimethylsilyl)tetrachloropyridine, gave the same compound.

The compounds from C_5Cl_4NLi and the corresponding chlorosilanes in THF have been found identical with those prepared via the Grignard reagents and chlorosilanes. We have not been able to isolate 2-silylsubstituted tetrachloropyridine from any of these reactions. It seems, in a more polar solvent, like THF, the major product is 4-substituted compound. It may be pointed out here that Cook and co-workers[4] have reported the formation of both 2- and 4-substituted compounds when lithiation is carried out in ether, the major product being the 4-substituted derivative.

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