POLYCHLOROAROMATIC COMPOUNDS
II*. TETRACHLOROPYRIDYL DERIVATIVES OF LITHIUM, MAGNESIUM AND MERCURY**

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SUMMARY

Solutions of tetrachloropyridyllithium compounds have been made by the reaction of n-butyllithium with pentachloropyridine; in hydrocarbon solvents, 3,4,5,6-tetrachloro-2-pyridyllithium was the predominant isomer, whereas in diethyl ether, 2,3,5,6-tetrachloro-4-pyridyllithium was the major product. 2,3,5,6-Tetrachloro-4-pyridylmagnesium chloride was prepared from pentachloropyridine and magnesium. Bis(2,3,5,6-tetrachloro-4-pyridyl)mercury and 2,3,5,6-tetrachloro-4-pyridylmercuric chloride were made by the reaction of the 4-pyridyllithium compound with mercuric chloride. The 2,3,5,6-tetrachloro-4-pyridylmercuric chloride was isolated as a complex with 2,2'-bipyridine.

INTRODUCTION

Pentafluorophenyl derivatives of many of the metals, both typical and transition, have been prepared and studied[3]. Recently, pentachlorophenyl derivatives of lithium[4,5], magnesium[6,7] and mercury[8,9] have been prepared, and it is becoming apparent that significant differences exist between the fluorinated and chlorinated series[9,10,11]. The balance between the electron-withdrawing effect of the organic groups and the steric requirements of the o-halogen atoms may well be critical in determining some of the properties of the compounds (cf. ref. 9). We have now investigated the synthesis and properties of some tetrachloropyridyl derivatives of metals, with the object of comparing them with their pentafluoro- and pentachlorophenyl analogues, as well as of studying their utility in synthesis. Recently, the synthesis of some tetrafluoropyridyl derivatives of lithium, magnesium and mercury has also been reported[12].
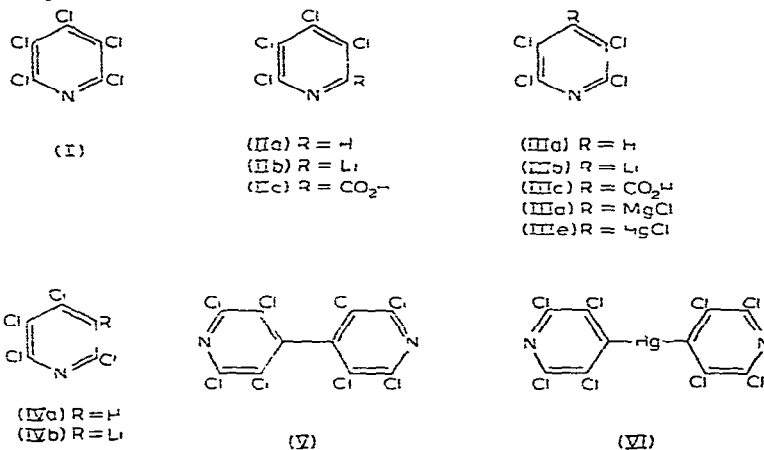
RESULTS AND DISCUSSION

The reaction of organolithium compounds with hexafluorobenzene[13,14] or pentafluoropyridine[15,16] leads to alkyl- or aryl-substituted products. However, hexa-

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* For Part I see ref 1.
** A preliminary account of the preparation of the lithium derivatives has been published[2].

chlorobenzene reacts with n-butyllithium by metal–halogen exchange, to give solutions of pentachlorophenyllithium[4]. We have found that n-butyllithium similarly reacts with pentachloropyridine mainly by metal–halogen exchange. However, we have also observed that the proportions of the tetrachloropyridyllithium compounds formed depend on the solvent used.

(I)

(IIa) R = H
(IIb) R = Li
(IIc) R = CO₂H → (IIc) R = CO_2-

(IIIa) R = H
(IIIb) R = Li
(IIIc) R = CO_2H
(IIId) R = MgCl
(IIIe) R = HgCl

(IVa) R = H
(IVb) R = Li

(V)

(VI)

When a solution of n-butyllithium in hexane was added to a suspension of pentachloropyridine (I) in methylcyclohexane at room temperature, a mildly exothermic reaction occurred, leading to a clear, though coloured, solution. Distillation of the products obtained from the solution after hydrolysis gave the following fractions: (a) a liquid mixture of tetrachloropyridines (43% yield), (b) a mixture of pentachloropyridine and another component of similar boiling point, and (c) a mixture of several high-boiling components. The mixture of tetrachloropyridines, (a), could not be separated into its components by distillation, TLC or GLC. However, its proton nuclear magnetic resonance (^{1}H NMR) spectrum showed three singlets in the aromatic region. By analogy with the signals for 2,3-dichloropyridine[17] (α-hydrogen, τ 1.70; β-hydrogen, τ 2.80; γ-hydrogen, τ 2.22), the signals for the mixture of tetrachloropyridines, which were at τ 1.65, 2.10 and 2.59 ($CDCl_3$ solution) were assigned to 2,3,4,5-tetrachloropyridine (IIa), 2,3,5,6-tetrachloropyridine (IIIa) and 2,3,4,6-tetrachloropyridine (IVa), respectively. Integration of the spectrum indicated that the isomers were present in the ratio 68:16:16. Further confirmation of the correctness of the NMR assignments came from subsequent experiments (see below), and it was concluded that the main product from the reaction of n-butyllithium with pentachloropyridine in methylcyclohexane is 3,4,5,6-tetrachloro-2-pyridyllithium (IIb). Similar results were obtained using other hydrocarbons (hexane, benzene) as solvents. The second component of fraction (b) of the reaction products could be partly separated from pentachloropyridine by GLC but has not been obtained in a pure state. However, the ^{1}H NMR spectrum [triplet, τ 7.25 (2 protons); multiplet, τ 8.7 (4 protons): triplet, τ 9.15 (3 protons)] indicated that an n-butyl group was present, and it seems probable that the substance is an n-butyltetrachloropyridine, of unknown orientation (or a mixture of isomers). No pure materials could be isolated from the mixture of high-boiling compounds (c). However, one major component had the same GLC retention volume as octachloro-4,4'-bipyridine (V)[18], and others

corresponded to components of the mixture of heptachloro- and octachloro-bi-pyridines obtained via the reaction of n-butyllithium with pentachloropyridine in furan[19].

When a solution of n-butyllithium in hexane was added to pentachloropyridine (I) in diethyl ether instead of in methylcyclohexane, the product obtained after hydrolysis and work-up was a solid. Experimental difficulties prevented efficient fractional distillation, but the bulk of the distillate was shown by GLC to consist of a mixture of tetrachloropyridines (yield approx. 45%) with a little pentachloro-pyridine. The spectrum of the product had singlets at τ 2.10 and τ 2.59, which were assigned to 2,3,5,6-tetrachloropyridine (IIIa) and 2,3,4,6-tetrachloropyridine (IVa), respectively. Integration of the spectrum indicated that the isomers were present in a ratio of 78 : 22. No 2,3,4,5-tetrachloropyridine (IIa) was detected. Sublimation and crystallisation of a sample of the mixed tetrachloropyridines gave material melting at 89–91°, and giving a singlet at τ 2.10, with only a weak signal at τ 2.59. 2,3,5,6-Tetra-chloropyridine is reported[20] to melt at 90–91°. It was thus concluded that the main product from the reaction of n-butyllithium with pentachloropyridine in diethyl ether is 2,3,5,6-tetrachloro-4-pyridyllithium (IIIb). No n-butylated compounds were detected. Some higher-boiling material appeared to be similar to the mixture of polychloropolypyridines obtained from the reaction in methylcyclohexane. When the reaction was carried out at −75°, the proportions of the tetrachloropyridines (IIIa) and (IVa) were unaltered, but the yield was raised to approximately 70%.

The absence of butylated products from the reactions in diethyl ether might be explained if the alkylation reaction were considered to involve initial electrophilic attack on chlorine by the lithium atom of the n-butyllithium rather than nucleophilic attack on the ring by the carbanionic butyl group. In diethyl ether, the electrophilicity of the n-butyllithium is satisfied by coordination.

The tetrachloropyridyllithium compounds behaved in general as expected. Their reactions with carbonyl compounds, nitriles, etc., will be described in a separate publication, as will their use as precursors of trichloropyridynes[19]. However, the products of their reactions with carbon dioxide provide further evidence for the orientation of the lithium compounds, and are therefore described here. Dry carbon dioxide was passed into the solutions in methylcyclohexane and in ether; when the solutions were poured onto solid carbon dioxide, only tetrachloropyridines were obtained. The reaction in methylcyclohexane yielded, by conventional working-up procedures, a mixture of acids (40%, calculated as tetrachloropyridinecarboxylic acids). Isolation of pure components proved difficult, but fractional crystallisation yielded a sample of 3,4,5,6-tetrachloropyridine-2-carboxylic acid (IIc) identical with an authentic specimen synthesised by Roedig et al.[21]. Similarly, the reaction of the ethereal lithium compounds with carbon dioxide yielded a mixture of acids from which a pure sample, m.p. 226–228°, of 2,3,5,6-tetrachloropyridine-4-carboxylic acid (IIIc) (lit.[22] m.p. 224–245°) was readily obtained by crystallisation.

We have suggested[2] two possible explanations for the solvent effect in the reaction of n-butyllithium with pentachloropyridine. The explanation which seems to us most attractive is that in a hydrocarbon solvent the pentachloropyridine, al-though it is only very weakly basic, coordinates with the highly electron-deficient n-butyllithium, holding the reagent in a favourable position for attack at the 2-posi-tion. On the other hand, n-butyllithium is strongly solvated by diethyl ether[23], and

if the very weakly basic pentachloropyridine is unable to displace ether molecules from the complex, reaction will take place at the position most susceptible to nucleophilic attack, *viz.* the 4-position[24,25].

Alternatively, the solvent effect might be due to steric factors. It has been established[24,25,26] that with bulky nucleophiles, pentachloropyridine undergoes substitution mainly in the 2-position. In ether, alkyllithium compounds are believed to be present mainly as solvated dimers[27,28], and a species of this type would be smaller than the hexamer which forms the bulk of the reagent in hydrocarbon solution[29].

We are not yet able to determine which of the alternative explanations is correct, although we hope to do so by means of experiments on polychlorobenzene derivatives. However, we have established that the 2-lithio compound (IIb) does not rearrange to the 4-lithio compound (IIIb) in the presence of ether. The addition of ether to a solution of the lithium compounds [mainly (IIb)] in methylcyclohexane apparently led to the rapid destruction of (IIb), as no 2,3,4,5-tetrachloropyridine (IIa) could be detected in the hydrolysed product even when hydrolysis was carried out immediately after the addition of ether. Parallel experiments, carried out with and without the addition of ether, disclosed (by quantitative analysis of the products by NMR) that the disappearance of the 2-lithio compound (IIb) was not accompanied by any increase in the amount of the 4-lithio compound (IIIb). In the experiments in which ether was added, part of the product consisted of insoluble material, presumably formed via decomposition of the 2-lithio compound (IIb).

Like hexachlorobenzene[30], pentachloropyridine is unaffected by ethereal Grignard reagents. We suspected that reaction might take place in the presence of very strong nucleophiles, which would enhance the carbanionic character of the reagents, but pentachloropyridine was recovered unchanged after treatment with the complex of n-butylmagnesium bromide with 1,4-diaza[2 2.2]bicyclooctane (*cf.* ref. 31).

Pentachloropyridine did react with unsolvated n-butylmagnesium bromide[32] in refluxing methylcyclohexane, but under these conditions any tetrachloropyridylmagnesium halide reacted as soon as it was formed, as the very complex mixture of products obtained after hydrolysis appeared to consist of butyl derivatives and chlorinated bipyridines, with only traces of tetrachloropyridines. Pentachloropyridine failed to react with magnesium in diethyl ether or in boiling decalin, even in the presence of iodine, alkoxides, etc., but a Grignard reagent could be made from pentachloropyridine by means of "entrainment" with 1,2-dibromoethane in diethyl ether (*cf.* ref. 6)*. Hydrolysis of this reagent gave mainly 2,3,5,6-tetrachloropyridine (IIIa), together with some unreacted pentachloropyridine, but only a small amount of 2,3,4,5-tetrachloropyridine (IIa). From the reaction of the Grignard reagent with carbon dioxide, 2,3,5,6-tetrachloropyridine-4-carboxylic acid (IIIc) was obtained. The reagent was thus largely a solution of 2,3,5,6-tetrachloro-4-pyridylmagnesium chloride (IIId).

On treatment with mercuric chloride (0.4 mole), the ethereal solution of tetrachloropyridyllithium compounds gave bis(2,3,5,6-tetrachloro-4-pyridyl)mercury (VI).

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* This reaction was first carried out by C. J. Clayton, and we are highly indebted to Dr. Clayton and Imperial Chemical Industries Ltd, Mond Division, for making this information available to us.

No complex was obtained between this mercury compound and 2,2'-bipyridine, although a stable 1 : 1 complex is formed between bis(2,3,5,6-tetrafluoro-4-pyridyl)-mercury and 2,2'-bipyridine[12]. A similar contrast exists between bis(pentachloro-phenyl)mercury and bis(pentafluorophenyl)mercury[9]. It is not clear whether these differences are due to polar or steric factors.

With an equimolar amount of mercuric chloride the tetrachloropyridyllithium reagent gave a product which was not purified, but which on treatment with 2,2'-bi-pyridine gave a product with a composition corresponding approximately to that of a 1 : 1 complex of 2,3,5,6-tetrachloro-4-pyridylmercuric chloride (IIIe) with 2,2'-bipyridine. Since the work described here was completed, it has been reported[11] that pentachlorophenylmercuric chloride forms a stable complex with 1,10-phenanthro-line.

EXPERIMENTAL

The ^1H NMR spectra were recorded at 60 mcps, in deuterochloroform or carbon tetrachloride solution with tetramethylsilane as internal standard.

Gas-liquid chromatography was generally carried out under two sets of conditions, as follows. (i) Column: 130 cm × 5 mm, 10% polyethylene glycol adipate on 100–120 mesh Celite. Carrier gas: nitrogen (40 ml/min). Temperature: 180°. (ii) Column: 130 cm × 5 mm, 5% Silicone E301 on 100–120 mesh Celite. Carrier gas: nitrogen (40 ml/min). Temperature: 290°.

Column chromatography on silica was carried out using "Kieselgel", 0.05–0.2 mm.

Elemental analyses were carried out by Drs. Weiler and Strauss, Oxford. M.p.'s are uncorrected.

Reactions of n-butyllithium with pentachloropyridine

Many experiments were performed, using various experimental conditions. Representative runs are described here.

(a). *In methylcyclohexane.* Pentachloropyridine (25.0 g) was suspended in methylcyclohexane (200 ml), and the mixture cooled in ice as n-butyllithium (50 ml of 2.24 M solution in hexane) was added slowly, with stirring. The ice-bath was withdrawn and the mixture stirred for 10 min at room temperature, before water (100 ml) was added. The solvents were distilled through a short column at atmospheric pressure, and the residue fractionally distilled using a spinning band column. The fractions were examined by GLC [conditions (i)]. Fraction 1 (0.42 g, b.p. 104–119°/3.5 mm) was a complex mixture, and was discarded. Fractions 2 (1.30 g, b.p. 119–134°/3.5 mm), 3 (2.63 g, b.p. 133°/3.0 mm) and 4 (5.35 g, b.p. 134.5°/3.0 mm) consisted almost entirely of tetrachloropyridines. Fraction 5 (2.13 g, b.p. 135.5–142°/3.0 mm) consisted of tetrachloropyridines, pentachloropyridine, and a third component, with a slightly longer retention time than pentachloropyridine. The residue from this prolonged distillation was charred, but rapid distillation of the products from other runs gave high-boiling fractions, which were shown by GLC [conditions (ii)] to contain a mixture of compounds, including octachloro-4,4'-bipyridine[18]. The ^1H NMR spectra of fractions 2, 3 and 4 were similar, and are described above, as is that of fraction5. Fraction 3 had n_D^{23} 1.5889, and was analysed. (Found: C, 27.7; H, 0.46; Cl, 65.5; N,

6.6. C_5HCl_4N calcd.: C, 27.7; H, 0.46; Cl, 65.3; N, 6.5%.) Lit.[33] b.p. of 2,3,4,5-tetra-chloropyridine, 135–137°/24 mm, m.p. 21–22°. Fractions 2–4 represent a 43% yield of tetrachloropyridines.

Similar results were obtained using hexane or benzene as the solvent. In some runs the tetrachloropyridines were separated by chromatography on silica gel, using light petroleum as the eluant; ^1H NMR showed that a mixture of similar proportions of isomers was obtained by this method.

(b). *In diethyl ether.* n-Butyllithium (10.0 ml of 2.20 M solution in hexane) was added to a solution of pentachloropyridine (5.0 g) in diethyl ether (100 ml) at 0°. The solution was allowed to warm to room temperature (15 min), with stirring, and stirred at room temperature for a further 30 min. Water (50 ml) was added. The mixed products were isolated via ether extraction. The resulting solid was shaken with light petroleum, b.p. 40–60° (a small amount of insoluble material was discarded). Chromatography of the solution on silica gel gave pentachloropyridine (0.34 g, 6.8%) and a mixture of tetrachloropyridines (1.73 g, 41%). The identities of the products were checked by GLC [conditions (i)], and the mixture of tetrachloropyridines was analysed by ^1H NMR. Similar proportions of the tetrachloropyridines were obtained when the crude products of the reaction were distilled, but it was not possible to use the spinning band column for these solid materials, and the tetrachloropyridines could not be separated from pentachloropyridine by this method. High-boiling mixtures of polychlorobipyridines, etc., were also obtained.

In subsequent runs, the n-butyllithium was added at −75°, and the mixture stirred at this temperature for 30 min before being allowed to warm to room temperature. The proportions of the tetrachloropyridines obtained were similar to those from the earlier runs, but yields were (65–70%).

A sample of the mixture of tetrachloropyridines was sublimed and then recrystallised from aq. ethanol, to give a white solid, m.p. 89–91°. 2,3,5,6-Tetrachloropyridine melts[18] at 90–91° and the ^1H NMR spectrum of the solid showed that it contained only a little 2,3,4,6-tetrachloropyridine.

Reactions of the lithium derivatives with carbon dioxide

(a). *Lithium derivatives prepared in methylcyclohexane.* A solution of the tetrachloropyridyllithium derivatives in methylcyclohexane was prepared as described above from pentachloropyridine (5.0 g) and cooled in ice. Carbon dioxide was passed into the solution for 1 h at 0°, then for a further $3\frac{1}{2}$ h at room temperature. The mixture was allowed to stand overnight, and water (50 ml) was added. The organic layer was separated, and extracted with 2 N sodium hydroxide (3 × 30 ml) and water (10 ml). The extract was acidified with hydrochloric acid, and extracted with ether, from which a gummy, semi-solid product (2.30 g) was obtained. Fractional crystallisation from mixtures of chloroform and light petroleum, b.p. 40–60°, gave 3,4,5,6-tetrachloro-pyridine-2-carboxylic acid (0.46 g, 9.0%), m.p. *ca.* 165° (dec.). On further recrystallisation the m.p. was raised to 170° (dec.). The acid was identical (mixed m.p., infrared) with an authentic specimen[21].

(b). *Lithium derivatives prepared in diethyl ether.* A solution of the tetrachloro-pyridyllithium derivatives in diethyl ether was prepared as described above from pentachloropyridine (3.0 g) and cooled to −75°. Carbon dioxide was passed into the solution as it warmed to room temperature, and the resulting mixture was allowed

to stand overnight before being hydrolysed with 2 N sodium hydroxide (50 ml). The organic layer was separated, and extracted with 2 N sodium hydroxide (50 ml) and water (50 ml). The combined aqueous layers were acidified with hydrochloric acid and filtered. The precipitated acids (2.01 g, 67%) were recrystallised from benzene/light petroleum, b.p. 60–80°, to yield 2,3,5,6-tetrachloropyridine-4-carboxylic acid (0.84 g, 29%), m.p. 220–222°. Further recrystallisation raised the m.p. to 226–228° (lit.[22] m.p. 224–225°).

Action of diethyl ether on solutions of the lithium derivatives in methylcyclohexane

Four solutions of tetrachloropyridyllithium compounds were prepared from pentachloropyridine (2.0 g) and n-butyllithium (1.1 mol.) at −75°. Solution A was in diethyl ether (50 ml) and solutions B, C and D in methylcyclohexane (50 ml). The solutions were allowed to warm to room temperature, and stirred at room temperature for $\frac{1}{2}$ h. Diethyl ether (50 ml) was added to solutions A, B and C, and methylcyclohexane (50 ml) to solution D. Water (50 ml) was added to each solution, with stirring. The organic layers were separated, filtered and dried, and most of the solvent distilled (using similar conditions for each sample). The residue from each experiment was dissolved in carbon tetrachloride (20 ml) and the NMR spectra of aliquots of the solutions were recorded. The results are shown in Table 1.

TABLE 1

HEIGHTS OF SIGNALS DUE TO THE ISOMERIC TETRACHLOROPYRIDINES (ARBITRARY UNITS)

Chemical shift, τ	Experiment			
	A	B	C	D
1.65 (2-H)	0	0	0	200
2.10 (4-H)	off scale	90	80	90
2.59 (3-H)	190	70	60	70

2,3,5,6-Tetrachloro-4-pyridylmagnesium chloride

A mixture of pentachloropyridine (5.0 g), magnesium turnings (3.88 g), 1,2-dibromoethane (0.1 ml), diethyl ether (50 ml) and iodine (small crystal) was warmed gently until the reaction was initiated (5 min). The solution was stirred and warmed as 1,2-dibromoethane (5.6 ml) in diethyl ether (50 ml) was added dropwise over $1\frac{1}{2}$ h. The product obtained via hydrolysis, work-up and column chromatography on silica gel was crude 2,3,5,6-tetrachloropyridine (2.0 g, 46.5%), m.p. 78–80°. GLC [conditions (*i*)] showed that a little pentachloropyridine was present. The ¹H NMR showed a singlet, τ 2.10, with only a very weak signal at τ 2.59. In another experiment, the solution of the Grignard reagent was treated with carbon dioxide using the procedure described above for the lithium derivatives. 2,3,5,6-Tetrachloropyridine-4-carboxylic acid (14%), m.p. 221–222°, was obtained.

Bis(2,3,5,6-tetrachloro-4-pyridyl)mercury

To a solution of the lithium derivative from pentachloropyridine (5.0 g) in diethyl ether (100 ml) at −75° was added mercuric chloride (1.5 g). The mixture was

stirred at $-75°$ for 1 h, then allowed to stand at room temperature for 3 h. Water (50 ml) was added. The product obtained from the ether layer was purified by chromatography on silica (chloroform eluant), to yield bis(2,3,5,6-tetrachloro-4-pyridyl)-mercury (1.53 g, 12%). The compound could not be recrystallised, and decomposed on heating, but was further purified by washing with small volumes of diethyl ether. (Found: C, 19.3; N, 4.5. $C_{10}Cl_8HgN_2$ calcd.: C, 19.0; N, 4.4%.)

When equimolar amounts of the mercury derivative and 2,2'-bipyridine in diethyl ether were mixed, no complex was obtained.

When an experiment was carried out as described above, but using mercuric chloride (3.0 g) no pure product could be isolated. Addition of 2,2'-bipyridine to a solution of the reaction products in ether yielded an impure sample of a 1:1 complex of 2,3,5,6-tetrachloro-4-pyridylmercuric chloride and 2,2'-bipyridine. (Found: C, 27.5; H, 0.9; N, 6.2. $C_{15}H_8Cl_5HgN_3$ calcd.: C, 29.6; H, 1.3; N, 6.8%.)

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