

## Polyhalogenoaromatic Compounds. Part XXXI.<sup>1</sup> Synthesis and Attempted Cyclisation of Polychlorophenyl- and Polychloropyridyl-alkanols

By Norman J. Foulger and Basil J. Wakefield,\* The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT

Several 2-polychloroarylethanols were synthesised by the reaction of polychloroaryl-lithium compounds with ethylene oxide. The products did not undergo cyclisation by intramolecular nucleophilic substitution except in the case of 2-(heptachloro-4,4'-bipyridyl-3-yl)ethanol, which gave 5,6-dichloro-2,3-dihydro-4-(tetrachloro-4-pyridyl)furo[2,3-*b*]pyridine.

Metal-halogen exchange between *n*-butyl-lithium and 2-pentachlorophenylethanol took place at the *m*- and *p*-positions. On heating, the mixture of lithiated compounds gave 4,5,6-trichloro-2,3-dihydrobenzo[*b*]furan *via* intramolecular addition to an aryne intermediate. 2-(Tetrachloro-4-pyridyl)ethanol underwent metal-halogen exchange at both positions 2 and 3 of the ring, but cyclisation was not achieved in this case.

CYCLISATION by intramolecular nucleophilic substitution in polyfluoroaromatic compounds is well known, but few examples of analogous reactions of polychloroaromatic compounds have been recorded. However, we and our colleagues have synthesised quinazolines and triaza-naphthalenes by the reaction of pentachlorophenyl-lithium and polychloropyridyl-lithium compounds with aromatic nitriles,<sup>2,3</sup> and thienopyridines by the reaction of tetrachloropyridine-4-thiolate with dimethyl acetylenedicarboxylate<sup>4</sup> and by treatment of tetrachloro-4-pyridylmethylenetherhodanine with base.<sup>5</sup> The experiments now described were carried out in order to test the feasibility of cyclisations involving intramolecular nucleophilic substitution by alkoxide ions.

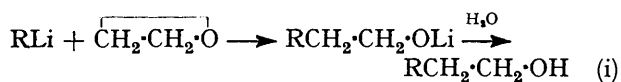
The preparation of suitable starting materials by the reaction of the polychloroaryl-lithium compounds (1)—

<sup>1</sup> Part XXX, N. J. Foulger and B. J. Wakefield, *J. Organometallic Chem.*, in the press.

<sup>2</sup> D. J. Berry and B. J. Wakefield, *J. Chem. Soc. (C)*, 1971, 642.

<sup>3</sup> D. J. Berry, J. D. Cook, and B. J. Wakefield, *J.C.S. Perkin I*, 1972, 2190.

(6) with ethylene oxide was first examined. Although steric hindrance has been reported to favour proton abstraction rather than nucleophilic ring-opening,<sup>6</sup> we obtained the expected  $\beta$ -substituted ethanols (7)—(12) [equation (i) and Table 1]. The structures of the



products were established by their elemental analyses and n.m.r. (Table 1), i.r. ( $\nu_{\text{max}}$  near 3400  $\text{cm}^{-1}$ ), and mass spectra. The yields based on the precursors for the organolithium intermediates were moderate, but were in most cases good if based on the estimated yield of organolithium compound. The main products were accompanied by small amounts of the 'hydrolysis product' of the organolithium compound, but we have

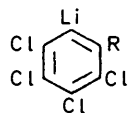
<sup>4</sup> E. Ager, Ph.D. Thesis, Salford, 1970.

<sup>5</sup> A. W. Thompson, Ph.D. Thesis, Salford, 1973.

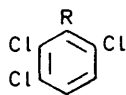
<sup>6</sup> J. K. Crandall and L.-H. C. Lin, *J. Amer. Chem. Soc.* 1967, **89**, 4527.

not determined whether this arose by proton abstraction from ethylene oxide or from adventitious water.

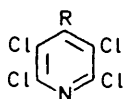
Attempts were made to cyclise 2-pentachlorophenylethoxide and 2-(tetrachloro-4-pyridyl)ethoxide under a variety of conditions, ranging from heating the ethoxides, prepared *in situ*, in diethyl ether, to heating the ethanols with lithium hydride in boiling tetrahydrofuran or



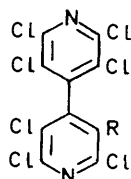
- (1) R = Li  
(2) R = H



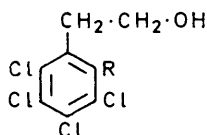
- (3) R = Li  
(9) R = CH<sub>2</sub>·CH<sub>2</sub>·OH



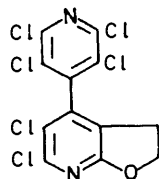
- (4) R = Li  
(5) R = CH<sub>2</sub>Li  
(10) R = CH<sub>2</sub>·CH<sub>2</sub>·OH  
(11) R = CH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·OH



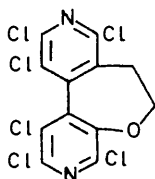
- (6) R = Li  
(12) R = CH<sub>2</sub>·CH<sub>2</sub>·OH



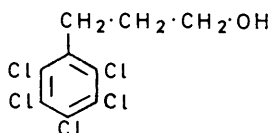
- (7) R = Cl  
(8) R = H



(13)



(14)



(15)

pyridine. No cyclisation was observed, although compounds such as hexachlorobenzene readily undergo substitution by alkoxides under similar conditions.<sup>7</sup> We attribute the failure of our alkoxides to cyclise to deactivation by the electron-donating  $\beta$ -hydroxyethyl substituent, and to steric hindrance; models show that attack of the alkoxide group at an *ortho*-carbon atom is rendered difficult by the presence of the *ortho*-chlorine atoms. The facts that *intermolecular* substitution was not observed and that the starting materials were

\* The physical evidence for the structure of compound (13) (see Experimental section) does not exclude the alternative isomeric structure (14). However, the formation of compound (14) would involve attack at a less reactive, more hindered site.

<sup>7</sup> A. L. Rocklin, *J. Org. Chem.*, 1956, **21**, 1478.

<sup>8</sup> S. Searles, *J. Amer. Chem. Soc.*, 1951, **73**, 124.

<sup>9</sup> R. B. Bates, L. M. Kroposki, and D. E. Potter, *J. Org. Chem.*, 1972, **37**, 560.

recovered indicate that deactivation was the more important factor preventing cyclisation. In marked contrast, the reaction of heptachloro-3-lithio-4,4'-bipyridyl (6) with ethylene oxide in boiling diethyl ether gave, besides the  $\beta$ -substituted ethanol (12), the dihydrofuro-pyridine derivative (13).<sup>\*</sup> In this case, the '*ortho*-position' is the reactive 2-position in the pyridine ring, and there is less steric hindrance to cyclisation. Compound (13) was also formed when the alkoxide derived from the 2-bipyridylethanol (12) was heated under reflux in diethyl ether.

Cyclisation of  $\gamma$ -polychloroarylpropanols should be less subject to steric hindrance than that of the corresponding  $\beta$ -substituted ethanols. The reaction of organolithium compounds with oxetan has been little studied,<sup>8</sup> but proved to furnish a convenient route to the required 3-pentachlorophenylpropan-1-ol (15) and 3-(tetrachloro-4-pyridyl)propan-1-ol (11). [The latter was also prepared by the reaction of (tetrachloro-4-pyridyl)-methyl-lithium with ethylene oxide.] Attempts were made to cyclise the alkoxides derived from the 3-polychloroarylpropanols (11) and (15) under conditions similar to those used for the 2-polychloroarylethanol, but no chromans were obtained.

The reactions of organolithium compounds with tetrahydrofuran normally give ethylene and the lithium enolate of acetaldehyde.<sup>9</sup> The 4-substituted butanol has been obtained only from triphenylsilyl-lithium<sup>10</sup> and (probably) from triphenylmethyl-lithium<sup>11</sup> and diphenylmethyl-lithium<sup>12</sup> (in the last two cases the products were not characterised). It has been noted<sup>13</sup> that pentachlorophenyl-lithium decomposes in tetrahydrofuran, but the products were not recorded; we have investigated them but we have not detected any 4-pentachlorophenylbutan-1-ol.

Since cyclisation by 'direct' intramolecular nucleophilic substitution was so difficult to achieve, the possibility of cyclisation by intramolecular addition to an aryne intermediate was investigated. Examples of such reactions have been reported, although they are apparently much less efficient than the corresponding reactions involving intramolecular addition of amines.<sup>14</sup>

The reaction of 2-pentachlorophenylethanol (10) with 2 mol. equiv. of *n*-butyl-lithium in diethyl ether at  $-70$  to  $-20^\circ$ , followed by hydrolysis, gave a mixture of 2-(tetrachlorophenyl)ethanols, which must have been derived from the organolithium intermediates (16), (17), or (18). When a similar reaction mixture was heated under reflux before being hydrolysed, the products included 4,5,6-trichloro-2,3-dihydrobenzo[*b*]furan (19),

<sup>10</sup> A. G. Evans, M. L. Jones, and N. H. Rees, *J. Chem. Soc. (B)*, 1969, 894.

<sup>11</sup> J. G. Carpenter, A. G. Evans, and N. H. Rees, *J.C.S. Perkin II*, 1972, 1598.

<sup>12</sup> H. Gilman and B. J. Gaj, *J. Org. Chem.*, 1963, **28**, 1725.

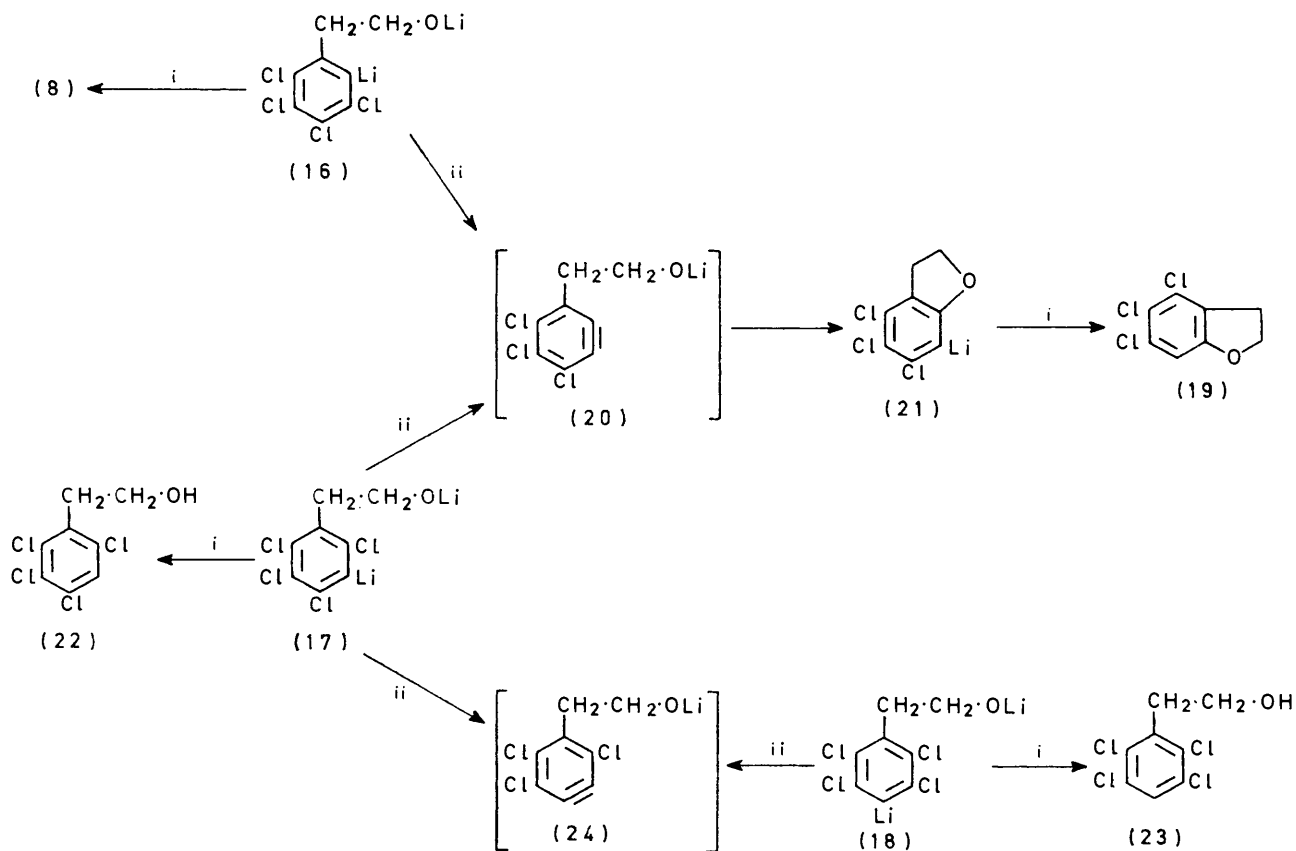
<sup>13</sup> M. D. Rausch, F. E. Tibbets, and H. B. Gordon, *J. Organometallic Chem.*, 1966, **5**, 493.

<sup>14</sup> R. Huisgen, H. König, and A. R. Lepley, *Chem. Ber.*, 1960, **93**, 1496; R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1967; cf. T. Kauffmann and H. Fischer, *Chem. Ber.*, 1973, **106**, 220.

identified by its mass and n.m.r. spectra (see Experimental section). Compound (19) must have arisen by cyclisation of the aryne (20), followed by hydrolysis of the intermediate (21). The yield of compound (19) was only 7%. However, the maximum yield possible depended on the proportions of the isomeric intermediates (16), (17), and (18), since only (16) and (17) could lead to the requisite aryne (20) (see Scheme). The

apparently more reactive than its unsubstituted analogue.<sup>14</sup> However, the reaction of 3-pentachlorophenylpropan-1-ol (15) with 2 equiv. of *n*-butyl-lithium failed to yield a chroman derivative.

The reaction of 2-(tetrachloro-4-pyridyl)ethanol (10) with 2 equiv. of *n*-butyl-lithium at  $-70$  to  $-20^\circ$ , followed by hydrolysis, gave an oil, which was distilled and separated by preparative t.l.c. into two components.



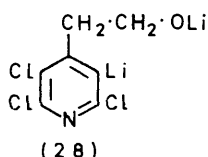
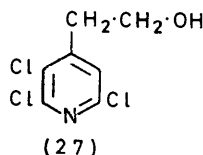
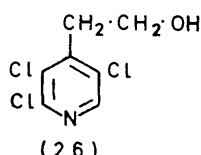
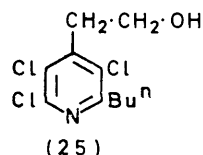
n.m.r. spectrum of 2-(2,3,4,5-tetrachlorophenyl)ethanol prepared as described above (see Table 2) showed a singlet due to the aromatic proton at  $\tau$  2.56. Since the mixture of 2-(tetrachlorophenyl)ethanols referred to above showed no signal at  $\tau$  2.56, but two singlets at  $\tau$  2.45 and 2.50 in a ratio of 3 : 7, it was clear that the reaction of 2-pentachlorophenylethanol with 2 mol. equiv. of *n*-butyl-lithium gave (17) and (18) but not (16) (*cf.* ref. 15). The signal at  $\tau$  2.45 was attributed to the *meta*-isomer (22) and that at  $\tau$  2.50 to the *para*-isomer (23) (*cf.* ref. 15). Thus, even if all the *meta*-lithio-isomer (17) gave aryne (20) rather than aryne (24), the maximum yield of compound (19) was *ca.* 30%. [Besides compound (19), the reaction gave an uncharacterised mixture, whose mass spectrum suggested that it consisted of compounds derived from intermolecular additions to arynes such as (24).] The halogenated aryne (20) is

The minor component showed <sup>1</sup>H n.m.r. signals at  $\tau$  6.06 (2H, t), 6.69 (2H, t), 7.05 (2H, t), 8.03 (1H, s, exchangeable), and 8.5 (7H, m) and its mass spectrum showed a molecular ion at *m/e* 281, with accompanying ions appropriate for three chlorine atoms. This component was thus probably the butylated derivative (25). The major component of the mixture comprised the two isomers (26) and (27); the mass spectrum showed a molecular ion at *m/e* 225 (Cl<sub>3</sub>), and the n.m.r. spectrum showed signals due to ring protons at  $\tau$  1.68 and 2.62 which were attributed to compounds (26) and (27), respectively (*cf.* ref. 16; this is one of the few cases where any metal-halogen exchange at the 2-position of a 4-substituted tetrachloropyridine has been observed). From the n.m.r. spectrum of the crude reaction mixture, the relative amounts of compounds (25)—(27) were estimated to be 37 : 13 : 50. However, although the

<sup>15</sup> D. J. Berry, I. Collins, S. M. Roberts, H. Suschitzky, and B. J. Wakefield, *J. Chem. Soc. (C)*, 1969, 1285.

<sup>16</sup> J. D. Cook and B. J. Wakefield, *J. Organometallic Chem.*, 1968, 13, 15.

precursor of compound (27), namely the dilithio-intermediate (28), might be expected to generate the required



2-pyridyne,<sup>17</sup> no cyclised products were obtained even when the solution was heated after the addition of n-butyl-lithium.

#### EXPERIMENTAL

All experiments involving organolithium compounds were carried out in dried solvents, under dry, oxygen-free

oxide (slight excess) in diethyl ether. The mixture was stirred at room temperature during 1–2 h and hydrolysed with water. Conventional work-up, followed by chromatography on silica, gave the  $\beta$ -substituted ethanol derivatives (7)–(12) in the yields shown in Table 1 and with the properties shown in Table 2.

In each case ca. 15% of the 'hydrolysis' product from the organolithium compound was also obtained. In the case of heptachloro-3-lithio-4,4'-bipyridyl, elution with 20% benzene in light petroleum gave 3H-heptachloro-4,4'-bipyridyl (17%); elution with benzene gave 5,6-dichloro-2,3-dihydro-4-(tetrachloro-4-pyridyl)furo[2,3-b]pyridine (12%), m.p. 237–238°,  $\tau$  (CDCl<sub>3</sub>) 5.20 (2H, t), 6.98 (2H, t) (Found: C, 34.9; H, 1.15; N, 6.7%;  $M^+$ , 401.8438. C<sub>12</sub>H<sub>4</sub>Cl<sub>6</sub>N<sub>2</sub>O requires C, 35.55; H, 1.0; N, 6.9%;  $M$ , 401.8452); elution with chloroform gave compound (12), as detailed in Tables 1 and 2.

(ii) *With oxetan.* The reaction and work-up were carried out as described in (i). Pentachlorophenyl-lithium gave 3-pentachlorophenylpropan-1-ol (43%), m.p. 97–98°,  $\tau$  (CDCl<sub>3</sub>) 6.28 (2H, t), 6.90 (1H, t), 8.14 (2H, m), and 8.31 (1H, s, exchangeable) (Found: C, 35.5; H, 2.4%;  $M^+$ , 306. C<sub>9</sub>H<sub>7</sub>Cl<sub>5</sub>O requires C, 35.05; H, 2.3%;  $M$ , 306). Tetrachloro-4-pyridyl-lithium gave 3-(tetrachloro-4-pyridyl)propan-1-ol (40%), b.p. 121° at 0.55 mmHg,  $\tau$  (CDCl<sub>3</sub>) 6.26

TABLE 1  
Synthesis of 2-polychloroarylethanol derivatives

Precursor for intermediate	Organolithium intermediate (estimated % yield)	Product	% Yield (% yield based on intermediate)
C <sub>6</sub> Cl <sub>6</sub>	C <sub>6</sub> Cl <sub>5</sub> Li (1) (82) <sup>a</sup>	C <sub>6</sub> Cl <sub>5</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·OH (7)	64 (78)
2,3,4,5-C <sub>6</sub> HCl <sub>4</sub> I	2,3,4,5-C <sub>6</sub> HCl <sub>4</sub> Li (2) (59) <sup>b</sup>	2,3,4,5-C <sub>6</sub> HCl <sub>4</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·OH (8)	31 (53)
1,2,3,4-C <sub>6</sub> H <sub>2</sub> Cl <sub>4</sub>	2,3,6-C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> Li (3) (62) <sup>c</sup>	2,3,6-C <sub>6</sub> H <sub>2</sub> Cl <sub>3</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·OH (9)	24 (39)
C <sub>6</sub> Cl <sub>5</sub> N	4-C <sub>6</sub> Cl <sub>4</sub> NLi (4) (66) <sup>d</sup>	4-C <sub>6</sub> Cl <sub>4</sub> N·CH <sub>2</sub> ·CH <sub>2</sub> ·OH (10)	65 (98)
4-MeC <sub>5</sub> Cl <sub>4</sub> N	4-LiCH <sub>2</sub> C <sub>5</sub> Cl <sub>4</sub> N (5) (73) <sup>e</sup>	4-C <sub>5</sub> Cl <sub>4</sub> N·CH <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·OH (11)	44 (60)
(4-C <sub>5</sub> Cl <sub>4</sub> N) <sub>2</sub>	C <sub>10</sub> Cl <sub>7</sub> N <sub>2</sub> Li (6) (77) <sup>f</sup>	C <sub>10</sub> Cl <sub>7</sub> N <sub>2</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> ·OH (12) <sup>g</sup>	42 (55) <sup>h</sup>

<sup>a</sup> Ref. 13. <sup>b</sup> N. J. Foulger and B. J. Wakefield, *J. Organometallic Chem.*, in the press. <sup>c</sup> I. Haiduc and H. Gilman, *Rev. Roumaine Chim.*, 1971, **16**, 907. <sup>d</sup> J. D. Cook, Ph.D. Thesis, Salford, 1969; cf. ref. 16. <sup>e</sup> Ref. 17. <sup>f</sup> J. D. Cook, N. J. Foulger, and B. J. Wakefield, *J.C.S. Perkin I*, 1972, 995. <sup>g</sup> The 2-substituted ethanol (12) was accompanied by the furopyridine (13), which was obtained in 12(16)% yield; see text.

TABLE 2  
Properties of 2-(polychloroaryl)ethanols

Compound <sup>a</sup>	M.p. or b.p. (°) [mmHg]	Formula	Found			Required			<sup>1</sup> H N.m.r. $\tau$ <sup>b</sup>
			C (%)	H (%)	$M^+$	C (%)	H (%)	$M$	
(7)	128	C <sub>6</sub> H <sub>5</sub> Cl <sub>5</sub> O	32.2	2.1	292	32.6	1.7	292	6.00 (2H, t), 6.54 (2H, t), 8.26 (1H, s, exch.)
(8)	72–73	C <sub>6</sub> H <sub>5</sub> Cl <sub>4</sub> O	37.4	2.4	258	36.95	2.3	258	2.56 (1H, s), 6.10 (3H, m), 7.00 (2H, t)
(9)	89 [1.5]	C <sub>6</sub> H <sub>7</sub> Cl <sub>3</sub> O	43.0	3.3	224	42.6	3.1	224	2.73 (2H, s), 6.16 (2H, t), 6.69 (2H, t), 8.30 (1H, s, exch.)
(10)	97–98	C <sub>7</sub> H <sub>5</sub> Cl <sub>4</sub> NO	32.65	2.3 <sup>d</sup>	259	32.2	1.9 <sup>d</sup>	259	6.05 (2H, t), 6.67 (2H, t), 8.22 (1H, s, exch.)
(11)	121 [0.55]	C <sub>8</sub> H <sub>7</sub> Cl <sub>4</sub> NO	34.7	3.0	271	35.2	2.6	271	6.26 (2H, t), 6.89 (2H, t), 8.12 (2H, m), 8.39 (1H, s, exch.)
(12)	216–218	C <sub>12</sub> H <sub>5</sub> Cl <sub>7</sub> N <sub>2</sub> O			437.8218			437.8218	6.22 (2H, t), 7.28 (2H, t), 8.29 (1H, s, exch.)

<sup>a</sup> All new compounds. <sup>b</sup> In CDCl<sub>3</sub>. <sup>c</sup> After addition of D<sub>2</sub>O, 2H, t. <sup>d</sup> Found: N, 5.1; required: N, 5.4%.

nitrogen. n-Butyl-lithium was used as a commercial solution in hexane. N.m.r. spectra were recorded at 60 MHz, with tetramethylsilane as internal reference and in carbon tetrachloride solution unless otherwise stated. Calculated *m/e* values refer to the ions containing <sup>35</sup>Cl only.

*Reactions of Polychloroaryl-lithium Compounds.*—(i) *With ethylene oxide.* To a stirred solution of the polychloroaryl-lithium compound in diethyl ether at –40 to –20° (see Table 1 for references) was added a solution of ethylene

(2H, t), 6.89 (2H, t), 8.12 (2H, m), and 8.39 (1H, s, exchangeable) (Found: C, 34.7; H, 3.0%;  $M^+$ , 271. C<sub>8</sub>H<sub>7</sub>Cl<sub>4</sub>NO requires C, 35.2; H, 2.6%;  $M^+$ , 271).

(iii) *With tetrahydrofuran.* A solution of pentachlorophenyl-lithium in tetrahydrofuran <sup>13</sup> was stirred at room temperature during 24 h. Hydrolysis with water, followed by conventional work-up and chromatography on silica

<sup>17</sup> J. D. Cook and B. J. Wakefield, *J. Chem. Soc. (C)*, 1969, 1973.

gave only hexachlorobenzene, pentachlorobenzene, and unidentified 'polymeric' materials.

*Attempted Cyclisation of  $\omega$ -Polychloroarylalkoxides.*—The  $\omega$ -polychloroarylalkoxides were prepared by one of two methods: (a) the reaction of a polychloroaryl-lithium compound with ethylene oxide or oxetan, as described above; (b) the reaction of the  $\omega$ -polychloroarylalkanol with 1 mol. equiv. of lithium hydride or *n*-butyl-lithium in the appropriate solvent.

Solutions of the alkoxides, prepared as described above, were heated under reflux during 3 h, (a) in diethyl ether, (b) in tetrahydrofuran, and (c) in pyridine. Starting material was recovered in good yield except in the case of 2-(heptachloro-4,4'-bipyridyl-3-yl)ethanol, which in diethyl ether gave 5,6-dichloro-2,3-dihydro-4-(tetrachloro-4-pyridyl)furo[2,3-*b*]pyridine (11%), identical with the compound described above.

*Reactions of  $\omega$ -Polychloroarylalkanol with Two Molar Equivalents of *n*-Butyl-lithium.*—(i) To 2-pentachlorophenyl-ethanol (10 mmol) in diethyl ether (150 ml) at  $-70^\circ$  was added 2.1M-*n*-butyl-lithium (10 ml). The mixture was stirred at  $-70^\circ$  during 15 min and at  $-20^\circ$  during 30 min. Water (100 ml) was added, and the crude product (2.7 g) was obtained by conventional work-up. Recrystallisation from light petroleum gave a mixture (1.8 g, 69%) of 2-(2,3,4,6-tetrachlorophenyl)ethanol and 2-(2,3,5,6-tetrachlorophenyl)ethanol, m.p. 69–70°,  $\tau$  2.45 and 2.50 (both s, total 1H), 6.20 (2H, t), and 6.65 (3H, m; after addition of  $D_2O$ , 2H, t) (Found: C, 36.6; H, 2.6%;  $M^+$ , 258. Calc. for  $C_6H_6Cl_4O$ : C, 37.0; H, 2.4%;  $M$ , 258).

(ii) The reaction was carried out as described above, except that the solution was stirred at room temperature during 3 h and under reflux during 1.5 h. Chromatography of the crude product (silica; 25% benzene–light petroleum) gave 4,5,6-trichloro-2,3-dihydrobenzo[*b*]furan (7%), m.p. 62°,

$\tau$  3.14 (1H, s), 5.34 (2H, t), and 6.75 (2H, t) (Found:  $M^+$ , 221.9404.  $C_8H_5Cl_3O$  requires  $M$  221.9404), and a mixture (1.3 g); the principal group of peaks at the high mass end of the mass spectrum of the mixture was at  $m/e$  ca. 480, corresponding to  $C_{16}H_{11}Cl_7O_2$ .

(iii) To 2-(tetrachloro-4-pyridyl)ethanol (5 mmol) in diethyl ether (100 ml) at  $-70^\circ$  was added 2.1M-*n*-butyl-lithium (5 ml). The mixture was stirred at  $-70^\circ$  during 15 min and as it warmed to room temperature during 30 min. Hydrolysis with water, followed by conventional work-up and distillation (Kugelrohr), gave an oil (0.70 g), b.p. 132° (at 2.5 mmHg). The components of the mixture could not be adequately purified, but preparative t.l.c. (silica; chloroform) gave components formulated as 2-butyl-3,4,6-trichloro-4-(2-hydroxyethyl)pyridine (0.15 g, 10%),  $\tau$  6.06 (2H, t), 6.69 (2H, t), 7.05 (2H, t), 8.03 (1H, s, exchangeable), and 8.5 (7H, m),  $M^+$  281 (Calc. for  $C_{11}H_{14}Cl_3NO^+$ :  $M$ , 281) and a mixture (0.33 g, 29%) of 2-(2,3,6-trichloro-4-pyridyl)ethanol and 2-(2,3,5-trichloro-4-pyridyl)ethanol,  $\tau$  ( $CDCl_3$ ) 1.68 and 2.62 (both s, total 1H), 6.02 (2H, t), and 7.0 (3H, m; after addition of  $D_2O$ , 2H, t),  $M^+$  225 (Calc. for  $C_7H_6Cl_3NO^+$ :  $M$ , 225).

(iv) A reaction was carried out as described in (iii). Before hydrolysis, diethyl ether was distilled off as methylcyclohexane (100 ml) was added, and the mixture was heated at 55° during 1 h. Hydrolysis with water followed by conventional work-up and chromatography on silica gave no identifiable products. Similar reactions with 3-(tetrachloro-4-pyridyl)propanol and 3-pentachlorophenylpropanol also failed to give identifiable products.

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