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POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS.
XIV*. SOME POLYCHLOROPHENYL COMPOUNDS CONTAINING SILICON AND TIN

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As an extension of our studies on thermally stable polymers and our related previous findings on the facile formation of tetrakis(trimethylsilyl)allene[2,3] from hexachlorobenzene and other polyhalogenated types by reaction with excess lithium and chlorotrimethylsilane, it was of interest to extend this novel reaction to some simple halogenated derivatives containing silicon and tin substituents, incidental to our studies[4] on highly halogenated polymers. The previously described organometallic reagents, pentachlorophenylmagnesium chloride[5-8] (I) pentachlorophenyllithium[9,10] (II) and 1,4-dilithiotetrachlorobenzene[9] (III) offered direct routes to the required derivatives.

Pentachlorophenylmagnesium chloride[5-8] (I) was prepared from hexachlorobenzene and excess magnesium in tetrahydrofuran (THF) using ethylene bromide to initiate the reaction. The corresponding lithio reagent, pentachlorophenyllithium (II), was prepared in THF solution by the proven procedure of halogen–metal exchange of hexachlorobenzene[10] or metalation of pentachlorobenzene[9] with n-butyllithium, respectively. Compounds herein described derived from (I) and (II) by derivatization with the appropriate chlorosilane or chlorostannane are: (pentachlorophenyl)dimethylsilane (IV), (pentachlorophenyl)triethylsilane (V) and (pentachlorophenyl)trimethyltin (VI).

The reactivity of the silicon–hydrogen bond of (pentachlorophenyl)dimethylsilane (IV) was of interest. It has previously been reported[11] that methyllithium effects cleavage of the silicon–pentachlorophenyl bond of (pentachlorophenyl)diphenylsilane to give, subsequent to derivatization with chlorotrimethylsilane, (pentachlorophenyl)-trimethylsilane and methyldiphenylsilane. Similar cleavage of the silicon–polyhalophenyl bond has been shown to occur on treatment of (pentafluorophenyl)diphenylsilane with methyllithium and with n-butyllithium, respectively[12].

Attempted phenylation of (IV) with phenyllithium in THF lead to cleavage of the silicon–aryl bond to give, subsequent to derivatization with chlorotrimethylsilane, (pentachlorophenyl)trimethylsilane (VII) and dimethylphenylsilane. The silicon–hydrogen bond in certain silanes can be alkylated by appropriate organolithium reagents in diethyl ether or by Grignard reagents in THF[13]. Most silanes are invariably inert to the action of Grignard reagents in diethyl ether[13]. The cleavage

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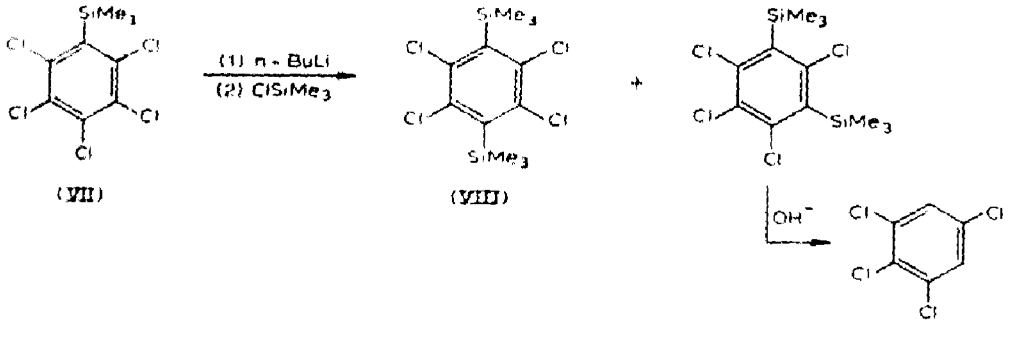
* For Part XIII see ref. 1.

observed in the present case is evidence for the lability of the silicon–polychlorophenyl bond in (IV).

Metalation of 1,2,4,5-tetrachlorobenzene with n-butyllithium (two equiv.) in either THF or ether according to the procedure of Tamborski[9] usually gives a mixture of 1,4-dilithiotetrachlorobenzene (III) and 2,3,5,6-tetrachlorophenyllithium. This mixture of organolithium reagents has previously[9] been carbonated to the corresponding carboxylic acids, tetrachloroterephthalic acid (43%) and 2,3,5,6-tetrachlorobenzoic acid (30%). We have observed that derivatization of such a mixture with chlorotrimethylsilane gave 1,4-bis(trimethylsilyl)tetrachlorobenzene (VIII) and (2,3,5,6-tetrachlorophenyl)trimethylsilane. In the present work, it was found advantageous in some cases to use n-butyllithium in excess of two equiv. (2.25–2.5 equiv.) with respect to 1,2,4,5-tetrachlorobenzene; such a procedure usually gave an improved yield of the 1,4-bis derivative subsequent to derivatization, and by inference an increased yield of the 1,4-dilithio intermediate. The use of excess n-butyllithium did not apparently increase the proportion of side-reactions involving nuclear chlorine; Color Test II[14] indicated the presence of unreacted n-butyllithium even after prolonged periods of reaction. 1,4-Dibromotetrachlorobenzene was used in some cases for the preparation of 1,4-dilithiotetrachlorobenzene (III); improved yields of derivatized products resulted.

The dilithio reagent (III) exhibits moderate stability in THF at −78°. However, in an unsuccessful attempt to prepare directly 1,4-bis(chlorodimethylsilyl)tetrachlorobenzene, it was desirable to add a THF solution of (III) to a large excess of dimethyldichlorosilane. The momentary rise in temperature which was inevitable during such addition caused considerable decomposition of 1,4-dilithiotetrachlorobenzene when dissolved in THF. No such decomposition was apparent when the dilithio compound (III) was prepared in diethyl ether.

Derivatization of 1,4-dilithiotetrachlorobenzene with chlorotrimethylsilane offers a direct route to 1,4-bis(trimethylsilyl)tetrachlorobenzene (VIII). It was found, in addition, that (pentachlorophenyl)trimethylsilane (VII)[15,16] on treatment with n-butyllithium (one equiv.) undergoes halogen–metal exchange at the *para* and *meta* positions to give, subsequent to derivatization with chlorotrimethylsilane, a mixture of (VIII) and 1,3-bis(trimethylsilyl)tetrachlorobenzene. The isomeric structure of the latter was deduced by basic hydrolysis to 1,2,3,5-tetrachlorobenzene:



Compounds described herein derived from 1,4-dilithiotetrachlorobenzene by derivatization with the appropriate chlorosilane or chlorostannane are: 1,4-bis(trimethylsilyl)tetrachlorobenzene (VIII), 1,4-bis(dimethylsilyl)tetrachlorobenzene (IX), 1,4-bis(dimethylphenylsilyl)tetrachlorobenzene (X), 1,4-bis(diphenylmethylsilyl)-tetrachlorobenzene (XI) and 1,4-bis(trimethylstannyl)tetrachlorobenzene (XII).

By analogy with the cleavage reaction of (pentachlorophenyl)dimethylsilane (IV) by phenyllithium in THF, it was also observed that 1,4-bis(dimethylsilyl)tetrachlorobenzene (IX) underwent cleavage of the silicon–polychlorophenyl bond on treatment with phenyllithium in ether or in THF. When the intermediate organometallic species, 1,4-dilithiotetrachlorobenzene, produced by such cleavage, was derivatized with chlorotrimethylsilane while the reaction mixture was maintained at low temperature, the products isolated were dimethylphenylsilane and 1,4-bis-(trimethylsilyl)tetrachlorobenzene (VIII). The silane (IX) was inert to phenylmagnesium bromide in both ether and THF.

EXPERIMENTAL

All reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. THF was dried and freed from peroxides by drying over sodium wire and distillation from sodium benzophenone ketyl before use. IR and NMR spectra were obtained using Perkin–Elmer Model 21 and Varian HR-60 spectrometers, respectively. Mol. wts. were determined mass spectrometrically. 1,4-Dibromotetrachlorobenzene was obtained by bromination of 1,2,4,5-tetrachlorobenzene according to a published procedure[17]. In certain cases, the identities of some products were confirmed by a comparison of their physical data with those of authentic materials.

(Pentachlorophenyl)dimethylsilane (IV)

Pentachlorophenyllithium was prepared by addition of n-butyllithium (0.15 mole) to pentachlorobenzene (37.57 g, 0.15 mole) in THF (200 ml) at −78°. After 3 h, Color Test II[14] was negative: Color Test I[18] was positive. Chlorodimethylsilane (18.9 g, 0.2 mole) was added dropwise to the organolithium solution at −78°; the mixture was stirred at low temperature overnight and then allowed to reach room temperature. A general work-up procedure was then employed: (1) concentrate the reaction mixture; (2) extract the residue with boiling petroleum ether (b.p. 60–70°) or with boiling benzene as appropriate according to the expected solubility of the product; (3) filter and concentrate the filtrate. Crystallization of the product thus obtained from ethanol gave (pentachlorophenyl)dimethylsilane (28.2 g, 60.9 %), m.p. 94–95°. The IR spectrum of the product showed characteristic bands (cm^{-1}) in accordance with this structure: Si–Me (1250); Si–H (2190) and Si–C_6Cl_5 (875, 1090). (Found: C, 31.52; H, 2.20. $C_8H_7Cl_5Si$ calcd.: C, 31.14; H, 2.29 %.)

Attempted arylation of (pentachlorophenyl)dimethylsilane (IV)

Phenyllithium (0.05 mole) was added to (IV) (15.4 g, 0.05 mole) in THF (100 ml) at −78°. The mixture was stirred at −78° for 6 h; Color Test I was still positive. Chlorotrimethylsilane (10.85 g, 0.1 mole) was then added and the mixture allowed to reach 20°. Normal work-up and distillation of the residue so obtained gave dimethylphenylsilane (4.5 g, 66.18 %), b.p. 48–50°/15 mm, n_D^{20} 1.4983 (lit.[19] values: b.p. 159.3°/760 mm; n_D^{20} 1.4995). The IR spectrum of this silane showed bands (cm^{-1}) attributable to Si–Me (1250), Si–H (2120) and Si–Ph (1430, 1114) groups. The residue from the distillation was crystallized from ethanol to give (pentachlorophenyl)trimethylsilane (VII) (7.5 g, 46.59%), m.p. and mixed m.p. 116–117°.

(Pentachlorophenyl)triethylsilane (V)

Pentachlorophenylmagnesium chloride was prepared from hexachlorobenzene (42.6 g, 0.15 mole) and magnesium (4.0 g, 0.165 g-atom) in THF (170 ml). To this filtered Grignard solution was added chlorotriethylsilane (25 g, 0.167 mole) and the resulting mixture was heated at reflux for 7 h. Work-up as before and fractionation of the reaction residue gave (pentachlorophenyl)triethylsilane (37.7 g, 70.7%), b.p. 143–147°/0.2 mm, n_D^{20} 1.5825, d_4^{20} 1.3725. (Found: Si, 8.0; MR_D, 88.7. $C_{12}H_{15}Cl_5Si$ calcd.: Si, 7.7%; MR_D, 88.2.)

(Pentachlorophenyl)trimethyltin (VI)

Pentachlorophenyllithium was prepared by the Tamborski procedure[9] from pentachlorobenzene (25.05 g, 0.1 mole) and n-butyllithium (0.1 mole) in THF (100 ml) at −78°. After 5 h, chlorotrimethyltin (19.93 g, 0.1 mole) in THF (25 ml) was added to the organolithium reagent at −78°. Work-up as before gave (pentachlorophenyl)-trimethyltin (30.3 g, 73.3%), m.p. 119–120° [from petroleum ether (b.p. 60–70°)]. (Found: C, 26.54; H, 1.85; Sn, 28.51; mol. wt., 413. $C_9H_9Cl_5Sn$ calcd.: C, 26.13; H, 2.18; Sn, 28.73%; mol. wt., 413.19.)

Preparation of 1,4-bis(trimethylsilyl)tetrachlorobenzene (VIII) in THF and in ether

n-Butyllithium (0.2 mole) was added to a suspension of 1,2,4,5-tetrachlorobenzene (21.6 g, 0.1 mole) in THF (200 ml) at −78°. After 5 h, Color Test II was negative; Color Test I was positive. Chlorotrimethylsilane (32.55 g, 0.3 mole) was added to the organolithium reagent at −78°; subsequent to the addition, Color Test I was negative.

A similar reaction using the same quantities of reactants was run in ether (200 ml) as solvent. Both reaction mixtures showed the presence of two main products by VPC after derivatization with chlorotrimethylsilane. The THF reaction mixture gave on work-up: (1) (2,3,5,6-tetrachlorophenyl)trimethylsilane (10.1 g, 35.0%), b.p. 90–95°/0.2 mm, m.p. 38–40°. The ^1H NMR spectrum of this product showed Si-Me (singlet, τ 9.37 ppm) and aromatic (singlet, 2.43 ppm) protons in the integrated ratio 9.5 : 1 (calcd. ratio 9 : 1) (Found: Si, 9.9. $C_9H_{10}Cl_4Si$ calcd.: Si, 9.75%.); (2) 1,4-bis(trimethylsilyl)tetrachlorobenzene (VIII) (17.5 g, 49%), b.p. 135–140°/0.075 mm, m.p. 81–83°. The ^1H NMR spectrum of (VIII) showed only Si-Me protons (singlet, τ 9.50 ppm) (Found: Si, 15.4. $C_{12}H_{18}Cl_4Si_2$ calcd.: Si, 15.5%.). The ether reaction mixture gave similarly: (2,3,5,6-tetrachlorophenyl)trimethylsilane (6.9 g, 23.9%) and (VIII) (20.3 g, 56.4%).

Lithiation of (pentachlorophenyl)trimethylsilane (VII)

n-Butyllithium (0.02 mole) was added to (VII) (6.4 g, 0.02 mole) in ether (100 ml) at −78°. After 3 h, Color Test II was negative; Color Test I was positive. The organolithium intermediate was derivatized with chlorotrimethylsilane (3.0 g, 0.028 mole). The reaction mixture was stirred at low temperature overnight and then allowed to reach 20°. Work-up gave a solid product which on crystallization from acetone gave a mixture of needle crystals and amorphous solid. Repeated fractional crystallization from acetone gave 1,4-bis(trimethylsilyl)tetrachlorobenzene (3.2 g, 44.4%), m.p. and mixed m.p. 81–83°, and needle crystals (0.8 g), m.p. 114–116°. The IR spectrum of this latter product showed Si-Me absorption (1250–1280 cm^{-1}) and no band due to aromatic hydrogen. The ^{1}H NMR spectrum showed only Si-Me protons (singlet, τ 9.48 ppm) to be present. Basic hydrolysis of this latter product (0.5 g) in THF (15 ml) with 0.1 *N* sodium hydroxide (1 ml) gave 1,2,3,5-tetrachlorobenzene (0.25 g), m.p. 51–52° (from ethanol), mixed m.p. with an authentic sample of 1,2,3,5-tetrachlorobenzene 50–52°. This evidence suggested this latter secondary product to be 1,3-bis(trimethylsilyl)tetrachlorobenzene. (Found: Si, 15.1. $C_{12}H_{18}Cl_4Si_2$ calcd.: Si, 15.5%.)

1,4-Bis(dimethylsilyl)tetrachlorobenzene (IX)

1,4-Dilithiotetrachlorobenzene, prepared from 1,2,4,5-tetrachlorobenzene (43.2 g, 0.2 mole) and n-butyllithium (0.4 mole) in THF (300 ml) at −78°, was derivatized with chlorodimethylsilane (56.7 g, 0.6 mole). The product obtained after the normal work-up was sublimed at 130°/0.05 mm to give 1,4-bis(dimethylsilyl)tetrachlorobenzene (10.1 g, 15.2%), m.p. 80–90°. Repeated crystallization from absolute ethanol gave a material of m.p. 90–91°. The ^{1}H NMR spectrum of the product showed Si-Me (doublet, τ 9.48, 9.54 ppm) and Si-H (multiplet, 4.87–5.14 ppm) in the integrated ratio 5.93:1 (calcd. ratio 6:1). (Found: C, 36.8; H, 4.27. $C_{10}H_{14}Cl_4Si_2$ calcd.: C, 36.15; H, 4.25%.)

Treatment of 1,2,4,5-tetrachlorobenzene (21.6 g, 0.1 mole) in THF (250 ml) with n-butyllithium (2.5 equiv.) at −78° and subsequent derivatization of the organolithium intermediate with chlorodimethylsilane (28.35 g, 0.3 mole) gave 1,4-bis(dimethylsilyl)tetrachlorobenzene (19.3 g, 58.15%), m.p. and mixed m.p. 90–91° (from ethanol).

Addition of n-butyllithium (0.15 mole) to 1,4-dibromotetrachlorobenzene (24.1 g, 0.65 mole) in THF (150 ml) at −78° and subsequent derivatization of the reaction mixture with chlorodimethylsilane (18.9 g, 0.2 mole) gave, after the usual work-up, 1,4-bis(dimethylsilyl)tetrachlorobenzene (8.7 g, 40.32%), m.p. and mixed m.p. 90–91°.

Attempted arylation of 1,4-bis(dimethylsilyl)tetrachlorobenzene (IX)

(*a*) *With phenyllithium in ether.* Phenyllithium (0.06 mole) was added to (IX) (9.96 g, 0.03 mole) in ether (100 ml) at −78°. After 2 h, the mixture was allowed to reach 20° whereupon Color Test I soon became negative. The product obtained after normal work-up was distilled to give dimethylphenylsilane (3.0 g, 36.7%), b.p. 47°/15 mm, n_D^{21} 1.4963. The IR spectrum of this product showed Si–Me, Si–H and Si–Ph bands and was identical with that of authentic dimethylphenylsilane.

(*b*) *With phenyllithium in THF.* Phenyllithium (0.06 mole) was added to (IX) (9.96 g, 0.03 mole) in THF (100 ml) at −78°. After 4 h at −78°, Color Test I was still positive. Chlorotrimethylsilane (excess) was added to the reaction mixture at −78° and the solution then allowed to warm to room temperature. Normal work-up and distillation of the reaction residue gave dimethylphenylsilane (2.3 g, 29%), b.p. 63°/30 mm, n_D^{20} 1.4985. Neutral alumina chromatography of the distillation residue using petroleum ether (b.p. 60–70°) as eluting agent, gave 1,4-bis(trimethylsilyl)tetrachlorobenzene (VIII) (3.5 g, 32.4%), m.p. and mixed m.p. 74–76°.

(*c*) *With phenylmagnesium bromide in ether and in THF.* Phenylmagnesium bromide (excess) was added to (IX) (9.96 g, 0.03 mole) in ether (100 ml) at room temperature. After 6 h, chlorotrimethylsilane (excess) was added to the reaction mixture. Subsequent to the usual work-up, 1,4-bis(dimethylsilyl)tetrachlorobenzene (IX) (6.0 g, 60.24%), m.p. and mixed m.p. 90–91°, was recovered unchanged. A similar result was obtained on reaction of (IX) with phenylmagnesium bromide in THF.

1,4-Bis(dimethylphenylsilyl)tetrachlorobenzene (X)

1,4-Dilithiotetrachlorobenzene, prepared from 1,2,4,5-tetrachlorobenzene (10.8 g, 0.05 mole) and n-butyllithium (0.1 mole) in THF (150 ml) at −78°, was derivatized with chlorodimethylphenylsilane (17.07 g, 0.1 mole). The mixture was stirred at −78° overnight and then allowed to reach 20°. The usual work-up gave 1,4-bis(dimethylphenylsilyl)tetrachlorobenzene (16.1 g, 66.53%), m.p. 114–115° (from acetone). The ^{1}H NMR spectrum of this product showed Si-Me (singlet, τ 9.24 ppm) and aromatic (multiplet, 2.44–2.83 ppm) protons in the integrated ratio 6:4.9 (calcd. ratio 6:5). (Found: Si, 10.9. $C_{22}H_{22}Cl_4Si_2$ calcd.: Si, 11.5%.)

1,4-Bis(diphenylmethylsilyl)tetrachlorobenzene (XI)

1,4-Dilithiotetrachlorobenzene, prepared from 1,2,4,5-tetrachlorobenzene (10.8 g, 0.05 mole) and n-butyllithium (0.1 mole) in THF (150 ml) at −78°, was derivatized with chlorodiphenylmethylsilane (23.3 g, 0.1 mole). The normal work-up procedure gave (XI) (18.9 g, 62.1%), m.p. 220–222°. The ^{1}H NMR spectrum of this product showed Si-Me (singlet, τ 9.03 ppm) and aromatic (multiplet, 2.48–2.84 ppm) protons in the integrated ratio 3:9.9 (calcd. ratio 3:10). (Found: Si, 8.6. $C_{32}H_{26}Cl_4Si_2$ calcd.: Si, 9.2%.)

1,4-Bis(trimethylstannyl)tetrachlorobenzene (XII)

1,4-Dilithiotetrachlorobenzene, prepared from 1,2,4,5-tetrachlorobenzene (21.6 g, 0.1 mole) and n-butyllithium (0.2 mole) in THF (100 ml) at −78°, was derivatized with a solution of chlorotrimethyltin (39.8 g, 0.2 mole) in THF (50 ml). The reaction mixture was stirred at low temperature overnight and then allowed to reach 20°. The normal work-up gave a semi-solid which on crystallization from petroleum ether (b.p. 60–70°) gave (XII) (17.3 g, 31.9%), m.p. 148–149.5°. (Found: C, 26.84; H, 3.25; Sn, 43.84; mol. wt., 541. $C_{12}H_{18}Cl_4Sn_2$ calcd.: C, 26.61; H, 3.33; Sn, 43.84%; mol. wt., 541.38.)

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SUMMARY

Pentachlorophenylmagnesium chloride (I), pentachlorophenyllithium (II) and 1,4-dilithiotetrachlorobenzene (III) have been employed for the preparation and characterization of some polychlorophenyl derivatives of silicon and tin by derivatiza-

tion of the respective organometallic reagents with the appropriate chlorosilane or chlorostannane. 1,4-Bis(trimethylsilyl)tetrachlorobenzene (VIII) was obtained indirectly, in addition to 1,3-bis(trimethylsilyl)tetrachlorobenzene, by lithiation of (pentachlorophenyl)trimethylsilane (VII) with n-butyllithium and derivatization of the organolithium intermediates with chlorotrimethylsilane. (Pentachlorophenyl)dimethylsilane (IV) underwent cleavage of the silicon–polychlorophenyl bond on treatment with phenyllithium in THF to give dimethylphenylsilane and (pentachlorophenyl)trimethylsilane subsequent to derivatization with chlorotrimethylsilane. Phenyllithium also effected the cleavage of the silicon–aryl bonds of 1,4-bis(dimethylsilyl)tetrachlorobenzene (IX) to give analogously, dimethylphenylsilane and 1,4-bis(trimethylsilyl)tetrachlorobenzene (VIII); (IX) was inert to phenylmagnesium bromide in THF and in ether.

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