

POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL
COMPOUNDS
XIII*. SOME PENTAHALOPHENYL-SUBSTITUTED POLYSILANES

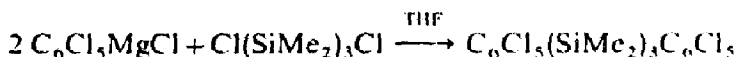
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Until recently the only pentachlorophenyl-silicon compound reported in the literature was (pentachlorophenyl)trichlorosilane, formed in low yield by the catalytic chlorination of phenyltrichlorosilane¹. The preparation of pentafluorophenylmagnesium halides^{2,3} and pentafluorophenyllithium^{4,5} led to the formation of silanes containing one or more pentafluorophenyl groups directly bonded to a silicon atom^{6,7}. By the use of pentachlorophenylmagnesium chloride^{8,9} or pentachlorophenyllithium^{10,11}, (pentachlorophenyl)trimethylsilane¹¹ together with a number of novel pentachlorophenyl-substituted chlorosilanes¹² and phenylsilanes¹³ have now been prepared. In a preliminary communication we reported the ultraviolet properties of a series of novel permethylated silanes containing pentahalophenyl groups¹⁴, and we now wish to report the syntheses of these compounds together with some of their spectral properties.

The pentachlorophenyl derivatives were prepared by coupling of the appropriate chloro- or dichloropermethylated silane in tetrahydrofuran (THF) with pentachlorophenylmagnesium chloride, formed in high yield by a modified procedure¹³.



However, an attempt to prepare hexamethyl(pentachlorophenyl)trisilane by coupling of the Grignard reagent in THF with chlorohexamethyltrisilane gave no tractable products, similar failure resulting from the use of the Grignard reagent in diethyl ether^{15,16} and pentachlorophenyllithium in THF.

Pentafluorophenyllithium⁴ was coupled with the appropriate dichloropermethylated silane in diethyl ether to give bis(pentafluorophenyl)dimethylsilane and -hexamethyltrisilane. As solutions of pentafluorophenyllithium are more stable in diethyl ether than THF¹¹, diethyl ether was used as solvent.

All attempts to prepare some of the perphenylated analogs have so far been unsuccessful. At the temperatures necessarily employed no pentahalophenyl derivatives were obtained from reactions of pentachlorophenylmagnesium chloride with 1,4-dichlorooctaphenyltetrasilane or 1,5-dichlorodecaphenylpentasilane; of penta-

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chlorophenyllithium with 1,4-dichlorooctaphenyltetrasilane, 1,4-dibromooctaphenyltetrasilane, or 1,2-dibromotetraphenyldisilane; or of pentafluorophenyllithium with 1,4-dichlorooctaphenyltetrasilane.

Preparation of pentachlorophenylmagnesium chloride in THF usually resulted in the formation of a small amount (*ca.* 5%) of 1,2,4,5-tetrachlorobenzene in a hydrolysed aliquot, indicating the presence of the 1,4-di-Grignard reagent¹³. Several attempts were made to produce a high proportion of this perchlorinated reactive species, but these attempts, either by the use of di-*n*-butyl ether as solvent, or by means of an exchange reaction between benzylmagnesium chloride and hexachlorobenzene¹³, were unsuccessful. The 3,6-dimetallation of 1,2,4,5-tetrachlorobenzene by the procedure of Tamborski *et al.* using *n*-butyllithium¹⁰ was successfully carried out but no tractable products resulted following treatment with chlorotrimethylsilane.

As expected, all the pentachlorophenyl derivatives were white, crystalline solids with fairly sharp melting points, whereas the two bis(pentafluorophenyl)-derivatives of the mono- and trisilanes were colorless, high-boiling liquids. Table 1 lists the melting points of the pentachlorophenyl derivatives: the bis(pentafluorophenyl)dimethylsilane and -hexamethyltrisilane had boiling points of 138–140°/14 mm and 116°/0.07 mm, respectively.

TABLE 1

MELTING POINTS OF THE PENTACHLOROPHENYL COMPOUNDS

Compound	M.p. (°C)	Compound	M.p. (°C)
C ₆ Cl ₅ SiMe ₃	116–117	C ₆ Cl ₅ (SiMe ₂) ₄ C ₆ Cl ₅	143–145
C ₆ Cl ₅ SiMe ₂ C ₆ Cl ₅	232–234	C ₆ Cl ₅ (SiMe ₂) ₅ C ₆ Cl ₅	129–130
C ₆ Cl ₅ (SiMe ₂) ₂ C ₆ Cl ₅	223–224	C ₆ Cl ₅ (SiMe ₂) ₆ C ₆ Cl ₅	148–149
C ₆ Cl ₅ (SiMe ₂) ₃ C ₆ Cl ₅	165–166		

During the course of the present work, Rausch and co-workers independently prepared (pentachlorophenyl)trimethylsilane by the reaction of chlorotrimethylsilane with pentachlorophenyllithium¹¹. Their observed melting point (116.5–117.5°) for this compound is in excellent agreement with ours.

The infrared spectra of all the pentachlorophenyl compounds in carbon tetrachloride solution were consistent with the formation of direct bonds between the silicon atom and the pentachlorophenyl moiety in place of the silicon–chlorine bonds of the initial chlorosilane. Thus a strong doublet occurred at 9.4 μ, doubtless arising from the silicon–aromatic carbon bond. The absorption due to a silicon–phenyl bond vibration occurs at *ca.* 9.0 μ, and in the present series of pentachlorophenyl compounds this vibration is shifted to a slightly longer wavelength by the chlorine atoms. A second absorption occurring as a strong singlet at 11.3 μ also appeared to be characteristic of the pentachlorophenyl moiety, both absorptions being consistent with those found for (pentachlorophenyl)trimethylsilane¹¹. Other absorptions appearing in the spectra were those expected for permethylated silanes.

Similarly, the spectra of the two bis(pentafluorophenyl) derivatives were consistent with the formation of direct silicon–pentafluorophenyl bonds. A strong

absorption occurred at 9.1μ , this silicon-phenyl vibration being shifted less than with the pentachlorophenyl moiety. The spectrum of tetrakis(pentafluorophenyl)silane also shows a strong absorption at 9.1μ .⁶

Ultraviolet spectral data of these pentahalophenyl derivatives in cyclohexane solution were published and discussed earlier¹⁴. All the pentachlorophenyl compounds had a major absorption at 216–217 $m\mu$, with an unusually high molar absorptivity which increased with the length of the silicon chain. For the two permethylated monosilanes the molar absorptivity was found to increase with the number of pentachlorophenyl moieties, as observed for the perphenylated pentachlorophenyl derivatives of silicon and tin¹³. The major absorption of the bis(pentafluorophenyl) compounds occurred at a shorter wavelength, and had a considerably lower molar absorptivity than the corresponding pentachlorophenyl derivative, as expected.

Nuclear magnetic resonance data for the bis(pentachlorophenyl) derivatives of the tri- and hexasilanes in carbon tetrachloride solutions were consistent with the formulation $C_6Cl_5(SiMe_2)_n C_6Cl_5$, where $n=3$ and 6. The spectrum of the trisilane showed two separate methyl absorptions as singlets at 9.42 and 9.68 τ in the ratio of 2:1, with the larger absorption at the lower field. Such splitting would be expected for a symmetrical, linear, hexamethylated trisilane containing pentachlorophenyl groups on the terminal silicon atoms. The presence of the pentachlorophenyl groups would cause the greater chemical shift for the adjacent four methyl groups, as observed. In the spectrum of the hexasilane, the anticipated three singlet absorptions occurred at 9.34, 9.77, and 9.86 τ , each of equal intensity, resulting from the methyl groups on pairs of equivalent silicon atoms. The spectrum of (pentachlorophenyl)trimethylsilane shows a singlet at 9.46 τ in solutions of carbon disulfide and carbon tetrachloride¹¹.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. The glassware was dried in an oven at 130°, assembled while hot, and purged with a stream of nitrogen. Tetrahydrofuran (THF) was dried over sodium wire. The α , ω -dichloropermethylated polysilanes and chlorohexamethyltrisilane were not commercially available and were prepared according to established procedures^{17–18}, as were the 1,4-¹⁹ and 1,5-dichloro-²⁰ and 1,4-dibromoperphenylated polysilanes²¹.

Molecular weight determinations were made using a Mechrolab vapor pressure osmometer, Model 201A. The infrared spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer, and ultraviolet data were recorded using a Beckman DK-2A spectrophotometer. Nuclear magnetic resonance data were measured with a Varian HR-60 spectrometer operating at 60 Mc. Melting points and boiling points are uncorrected.

(Pentachlorophenyl)trimethylsilane

A solution of pentachlorophenylmagnesium chloride¹³ (0.10 mole) in THF was added dropwise over 60 min to chlorotrimethylsilane (10.9 g, 0.10 mole) in THF (50 ml). After the addition a Color Test¹²² was negative, and the dark brown mixture was stirred overnight at room temperature before hydrolysis with dilute hydrochloric acid. The organic material was extracted into diethyl ether, and the aqueous portion discarded. Removal of the ether gave the crude product (20.0 g), m.p. 100–108°.

Recrystallisation from petroleum ether (b.p. 60–70°) gave 17.0 g (52%) of a white, crystalline solid, m.p. 116–117°. (Found: Si, 9.3; mol. wt., 322. C₉H₉Cl₅Si calcd.: Si, 8.7%; mol. wt., 322.5.)

Bis(pentachlorophenyl)dimethylsilane

Using a procedure essentially the same as that described above, pentachlorophenylmagnesium chloride (0.10 mole) was caused to react with dichlorodimethylsilane (6.5 g; 0.05 mole). The crude product (22.0 g), m.p. 216–222°, was recrystallised from petroleum ether (60–70°) to give 18.0 g (65%) of pure product, m.p. 232–234°. (Found: Si, 5.5; mol. wt., 565. C₁₄H₆Cl₁₀Si calcd.: Si, 5.0%; mol. wt., 556.8.)

1,2-Bis(pentachlorophenyl)tetramethyldisilane

Pentachlorophenylmagnesium chloride (0.10 mole) and 1,2-dichlorotetramethyldisilane (9.4 g, 0.05 mole) reacted to give 21.0 g of crude product, m.p. 218–222°. Recrystallisation from toluene gave 19.0 g (62%) of a white, crystalline product, m.p. 223–224°. (Found: Si, 9.2; mol. wt., 615. C₁₆H₁₂Cl₁₀Si₂ calcd.: Si, 9.15%; mol. wt., 615.0.)

1,3-Bis(pentachlorophenyl)hexamethyltrisilane

A reaction between the Grignard reagent (0.10 mole) and 1,3-dichlorohexamethyltrisilane (12.3 g, 0.05 mole) resulted in the formation of 18.0 g of crude product, m.p. 150–158°. Recrystallisation from petroleum ether (60–70°) gave 14.7 g of pure product, m.p. 165–166°. (Found: Si, 12.8; mol. wt., 686. C₁₈H₁₈Cl₁₀Si₃ calcd.: Si, 12.5%; mol. wt., 673.3.)

1,4-Bis(pentachlorophenyl)octamethyltetrasilane

By the usual procedure a reaction was carried out between the Grignard reagent (0.05 mole) and 1,4-dichlorooctamethyltetrasilane (7.6 g, 0.025 mole). The crude product (9.0 g), m.p. 130–134°, was recrystallised from petroleum ether (60–70°) to give 5.9 g (32%) of pure product, m.p. 143–145°. (Found: Si, 15.4.; mol. wt., 738. C₂₀H₂₄Cl₁₀Si₄ calcd.: Si, 15.4%; mol. wt., 731.3.)

1,5-Bis(pentachlorophenyl)decamethylpentasilane

The reaction between pentachlorophenylmagnesium chloride (0.0083 mole) and 1,5-dichlorodecamethylpentasilane (1.50 g, 0.00415 mole) gave 1.30 g of crude product, m.p. 115–119°. Recrystallisation from petroleum ether (60–70°) gave 1.0 g (31%) of pure product, m.p. 129–130°. (Found: Si, 17.7; mol. wt., 774. C₂₂H₃₀Cl₁₀Si₅ calcd.: Si, 17.8%; mol. wt., 789.4.)

1,6-Bis(pentachlorophenyl)dodecamethylhexasilane

A reaction was carried out in the usual manner between the Grignard reagent (0.062 mole) and 1,6-dichlorododecamethylhexasilane (13.0 g, 0.031 mole). The crude solid product (10.0 g), m.p. 138–142°, which partially separated from the reaction mixture, was recrystallised from petroleum ether (60–70°) to give 7.5 g (29%) of a white, crystalline product, m.p. 148–149°. (Found: Si, 20.2; mol. wt., 862. C₂₄H₃₆Cl₁₀Si₆ calcd.: Si, 19.9%; mol. wt., 847.6.)

Bis(pentafluorophenyl)dimethylsilane

Pentafluorophenyllithium (0.10 mole) was prepared in diethyl ether at *ca.* -65° by an exchange reaction between *n*-butyllithium (preformed in *n*-hexane by Foote Mineral Co., Exton, Penn.) and bromopentafluorobenzene⁴. The solution, maintained at *ca.* -65° , was divided into two equal portions. One-half was added, from an addition funnel surrounded by Dry Ice, to dichlorodimethylsilane (3.23 g, 0.025 mole) over 45 min. Throughout the addition the temperature of the reaction mixture was kept at *ca.* -65° . The mixture was then allowed to attain room temperature overnight, and hydrolysed with dilute hydrochloric acid. Extraction with diethyl ether, followed by distillation, gave 6.8 g (70%) of a colorless liquid, b.p. $138-140^{\circ}/14$ mm, shown by vapor phase chromatography to contain only one component. (Found: Si, 6.8; mol. wt., 397. $C_{14}H_6F_{10}Si$ calcd.: Si, 7.15%; mol. wt., 392.3.)

1,3-Bis(pentafluorophenyl)hexamethyltrisilane

The second portion of pentafluorophenyllithium (0.05 mole) in diethyl ether, maintained at *ca.* -65° , was added over 45 min to 1,3-dichlorohexamethyltrisilane (6.14 g, 0.025 mole). Distillation gave 9.0 g (71%) of a colorless liquid, b.p. $116^{\circ}/0.07$ mm, shown by vapor phase chromatography to be a single compound. (Found: Si, 16.4; mol. wt., 500. $C_{18}H_{18}F_{10}Si_3$ calcd.: Si, 16.55%; mol. wt., 508.6.)

Attempted reactions of some α, ω -dihaloperphenylated polysilanes

(a) *With pentachlorophenylmagnesium chloride.* Coupling of the Grignard reagent in THF with 1,4-dichlorooctaphenyltetrasilane and 1,5-dichlorodecaphenylpentasilane was attempted by the usual procedure, on a 0.05 mole scale. Even after the reaction mixtures had been refluxed for 24 h, Color Test 1²² was positive in both cases, and hydrolysed samples were shown by vapor phase chromatography to each contain pentachlorobenzene as the major component. In both cases the Color Test was negative after 2 days. Work-up by the usual method gave white solids which were identified as the α, ω -dihydroxy derivatives (mixed m.p.). Thus no reaction of the dichloro compounds would appear to have occurred until the final hydrolysis stage.

(b) *1,4-Dichlorooctaphenyltetrasilane with pentachlorophenyllithium.* The pentachlorophenyllithium was prepared in THF by an exchange reaction between *n*-butyllithium (0.05 mole) in *n*-hexane and hexachlorobenzene (14.24 g, 0.05 mole), following a procedure similar to that used for the preparation of pentafluorophenyllithium. To this lithium compound was added 1,4-dichlorooctaphenyltetrasilane (20.0 g, 0.025 mole). After 15 h with the reaction mixture maintained at *ca.* -65° a Color Test I was still strongly positive, and pentachlorobenzene was the predominant product formed on hydrolysis of an aliquot (vapor phase chromatography). The temperature of the mixture was gradually raised, but the Color Test I persisted until the temperature had been at 0° for 5 h. A trace of pentachlorobenzene was still apparent. The residual solid (6.4 g) was filtered off and shown to be the unchanged dichloro-compound (mixed m.p.). Following hydrolysis and extraction as usual, the diethyl ether was removed and petroleum ether ($60-70^{\circ}$) added. The solid thus formed (9.9 g), m.p. $170-188^{\circ}$, was an unidentified mixture.

(c) *Dibromo compounds with pentachlorophenyllithium.* Reactions of 1,2-dibromotetraphenyldisilane and 1,4-dibromooctaphenyltetrasilane with pentachlorophenyllithium in THF were attempted following the usual general procedure. In both

cases Color Test I was strongly positive after 20 h with the reaction mixtures at *ca.* -65° , and pentachlorobenzene was predominant in hydrolysed aliquots. Only after the reaction mixture had been at 0° for several hours did the Color Tests^{22,23} give a negative result. No solid was apparent in either reaction mixture, and, following hydrolysis and extraction, no tractable products were isolated.

(d) *1,4-Dichlorooctaphenyltetrasilane with pentafluorophenyllithium.* Pentafluorophenyllithium (0.05 mole), prepared in diethyl ether by the exchange reaction⁴, was added at *ca.* -65° to 1,4-dichlorooctaphenyltetrasilane (20.0 g, 0.025 mole) over 60 min. The reaction mixture was maintained at *ca.* -65° for 4 h. After this time a Color Test I was still strongly positive, and the mixture was allowed to attain room temperature overnight. The Color Test was then negative. However, 19.5 g (98%) of the 1,4-dichlorooctaphenyltetrasilane was reclaimed (mixed m.p.), showing that reaction had taken place to a negligible extent.

Attempted reactions of chlorohexamethyltrisilane

(a) *With pentachlorophenylmagnesium chloride in THF.* The Grignard reagent (0.10 mole) in THF was added over 2 h to chlorohexamethyltrisilane (21.09 g, 0.10 mole). Color Test I was negative after a further hour, and the dark brown reaction mixture was hydrolysed and extracted as usual. Removal of the solvent gave an intractable brown tar.

(b) *With pentachlorophenylmagnesium chloride in diethyl ether.* The Grignard reagent was prepared in diethyl ether using the modified entrainment method of Pearson *et al.*^{15,16}, and 0.01 mole of the solution added to chlorohexamethyltrisilane (2.11 g, 0.01 mole) over 30 min. After 48 h at room temperature, pentachlorobenzene was still the major component in a hydrolysed aliquot of the reaction mixture (vapor phase chromatography). Only a trace of the pentachlorobenzene remained after the mixture had been refluxed for 36 h. Following hydrolysis and extraction as usual, no tractable products were isolated.

(c) *With pentachlorophenyllithium in THF.* Pentachlorophenyllithium was prepared as usual in THF, and 0.01 mole of the solution added at *ca.* -65° to chlorohexamethyltrisilane (2.11 g, 0.01 mole) over 30 min. Color Test I was negative after the addition. The reaction mixture was allowed to attain room temperature, and was then hydrolysed and extracted. Removal of the solvent gave a yellow solid (0.7 g), m.p. $200-213^{\circ}$. The infrared spectrum of this material showed broad bands characteristic of polymers with no Si-H absorption. Attempts to recrystallise the solid were unsuccessful.

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SUMMARY

The synthesis of a series of novel, permethylated silanes containing pentachlorophenyl groups by the reaction of pentachlorophenylmagnesium chloride with

the appropriate chlorosilane is described. Two bis(pentafluorophenyl) analogs have also been synthesised using pentafluorophenyllithium, but attempts to prepare similar perphenylated silanes have failed. Infrared, ultraviolet, and nuclear magnetic resonance spectral data are presented to confirm the structure of these compounds.

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