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(Pentachlorophenyl)tris(trimethylsilyl)silane and 1,4-bis[tris(trimethylsilyl)silyl]tetrachlorobenzene

In connection with studies concerned with thermally stable compounds an examination is being made of some organosilicon compounds containing a perhalogenated aryl group and the highly branched symmetrical tris(trimethylsilyl) moiety. One of the simpler compounds in this series is (pentachlorophenyl)tris(trimethylsilyl)silane (I). This has been synthesized by the following three reactions:

$$\left.\begin{array}{l} C_6Cl_5MgCl + ClSi(SiMe_3)_3 \\ C_6Cl_6 + LiSi(SiMe_3)_3 \\ C_6Cl_6 + NaSi(SiMe_3)_3 \end{array}\right] \rightarrow \underset{\text{(I)}}{C_6Cl_5Si(SiMe_3)_3}$$

The structure of (I) was established by: (*a*) appropriate analytical procedures; (*b*) the three syntheses illustrated above; and (*c*) hydrolysis to pentachlorobenzene.

We are also reporting at this time some orienting studies concerned with the introduction of more than one $(Me_3Si)_3Si$ group to give 1,4-bis[tris(trimethylsilyl)silyl]tetrachlorobenzene. This was prepared by the following reactions:

$$\left.\begin{array}{l} C_6Cl_6 + 2\ LiSi(SiMe_3)_3 \\ C_6Cl_6 + 2\ NaSi(SiMe_3)_3 \end{array}\right] \rightarrow p\text{-}(Me_3Si)_3Si{-}C_6Cl_4{-}Si(SiMe_3)_3$$

The positions of the $(Me_3Si)_3Si$ groups were established by alkaline cleavage to give 1,2,4,5-tetrachlorobenzene. In addition, the 1,4-positions were shown to be the ones involved by the following reaction sequences:

$$1,2,4,5\text{-}C_6Cl_4H_2 + n\text{-}BuLi \rightarrow p\text{-}LiC_6Cl_4Li$$
$$p\text{-}LiC_6Cl_4Li + 2\ ClSi(SiMe_3)_3 \rightarrow p\text{-}(Me_3Si)_3SiC_6Cl_4Si(SiMe_3)_3$$

Experimental

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Glassware was dried in an oven at 130°, assembled while hot and purged with a stream of nitrogen. The tetrahydrofuran was dried and purified by refluxing over sodium wire, followed by distillation into lithium aluminum hydride, from which it was distilled immediately before use. Melting and boiling points are uncorrected.

Reaction of pentachlorophenylmagnesium chloride with tris(trimethylsilyl)chlorosilane. To a solution of 1.77 g (0.00635 mole) of tris(trimethylsilyl)chlorosilane in 10 ml of THF was added a solution of 0.007 mole of pentachlorophenylmagnesium chloride. After stirring for 18 h at room temperature the mixture was hydrolyzed. Work-up gave 1.3 g (41%) of (pentachlorophenyl)tris(trimethylsilyl)silane, melting at 126–127.5° after crystallization from ethanol. [Found: Si, 23.1, 23.3; mol. wt. (vapor pressure osmometer), 508. $C_{15}H_{27}Si_4Cl_5$ calcd.: Si, 22.5%; mol. wt., 497.]

The infrared spectrum was consistent with the assigned structure and showed absorptions at the following positions (cm^{-1}): 2970 (w), 2940 (w), 2890 (w), 1387 (w), 1330 (w), 1310 (w), 1285 (m), 1238 (s), 1080 (m), 833 (s). The band at 1080 cm^{-1}

is probably due to the presence of the pentachlorophenyl group.

1,4-Bis[tris(trimethylsilyl)silyl] tetrachlorobenzene. First, the 1,4-dilithiotetrachlorobenzene was prepared in accordance with the procedure of Tamborski and co-workers[1] using 4.3 g (0.02 mole) of 1,2,4,5-tetrachlorobenzene in 80 ml of THF at −50° with a solution of 25.6 ml of n-butyllithium (0.04 mole) in hexane. After 5 h of stirring Color Test II[2] was negative. A solution of 11.3 g (0.04 mole) of tris(trimethylsilyl)chlorosilane in 35 ml of THF was added to the dilithio compound during 1 h at −50°. After stirring for 10 hours at −50° and then allowing the mixture to come to room temperature, work-up gave 2.35 g (20.1 %) of solid melting over the range 240–262°, subsequent to crystallizations from ethyl acetate or benzene. Additional recrystallizations or chromatography on alumina had no effect on the melting range. The infrared spectrum showed the expected absorptions for Si–Me and a strong band at 1065 cm^{-1}. The latter is probably due to the tetrachlorobenzene moiety.

1 : 1 *Ratio of hexachlorobenzene and tris(trimethylsilyl)silyllithium in THF.* The 0.044 mole of tris(trimethylsilyl)silyllithium [prepared[3] in a conventional manner from tetrakis(trimethylsilyl)silane] was added during 1.5 h to a mixture of 12.5 g (0.044 mole of hexachlorobenzene in 200 ml of THF maintained at −35°. Color Test I[4] was negative just after completion of the addition; and the mixture was stirred overnight during which time it had reached room temperature. Subsequent to concentration by rotary evaporation the mixture was poured into an ice-water mixture to precipitate 23.6 g of a solid which after sublimation gave 10 g of product. Recrystallizations from benzene yielded 5.6 g of hexachlorobenzene, and 1.5 g (7.2%) of (pentachlorophenyl)tris(trimethylsilyl)silane, m.p. 125–126.5°. This compound was obtained by ethanol crystallization of the solid remaining after removal of the hexachlorobenzene, and a mixed melting point with the compound from pentachlorophenylmagnesium chloride and tris(trimethylsilyl)chlorosilane was not depressed.

1 : 1 *Ratio of hexachlorobenzene and tris(trimethylsilyl)silyllithium in THF.* In this experiment the tris(trimethylsilyl)silyllithium was prepared from 16 g (0.05 mole) of tetrakis(trimethylsilyl)silane, 1.4 g (0.2 g-atom) of lithium (1% sodium content), and 2 g of biphenyl in 100 ml of THF[5]. Titration showed 0.0904 mole of basic material, and this solution was added (during 1.5 h) to 25.6 g (0.09 mole) of hexachlorobenzene in 300 ml of THF kept at −30°. After customary work-up there was obtained 7.5 g of hexachlorobenzene, and 7.6 g (30.6%) of pure (pentachlorophenyl)tris(trimethylsilyl)silane (m.p. and mixed m.p. 126.5–127.5°).

1 : 1 *Ratio of hexachlorobenzene and tris(trimethylsilyl)silylsodium in THF.* To a mixture of 21.8 g (0.077 mole) of hexachlorobenzene in 200 ml of THF kept at −30° was added a 0.027 molar solution of tris(trimethylsilyl)silylsodium prepared from 16 g (0.05 mole) of tetrakis(trimethylsilyl)silane, 4.6 g (0.2 g-atom) of sodium and 1.5 g of biphenyl in 100 ml of THF. The mixture was stirred overnight (negative Color Test I). From the dark colored reaction mixture there was obtained 3.75 g of hexachlorobenzene and 8.5 g (24.1%) of (pentachlorophenyl)tris(trimethylsilyl)silane (m.p. and mixed m.p. 125.5–127.5°).

1 : 2 *Ratio of hexachlorobenzene and tris(trimethylsilyl)silyllithium in THF.* A reaction was carried out between 12.5 g (0.044 mole) of hexachlorobenzene and 0.088 mole of tris(trimethylsilyl)silyllithium [prepared from tetrakis(trimethylsilyl)silane and methyllithium] in 100 ml of THF. One-half of the tris(trimethylsilyl)silyllithium solution was added during 1.5 h at room temperature, and the remainder below −40°

during a two-hour period. The mixture became black and Color Test I was negative after stirring overnight. Subsequent to concentration, the mixture was poured into iced-water; the organic material was extracted by ether; removal of the ether gave a tar which was dissolved in a small volume of petroleum ether (b.p. 90–100°). On working up the reaction mixture there was obtained 3.0 g (11%) of 1,4-bis[tris(trimethylsilyl)silyl]tetrachlorobenzene (m.p. range 241–261°). The compound was shown to be identical (IR, m.p. and mixed m.p.) with the product obtained by reaction of 1,4-dilithiotetrachlorobenzene and tris(trimethylsilyl)chlorosilane.

In an orienting experiment in which a 1:2 ratio of hexachlorobenzene and tris(trimethylsilyl)silyllithium prepared from tetrakis(trimethylsyl)silane, lithium (1% sodium), and 2 g of biphenyl, there was isolated 1.3 g of (pentachlorophenyl)tris(trimethylsilyl)silane melting at 125–127.5° (mixed m.p.).

1:2 *Ratio of hexachlorobenzene and tris(trimethylsilyl)silylsodium.* The silylsodium compound was prepared from tetrakis(trimethylsilyl)silane, sodium, and biphenyl. There was obtained 3.8 g (20.7%) of 1,4-bis[tris(trimethylsilyl)silyl]tetrachlorobenzene, melting range 241–262°. The compound was shown to be the same as that obtained from the 1,4-dilithiotetrachlorobenzene reaction.

1:3 *Ratio of hexachlorobenzene and tris(trimethylsilyl)silylsodium.* The silylsodium compound was prepared from tetrakis(trimethylsilyl)silane, sodium, and biphenyl. There was isolated from among the reaction products 9.3 g (34.4%) of the 1,4-bis[tris(trimethylsilyl)silyl]tetrachlorobenzene, melting over the range 242–261°. The compound was shown to be the same as that from the 1,4-dilithiotetrachlorobenzene reaction.

Alkaline hydrolyses. From the hydrolysis of (0.5 g) of (pentachlorophenyl)-tris(trimethylsilyl)silane in aqueous THF/sodium hydroxide there was isolated 0.17 g (68%) of pentachlorobenzene (m.p. and mixed m.p. 85–87°).

In like manner, 0.5 g of 1,4-bis[tris(trimethylsilyl)silyl]tetrachlorobenzene gave 0.1 g (66.6%) of 1,2,4,5-tetrachlorobenzene (m.p. and mixed m.p. 141–142°).

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