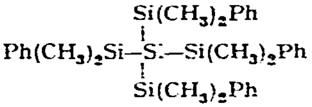
The preparation of tetrakis(dimethylphenylsilyl)silane

Since the preparation of the first branched-chain polysilane having contiguous silicon atoms, tris(triphenylsilyl)silane, in 1959[1], the synthesis and characterization of some novel, highly symmetrical tetrasilyl-substituted compounds of the type: $[R(CH_3)_2Si]_4E$ (where R = H, CH_3, OCH_3 or OC_2H_5, and E = C[2-5]; R = H or CH_3, and E = Si[6,7]) have recently been described. A number of structurally related compounds, $[Ph_3E]_4E'$ (where E = Pb or Sn and E' = C, Pb, Sn or Ge), has also been reported[8-13]. To date, attempts to prepare similar phenylated tetrasilyl-substituted polysilanes have failed[1,2,14].

We are now reporting the preparation of tetrakis(dimethylphenylsilyl)silane(I).



$$Ph(CH_3)_2Si{-}\overset{\displaystyle Si(CH_3)_2Ph}{\underset{\displaystyle Si(CH_3)_2Ph}{Si}}{-}Si(CH_3)_2Ph$$

(I)

Compound (I) was prepared by two independent methods: the reaction between silicon tetrachloride, chlorodimethylphenylsilane and lithium;

$$SiCl_4 + 4\ Ph(CH_3)_2SiCl + 8\ Li \xrightarrow{THF} (I) + Ph(CH_3)_2SiSi(CH_3)_2Ph \qquad (1)$$

and the reaction between dimethylphenylsilyllithium and silicon tetrachloride.

$$SiCl_4 + 4\ Ph(CH_3)_2SiLi \xrightarrow{THF/Et_2O} (I) + Ph(CH_3)_2SiSi(CH_3)_2Ph \qquad (2)$$

Reaction (1) was carried out at room temperature in tetrahydrofuran (THF) and the yield of (I) obtained by this procedure was quite low (3.5 %). The conditions used in Method (2), namely, a low temperature (−40°) and THF/ether as solvents, seemed more favorable for the formation of (I), giving a 14.6 % yield.

It seems reasonable that the low yield of (I) might be due to steric crowding of atoms in the molecule imposed by the four bulky phenyl groups, and that a high order of orientation of reactant species is necessary for the formation of the product. The rigorous steric requirement presumably increases the probability of some secondary reactions leading to the formation of the less sterically hindered compound, 1,1,2,2-tetramethyl-1,2-diphenyldisilane, in high yields (60–65 %). Presumably these reactions involve: (1) cleavage of an intermediate disilane by silyllithium,

$$Ph(CH_3)_2SiLi + SiCl_4 \longrightarrow Ph(CH_3)_2SiSiCl_3 + LiCl$$

$$Ph(CH_3)_2SiLi + Ph(CH_3)_2SiSiCl_3 \longrightarrow Ph(CH_3)_2SiSi(CH_3)_2Ph + LiSiCl_3$$

and (2) direct coupling of chlorodimethylphenylsilane and dimethylphenylsilyllithium*.

$$Ph(CH_3)_2SiCl + Ph(CH_3)_2SiLi \longrightarrow Ph(CH_3)_2SiSi(CH_3)_2Ph + LiCl$$

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* Dimethylphenylsilyllithium could be formed by Method (1) from the reaction between chlorodimethylphenylsilane and lithium[15]. A halogen–metal interconversion reaction between dimethylphenylsilyllithium and silicon tetrachloride (Method 2) would afford chlorodimethyl phenylsilane[16].

Thus, it is not surprising that tris(triphenylsilyl)silane was prepared in a 4.4 % yield and attempts to synthesize tetrakis(triphenylsilyl)silane gave only hexaphenyldisilane, triphenylsilane and some polymeric material[1]. It is also noteworthy that whereas tetrakis(dimethylsilyl)methane and tetrakis(trimethylsilyl)methane can be prepared by a reaction between a chlorosilane, polyhalo methane and magnesium, application of the technique to the attempted preparation of tetrakis(dimethylphenylsilyl)methane gave good yields of bis(dimethylphenylsilyl)methane; and no tetrakis compound was isolated[2]. It appears that the formation of tetrasilyl-substituted methanes and silanes is limited by the number of large groups bonded to the peripheral silicon atoms.

Compound (I), a white crystalline solid, is very soluble in nonpolar solvents; sparingly soluble in ethanol; and insoluble in methanol. Its melting point, 133–134°, is appreciably lower than that of tetrakis(trimethylsilyl)silane (II) (m.p. 319–321°, sealed tube)* but higher than tetrakis(dimethylsilyl)silane (III) (m.p. 40–42°)[6].

$[(CH_3)_3Si]_4Si$ (II) $[H(CH_3)_2Si]_4Si$ (III)

Unlike (II), compound (I) does not sublime under ordinary conditions and both compounds melt without decomposition.

The ^1H NMR spectrum of (I) (CS_2) shows a sharp singlet at 9.72τ for the Si–CH_3 protons and a multiplet for the Si–Ph protons centered at 2.91τ (aliphatic/aromatic proton ration = 1.2; calcd. 1.2), and its ultraviolet spectrum consists of a band at λ_{max} in cyclohexane 242 mμ (ε 38,600). The analyses and its infrared spectrum are in agreement with the proposed structure.

Experimental

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Melting and boiling points are uncorrected. The THF was freed from peroxide and moisture by refluxing over sodium, followed, by distillation from lithium aluminum hydride immediately before use.

Preparation of tetrakis(dimethylphenylsilyl)silane (I)

(1) The reaction of chlorodimethylphenylsilane, silicon tetrachloride and lithium. To 81.6 g (0.48 mole) of chlorodimethylphenylsilane, 6.72 g (0.96 g-atom) of lithium and 200 ml of THF was added dropwise 20 g (0.12 mole) of silicon tetrachloride dissolved in 50 ml of THF over a period of 3 h. Upon complete addition, the reaction mixture was stirred for 20 h at room temperature prior to filtration through glass wool. The organic layer was separated and dried over sodium sulfate subsequent to acid hydrolysis. Removal of the organic solvents under reduced pressure gave an oil which was chromatographed on neutral alumina. Elution with petroleum ether (b.p. 60–70°) gave a liquid which had the same retention time (VPC) as a known sample of 1,1,2,2-tetramethyl-1,2-diphenyl-disilane. Purification of this liquid by distillation afforded 25.9 g (63.6 %) of pure 1,1,2,2-tetramethyl-1,2-diphenyldisilane, b.p. 125–128°/1.8 mm, m.p. 34–35° (mixed m.p.) (lit. value[17]: b.p. 128–130°/1.8 mm, m.p. 34–35°). Further elution with benzene gave 2.4 g (3.5 %) of (I), m.p. 133–135°,

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* The previously reported[7] melting point of 261–263° is presumably a transition point. The authors are grateful to R. L. HARRELL and S.-Y. SIM for their assistance in checking this melting point.

subsequent to purification by crystallization from benzene. (Found: Si, 24.5; mol. wt. vapor pressure osmometer, 506. $C_{32}H_{44}Si_5$ calcd.: Si, 24.6%; mol. wt., 507.)

The infrared spectrum (CCl_4) showed prominent absorptions in μ at: 3.26 (m), 3.38 (m), 3.45 (m), 7.0 (s), 7.12 (w), 8.06 (s) and 9.06 (s).

(2) *The reaction of dimethylphenylsilyllithium and silicon tetrachloride.* To 280 ml of a THF/ether (1:2) solution of 0.12 mole of freshly prepared dimethylphenylsilyllithium (prepared by the cleavage of 1,1,2,2-tetramethyl-1,2-diphenyldisilane with lithium in THF[16]), cooled to —40° was added dropwise 5.1 g (0.03 mole) of silicon tetrachloride dissolved in 20 ml of ether. Color Test I[18] was negative upon complete addition and the reaction mixture was stirred at room temperature for *ca.* 1 h. Hydrolysis of the reaction mixture with 200 ml of a saturated ammonium chloride solution followed by the usual work-up afforded an oil which was chromatographed on neutral alumina. Elution with petroleum ether (b.p. 60–70°) gave 9 g (60%) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane, b.p. 126–127°/1.8 mm, m.p. 34–35° (mixed m.p.) after purification by distillation. Further elution with benzene gave, after crystallization from acetone, 2.5 g (14.6%) of (I), m.p. 133–134° (mixed m.p.).

Preparation of tetrakis(triphenylsilyl)silane (attempted)

A solution of 70.8 g (0.24 mole) of chlorotriphenylsilane, 10 g (0.06 mole) of silicon tetrachloride and 250 ml of THF was added dropwise to 3.36 g (0.48 g-atom) of lithium and 20 ml of THF. The reaction mixture immediately became exothermic and, after complete addition, the reaction was stirred overnight at room temperature. Subsequent to filtration through glass wool, the reaction mixture was hydrolyzed with 200 ml of 1 N hydrochloric acid. Hexaphenyldisilane, 41 g (66.5%), m.p. 355–358° (mixed m.p.), was removed by filtration. The organic layer of the filtrate was separated and dried over sodium sulfate. Removal of the solvents gave an oil which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave a solid after crystallization from ethyl acetate which did not melt when heated above 500°.

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Reactions of some thiolatotin compounds

During investigations of cyclic dithiolatotin compounds[1] we became interested in the general reactivity of the tin–sulphur bond about which there is little information. One method of investigation used was to examine the behaviour of triphenyltin thiophenoxide with various reagents and the results obtained, together with some reactions of cyclic dithiolatotin compounds are now reported. While this work was in progress, reactions of alkyltin thiolates with halogens[2] and metal halides[3] were described.

The tin–sulphur bond in triphenyltin thiophenoxide is stable to water and the compound can be recovered unchanged after several hours boiling in aqueous ethanol; addition of sodium hydroxide caused hydrolysis to triphenyltin hydroxide.

Reactions of triphenyltin thiophenoxide with metal halides gave similar results to those obtained by Abel[3] with cleavage of the tin–sulphur bond and formation of the metal thiophenoxide. One point of difference is that mercuric chloride gave chloromercury thiophenoxide whereas with trimethyltin butanethiolate only the fully thiolated product was formed[3].

A strikingly different reaction occurred when mercuric acetate was used in place of the chloride, under mild conditions tin–carbon bond cleavage accompanied the tin–sulphur cleavage and the principal product was phenylmercury thiophenoxide PhHgSPh. Although cleavage of phenyl–tin bonds by mercuric chloride is known[4] the conditions employed were much more energetic than in the present case. At present only speculative attempts can be made to interpret the course of the reaction since the other major product isolated appeared to be the partially hydrolysed compound $[Ph_2(AcO)Sn–O–SnPh_2(OAc)]_2$, an attempt to make diphenyltin diacetate by the treatment of diphenyltin oxide with acetic acid gave the same product.

Attempts to isolate compounds of the type $SnCl_x(SPh)_{4-x}$ by treatment of stannic chloride with less than 4 equivalents of triphenyltin thiophenoxide gave only tin tetrathiophenoxide and unchanged stannic chloride. Using a 1:4 ratio of the reactants good yields were obtained of tin tetrathiophenoxide which was characterised by formation of its 2,2'-bipyridine derivative, bipy–$Sn(SC_6H_5)_4$.

The reactions were extended to include some cyclic compounds and (ethane-1,2-dithiolato)dibutyltin reacted with iodine to give dibutyltin diiodide and the polymeric sulphide $(S–CH_2CH_2–S)_n$. The spirocyclic bis(ethane-1,2-dithiolato)tin with