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HEXAKIS(TRIMETHYLSILYL)DISILANE: A HIGHLY BRANCHED AND SYMMETRICAL ORGANOPOLYSILANE*

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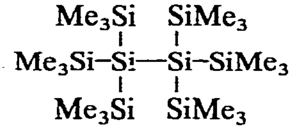
Recently, a number of reports from these Laboratories[1-6] have described the syntheses of several heretofore unavailable branched-chain organopolysilanes. These have been found to possess some very interesting physical and chemical properties. As a continuation of our interest in these novel compounds we are now reporting the synthesis of another highly-branched and symmetrical organopolysilane, namely, hexakis(trimethylsilyl)disilane, (I),



$$\begin{array}{ccc} & Me_3Si \quad SiMe_3 & \\ & | \qquad\quad | & \\ Me_3Si{-}&Si{-}Si&{-}SiMe_3 \\ & | \qquad\quad | & \\ & Me_3Si \quad SiMe_3 & \end{array}$$

(I)

Compound (I) was prepared in varying yields by a number of procedures, most of which involved the use of tris(trimethylsilyl)-silyllithium (II)[3,7] as a precursor. The results of several experiments are summarized in Table 1. These methods appeared attractive because analogous reactions with triphenylsilyllithium gave high yields of hexaphenyldisilane[8].

TABLE 1

PREPARATION OF HEXAKIS(TRIMETHYLSILYL)DISILANE FROM TRIS(TRIMETHYLSILYL)SILYLLITHIUM[a]

Run	*Reagent*	*Temp (°C)*	*Yield of (I) (%)*
1	$BrCH_2CH_2Br$	25	7.3
2[b]	$BrCH_2CH_2Br$	25	6.6
3[b]	$BrCH_2CH_2Br$	−70 (*ca.*)	51.0
4[b]	$BrCH_2CH_2Br$	−70	45.0
5[b]	I_2	25	9.9
6[b]	I_2	−70	19.5
7	$HgCl_2$	25	5.3
8	$(Me_3Si)_3SiCl$	25	6.4
9	$(Me_3Si)_3SiCl$	−70	25.0

[a] All reactions were run in a THF/ether mixture. [b] Reverse addition.

The reactions of compound (II) with 1,2-dibromoethane and iodine pre-

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* The synthesis of this compound was mentioned in a preliminary communication[6].

sumably involve halogen–metal exchange[8] resulting in the formation of a halosilane which couples with the excess silyllithium compound (II).

$$\underset{\text{(II)}}{(Me_3Si)_3SiLi} + BrCH_2CH_2Br \rightarrow (Me_3Si)_3SiBr + C_2H_4 + LiBr \qquad (1)$$

$$(Me_3Si)_3SiBr \xrightarrow{\text{(II)}} \text{(I)}$$

On the basis of results obtained by the treatment of 1,2-dibromoethane with magnesium[9], the incipient bromoalkyllithium compound should undergo a rapid internal Wurtz reaction to form ethylene.

Initially, the reactions shown in Table 1 were run at room temperature. Under this condition, tetrakis(trimethylsilyl)silane[2,10] (III) was found to be the major product (50–75%). It was later determined that the desired product (I) reacts with the silyllithium compound (II) to give tetrakis(trimethylsilyl)silane (III).

$$\text{(I)} + \text{(II)} \xrightarrow{\text{THF/Et}_2\text{O}} R_4Si + LiR_2SiSiR_3 \qquad R = Me_3Si \qquad (3)$$

This reaction proceeds rapidly at room temperature but very slowly at *ca.* −70°. Thus, when the experiments were repeated at the latter temperature higher yields of (I) were obtained. There were also corresponding decreases in the yields of (III).

The reaction of (II) with iodine appeared to involve more than just halogen–metal exchange as shown below. A 4 : 1 molar ratio of (II) to iodine should be required to convert one-half of the silyllithium to the iodosilane. However, about twice this quantity was needed to give a negative Color Test I[7].

$$\text{(II)} + \tfrac{1}{2}\, I_2 \rightarrow (Me_3Si)_3SiI \qquad (4)$$

$$(Me_3Si)_3SiI \xrightarrow{\text{(II)}} \text{(I)} \qquad (5)$$

The possibility that all of the silyllithium was converted to the iodosilane, due to a slowness of the coupling reaction, was readily dismissed when the infrared spectrum of the crude product mixture, after hydrolysis, did not show the presence of significant quantities of compounds containing Si–OH or Si–O–Si linkages.

It is not clear at this time why the reaction of (II) with tris(trimethylsilyl)-chlorosilane (IV) (Table 1) afforded much lower yields of (I) than the reaction involving 1,2-dibromoethane. If a bromosilane is formed in the latter case the yields from the two reactions should be comparable since both reactions would involve the coupling of (II) with a halosilane.

An attempt to prepare (I) by the sodium coupling of the chlorosilane (IV) gave, after hydrolysis, a mixture containing tris(trimethylsilyl)silane[7] and tetrakis(trimethylsilyl)silane (III). Compound (I) could not be detected by vapor phase chromatography.

$$(Me_3Si)_3SiCl + Na \xrightarrow{H_3O^+} (Me_3Si)_3SiH + \text{(III)} + \text{others} \qquad (6)$$

The reaction of the same chlorosilane (IV) with magnesium in THF gave a mixture of (I) and (III) in which the latter was the major product. The formation of (III) in this reaction possibly involves nucleophilic attack on a trimethylsilyl group by an intermediate silyl Grignard reagent.

$$(Me_3Si)_3SiMgCl + Me_3Si\text{–}SiR_3 \rightarrow (III) + R_3SiMgCl \qquad (7)$$

Although no stable species of this type has been prepared, silyl Grignard reagents have been postulated as intermediates[11,12].

Experiments designed to synthesize compound (I) via one-step reactions of tetrachlorosilane or hexachlorodisilane with lithium and chlorotrimethylsilane afforded high yields of compound (III) as the only isolable product. In contrast, the reaction of tetrachlorosilane with lithium and chlorodimethylsilane afforded both tetrakis(dimethylsilyl)silane and hexakis(dimethylsilyl)disilane[13].

The failure to obtain compound (I) from the reaction involving hexachlorodisilane is undoubtedly due to the rapid cleavage of (I) by lithium (*vide infra*) as well as by silyllithium compounds.

The results of the various synthetic procedures attempted clearly indicate the reaction of (II) with 1,2-dibromoethane at *ca.* −70° to be the method of choice.

PHYSICAL AND SPECTRAL PROPERTIES

Compound (I) is a crystalline solid that melts with decomposition at temperatures between 372 and 380°*. This high melting point is undoubtedly associated with the high degree of symmetry in the molecule. This is supported when one realizes that the linear isomer, octadecamethyloctasilane[14], melts at 61–62°. This trend has been observed with a number of other branched-chain polysilanes prepared in these laboratories. For example, the highly-symmetrical tetrakis(trimethylsilyl)silane melts at *ca.* 319° while the isomeric dodecamethylpentasilane is a liquid at room temperature[15].

As one would expect on the basis of trends in carbon chemistry[16], compound (I) is much more volatile than its normal isomer. The volatility of (I) is shown by the fact that it is sublimable and can readily pass through a VPC column despite its high melting point.

Compound (I) is very soluble in many of the common organic solvents but only slightly soluble in cold ethanol or acetone. The latter was found to be the best solvent for the recrystallization of (I).

The infrared spectrum of (I) was consistent with the assigned structure in that it only exhibited the expected bands due to the presence of trimethylsilyl groups[17]. The NMR spectrum (in CS_2, with TMS as internal standard) displayed a sharp singlet at 9.78 τ.

Although (I) is a substituted tetrasilane, it does not absorb ultraviolet radiation above 210 mμ. In contrast, decamethyltetrasilane absorbs at 235 mμ[18]. This was not unexpected since it has previously been reported that substitution of silyl groups on a silicon chain causes a decrease in the value of the position of maximum absorption.

CHEMICAL PROPERTIES

A few preliminary reactions were run with (I) as a means of further confirming the assigned structure. In the early stages of this investigation compound (I) was

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* All melting points were taken in a sealed tube to prevent sublimation from the capillary.

obtained in very low yields. Consequently, the reactions were run on a small scale and the products were detected and identified, when possible, by comparing their VPC retention times with those of authentic samples. All of these reactions involved cleavage of silicon–silicon bonds. Due to the symmetry of the molecule only three cleavage paths were possible:

$$(\mathrm{I}) + \mathrm{X{-}Y} \xrightarrow{(a)} \mathrm{R_3Si{-}X} + \mathrm{R_3Si{-}Y} \qquad (8)$$

$$(\mathrm{I}) + \mathrm{X^+Y^-} \begin{cases} \xrightarrow{(b)} \mathrm{R{-}X} + \mathrm{R_3Si{-}SiR_2{-}Y} \\ \xrightarrow{(c)} \mathrm{R{-}Y} + \mathrm{R_3Si{-}SiR_2X} \end{cases} \qquad (9)$$

$$\mathrm{R} = (\mathrm{CH_3})_3\mathrm{Si}$$

Methyllithium reacted with (I) by path (a) only, to give the known tris(trimethylsilyl)methylsilane and tris(trimethylsilyl)silyllithium which was converted to tris(trimethylsilyl)silane upon acid hydrolysis. It is noteworthy that hexakis(dimethylsilyl)disilane reacts with methyllithium in a manner analogous to path (c) (eqn. 9) with the subsequent formation of pentakis(dimethylsilyl)disilanyllithium[13]. The bulkier triphenylsilyllithium and tris(trimethylsilyl)silyllithium (II) reacted with (I) via path (c). This was determined by identifying the known products R–Y [$\mathrm{R} = (\mathrm{CH_3})_3\mathrm{Si}$, $\mathrm{Y} = \mathrm{R_3Si}$ and $\mathrm{Ph_3Si}$]. The resulting silyllithium compounds were unknown species, and authentic samples of their derivatives were not available. However, in the case of the reaction of (I) with (II) chemical evidence indicated that the two silyllithium compounds shown below (eqn. 10) were present.

$$\underset{(\mathrm{II})}{[(\mathrm{CH_3})_3\mathrm{Si}]_3\mathrm{SiLi}} + (\mathrm{I}) \rightarrow \underset{(\mathrm{III})}{[(\mathrm{CH_3})_3\mathrm{Si}]_4\mathrm{Si}} + \underset{(\mathrm{V})}{\mathrm{R_3Si{-}SiR_2Li}} + \underset{(\mathrm{VI})}{\mathrm{LiR_2Si{-}SiR_2Li}} \qquad (10)$$

$$(\mathrm{V}) + (\mathrm{VI}) \xrightarrow{\mathrm{H_3O^+}} \mathrm{R_3Si{-}SiR_2H} + \mathrm{HR_2Si{-}SiR_2H} \qquad (11)$$

$$(\mathrm{V}) + (\mathrm{VI}) \xrightarrow{(\mathrm{CH_3O})_3\mathrm{PO}} \underset{(\mathrm{VII})}{\mathrm{R_3Si{-}SiR_2CH_3}} + \underset{(\mathrm{VIII})}{\mathrm{CH_3R_2Si{-}SiR_2CH_3}} \qquad (12)$$

$$\uparrow \mathrm{CH_3MgI}$$

$$(\mathrm{I}) + \mathrm{X_2} \rightarrow \mathrm{R_3SiSiR_2X} + \mathrm{XR_2Si{-}SiR_2X} \qquad (13)$$

$$\mathrm{X} = \mathrm{Cl, Br};\ \mathrm{R} = (\mathrm{CH_3})_3\mathrm{Si}$$

Treatment of the mixture of (V) and (VI) with trimethyl phosphate[19] afforded products (VII) and (VIII). The latter is a known compound and was identified by VPC. Product (VII) had a higher retention time than (VIII). The reaction of (II) with (I) by path (a) cannot be excluded since it would only generate starting materials.

A single silyllithium compound was formed by treatment of I with an excess of triphenylsilyllithium. The retention time of the product, after hydrolysis, indicated that it was (VI). This was further confirmed by the infrared spectrum of the mixture of hydrolysis products. In addition to the absorption bands for the known compounds, a peak was present at 4.88 μ due to the Si–H moiety. The assignment of this band to a tertiary silicon hydride of the type suggested as a product is based on previous findings[4] that tertiary Si–H groups show a shift to lower stretching frequencies, relative to the usual 4.4–4.8 μ absorption region. No attempt was made to determine if (V) could be formed free of (VI) by using a 1 : 1 molar ratio of reactants.

Compound (I) reacted with chlorine or bromine by path (b) [(b) ≡ (c)] to give the corresponding halotrimethylsilane and two unknown halosilanes. Treatment of the mixture of products from the bromine reaction with methylmagnesium iodide converted one of the products to compound (VII). The second product had the same retention time as compound (VIII) (eqn. 12). On this basis the products are probably those shown in eqn. (13).

(I) was cleaved rapidly by lithium in tetrahydrofuran with the formation of (II) which was converted to tris(trimethylsilyl)silane by acid hydrolysis. A small quantity of (III) was also present. This latter product was probably formed by the reaction of the silyllithium (II) with (I). Many unsuccessful attempts to cleave silicon–silicon bonds of peralkylpolysilanes with lithium have been reported[20,21]. A recent example is the attempted reaction of (III) with this metal[10]. However, (III) is cleaved slowly by sodium/potassium alloy to give tris(trimethylsilyl)silylpotassium[10].

The facile reactivity of (I) towards lithium is probably due in part to the formation of a very stable silyllithium compound from both fragments, and to strain in the molecule. This reaction represents the first successful cleavage of an individual peralkylpolysilane by lithium metal alone. It was reported that the insoluble dimethylsilylene polymer, obtained from the uncatalyzed reaction of dichlorodimethylsilane with lithium, is cleaved by lithium metal[22]. An attempt to carry out the cleavage of (I) in diethyl ether was unsuccessful.

$$\text{(I)} + 2\,\text{Li} \xrightarrow{\text{THF}} 2\,\text{(II)} \xrightarrow{\text{H}_3\text{O}^+} [(\text{CH}_3)_3\text{Si}]_3\text{SiH}$$

In view of the facile reactivity of (I) with organolithium compounds, and the stability of (II)[7], an attempt was made to react (I) with methylmagnesium iodide and phenylmagnesium bromide. It was hoped that cleavage would occur according to path (a) (eqn. 8) to give a known compound and a stable silyl Grignard reagent. Only unchanged (I) could be detected by VPC.

$$\text{(I)} + \text{RMgX} \rightarrow [(\text{CH}_3)_3\text{Si}]_3\text{SiR} + [(\text{CH}_3)_3\text{Si}]_3\text{SiMgX}$$

$$\text{R} = \text{CH}_3,\ \text{X} = \text{I};\ \ \text{R} = \text{C}_6\text{H}_5,\ \text{X} = \text{Br}$$

It was also determined that (I) is not cleaved on basic alumina. There have been reports that silicon–silicon bonds of some organopolysilanes are cleaved under this condition[23,24].

EXPERIMENTAL

All reactions were carried out under an atmosphere of oxygen-free dry nitrogen. The melting points were taken with a Mel-Temp apparatus and are uncorrected. The silyllithium compound (II) was prepared from (III)* in accordance with a published procedure[7]. Tris(trimethylsilyl)chlorosilane was prepared by the reaction of tris(trimethylsilyl)silane with carbon tetrachloride[6]. All other reagents were commercially available. Tetrahydrofuran was refluxed over sodium and over

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* For a precautionary note on a hazard involved in the purification of tetrakis(trimethylsilyl)silane, see ref. 10.

lithium aluminum hydride before use. VPC analyses were carried out using columns packed with silicone gum rubber SE 30 on Chromosorb W (1 : 20). The instrument was a Perkin Elmer Model 500 gas chromatograph. The infrared spectrum was determined using a Perkin Elmer Model 21 spectrophotometer. The ultraviolet spectrum was run in cyclohexane with a Beckman DK-2A Spectrophotometer. The molecular weight of (I) was determined in benzene with a Mechrolab Vapor Pressure Osmometer, Model 301A.

General procedure for the purification of (I). When the reaction was complete the mixture was hydrolyzed with dilute hydrochloric acid. After the organic layer had been separated and dried over anhydrous sodium sulfate the solvents were removed on a rotary evaporator. Ethanol (95%) was then added to cause immediate precipitation of the products. Compound (III) was removed by fractional sublimation at *ca.* 75°/0.01 mm; the disappearance of (III) was usually followed by VPC. The residue was taken up in hot ethanol or a mixture of ethyl acetate and methanol. Usually 2–3 recrystallizations were required to give pure (I). Acetone was later found to be the best solvent for recrystallization.

In all cases the yield of (I) was based on the quantity of (III) converted to the silyllithium (II).

Preparation of (I)

From compound (II) and 1,2-dibromoethane. A solution of 7.7 g (0.04 mole) of the dibromide in 100 ml of THF was added during 2 h to a solution of 0.08 mole of (II). The reaction was exothermic and a red-brown color persisted until 85 ml of the solution had been added. Stirring was continued for an additional 2 h. At this time Color Test I[7] was negative. The products were then worked up as described above to give 9.2 g of (III), m.p. 288–295° (mixed m.p.), and 1.3 g (6.6%) of (I), m.p. 372–374° dec. (Found: Si, 45.1; mol. wt., 509.7. $C_{18}H_{54}Si_8$ calcd.: Si, 45.4%; mol. wt., 495.3.)

This reaction was repeated under the same conditions, with the exception that the reverse addition was used. From this run there was isolated 10.0 g of (III) and 1.5 g (7.6%) of (I).

Two runs at *ca.* −70° gave (I) in 51.0 and 45.0% yields. In both cases the dibromide was added to the silyllithium.

From (II) and iodine. To a solution of the silyllithium prepared from 0.082 mole of (III) was added 7.6 g (0.03 mole) of iodine in 150 ml of THF during 2 h. The reaction mixture was stirred overnight (Color Test I[7] was negative) and it was then added to cold dilute hydrochloric acid. The solution was washed with 10% sodium thiosulfate and water and then dried over sodium sulfate. The usual purification procedure gave 10.0 g of (III), m.p. 298–315° (mixed m.p.), and 1.8 g (9.1%) of (I), m.p. 372–377° dec. (mixed m.p.).

This reaction was repeated using initially a 4 : 1 molar ratio of (II) to iodine, but an additional quantity of the latter was required to give a negative Color Test I. The yield of (I) was 7.5%.

A repeat run at −70° gave (I) in 19.5% yield.

From (II) and mercury (II) chloride. To a flask containing 10.85 g (0.04 mole) of the chloride in 75 ml of THF was added a solution of (II) prepared from 0.082 mole of (III). An exothermic reaction began immediately and the mixture acquired a black color. The addition was complete in 2 h, and stirring was continued for another 3 h.

Filtration of the reaction mixture gave 7.3 g of mercury. Hydrolysis and the usual work-up afforded 9.3 g of (III) and 1.1 g (5.3 %) of (I), m.p. 373–378° dec. (mixed m.p.).

From tris(trimethylsilyl)chlorosilane and (II). To a solution of 20.4 g (0.073 mole) of the chlorosilane in 100 ml of THF was added a solution (250 ml) of 0.07 mole of the silyllithium compound. The addition was completed in 1 h, and stirring was continued for an additional 1.5 h. (Color Test I was negative.) The reaction mixture was then hydrolyzed with dilute acid and the combined organic layers were separated and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure and 95 % ethanol was added to the residue to cause immediate precipitation of the products. Subsequent to cooling in an ice bath for 1 h, filtration gave 21.1 g of impure product, m.p. 145–195°. Fractional sublimation at 70°/0.01 mm afforded 17.4 g of compound (III), m.p. 292–300° (mixed m.p.). The residue was taken up in hot ethanol. Upon standing there crystallized 2.5 g of material, m.p. 344–348°. Two recrystallizations from methanol/ethyl acetate and finally from cyclohexane produced 2.3 g (6.4 %) of compound (I), m.p. 373–376° dec. (mixed m.p.).

When the reaction was repeated at −70°, (I) was isolated in 25.0 % yield.

From tris(trimethylsilyl)chlorosilane and magnesium. To a flask containing 12.4 g (0.1 g-atom) of magnesium and 75 ml of THF was added 13.8 g (0.05 mole) of chlorosilane and 8 drops of ethyl iodide. After 4 h of stirring at reflux temp. there was no evidence that a reaction had started. Upon standing overnight the solution acquired a red-brown color. Stirring at reflux temp was then continued for 6 h. The reaction mixture was then cooled, filtered from the excess magnesium and hydrolyzed with dilute acid. After the usual work-up the organic solvents were removed to give a semi-solid residue which was taken up in a mixture of hot methanol and ethyl acetate. A fraction of the mixture was separated to give 1.0 g of (III), m.p. 292–300° (mixed m.p.), and 0.4 g of (I), m.p. 368–372° dec. (mixed m.p.).

The reaction could not be initiated when a repeat run was attempted.

From hexachlorodisilane, lithium, and chlorotrimethylsilane (attempted). The reaction was initiated in *ca.* 5 min by adding 10 ml of a solution of 26.9 g (0.1 mole) of hexachlorodisilane in 200 ml of THF to a rapidly stirred mixture of 14.0 g (2.0 g-atom) of lithium, 109 g (1.0 mole) of chlorotrimethylsilane and 200 ml of THF. The remainder of the solution was added in 6 h, and stirring was continued for a total of 48 h. The solution was then filtered from the excess lithium and hydrolyzed with a mixture of ice and hydrochloric acid. The organic layer was separated and the solvents were removed by steam distillation. Subsequent to the addition of methanol, the mixture was filtered to give 19 g of crude (III). Sublimation produced 17.1 g (26.6 %) of (III), m.p. 290–298° (mixed m.p.). The filtrate was concentrated and chromatographed on neutral alumina. Elution with petroleum ether (b.p. 60–70°) gave an additional 1.5 g of (III). Continued elution gave a heavy oil which was shown (VPC) to contain (III) but not (I).

From tetrachlorosilane, lithium and chlorotrimethylsilane (attempted). To a mixture of 94.2 g (0.87 mole) of chlorotrimethylsilane, 15.13 g (2.2 g-atom) of lithium, 3 ml of ethyl acetate and 150 ml of THF was added 25 ml of a solution of 35.6 g (0.21 mole) of tetrachlorosilane in 100 ml of THF. An exothermic reaction started after 30 min of stirring. Ethyl acetate (3 ml) was added to the addition funnel and the remainder of the solution was added dropwise during *ca.* 3 h. The reaction was maintained at *ca.* 40° during the first 5 h by external cooling. Subsequent to 20 h of stirring the reaction mixture was filtered to remove the insolubles. The filtrate was then hydrolyzed and worked up as usual. After the solvents were removed, 95% ethanol was added to cause precipitation of the crude products. Filtration and sublimation gave 26.9 g (40.1%) of (III). The presence of (I) was not detected (VPC) among the reaction products.

From tris(trimethylsilyl)chlorosilane and sodium (attempted). A mixture of 4.6 g (0.2 g-atom) of sodium, 2 ml of ethyl acetate and 100 ml of dry toluene was refluxed until the sodium became molten. There was then added in *ca.* 1 h a solution of 13.0 g (0.046 mole) of the chlorosilane and 5 ml of ethyl acetate in 75 ml of toluene. The solution acquired a green color after 1–5 h. Stirring at reflux temp. was continued for a total of 24 h. The reaction mixture was then cooled and filtered through glass wool. Ethanol was then added to destroy the excess sodium. The solution was then acidified and worked up in the usual manner. Removal of the solvents left an oily residue that was chromatographed on basic alumina. Petroleum ether (b.p. 60–70°) eluted a mixture of products. Analysis by VPC showed the presence of tris(trimethylsilyl)silane, (III), and three unidentified products but not (I). The presence of the former product was confirmed by IR. The spectrum showed a characteristic band[6] at 4.87 μ for the Si–H absorption.

Reactions of (I)

With methyllithium. To a solution of 0.5 g (0.001 mole) of (I) in 10 ml of THF was added *ca.* 0.01 mole of methyllithium[25] in ether. The solution gradually acquired a yellow color. After 4 h of stirring an aliquot was removed and hydrolyzed for analysis. VPC showed the presence of tris(trimethylsilyl)silane and tris(trimethylsilyl)methylsilane as the only products.

An attempt to react (I) with methyllithium, using only ether as the solvent, was unsuccessful.

With (II) followed by treatment with trimethyl phosphate. To a flask containing 0.004 mole of (II) in THF/ether (4:1) was added at once 0.5 g (0.001 mole) of (I) in 10 ml THF. After the reaction mixture was stirred for 1.5 h, an aliquot was removed and hydrolyzed for analysis by VPC. Uncleaved (I), (III) and two unidentified products were shown to be present. Subsequent to 12 h of stirring the reaction mixture was derivatized with trimethyl phosphate and hydrolyzed with dilute acid. Analysis of the organic layer (VPC) showed the presence of (III), 1,1,2,2-tetrakis(trimethylsilyl)dimethyldisilane[25] and a small amount of a product with a higher retention time. There was no starting material (I) present.

With triphenylsilyllithium. A solution of 0.5 g (0.001 mole) of (I) in 10 ml of THF was added dropwise to 0.1 mole of triphenylsilyllithium in THF. The reaction mixture was stirred for 10 min and an aliquot was hydrolyzed for analysis. The following known products were shown to be present: triphenylsilane, 1,1,1-trimethyl-2,2,2-triphenyldisilane and unchanged starting material. In addition, there was present a single product which presumably resulted from cleavage of two trimethylsilyl groups from (I).

After 3 h of stirring the reaction mixture was hydrolyzed and the organic layer was separated and dried over sodium sulfate. In addition to the expected absorption bands, the infrared spectrum of the product mixture showed a peak characteristic of a tertiary Si–H[6] at 4.78 μ.

With lithium. One ml of THF was added to a flask containing 1.0 g (0.002 mole) of (I) and 0.7 g (0.1 g-atom) of finely cut lithium wire. After *ca.* 5 min of stirring ,a yellow color appeared, indicating that the reaction had started. There was then added dropwise an additional 5 ml of THF. Subsequent to 1.5 h of stirring, analysis (VPC) of a hydrolyzed aliquot showed the presence of tris(trimethylsilyl)silane, and (III) as the major products. Small amounts of two products with retention times lower than (I), but greater than that of (III), were also present.

With bromine, followed by treatment with methylmagnesium iodide. To a solution of 1.8 g (0.004 mole) of (I) in 25 ml of dry benzene was added a solution of 3.2 g (0.02 mole) of bromine in 15 ml of benzene. The addition was completed in 30 min and stirring was continued for an additional 30 min. There was then added 25 ml of dry THF and an excess of methylmagnesium iodide. The mixture was stirred overnight and it was then hydrolyzed with acidified ice. Analysis of the organic layer showed the presence of 1,1,2,2-tetrakis(trimethylsilyl)dimethyldisilane[25], a second product that was not identified, and unchanged (I). A partial separation of the mixture gave 0.7 g of (I).

With chlorine. Chlorine gas was bubbled through a solution of (I) in carbon tetrachloride at *ca.* −10° for 30 min (no reaction occurred at *ca.* −20°). VPC analysis showed, in addition to unchanged (I), the presence of two products. These were probably compounds resulting from cleavage of one and two trimethylsilyl groups from (I) in a manner analogous to the bromine reaction. The retention times of these products were higher than that of tris(trimethylsilyl)chlorosilane.

Attempted cleavage of compound (I) on basic alumina. One gram of (I) (m.p. 373–382°) dissolved in 20 ml of petroleum ether (b.p. 60–70°) was left standing on a 3 × 20 cm column of basic alumina (Matheson Coleman and Bell Chromatographic Grade Activated Alumina, 80–200 mesh) for 4.5 hours. Elution with the same solvent and recrystallization from acetone gave 0.85 g (85%) of recovered (I), m.p. 373–382° (mixed m.p.).

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SUMMARY

Hexakis(trimethylsilyl)disilane (I), a novel, highly branched and symmetrical polysilane, was synthesized by a number of procedures. Many of these gave (I) in only 5–9% yield. The reaction of tris(trimethylsilyl)silyllithium (II) with 1,2-dibromoethane (*ca.* −70°) gave (I) in 45–50% yields, and proved to be the most satisfactory method of synthesis. The physical and spectral properties of (I) are discussed. Lithium and methyllithium reacted with (I) to cause cleavage of the symmetrical Si–Si bond, while (II), triphenylsilyllithium and halogens effected cleavage of peripheral trimethylsilyl groups.

REFERENCES

1 D. WITTENBERG, M. V. GEORGE AND H. GILMAN, *J. Am. Chem. Soc.*, 81 (1959) 4812.
2 H. GILMAN AND C. L. SMITH, *J. Am. Chem. Soc.*, 86 (1964) 1459.
3 H. GILMAN, J. M. HOLMES AND C. L. SMITH, *Chem. Ind. (London)*, (1965) 848.
4 H. GILMAN, W. H. ATWELL, P. K. SEN AND C. L. SMITH, *J. Organometal. Chem.*, 4 (1965) 163.
5 H. GILMAN AND G. L. SCHWEBKE, in press.
6 H. GILMAN AND R. L. HARRELL, JR., *J. Organometal. Chem.*, 5 (1966) 199.
7 H. GILMAN AND C. L. SMITH, *J. Organometal. Chem.*, 8 (1967) 245; see also H. GILMAN AND F. SCHULZE. *J. Am. Chem. Soc.*, 47 (1925) 2002.
8 H. GILMAN AND H. J. S. WINKLER, in H. ZEISS, *Organometallic Chemistry* Reinhold, New York, 1960, pp. 303–314.
9 M. S. KHARASCH AND O. REIMUTH, *Grignard reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954.
10 H. GILMAN AND C. L. SMITH, *J. Organometal. Chem.*, 8 (1967) 245.
11 T. G. SELIN AND R. WEST, *Tetrahedron*, 5 (1959) 97.
12 W. STEUDEL AND H. GILMAN, *J. Am. Chem. Soc.*, 82 (1960) 6129, and references cited therein.
13 H. GILMAN AND J. M. HOLMES, unpublished studies.
14 M. KUMADA, M. ISHIKAWA AND S. MAEDA, *J. Organometal. Chem.*, 5 (1966) 120.
15 M. KUMADA AND M. ISHIKAWA, *J. Organometal. Chem.*, 1 (1963) 153.
16 K. B. WIBERG, *Laboratory Technique in Organic Chemistry*, McGraw-Hill, New York, 1960, pp. 77–78.
17 A. L. SMITH, *Spectrochim. Acta*, 16 (1960) 87.
18 H. GILMAN, W. H. ATWELL AND G. L. SCHWEBKE, *J. Organometal. Chem.*, 2 (1964) 369.
19 H. GILMAN AND B. J. GAJ, *J. Org. Chem.*, 26 (1961) 2471.
20 H. GILMAN AND D. WITTENBERG, *Quart. Rev.*, 13 (1959) 116.
21 C. EABORN, *Organosilicon Compounds*, Butterworths, London, 1960, pp. 357–361.
22. H. GILMAN AND R. A. TOMASI, *J. Org. Chem.*, 28 (1963) 1651.
23 G. R. CHAINANI, S. COOPER AND H. GILMAN, *J. Org. Chem.*, 28 (1963) 2146.
24 H. GILMAN AND G. L. SCHWEBKE, *J. Am. Chem. Soc.*, 86 (1964) 2693.
25 H. GILMAN, E. A. ZOELLNER AND W. M. SELBY, *J. Am. Chem. Soc.*, 55 (1933) 1252.