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CLEAVAGE OF ORGANOPOLYSILANES BY LITHIUM ALUMINUM HYDRIDE. INTERMEDIATE(ORGANOSILYL)ALUMINUM COMPOUNDS

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SUMMARY

The reductive cleavage of silicon–silicon bonds in phenyl-substituted organopolysilanes by lithium aluminum hydride has been shown to occur in refluxing tetrahydrofuran. The reaction of hexaphenyldisilane was studied in greater detail, and the results show that the cleavage produces intermediate(organosilyl)aluminum compounds. The formation of the latter from reactions of triphenylsilyllithium with some aluminum compounds was also investigated.

INTRODUCTION

The reductive cleavage of aryl-substituted silicon–silicon bonds in organopolysilanes by alkali metals has been accomplished under a wide variety of conditions**. In aprotic solvents, the reactions afford organosilylmetallic compounds, according to the following equation:

$$R_3SiSiR_3 + 2\,M \rightarrow 2\,R_3SiM \qquad (1)$$

Only very low yields of trialkylsilylmetallic compounds have resulted from fission of 1,1,1-trialkyl-2,2,2-triphenyldisilanes. Thus, trimethylsilylpotassium was obtained utilizing sodium/potassium alloy in ether[2], and triethylsilyllithium was formed by the lithium cleavage of 1,1,1-triethyl-2,2,2-triphenyldisilane in tetrahydrofuran[3,4]. In contrast to the reactions of aryl-substituted compounds, numerous attempts to effect similar cleavages of hexamethyl- and hexaethyldisilane have proved unsuccessful[2,3,5–9]. Thus, it is apparent that aryl groups activate the silicon–silicon bond toward cleavage and/or stabilize the resulting organosilylmetallic. However, the cleavage of octamethyltrisilane and decamethyltetrasilane with sodium/potassium alloy in tetrahydrofuran has been reported[10]. Derivatization of the resulting silylmetallic species with chlorotrimethylsilane gave a variety of linear and cyclic permethylated polysilanes. Evidently, the presence of silicon–silicon bonds offers some stability to non-arylsubstituted silyl-metallics and/or facilitates cleavage.

A similar effect has also been observed in the reductive cleavage of silicon–silicon bonds by hydrogen over a "copper chromite" catalyst, with the phenyl-sub-

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** For comprehensive reviews on cleavages by alkali metals see ref. 1.

stituted compounds undergoing hydrogenolysis according to equation (2), while hexaethyldisilane was not affected under comparable conditions[11].

$$R_3SiSiR_3 + H_2 \rightarrow 2\,R_3SiH \qquad (2)$$

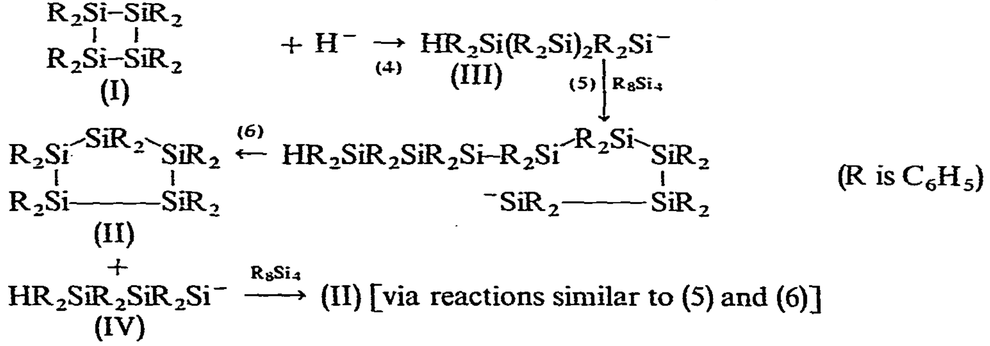
Hexaphenyldisilane has been shown to be unreactive towards lithium aluminum hydride in ether[12]. However, it has been noted that silicon–silicon bond cleavage occurs upon the addition of hexachlorodisilane to lithium aluminum hydride in tetrahydrofuran or in di-n-butyl ether, which afforded exclusively silane (SiH_4)[13], whereas disilane is obtained when diethyl ether was used as the solvent[14]. Also, cleavage of disilane by potassium hydride in ethylene glycol dimethyl ether yielded silane and silylpotassium[15], as illustrated by equation (3). Similarly, the fission of

$$x\,H_3SiSiH_3 + KH \rightarrow x\,SiH_4 + \left[\frac{1}{x}(SiH_2)_x\right] \xrightarrow{KH} KSiH_3 \qquad (3)$$

silicon–silicon bonds in mono- and dialkyldisilanes by potassium hydride has been observed, accompanied by redistribution of the alkyl groups[16].

DISCUSSION AND RESULTS

As compared to other organopolysilanes, octaphenylcyclotetrasilane[17] (I) is unusually reactive in silicon–silicon bond cleavage. Thus, it appeared likely that this compound, (I), might react with lithium aluminum hydride. After 168 h in refluxing ether, no evidence of reaction was indicated and octaphenylcyclotetrasilane was recovered in nearly quantitative amounts. However, after 20 h at room temperature in tetrahydrofuran (THF), no octaphenylcyclotetrasilane was recovered. The primary product of this reaction was decaphenylcyclopentasilane[18] (II), isolated in 64% yield. It seems likely that the mechanism involved in this reaction is analogous to that proposed for this same cyclotetrasilane to cyclopentasilane transformation brought about by organosilyllithium compounds[19,20] and other organometallic compounds[19,21]. The proposed mechanism of this conversion is shown in the following sequence of reactions. The fact that decaphenylcyclopentasilane was recovered in a 74% yield after similar treatment with lithium aluminum hydride is consistent with the accumulation of this compound in the reaction with octaphenylcyclotetrasilane. From these and other reactions of (I) and (II) with lithium aluminum hydride,



further support of the mechanistic pathway was obtained by the isolation of products containing one, two, three, four and five diphenylsilylene units, corresponding to hydrolysis of intermediate organosilylmetallics such as (III), (IV) and others predicted from subsequent cyclization cleavage steps.

The reactions of lithium aluminum hydride with hexaphenyldisilane, 1,2-dimethyl-1,1,2,2-tetraphenyldisilane, 1,1,2,2-tetramethyl-1,2-diphenyldisilane and hexaethyldisilane in refluxing tetrahydrofuran were also investigated. The general reaction is illustrated in equation (7). Under comparable conditions, the yields of

$$R_3Si\text{–}SiR_3 + H^- \rightarrow R_3SiH + R_3Si^- \xrightarrow{H^+} 2\,R_3SiH \qquad (7)$$

the corresponding products decreased, respectively, as the number of phenyl substituents decreased, with no triethylsilane being detected from hexaethyldisilane. 1,1,1-Trimethyl-2,2,2-triphenyldisilane also reacted, with trimethylsilane being obtained by distillation from the reaction mixture prior to hydrolysis, and triphenylsilane being isolated after hydrolysis. In addition, no reaction was observed with dodecamethylcyclohexasilane. The formation of organosilylmetallic species in these reactions is strongly suggested by the observation that the cleavages by lithium aluminum hydride closely follow the same general pattern of greater reactivity of aryl-substituted silicon–silicon bonds towards fission by alkali metals in the preparation of organosilylmetallic reagents[1-9].

The reaction of lithium aluminum hydride with hexaphenyldisilane was studied in some detail in order to get a better understanding of the cleavage reactions and, in particular, to investigate the nature of the proposed silylmetallic compounds, which could, conceivably, be associated with either lithium or aluminum.

To determine if appreciable amounts of triphenylsilyllithium were present, the reaction mixture obtained from the cleavage of hexaphenyldisilane was treated with excess chlorotrimethylsilane. Subsequent to acid hydrolysis, no 1,1,1-trimethyl-2,2,2-triphenyldisilane could be isolated, indicative of the absence of a silyllithium compound. Significantly, a 60% yield of triphenylsilane was obtained. Similar results were obtained upon repetition of this reaction on a little larger scale. In this case, the mixture was hydrolyzed in deuteriochloric acid. The overall yield of triphenylsilane in this instance was 78%. Of this, 31% was triphenylsilane-*d*, which established the presence of a silylmetallic compound other than lithium, namely, a (triphenylsilyl)-aluminum compound. The following sequence of reactions is consistent with these findings. The fact that no 1,1,1-trimethyl-2,2,2-triphenyldisilane was isolated is apparently due to a lower reactivity of (triphenylsilyl)aluminum dichloride, (VI).

$$\begin{tikzcd}
 & (C_6H_5)_6Si_2 + LiAlH_4 \arrow[r] & (C_6H_5)_3SiH + Li^+[(C_6H_5)_3SiAlH_3]^- \ \text{(V)} \arrow[dl, "3(CH_3)_3SiCl"] \\
(C_6H_5)_3SiD & (C_6H_5)_3SiAlCl_2 \ \text{(VI)} \arrow[l, "D_3O^+"'] \arrow[d, "(CH_3)_3SiCl"'] & \\
 & \text{No reaction} &
\end{tikzcd} \qquad (8)$$

Based on these reactions, the actual yield of triphenylsilane-*d*, and therefore of silylaluminum compound (VI), was 62%.

Similar conclusions may be drawn from cleavage reactions which were carbonated prior to hydrolysis. In the case of hexaphenyldisilane, triphenylsilane was obtained in a 62% yield. From the reaction involving 1,1,1-trimethyl-2,2,2-triphenyldisilane mentioned earlier, which was also treated with carbon dioxide prior to hydrolysis, triphenylsilane was obtained in a 63.9% yield. Although no triphenylsilanecarboxylic acid was isolated from these reactions, some oxygen-containing organosilicon compounds were obtained, which could have arisen from decarbonylation of the acid[22]. However, these products could also arise from basic hydrolysis of triphenylsilane by moisture condensed on the cold, carbonation mixture prior to hydrolysis. These reactions may be illustrated by equation (9).

$$(\mathrm{V})+\mathrm{CO_2} \rightarrow \underset{(\mathrm{VII})}{(\mathrm{C_6H_5})_3\mathrm{SiAl(OR)_2}} \xrightarrow{\mathrm{H^+}} (\mathrm{C_6H_5})_3\mathrm{SiH} \qquad (9)$$

(OR represents hydride reduction products of CO_2)

An alternate synthesis of lithium trihydro(triphenylsilyl)aluminate, (V), was carried out by the addition of triphenylsilyllithium to lithium aluminum hydride. The reaction, as illustrated by the following equation, is analogous to that reported for the reaction of metal alkyls with lithium aluminum hydride[23].

$$(\mathrm{C_6H_5})_3\mathrm{SiLi}+\mathrm{LiAlH_4} \rightarrow (\mathrm{V})+\mathrm{LiH} \qquad (10)$$

Using a 1:1 mole ratio of reactants, half of the resulting mixture was carbonated and, subsequent to hydrolysis, triphenylsilane was isolated in a 78.4% yield. The remaining portion of the reaction mixture was treated with excess chlorotrimethylsilane and yielded 68% of triphenylsilane after acidification. As previously noted, both of these routes show that triphenylsilyllithium was no longer present in appreciable amounts, and indicates the formation of (V).

An attempt to prepare lithium dihydrobis(triphenylsilyl)aluminate by the reaction of two molar equivalents of triphenylsilyllithium with lithium aluminum hydride was apparently unsuccessful. The yield of triphenylsilane subsequent to carbonation and acid hydrolysis was only 43%. In a similar experiment, using lithium aluminum deuteride, only a 34.6% yield of a mixture of triphenylsilane and triphenylsilane-*d* was obtained upon acid hydrolysis alone. Based on the triphenylsilyllithium used, the yield of triphenylsilane-*d* was 4.3%, the formation of which will be discussed subsequently. The fate of the second equivalent of triphenylsilyllithium used in these reactions was not established.

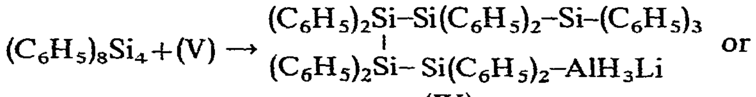
The hydrolysis reaction of the (triphenylsilyl)aluminum compounds formed in these experiments does not differentiate between (V) and a possible equilibrium product, (VIII), as shown in the following equation. Since it has been shown that lithium tetraphenylaluminate has an initial reactivity greater than triphenylaluminum[24], and further, that octaphenylcyclotetrasilane is cleaved by phenyllithium but not by the less reactive phenylmagnesium bromide under similar conditions[19], it appears more likely that (V) is the intermediate in the reactions, as it must be of sufficient reactivity to cleave silicon–silicon bonds. This same cleavage of octaphenylcyclotetrasilane, catenation, and cyclization was also brought about by treatment

$$\mathrm{Li[(C_6H_5)_3SiAlH_3]} \rightarrow \mathrm{LiH}+\underset{(\mathrm{VIII})}{(\mathrm{C_6H_5})_3\mathrm{SiAlH_2}} \qquad (11)$$

with (V), formed by the complete reaction of hexaphenyldisilane with a one-molar equivalent of lithium aluminum hydride. In addition, octaphenylcyclotetrasilane reacted similarly with the reaction mixture obtained from the addition of triphenylsilyllithium to aluminum hydride, another synthetic approach to (V), as illustrated in equation (12). Although this method was not thoroughly investigated, the results

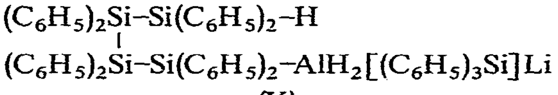
$$(C_6H_5)_3SiLi+AlH_3 \rightarrow Li[(C_6H_5)_3SiAlH_3] \qquad (12)$$

indicate the formation of (V). The first step in the reaction of (V) with octaphenylcyclotetrasilane could lead to the formation of either (IX) or (X). No products



$$(C_6H_5)_8Si_4+(V) \rightarrow \begin{array}{l}(C_6H_5)_2Si{-}Si(C_6H_5)_2{-}Si{-}(C_6H_5)_3\\ \qquad\quad | \\ (C_6H_5)_2Si{-}Si(C_6H_5)_2{-}AlH_3Li\end{array} \quad \text{or}$$

(IX)



$$\begin{array}{l}(C_6H_5)_2Si{-}Si(C_6H_5)_2{-}H\\ \qquad\quad | \\ (C_6H_5)_2Si{-}Si(C_6H_5)_2{-}AlH_2[(C_6H_5)_3Si]Li\end{array}$$

(X)

containing the triphenylsilyl group bound to silicon could be isolated from the resulting complex mixture of products, which would have established (IX) as the intermediate. Negative evidence suggesting that (IX) is the predominant species was obtained by the isolation of only 50% of triphenylsilane from the reaction involving the preparation of (V) by hydride reduction of hexaphenyldisilane, and only 30% from the experiment wherein triphenylsilyllithium had been added to aluminum hydride. Also, the results of the reactions of triphenylsilyllithium with lithium aluminum hydride indicated that compounds of the type $Li[AlH_2(SiR_3)_2]$ are not readily formed, which supports (IX) as the intermediate, rather than (X).

With regard to the existence and nature of (VI), the reaction of triphenylsilyllithium with aluminum chloride was also investigated briefly. This reaction had been carried out in an earlier study, but the formation of an (organosilyl)aluminum compound was not ascertained[25]. The addition of triphenylsilyllithium to aluminum chloride in a 1:1 molar ratio resulted in an almost colorless, clear solution. Color Test I[26] was essentially negative, indicating the absence of appreciable silyllithium reagent. Hydrolysis in deuteriochloric acid resulted in a 55% yield of a mixture of triphenylsilane-*d* and triphenylsilane in which the ratio of the deuterated to non-deuterated product was 1:1. Combination of triphenylsilyllithium and aluminum chloride in a 2:1 molar ratio resulted in a mixture which gave a marginally positive Color Test I[26]. Subsequent to treatment with deuteriochloric acid, a 63% yield of a mixture of triphenylsilane-*d* and triphenylsilane was isolated, and analysis showed a 1:3 ratio, respectively. When a 3:1 molar ratio of silylmetallic reagent to aluminum chloride was treated similarly, the ratio of triphenylsilane-*d* to triphenylsilane was 1:10. These results indicate that only the mono-substituted product, (VI), was formed in appreciable quantities, and that the bis- and tris(triphenylsilyl)aluminum chlorides, *if formed at all*, decomposed to afford triphenylsilane prior to hydrolysis. The fact that deuterated product was obtained does not establish the formation of di- and tri-substituted products in these latter two reactions, since a mono-substituted silylaluminum compound could arise in these cases.

The amount of non-deuterated triphenylsilane formed in the reaction using one equivalent of triphenylsilyllithium does not necessarily reflect an appreciable instability of (triphenylsilyl)aluminum dichloride, since a portion of the silyllithium compound could have interacted with the (triphenylsilyl)aluminum compound initially formed, resulting in triphenylsilane as in the other two cases.

Attempts to prepare(triphenylsilyl)aluminum compounds by cleavage of hexaphenyldisilane with aluminum metal in THF or by reaction of chlorotriphenylsilane with aluminum in the same solvent at reflux or at elevated temperatures under pressure were unsuccessful. In the latter cases, none of the easily isolable coupling product, hexaphenyldisilane, was obtained and there was not evidence of triphenylsilane subsequent to hydrolysis.

In the reactions involving the proposed (triphenylsilyl)aluminum compounds, the formation of some triphenylsilane, from sources other than hydrolysis, and hydride was detected. This became evident when the ratio of SiH to SiD in the triphenylsilane obtained from the cleavage by lithium aluminum deuteride followed by hydrolysis in hydrochloric acid was not the theoretical 1:1, but was of the order 1.5:1 of deuterated to non-deuterated product*. Nearly the reverse ratio was observed in the cleavage of hexaphenyldisilane by lithium aluminum hydride, followed by treatment with excess chlorotrimethylsilane and hydrolysis in deuteriochloric acid. The variances from the theoretical ratio may be explained by the fact that hydride/deuteride exchange was demonstrated between triphenylsilane and lithium aluminum deuteride in a separate experiment. Thus, in the cleavage of hexaphenyldisilane by deuteride ion, a larger than the expected amount of deuterated product would result if a portion of the silylaluminum complex were to decompose and afford triphenylsilane which could subsequently exchange with deuteride before hydrolysis. In the cleavage by lithium aluminum hydride, the triphenylsilane resulting from both sources would be constant upon hydrolysis in deuteriochloric acid, with only the remaining silylaluminum compound being deuterated. Similar reactions should explain the formation of the deuterated product from the reaction of triphenylsilyllithium with lithium aluminum deuteride. The mode of decomposition of the silylaluminum compounds was not determined, but may involve the formation of triphenylsilyl radicals and abstraction of hydrogen from solvent. A similar phenomenon has been observed in the reactions of triphenylsilyllithium with certain metallic halides, which has been proposed to result in unstable silylmetallic compounds[25]. Furthermore, recent studies have indicated that some silylmetallic derivatives of mercury[27], antimony, and bismuth[28] undergo decomposition affording silicon hydrides. However, lithium(triphenylsilyl)-triphenylborate, prepared by the reaction between triphenylsilyllithium and triphenylboron, apparently has appreciable stability[29].

In the reactions of hexaphenyldisilane with lithium aluminum hydride in tetrahydrofuran, there was always obtained a small amount of diphenylsilane, showing that some cleavage of silicon–phenyl bonds occurred. This was also observed upon treatment of triphenylsilane with lithium aluminum hydride under similar conditions.

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* A significant exchange of hydrogen between triphenylsilane and the aqueous media is precluded by the observation that triphenylsilane-*d*, prepared by the reduction of the chloride with lithium aluminum deuteride, followed by hydrolysis in hydrochloric acid, did not contain silicon–hydrogen absorption bands in its IR spectrum[35].

In addition to recovered starting material in this case, there was obtained about 3% of diphenylsilane and a lesser amount of tetraphenylsilane. The formation of these products may be illustrated by the following equation:

$$\begin{aligned}(C_6H_5)_3SiH + LiAlH_4 \rightarrow (C_6H_5)_2SiH_2 + LiAlH_3(C_6H_5) &\xrightarrow{(C_6H_5)_3SiH} \\ &\rightarrow (C_6H_5)_4Si + LiAlH_4\end{aligned}$$

Upon similar treatment, tetraphenylsilane was recovered in a 96% yield, and there was no evidence of products containing silicon–hydrogen groups. Recently, it has been reported that sodium hydride similarly cleaves silicon–carbon bonds when heated in cyclohexane at 200° under high pressure for 10 h[30]. Similarly, it has been demonstrated that silicon–phenyl bonds readily undergo hydrogenolysis when refluxed in dioxane in the presence of W-7 Raney nickel catalyst[31].

In addition to the reactions of $LiAlH_4$ in THF reported herein, some organopolysilanes were treated with the following reducing systems: $LiAlH_4$ in ether and in pyridine; NaH and LiH in THF; $NaH/AlCl_3$ in THF; $LiAlH_4/2\ AlCl_3$ in THF; $NaBH_4$ in dioxane; Zn(Hg)/HCl in a mixture of dioxane and toluene; Na/Hg in acetic acid; HI/P (red) in refluxing xylene; $Al(iso\text{-}OC_3H_7)_3$ in benzene and in THF; Mg in THF; Mg/MgI_2 in THF; and Al in THF. In the case of sodium hydride in THF, octaphenylcyclotetrasilane was converted into decaphenylcyclopentasilane in high yield after 20 h at reflux. Lithium hydride, after 72 h at reflux in THF, resulted in only a 3% yield of the cyclic pentasilane. None of the other treatments gave evidence of reductive cleavages. These reactions are summarized in Tables 5 and 6.

EXPERIMENTAL

All reactions were run in oven-dried glassware under atmospheres of oxygen-free, dry nitrogen. The tetrahydrofuran (THF) was dried and purified by refluxing over sodium for at least 24 h, followed by distillation into lithium aluminum hydride

TABLE 1

CLEAVAGE OF ORGANOPOLYSILANES BY LITHIUM ALUMINUM HYDRIDE IN THF

Compound		Mole ratio compd.: $LiAlH_4$	Reflux (h)	Yield of $(C_6H_5)_{2n}Si_nH_2$[a] (%)					Yield of $(C_6H_5)_{10}Si_5$[e] (%)
	(g)			$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	
$(C_6H_5)_8Si_4$[b]	10	4:1	[c]	[d]	[d]		3		64
	10	4:1	[c]	[d]	[d]		6		62
	7.3	1:1	1.5	[d]	[d]		16.5	8.2	16.5
$(C_6H_5)_{10}Si_5$[e]	10.9	4:1	0.2[f]	[d]	[d]		6		74
	10.9	1:1	41	[d]	10		7		9
	10.9	1:1	1.5	[d]	2	1	5	2	68
	10.9	1:2	44	16[g]	34		10		
$(C_6H_5)_8Si_4Cl_2$[a]	9.1	1:1	24	12	26	14.4	14		
$(C_6H_5)_8Si_4H_2$[a]	2	1:1	2	7.5[g]	10	30	5		

[a] Linear polysilanes. [b] Octaphenylcyclotetrasilane. [c] The reaction mixture was stirred at room temperature for 20 h. [d] No attempt was made to isolate these materials. [e] Decaphenylcyclopentasilane. [f] Refluxed for 12 min after stirring at room temperature for 18 h. [g] Obtained on distillation under reduced pressure.

and redistillation from the hydride immediately before use. All temperatures recorded are uncorrected. Products were identified by comparison of physical properties and infrared spectra with known samples. Mixed-melting point determinations were carried out on solid products.

Organopolysilanes and $LiAlH_4$

The reagents, reaction conditions, and results are listed in Table 1. In general, *ca.* 100 ml of THF was used in each case. The resulting reaction mixtures were hydrolyzed by cautiously pouring onto excess dilute acid. Subsequent to the usual work-up, products were isolated either by distillation under reduced pressure or by crystallization. The yields reported in Table 1 are for pure products, many of which were obtained only after repeated fractional recrystallizations.

Organodisilanes and $LiAlH_4$

The organodisilanes listed in Table 2 were treated with $LiAlH_4$ in 1:1 mole ratios using *ca.* 100 ml of THF in each run. Subsequent to hydrolysis in excess acid and the customary work-up, the products were isolated by distillation. The reaction conditions and results are shown in Table 2.

TABLE 2

CLEAVAGE OF ORGANODISILANES BY LITHIUM ALUMINUM HYDRIDE IN THF

Compound		Reflux	Treatment	Products	
	(g)	(h)			(%)
$(C_6H_5)_6Si_2$[a]	10.4	72	Acid hydrolysis	$(C_6H_5)_3SiH$	60
$[(CH_3)(C_6H_5)_2Si]_2$	6.0	67	Acid hydrolysis	$(CH_3)(C_6H_5)_2SiH$[b]	40
$[(CH_3)_2(C_6H_5)Si]_2$	10.0	65	Acid hydrolysis	$(CH_3)_2(C_6H_5)SiH$ (impure)[c]; $[(CH_3)_2(C_6H_5)Si]_2$	23 41.5
$(CH_3)_3SiSi(C_6H_5)_3$	6.0	61	Carbonation, acid hydrolysis	$(CH_3)_3SiH$;[d] $(C_6H_5)_3SiH$; $(C_6H_5)_3SiOH$	50 63.9 14
$(C_2H_5)_6Si_2$	12.5	65–67	Acid hydrolysis	$(C_2H_5)_3SiH$ $(C_2H_5)_6Si_2$	0[e] 72.8[e]

[a] A representative sample; see Table 3 for more complete information. [b] B.p. 107–110° (2.3 mm), n_D^{20} 1.5717; reported[36] n_D^{20} 1.5717. [c] Collected in three fraction, b.p. 50–70° (50–70 mm), with n_D^{20} values ranging from 1.4928–1.4988; reported[37] n_D^{20} 1.4988. [d] Collected prior to hydrolysis by means of a trap cooled to −65°, which was attached to the end of the reflux condenser. Identification was made by its IR spectrum as solutions in carbon disulfide and carbon tetrachloride. [e] The results of two runs. The solvent was carefully distilled through an 18″ spinning band column, rated at 23 theoretical plates. No evidence of triethylsilane was detected during the distillation or in the IR spectra of any of the distillation fractions.

Hexaphenyldisilane and $LiAlH_4$

The amounts of reagents, reaction conditions, subsequent treatments, and results are given in Table 3. In general, the reactions were carried out by simply mixing a 1:1 mole ratio of hexaphenyldisilane and $LiAlH_4$ in *ca.* 100 ml of THF and bringing to reflux the recorded length of time. The reaction mixtures usually took on a

TABLE 3

CLEAVAGE OF HEXAPHENYLDISILANE BY LITHIUM ALUMINUM HYDRIDE IN THF[a]

$(C_6H_5)_6Si_2$ (g)	Reflux (h)	Treatment	Yield of $(C_6H_5)_3SiH$[b] (%)	Other products[c]	(%)
5.2	48	$(CH_3)_3SiCl$ (excess); acid hydrolysis	60		
10.4	72	Acid hydrolysis	65.6	$(C_6H_5)_2SiH_2$	3
10.4	24	Carbonation[d]; acid hydrolysis	62.0[e]	$(C_6H_5)_6Si_2$	10
10.4	60	Acid hydrolysis	60.1	$(C_6H_5)_2SiH_2$	2
6.2	24	($LiAlD_4$ was used) hydrolyzed in H_3O^+	31[f] (62)[g]	$(C_6H_5)_3SiD$	44.3[f] (88.6)[g]
10.4	96	reflux with excess $(CH_3)_3SiCl$; hydrolized in D_3O^+	47[e,f] (94)[g]	$(C_6H_5)_3SiD$ $(C_6H_5)_6Si_2$	31[e,f] (62)[g] 36.5
5.2	26	$(C_6H_5)_8Si_4$[h], 7.2 g stirred at room temp. (36 h), acid hydrolysis	52	$(C_6H_5)_8Si_4$[h] $(C_6H_5)_{10}Si_5$[i] polysilanes[k]	45.2 55[j]

[a] The reactions were carried out as described in the experimental part, with the mole ratio of reactants being 1:1 in each case. [b] Yield based on two moles of product from one mole of disilane. [c] In addition to the products listed, distillation residues yielded varying amounts of viscous oils, which resisted attempts to purify. The IR spectra indicated the presence of SiOH and SiOSi groups. [d] Carbonation was accomplished by pouring the reaction mixture onto a slurry of Dry-Ice and ether, and allowing to warm to room temperature before hydrolyzing. [e] The yield was based on unrecovered starting material. [f] See the experimental part for the analysis of the mixture of $(C_6H_5)_3SiH$ and $(C_6H_5)_3SiD$. [g] The yield in parentheses is based on one mole of disilane forming one mole each of $(C_6H_5)_3SiH$ and $(C_6H_5)_3SiD$. [h] Octaphenylcyclotetrasilane. [i] Decaphenylcyclopentasilane. [j] Yield based on unrecovered octaphenylcyclotetrasilane. [k] Two additional solids were isolated. One, 0.5 g, m.p. 140–150° was obtained as crystals before distillation; the second, 0.7 g, m.p. 67–80°, was recovered from the distillation residue. Attempts to purify these materials were unsuccessful. Their IR spectra indicated the presence of silicon–phenyl and silicon–hydrogen groups.

greyish-green coloration. In one case, the grey lithium aluminates present in the lithium aluminum hydride were removed by filtration of a THF solution through a sintered-glass funnel prior to mixing with hexaphenyldisilane. After 24 h of reflux, an almost clear, light-yellow solution resulted. Subsequent to the treatment as given in Table 3 and hydrolysis, the mixtures were filtered to remove any unreacted hexaphenyldisilane. Following the usual work-up, the products were distilled under reduced pressure. Usually, a small amount of diphenylsilane was obtained at about 60° (0.3 mm) which was identified by IR spectral analyses and by its characteristic odor. Triphenylsilane was normally collected at temperatures of *ca.* 125–130° (0.16 mm), and solidified on cooling, m.p. 44–46°.

Triphenylsilyllithium and aluminum compounds

Triphenylsilyllithium was prepared in THF by cleavage of hexaphenyldisilane by lithium[32]. Subsequent to decantation from the excess lithium, the solution was added dropwise to a stirred solution of the aluminum compounds in THF. The triphenylsilane was isolated by distillation under reduced pressure. The reactants, molar quantities, reaction conditions and results are shown in Table 4.

TABLE 4

REACTIONS BETWEEN TRIPHENYLSILYLLITHIUM AND ALUMINUM COMPOUNDS

$(C_6H_5)_3SiLi$[a] (mmoles)	Aluminum compound (mmoles)	Treatment	$(C_6H_5)_3SiH$ (%)	Other products	
					(%)
30[b]	$LiAlH_4$ (30)	Stirred at room temp. (3h), added $(CH_3)_3SiCl$, (160 mmole), in ether, reflux (1 h), acid hydrolysis	68	$(C_6H_5)_3SiOH$	2.4
30[b]	$LiAlH_4$ (30)	Stirred at room temp. (3 h), carbonated, acid hydrolysis	78.4	[c]	
40	$LiAlH_4$ (20)	Stirred at room temp. (72 h), carbonated, acid hydrolysis	43	[c]	
10	$LiAlD_4$ (5)	Stirred at room temp. (7 h), hydrolyzed in dil. HCl	30.2	$(C_6H_5)_3SiD$[c]	4.4
20	AlH_3[d] (20)	Stirred at room temp. (1 h), followed by stirring with $(C_6H_5)_8Si_4$[e] (20 mmole), at room temp. (30 h); acid hydrolysis	30.8	$(C_6H_5)_8Si_4$[e] $(C_6H_5)_{10}Si_5$[f]	11.7 48.8[f]
14	$AlCl_3$[g] (14)	Stirred at room temp. (15 min)[h], hydrolyzed in dil. DCl	28	$(C_6H_5)_3SiD$	27
14	$AlCl_3$[g] (7)	Hydrolyzed in dil. DCl after 15 min	50	$(C_6H_5)_3SiD$	15
21	$AlCl_3$[g] (7)	Hydrolyzed in dil. DCl[i]	20[j]	$(C_6H_5)_3SiD$	2[j]

[a] Based on the amount of hexaphenyldisilane used in the preparation. [b] Originally, 60 mmoles each of $(C_6H_5)_3SiLi$ and $LiAlH_4$ were combined together. The resulting mixture was divided in half and each portion treated individually as described in the first two experiments. [c] IR spectra on the distillation residues indicated the presence of Si–phenyl, Si–OH, and Si–O–Si groups. [d] Prepared from 15 mmoles of $LiAlH_4$ and 5 mmoles of $AlCl_3$, according to the method of Wiberg[38]. [e] Octaphenylcyclotetrasilane. [f] Decaphenylcyclopentasilane; yield based on unrecovered $(C_6H_5)_8Si_4$. [g] Freshly sublimed; dissolved in THF at -30° to prevent interaction between solvent and $AlCl_3$. [h] The resulting light-pink solution gave a negative or very weakly positive Color Test I[26]. [i] Prior to hydrolysis, the reddish-brown mixture gave a marginally positive Color Test I[26]. [j] Color Test I[26] was essentially negative after 15 min. Aprox. one-fourth of the solution was withdrawn and hydrolyzed in dil. DCl; the ratio of deuterated to non-deuterated triphenylsilane was about 1:10, resp. Octaphenylcyclotetrasilane had been added to the rest of the reaction mixture, which was subsequently refluxed for 24 h; following hydrolysis in dil. DCl, octaphenylcyclotetrasilane was recovered nearly quantitatively.

Perphenylated cyclic polysilanes and other metallic hydrides

Various other metallic hydride systems were used in attempts to effect silicon–silicon bond reductions. The reagents, reaction conditions, and results are listed in Table 5. The reaction mixtures were all hydrolyzed in crushed ice containing excess dilute acid. Any solids were filtered off, washed with benzene, and dried. The soluble materials were worked up in the usual manner.

Organopolysilanes and various reducing agents (attempted)

The reagents, reaction conditions and results are given in Table 6.

Analyses of mixtures of triphenylsilane and triphenylsilane-d

IR analyses of mixtures of triphenylsilane and triphenylsilane-*d* were carried

TABLE 5

ATTEMPTED REDUCTION OF PERPHENYLATED POLYSILANES WITH METALLIC HYDRIDES[a]

Compound		Reducing agent	Reaction conditions	Starting material (%)	Products[b]	
	(g)					(%)
$(C_6H_5)_8Si_4$	10	$LiAlH_4$	Reflux 7 days in ether	98.7		
	10	NaH	Reflux 20 h in THF	0	$(C_6H_5)_{10}Si_5$	77
	10	LiH	Reflux 72 h in THF	88	$(C_6H_5)_{10}Si_5$	3
	10	$NaBH_4$	Reflux 5 days in dioxane	64[c]	Siloxane[b]	*ca.* 20
	10	$NaH/AlCl_3$	Reflux 72 h in THF	97		
	10	$LiAlH_4/2AlCl_3$	Reflux 6 days in THF	95		
$(C_6H_5)_{10}Si_5$	10.9	$LiAlH_4$	Reflux 6 days in ether	99		
	10.9	NaH	Reflux 18 h in THF	93.2		
	10.9	LiH	Reflux 72 h in THF	92.8		
	10.9	$NaBH_4$	Reflux 5 days in dioxane	96		
	10.9	$LiAlH_4/2AlCl_3$	Reflux 25 h in THF	95.8		
$(C_6H_5)_6Si_2$	5.2	$LiAlH_4$	Reflux 54 h in pyridine	96		

[a] The mole ratio of reactants was 1:1 in each case. [b] The IR spectrum of the remaining material, m.p. range 170–190°, showed bands characteristic of siloxane groups, but no silicon hydrogen groups. Material having a similar m.p. range and IR spectrum was also obtained during an attempted recrystallization of octaphenylcyclotetrasilane from boiling dioxane.

TABLE 6

ATTEMPTED REDUCTIVE CLEAVAGES OF PERPHENYLATED ORGANOPOLYSILANES BY VARIOUS REDUCING AGENTS

Compound[a]	Reducing agent	Mole ratio compound red. ag.	Reactions conditions	Recovery (%)
$(C_6H_5)_8Si_4$	Zn(Hg)/HCl	7:100	Reflux until H_2 evol. ceased (16 h) in a suspension of conc. HCl, toluene, and dioxane	90
$(C_6H_5)_{10}Si_5$	Zn(Hg)/HCl	7:100	Reflux until H_2 evol. ceased (16 h) in a suspension of conc. HCl, toluene, and dioxane	98
$(C_6H_5)_8Si_4$	3% $Na(Hg)/HC_2H_3O_2$	1:10	Room temp. until H_2 evol. ceased (8 h)	98
$(C_6H_5)_{10}Si_5$	3% $Na(Hg)HC_2H_3O_2$	1:10	Room temp. until H_2 evol. ceased (8 h)	90
$(C_6H_5)_8Si_4$	HI/P(red)	1:2	Reflux in xylene (64 h)	0[b]
$(C_6H_5)_{10}Si_5$	HI/P(red)	1:2	Reflux in xylene (64 h)	71[b]
$(C_6H_5)_8Si_4$	$Al(iso\text{-}OC_3H_7)_3$	1:1	Reflux (48 h) in benzene	96
$(C_6H_5)_8Si_4$	Mg[c]	1:10	Reflux (5 days) in THF	96
$(C_6H_5)_8Si_4$	Mg/MgI_2[d]	1:10	Reflux (30 h) in THF	96
$(C_6H_5)_6Si_2$	Mg/MgI_2[d]	1:10	Stirred with a few ml of THF (20 h), reflux with 60 ml THF (24 h)	99
$(C_6H_5)_6Si_2$	Al	1:4	Reflux (5 days) in THF	99

[a] Five grams of compound was used in each case. [b] There was a considerable amount of material admixed with the red phosphorus, which was insoluble in organic solvents. An IR spectrum as a KBr pellet showed no absorption bands for organic groups. The material was apparently a mixture of silica and silicic acid. Refluxing octaphenylcyclotetrasilane with conc. HI in xylene for 64 h produced a similar material which was analyzed for silicon. (Found: Si, 42.39, 41.11. SiO_2 calcd.: Si, 46.72%.) [c] Powdered Mg, which had been washed successively with dil. HCl, ethanol, and ether, followed by drying at 130° for 3 h. [d] Prepared by the reaction of iodine with magnesium turnings in ether, using a 1:2 g-atom ratio, respectively. The ether was removed by distillation and replaced with THF.

out on a Perkin Elmer "Model 21" double-beam spectrophotometer using a 0.5 mm, sodium chloride cell. The samples were analyzed for triphenylsilane-*d* using the absorption band at 6.45 microns, which is characteristic of silicon–deuterium bonds[33]. The solvent used was Eastman spectral grade bromoform. The determinations were carried out at 25°. The results were an average of at least three runs. Conformity with Beer's law was established by the standardization plot, which was a good straight line nearly passing through the origin. The analysis of a prepared mixture containing 12.2 mg/ml of triphenylsilane-*d* and 40.0 mg/ml of triphenylsilane gave a result of 12.8 mg/ml, a value 5% higher than the theoretical. The amount of triphenylsilane in the mixtures was calculated by subtracting the quantity of triphenylsilane-*d* from the total weight of the sample. The results are given with each individual case.

Triphenylsilane and $LiAlH_4$

A mixture of 10.0 g (0.04 mole) of triphenylsilane (free of di- and tetraphenylsilane) and 1.5 g (0.04 mole) of $LiAlH_4$ was refluxed in *ca.* 100 ml of THF for 46 h. Subsequent to hydrolysis by slowly pouring upon a mixture of crushed ice and dilute acid, and the usual work-up, the products were distilled under reduced pressure to give 0.2 g (2.8%) of impure diphenylsilane, b.p. 60–70° (0.15 mm), n_D^{20} 1.5828 (lit. value[34], n_D^{20} 1.5975), identified by its IR spectrum and characteristic odor. Further distillation afforded 8.5 g (85%) of recovered starting material, b.p. 125–130° (0.17 mm), m.p. 44–46° (mixed m.p.). The distillation residue partially solidified on cooling. The solid material was washed with petroleum ether (b.p. 60–70°) and recrystallized from ethyl acetate to give 0.2 g (1.5%) of tetraphenylsilane, m.p. 232–235° (mixed m.p.).

Similar results were obtained in a second run under the same conditions.

Triphenylsilane and $LiAlD_4$

A mixture of 5.2 g (0.02 mole) of triphenylsilane and 0.84 g (0.02 mole) of $LiAlD_4$ was refluxed in 65 ml of THF for 24 h. Subsequent to hydrolysis and work-up as described in the preceding experiment, there was obtained 0.1 g (2.8%) of impure diphenylsilane, b.p. 40–50° (0.17 mm) and 4.1 g (78%) of triphenylsilane, b.p. 125–130° (0.17 mm), m.p. 42–45° (mixed m.p.). The IR spectra of these materials contained strong absorption bands for both silicon–hydrogen and silicon–deuterium bonds. From the distillation residue, there was obtained 0.1 g (1.5%) of tetraphenylsilane, m.p. 232–235° (mixed m.p.).

Tetraphenylsilane and $LiAlH_4$

A solution of 10.0 g (0.03 mole) of tetraphenylsilane and 1.5 g (0.4 mole) of $LiAlH_4$ in 100 ml of THF was refluxed for 89 h. The reaction mixture was poured onto a slurry of Dry Ice and ether. After allowing the carbonation mixture to warm to room temperature, dilute acid was added, and the solids filtered. The solids were washed with ether and dried to give 9.3 g (93%) of tetraphenylsilane, m.p. 234–236° (mixed m.p.). The ether washings and the filtrate were combined and extracted with 5% sodium hydroxide solution. The aqueous layer was acidified with conc. hydrochloric acid, and extracted with ether. Evaporation of the ether gave only a trace of solid, m.p. 222–228°, identified as impure tetraphenylsilane by its IR spectrum. An additional 0.3 g (3%) of tetraphenylsilane was obtained from the original organic layer. The small amount of residue obtained from evaporation of the mother liquor did not show absorption bands for SiH, SiOH or SiOSi groups.

Chlorotriphenylsilane and aluminum (attempted)

Run 1. A mixture of 6.0 g (0.02 mole) of chlorotriphenylsilane and 1.0 g (0.04 g-atom) of freshly turned aluminum metal chips was refluxed in 25 ml of THF for 5 days. The reaction mixture was hydrolyzed in excess dilute acid. After hydrogen evolution ceased, there remained no insoluble material, *i.e.*, hexaphenyldisilane. Subsequent to the usual work-up, the solvents were removed by distillation and petroleum ether (b.p. 60–70°) added. The solids were removed by filtration and the filtrate chromatographed on an alumina column. Evaporation of the solvent from the petroleum ether eluate left only a trace of material, the IR spectrum of which did not show the presence of triphenylsilane. The petroleum ether insoluble material was identified as triphenylsilanol, resulting from hydrolyzed starting material.

Run 2. The same quantities of starting materials and solvent which were used in Run 1, were heated at 140–150° for 18 h and at 220–250° for 3 h in a steel bomb, agitated by a rocking assembly, under nitrogen pressure (initially at 500 p.s.i.g. at room temp.). The work-up and results were identical to those described in Run 1.

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