THE CHARACTERIZATION OF DODECAPHENYLCYCLOHEXASILANE

HENRY GILMAN AND GERALD L. SCHWEBKE
Department of Chemistry, Iowa State University, Ames, Iowa (U.S.A.)
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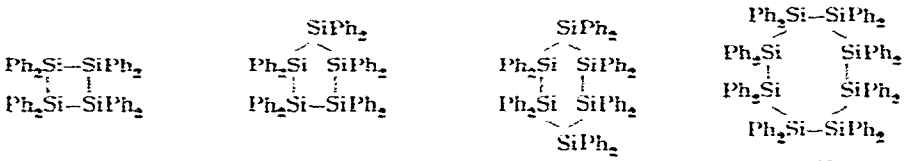
The preparation of phenylated cyclosilanes from the treatment of dichlorodiphenylsilane with sodium was first described by Kipping[1,2]. Three crystalline compounds, designated as Compounds A, B, and C, were isolated from this reaction, and the first two have been shown to be octaphenylcyclotetrasilane (I)[3,4] and decaphenylcyclopentasilane (II)[5,6], respectively. The structure of Compound B had earlier been reported to consist of a four-membered cycle (I) in one case[7] and a six-membered cycle (III) in another[8,9].



(I) (II) (III) (IV)

The third crystalline compound (Compound C) isolated by Kipping from the Wurtz coupling reaction of dichlorodiphenylsilane was usually obtained in a mixture with octaphenylcyclotetrasilane (I), from which it was separated either by fractional crystallization or by conversion of the octaphenylcyclotetrasilane to its more soluble 1,4-diiodide or 1,4-dichloride. Kipping found that Compound C did not react with the reagents which attack octaphenylcyclotetrasilane. Compound C was described as a crystalline material which, when heated in a test tube, did not melt at high temperatures, charred slightly and gave vapors which took fire with distinct explosion[2].

Kipping suggested that C, due to its unreactivity, resembled Compound B (later shown to be decaphenylcyclopentasilane[5,6]), but was probably more complex. He proposed as possible structures dodecaphenylcyclohexasilane (III) or hexadecaphenylcyclooctasilane (IV)[2]. The former is a very likely structure, because it is the next in the homologous series of phenylated cyclosilanes and is not an unexpected product in the reaction of dichlorodiphenylsilane with metals.

EXPERIMENTAL

All reactions involving organometallic compounds were carried out under an atmosphere of dry oxygen-free nitrogen. Unless otherwise specified the tetrahydrofuran was dried by refluxing it over sodium metal for at least 24 h and then was distilled from lithium aluminum hydride immediately before use. All melting points are uncorrected and were determined using a Mel-Temp apparatus.

Compound C

To 15.3 g (2.2 g-atom) of lithium metal was added 2 g of dichlorodiphenylsilane dissolved in 20 ml of sodium-dried tetrahydrofuran*. The reaction started within a few min, as indicated by the evolution of heat and formation of the usual silyllithium color (red-brown).

To this highly rapidly stirred mixture was added 253 g (1.01 moles total) of dichlorodiphenylsilane dissolved in 300 ml of tetrahydrofuran. The rate of addition was regulated to maintain a low concentration of silyllithium compounds and a vigorous, spontaneous reflux. The addition was complete within 2 h and the resulting reaction mixture was stirred with refluxing for 48 h. At the end of this time one ml of water was added to decompose the silyllithium compounds present.

The insoluble material was removed by filtration and boiled with 200 ml of a methanol–water mixture. After drying, the water-insoluble material (52.2 g) was extracted four times with cold benzene to leave 5.7 g (3.1 %) of Compound C, m.p. 500–504° (decomp.). From the benzene and tetrahydrofuran soluble materials was isolated 92 g (50 %) of decaphenylcyclopentasilane, m.p. 460–464°.

Purification of Compound C. For the purpose of study and reactions, Compound C was prepared as described above or was collected from the several preparations of decaphenylcyclopentasilane which were carried out and from treatment of unpurified octaphenylcyclotetrasilane in which Compound C occurs as a minor constituent, with various halogenating agents and hydrogen halides. Purification of the compound can be carried out by several crystallization methods.

Small amounts of Compound C can be recrystallized from benzene, in which it is very sparingly soluble (about 0.35 g/100 ml at reflux temperature). From this solvent the compound can be obtained in much better crystal form than others which have been investigated. Larger amounts of Compound C can be recrystallized from refluxing tetralin (3 g/100 ml) or from refluxing benzyl alcohol, in which the compound is significantly more soluble.

The most efficient method employed was one of Soxhlet extraction with benzene employing an apparatus in which the extracting mixture could be efficiently stirred.

The pure Compound C obtained by any of these methods melted, when placed in the melting point block at 490°, at 502–504°, decomposing to a lemon yellow froth or liquid with condensation of a colorless material in the upper part of the melting zone. Compound C maintained at temperatures above 450°, but below its melting point, for extended periods underwent significant sintering and softening.

Dodecaphenylcyclohexasilane

From dichlorodiphenylsilane and 1,5-dilithiodecaphenylpentasilane. To 4.04 g (0.0159 mole) of dichlorodiphenylsilane dissolved in 200 ml of tetrahydrofuran was added dropwise 166 ml of a tetrahydrofuran solution containing 0.0157 mole of 1,5-dilithiodecaphenylpentasilane[5,6]. After about three-fourths of this solution had been added, the silyllithium color began to persist in the reaction mixture. Therefore, an additional 1.21 g (0.0048 mole) of dichlorodiphenylsilane was introduced and the

* This method of preparation of Compound C was first developed in our laboratories by Dr. S. L. Liu (unpublished studies).

addition of silyllithium solution completed. A slight orange-yellow color remained at the end of the addition. After stirring overnight the reaction mixture was colorless.

Hydrolysis with 1*N* hydrochloric acid caused the precipitation of 1.50 g (13.1 %) of octaphenylcyclotetrasilane, m.p. 307–317° (mixed m.p.). The usual work-up provided a residue which was treated with benzene to give 0.4 g (2.7 %) of crude Compound C, melting with decomposition over the range 470–500°. Recrystallization from tetralin raised its melting point to 500° (mixed m.p.).

Concentration of the benzene soluble portion of the reaction residue and addition of petroleum ether (b.p. 60–70°) gave 3.50 g (24.5 %) of decaphenylcyclopentasilane, m.p. 435–445°.

From 1,3-dichlorohexaphenyltrisilane and sodium. A mixture of 3.09 g (0.005 mole) of 1,3-dichlorohexaphenyltrisilane[10], 0.25 g (0.0109 g-atom) of sodium metal and 50 ml of sodium-dried xylene was refluxed for 5 h with the formation of a blue-colored precipitate.

After standing overnight the reaction mixture was treated with 20 ml of ethanol to destroy excess sodium. The mixture was then filtered and the insoluble material was treated with water. The water-insoluble material amounted to 0.070 g and melted over the range 360–380° (decomp.). Extraction of this with 200 ml of boiling benzene left 0.40 g (14.7 %) of a tan solid melting 370–377° (decomp.). This material did not alter the melting point characteristics of a sample of Compound D* when the two were admixed.

The benzene-soluble material precipitated upon cooling of the solution to room temperature. There was obtained 0.25 g (9.2 %) of pure Compound C, m.p. 502–504° (mixed m.p.).

From the original xylene-soluble material there was obtained 0.41 g (15 %) of decaphenylcyclopentasilane, which melted 430–440° (mixed m.p.) after recrystallization from benzene–petroleum ether (b.p. 60–70°). A trace of octaphenylcyclotetrasiloxane, m.p. 188–189° (mixed m.p.) was also isolated.

From 1,3-dichlorohexaphenyltrisilane and magnesium (attempted). Magnesium metal (1.00 g, 0.041 g-atom) and a small crystal of iodine were treated with 10 ml of a solution of 3.09 g (0.005 mole) of 1,3-dichlorohexaphenyltrisilane in 56 ml of tetrahydrofuran at the reflux temperature for half an hour. Apparently the reaction did not initiate. The remainder of the chlorosilane solution was added along with a second iodine crystal, and the reaction mixture was refluxed overnight producing a slight green color. A third crystal of iodine was added and the reaction mixture was refluxed for an additional 24 h with no change in its appearance.

Work-up was effected with 1*N* hydrochloric acid followed by the usual extractive procedure yielding 2.38 g (82 %) of hexaphenyltrisilane-1,3-diol, m.p. 145–147°. Recrystallization from petroleum ether (b.p. 60–70°) gave the pure product, m.p. 146.5–148°. No other pure products were isolated for identification.

From 1,3-dihalohexaphenyltrisilane and sodium-potassium alloy (attempted). One milliliter of sodium–potassium alloy suspended in 20 ml of tetrahydrofuran was treated over a period of 2.5 h with 4.00 g (0.00567 mole) of the dihalo compound[6]

* This material can be obtained from the reaction of dichlorodiphenylsilane with sodium in refluxing toluene and is apparently similar to the amorphous, highly insoluble substance first characterized by Kipping[2].

prepared by the reaction of *N*-bromosuccinimide with *1H,3H*-hexaphenyltrisilane in carbon tetrachloride. At the end of this time the reaction solution was bright red in color and Color Test I[11] was positive. The mixture was stirred for an additional 2 h at room temperature and then about 15 g of mercury was added to amalgamate the excess alloy.

The mixture was stirred overnight and the silylmetallic solution, along with an insoluble solid material, was decanted from the amalgam. Analysis by double titration (allyl bromide)[12] indicated the presence of 0.0126 mole of silylmetallic compounds.

The resulting solution was added rapidly to 3.36 g (0.0126 mole) of tri-*n*-butyl phosphate and after 15 min Color Test I was negative. Hydrolysis with 200 ml of 1*N* hydrochloric acid and the usual work-up provided a residual oil from which was isolated by trituration with petroleum ether (b.p. 60–70°) 0.51 g (16%) of decaphenylcyclopentasilane, melting after recrystallization from ethyl acetate at 460–464° (mixed m.p.).

The petroleum ether-soluble material was chromatographed on alumina to give 0.43 g (8.6%) of 1,2-di-*n*-butyltetraphenyldisilane[6], m.p. 97–98° (mixed m.p.) after recrystallization from ethanol. Also isolated was 0.37 g (8.3%) of 1,3-di-*n*-butylhexaphenyltrisilane[6], m.p. 145–147° (mixed m.p.) after recrystallization from benzene–ethanol. No other products were identified.

Tetradecaphenylcycloheptasilane (attempted)

Eight grams (0.0153 mole) of 1,2-dibromotetraphenyldisilane suspended in 10 ml of tetrahydrofuran was treated in a dropwise manner with 0.014 mole of 1,5-dilithiodecaphenylpentasilane in 155 ml of tetrahydrofuran solution. At no time during the addition was Color Test I observed to be positive. The reaction mixture was stirred overnight at room temperature and then hydrolyzed (1*N* hydrochloric acid). The usual work-up provided octaphenylcyclotetrasilane (14.5%), m.p. 322–328° (mixed m.p.), and decaphenylcyclopentasilane (31.9%), m.p. 460–466° (mixed m.p.) as the only identifiable products.

Lithium cleavage of Compound C

Reaction with trimethyl phosphate. Two grams (0.00183 mole) of Compound C and 0.52 g (0.075 g-atom) of lithium metal were treated with a few ml of tetrahydrofuran. After 7 h of stirring, the reaction started, as indicated by a yellow color in the mixture. The remainder of the tetrahydrofuran (50 ml) was added slowly and the silyllithium color deepened as the addition progressed. Then the reaction mixture was stirred at room temperature for 14 h. At the end of this time a simple base titration indicated the presence of 0.0071 mole of silyllithium compounds.

The solution was filtered through glass wool and then added to 1.20 g (0.086 mole) of trimethyl phosphate[13] dissolved in 50 ml of tetrahydrofuran. After acid hydrolysis there was recovered 0.1 g (5%) of Compound C, m.p. 496° (decomp.). Work-up of the organic solvent-soluble material by chromatography on an alumina column, provided 0.20 g (14.9%) of 1,2-dimethyltetraphenyldisilane, which melted at 141–143° (mixed m.p.) after recrystallization from petroleum ether (b.p. 60–70°).

Cyclohexane eluted 1.09 g (55.6%) of crude 1,3-dimethylhexaphenyltrisilane, m.p. 90–93°. This material was recrystallized from ethanol to give the pure compound, m.p. 92–93° (mixed m.p.)[14]. There was also isolated a trace of 1,4-dimethyloctaphenyl-

tetrasilane, m.p. 217–220° (mixed m.p.). The yields cited here are based on unrecovered Compound C. No other products were isolated.

Reaction with tri-n-butyl phosphate. To 3.5 g (0.0032 mole) of Compound C and 0.60 g (0.086 g-atom) of lithium metal was added sufficient tetrahydrofuran to form a thin paste. This mixture was stirred for half an hour at slight reflux before the reaction started. The remainder of the tetrahydrofuran (100 ml) was added dropwise while the reaction mixture was warmed gently. After stirring the resulting mixture for 13 h at slight reflux, double titration (allyl bromide) indicated the presence of 0.0105 mole of silyllithium.

The reaction mixture, filtered free of lithium, was added to 3.42 g (0.0128 mole) of tri-*n*-butyl phosphate[13]. After Color Test I was negative, hydrolysis with 200 ml of 1.N hydrochloric acid was carried out to yield 0.20 g (5.7 %) of insoluble Compound C, m.p. 498–500° (decomp.). Alumina chromatography of the ether-soluble residue provided 0.58 g (21.7 %) of crude 1,2-di-*n*-butyltetraphenyldisilane[6], which melted at 98–100° (mixed m.p.) after recrystallization from ethanol. Also isolated with petroleum ether (b.p. 60–70°) as the eluent was 1.06 g (28.7 %) of 1,3-di-*n*-butylhexaphenyltrisilane[6], m.p. 146–147.5°, after it was recrystallized from petroleum ether (b.p. 60–70°).

A second reaction employing 8 h cleavage time at room temperature yielded 11.4 % of recovered Compound C, 13.4 % of 1,2-di-*n*-butyltetraphenyldisilane and 39.2 % of 1,3-di-*n*-butylhexaphenyltrisilane. In a third run for 5 h at room temperature there was obtained 42 % of recovered Compound C, 4.5 % of 1,2-di-*n*-butyltetraphenyldisilane; and 41.5 % of 1,3-di-*n*-butylhexaphenyltrisilane. All product yields are based on unrecovered Compound C.

Short contact time followed by trimethyl phosphate. Into a reaction flask provided with a sintered glass filter and stopcock at the bottom was introduced 5.00 g (0.0046 mole) of Compound C and 2.0 g (0.29 g-atom) of lithium metal. A few ml of tetrahydrofuran was introduced and after 10 min of stirring the reaction began. The silyllithium compounds thus formed were continuously filtered through the sintered glass into a lower reaction flask which contained 4.2 g (0.03 mole) of trimethyl phosphate. Over a period of three and one-half hours, 120 ml of tetrahydrofuran was added to the cleavage mixture and the solution of silyllithium compounds thus formed was filtered and allowed to react with the trimethyl phosphate. Subsequent to acid hydrolysis, 1.2 g (24 %) of Compound C was recovered. The remainder of the reaction residue was chromatographed on alumina to give 0.1 g (2.4 %) of crude 1,2-dimethyltetraphenyldisilane, m.p. 119–130°. It was recrystallized from petroleum ether (b.p. 60–70°) to give the pure product, m.p. 140–142° (mixed m.p.).

Cyclohexane elution of the column provided 1.72 g (43 %) of 1,3-dimethylhexaphenyltrisilane, which melted at 92–93° (mixed m.p.) after recrystallization from petroleum ether. With carbon tetrachloride there was eluted 0.05 g (1.3 %) of crude 1,6-dimethyldodecaphenylhexasilane, melting over the range 190–200°. Two recrystallizations from petroleum ether raised its melting point to 205–207° (mixed m.p.)[15].

In a second reaction using the same apparatus 6.00 g (0.0055 mole) of Compound C was cleaved with 0.85 g (0.12 g-atom) of lithium metal. The silyllithium compounds were allowed to react with 3.66 g (0.026 mole) of trimethyl phosphate. One liter of tetrahydrofuran was added to the cleavage mixture and the resulting solution re-

moved over a period of 7 h. Compound C (54.3 %) was recovered from the reaction mixture. Also isolated were 0.35 g of diphenylsilanediol, m.p. 136–140° and, by fractional crystallization, 0.15 g (5.3 %) of crude 1,6-dimethyldodecaphenylhexasilane, m.p. 195–200°. Recrystallization of the crude product from petroleum ether gave white crystals, m.p. 206–208° (mixed m.p.). (Found: mol. wt. vapor pressure osmometer in benzene with decaphenylcyclopentasilane as standard, 1155, 1141. $C_{74}H_{66}Si_6$ calcd.: mol. wt., 1124.)

Short contact time followed by tri-n-butyl phosphate. In an apparatus similar to that described for the previous reactions, but with a finer sintered glass filter, 8.00 g (0.0073 mole) of Compound C was cleaved with 2.00 g (0.288 g-atom) of lithium metal using 1250 ml of tetrahydrofuran over a period of 9 h. At the end of this time only a small amount of dark-brown insoluble material remained in the upper reaction flask.

The solution from the lower flask was hydrolyzed by addition to one liter of distilled water containing 15 ml of concentrated hydrochloric acid. After the addition of some diethyl ether the water layer was removed and the organic layer filtered to give 0.50 g (6.2 %) of recovered Compound C, m.p. 495–500° (decomp.).

The ether solution was dried with anhydrous sodium sulfate and the solvent removed by evaporation. The residue which resulted was chromatographed on an alumina column. There was isolated from the petroleum ether (b.p. 60–70°) eluates 1.91 g (21.5 %) of crude 1,3-di-*n*-butylhexaphenyltrisilane, which melted at 145–147° (mixed m.p.) after recrystallization from petroleum ether. Continued elution with the same solvent afforded 0.30 g (5.2 %) of 1,4-di-*n*-butyloctaphenyltetrasilane, m.p. 217–220°. When recrystallized from benzene–petroleum ether the compound melted at 221–222° (mixed m.p.).

Elution of the column with carbon tetrachloride provided 0.29 g (5.1 %) of decaphenylcyclopentasilane, m.p. 450–460° (mixed m.p.), and benzene and ethyl acetate eluted 2.11 g (27 %) of crude tri-*n*-butyl phosphate. No significant quantities of material were eluted with tetrahydrofuran or ethanol.

Finally the alumina column was stripped with a 5 % solution of acetic acid in tetrahydrofuran to give 4.45 g (about 55 %) of very viscous siloxane polymer, the infrared spectrum of which showed the presence of SiOH and SiOSi groupings in addition to the *Si*-phenyl group.

A repeat of this reaction under the same conditions, but using 8.87 g (0.096 mole) of *n*-butyl chloride for the formation of the derivatives, resulted in the recovery of 0.35 g (4.2 %) of Compound C and the isolation of 0.30 g (3.6 %) of diphenylsilanediol, m.p. 151–155° (mixed m.p.) prior to the chromatographic step. In this case the only product isolated by chromatography with petroleum ether and with cyclohexane was 2.59 g (28.0 %) of 1,3-di-*n*-butylhexaphenyltrisilane, m.p. 145–147° (mixed m.p.). The chromatography was continued no further.

Compound C with phosphorus pentachloride in sym-tetrachloroethane

A stirred mixture of 2.00 g (0.0018 mole) of Compound C, 0.82 g (0.0039 mole) of phosphorus pentachloride and 75 ml of *sym*-tetrachloroethane was heated to 135° for 2 h. No detectable change in the appearance of the reaction mixture occurred during this time. An additional 1.64 g (0.0078 mole) of phosphorus pentachloride was introduced and the mixture was heated at 135° for 5 h to give a clear solution.

The solvent was removed at reduced pressure and the residue was treated with sodium-dried petroleum ether (b.p. 60–70°) to give 0.30 g (15%) of recovered Compound C, m.p. 495–500° (decomp.). The residual oil failed to crystallize from petroleum ether; only an oil formed when the solution was cooled.

The petroleum ether was evaporated and the residual oil was treated with acetone to give 0.19 g (15%) of a compound, m.p. 217–221°. Recrystallization of this compound from benzene–petroleum ether afforded pure octaphenyl-1,4-dioxacyclohexasilane, m.p. 223–225° (mixed m.p.). The infrared spectrum of the compound and that of an authentic sample of octaphenyl-1,4-dioxacyclohexasilane were superimposable. No other products were isolable.

When Compound C was refluxed with *sym*-tetrachloroethane alone for 48 h, 98% of the starting material was recovered.

Compound C with mercuric chloride (attempted)

In benzene. A mixture of 1.99 g (0.0073 mole) of mercuric chloride, 2.00 g (0.0018 mole) of Compound C and 160 ml of sodium-dried benzene was stirred at reflux temperature for 18 h. Filtration of the mixture provided 2.76 g of insoluble material which was treated with hot water, to give 1.84 g (92%) of recovered Compound C, m.p. 500–503°.

In tetrahydrofuran. A suspension of 2.00 g (0.0018 mole) of Compound C in 75 ml of tetrahydrofuran was refluxed with 1.99 g (0.0073 mole) of mercuric chloride for 24 h with no appreciable change in the appearance of the reaction mixture. There was recovered 1.85 g (92.5%) of Compound C, m.p. 498–500° (decomp.).

Compound C with chlorine

Several reactions of Compound C with chlorine gas were attempted in either benzene, carbon tetrachloride or *o*-dichlorobenzene, with the recovery of varying amounts of Compound C. The compound does react with chlorine at elevated temperatures, but the complexity of the mixture of products made isolation by the usual techniques difficult. In order to cause significant amounts of Compound C to react, large excesses of chlorine had to be used, which evidently caused secondary cleavage reactions with whatever products had initially been formed.

Compound C with bromine (attempted)

A mixture of 1.5 g (0.0014 mole) of Compound C and 0.0028 mole of bromine in 110 ml of sodium-dried benzene was refluxed for 5 h. The red-brown color of the bromine remained. Filtration of the cooled reaction mixture afforded 1.44 g (96%) of recovered Compound C, m.p. 502–504°.

Compound C with methyllithium (attempted)

Two grams (0.0018 mole) of Compound C suspended in 100 ml of tetrahydrofuran was stirred at room temperature for 24 h with 0.0146 mole of methyllithium prepared in diethyl ether. Hydrolysis and filtration gave 1.91 g (96%) of recovered Compound C, m.p. 495–500°.

Compound C with benzyllithium

To 4.00 g (0.0036 mole) of Compound C suspended in 50 ml of tetrahydrofuran

was added 0.051 mole of benzyllithium in 45 ml of solution. The mixture was stirred for 15 h at room temperature and then hydrolyzed with 200 ml of 1*N* hydrochloric acid.

Filtration of the hydrolysis mixture provided 2.86 g (71.5%) of recovered Compound C, m.p. 500–502°. From the organic layer the only product which could be isolated was a trace of diphenylsilanediol, m.p. 160–162°. This product was insoluble in carbon tetrachloride and carbon disulfide, but the infrared spectrum (KBr) was identical with that of an authentic sample of diphenylsilanediol.

DISCUSSION

Physical evidence concerning the structure of Compound C is quite inconclusive although molecular weight values (1211 average of four values)* indicate that the compound probably contains no *more* than seven diphenylsilylene units. Several attempts to prepare dodecaphenylcyclohexasilane and tetradecaphenylcycloheptasilane were also inconclusive as to the identity of Compound C with either structure. The infrared spectrum of Compound C[6] is strikingly similar to those of octaphenylcyclotetrasilane and decaphenylcyclopentasilane, indicating the close similarity in structure, *i.e.* a closed ring of diphenylsilylene units. Chemical reactions of Compound C provide an indication that it is dodecaphenylcyclohexasilane.

Compound C is relatively nonreactive in comparison with octaphenylcyclotetrasilane and decaphenylcyclopentasilane**. Thus, it does not react with iodine, *sym*-tetrachloroethane or refluxing nitrobenzene, nor does it react appreciably with alkali or aqueous piperidine[2].

Lithium reacts slowly with Compound C to give a mixture of disilanyllithium compounds. Treatment of these mixtures with trimethyl phosphate and with tri-*n*-butyl phosphate leads to 1,2- and 1,3-dialkyl compounds as the major products, (V), (VI). The slowness of reaction might be attributed to a less reactive silicon–silicon bond; however, the insolubility of the compound in tetrahydrofuran is quite probably a contributing factor.

Table 1 contains data concerning the lithium cleavage of Compound C over extended periods of time.

TABLE 1

CLEAVAGE OF COMPOUND C BY LITHIUM IN TETRAHYDROFURAN

Time (h)	*Temperature*	*Treated with*	*Recovered C (%)*	*Derivatives (%)*[a]	
				1,3-	*1,2-*
5	25°	$(n\text{-}C_4H_9O)_3PO$	42.0	41.5	4.5
8	25°	$(n\text{-}C_4H_9O)_3PO$	11.4	39.3	13.4
13	65°	$(n\text{-}C_4H_9O)_3PO$	5.7	28.7	21.7
14	25°	$(CH_3O)_3PO$	5.0	55.6	14.9[b]

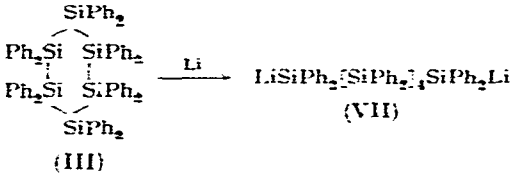
[a] Based on unrecovered C. [b] A trace of 1,4-dimethyloctaphenyltetrasilane was also isolated.

* Determined for us by Dr. C. A. GLOVER of the Tennessee Eastman Co.[16].

** For a comprehensive review of compounds of this type see ref. 17.

$$\text{Compound C} \xrightarrow[2.\ [n\text{-}C_4H_9O]_3PO]{1.\ Li} \underset{(V)}{n\text{-}C_4H_9SiPh_2SiPh_2SiPh_2C_4H_9\text{-}n} + \underset{(VI)}{n\text{-}C_4H_9SiPh_2SiPh_2C_4H_9\text{-}n}$$

On the basis that Compound C is dodecaphenylcyclohexasilane (III), then the cleavage with lithium may be represented as in the reaction scheme below. The 1,6-dilithiododecaphenylhexasilane (VII) might be expected to undergo further cleavage with lithium to give 1,3-dilithiohexaphenyltrisilane (VIII). A less favorable cleavage



$$\underset{(III)}{} \xrightarrow{Li} \underset{(VII)}{LiSiPh_2[SiPh_2]_4SiPh_2Li}$$

$$(VII) \xrightarrow{Li} \underset{(VIII)}{2LiSiPh_2SiPh_2SiPh_2Li}$$

$$(VII) \xrightarrow{Li} \underset{(IX)}{LiSiPh_2SiPh_2Li} + \underset{(X)}{LiSiPh_2[SiPh_2]_2SiPh_2Li}$$

would give 1,2-dilithiotetraphenyldisilane (IX) and 1,4-dilithiooctaphenyltetrasilane (X). Apparently a secondary cleavage which results in 1,2-dilithiotetraphenyldisilane is comparatively slow[6].

When the lithium cleavage of Compound C was carried out in such a manner that prolonged contact of the silyllithium compounds formed with lithium metal was minimized there could be isolated small quantities of 1,6-dimethyldodecaphenylhexasilane (XI) after the cleavage reaction solution was treated with trimethyl phos-

$$VII + [CH_3O]_3PO \longrightarrow \underset{(XI)}{CH_3SiPh_2[SiPh_2]_4SiPh_2CH_3}$$

phate. This is good evidence that Compound C is dodecaphenylcyclohexasilane. However, even under these special conditions the apparent yields of 1,6-dilithiododecaphenylhexasilane (VII) are low indicating that it undergoes secondary cleavage with great ease.

In addition to the fact that Compound C does not react with iodine, it has been found that C is not cleaved by bromine in refluxing benzene. Under the same condition, chlorine also does not react; however, when refluxing *o*-dichlorobenzene is used as the solvent, cleavage is complete within 5 min. The reaction products consist of a mixture of dichloropolysilanes and viscous polymers from which no materials of greater chain length than tetrasilanes could be isolated. Similar results were obtained from the extended reaction of phosphorus pentachloride with Compound C in refluxing *sym*-tetrachloroethane. Compound C was also found to be unreactive with mercuric chloride in refluxing benzene or tetrahydrofuran, which is in direct contrast with the reactivity of octaphenylcyclotetrasilane[18].

In contrast to octaphenylcyclotetrasilane and decaphenylcyclopentasilane,

Compound C is resistant to methyllithium cleavage. Benzyllithium, which is known to cause rapid cleavage of hexaphenyldisilane[19], reacts only very slowly with C. The only product, other than recovered Compound C, isolated from this reaction was diphenylsilanediol.

Recently Neumann[20] has compared the ultraviolet spectrum* of Compound C with that of dodecaphenylcyclohexagermane and has found them strikingly similar. It appears that the Compound C of Kipping and the one isolated by us from the reaction of lithium with dichlorodiphenylsilane are the same and that it is dodecaphenylcyclohexasilane. Difficulties encountered in obtaining molecular weights can be laid to solubility problems. The relative chemical inertness of the compound is probably due to steric bulkiness of the phenyl groups which in effect protect the silicon–silicon bonds from attacking reagents. Some support for this idea may be gained from the observation that atoms of small size (lithium and chlorine) are apparently more effective at cleaving the silicon–silicon bond.

However, the structure of cyclohexasilane with its possibility of gaining completely tetrahedral angles may possess some added stability over cyclotetrasilanes or cyclopentasilanes. This is indicated from the fact that when dichlorodimethylsilane is treated with lithium in a manner similar to that used with dichlorodiphenylsilane, the major product is dodecamethylcyclohexasilane. In this case the steric requirements are much less stringent in converting a straight chain polysilane to a cyclohexasilane.

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SUMMARY

The higher melting crystalline compound which can be obtained from the reaction of dichlorodiphenylsilane with lithium has been investigated with regard to its structure and reactivity. This compound is apparently identical with one isolated and described previously by F. S. Kipping and has been found to be dodecaphenylcyclohexasilane. The structure was indicated mainly through lithium cleavage of the cyclosilane followed by characterization of 1,6-dilithiododecaphenylhexasilane as its corresponding dimethyl derivative. Dodecaphenylcyclohexasilane was found to be very resistant to silicon–silicon bond cleavage by many reagents, with the exception of lithium, which had been previously shown to cause ring opening in other cyclosilanes.

* In our laboratories a study of the ultraviolet spectra of a large variety of polysilanes is in progress[21].

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