

m.p. 213–219°, $[\alpha]_D^{25} +155^\circ$, $+160^\circ$ (*c* 1.1), λ_{\max} (neutral) 247 $\mu\mu$ (ϵ 15,500), λ_{\max} (alkaline) 321 $\mu\mu$ (ϵ 2,200); ν_{\max}^{KBr} 1760(s), 1740(s), 1720(s), 1685(s), 1620(m), 1240(s) and 1200 cm.^{-1} ; $\nu_{\max}^{\text{CHCl}_3}$ 1755(s), 1725(s), 1685(s) and 1620(m) cm.^{-1} .

Anal. Calcd. for $\text{C}_{26}\text{H}_{32}\text{O}_7$: C, 67.55; H, 7.26; O, 25.20; Ac, 19.31. Found: C, 67.66; H, 7.26; O, 25.33; Ac, 21.60.

The diacetate XII (*R* = Ac) gave no color with ferric chloride in ethanol or with tetranitromethane.

(b) From the Monoacetate (XII, *R* = H).—Similar acetylation of this monoacetate (10 mg.) gave the same diacetate (XII, *R* = Ac).

Treatment of the diacetate (XII, *R* = Ac; 50 mg.) in methanol (10 ml.) with aqueous sodium hydroxide (1.24 ml.; 14.1 mg. of NaOH) under reflux for 15 min. gave, after crystallization from ethyl acetate, the 21-alcohol (as XII, *R* = H; 5 mg.) identical with material already described.

Preparation of the Triacetate (XVI).—The diacetate (XII, *R* = Ac; 20 mg.) in pyridine (8 ml.) and acetic anhydride (4 ml.) was refluxed for 48 hours. The dark mixture was decomposed with water, extracted with methylene chloride, and the product chromatographed on alumina (11 g.). The crystalline fractions of lowest polarity crystallized from ethyl acetate-hexane to give the triacetate XVI as colorless prisms, m.p. 190–209°, $[\alpha]_D +32^\circ$ (*c* 1.1), λ_{\max} 237 $\mu\mu$ (ϵ 18,000), λ_{\max} (alkaline) 232 and 346 $\mu\mu$ (ϵ 7,400 and 3,500, resp.); ν_{\max}^{KBr} 1765(s), 1745(s), 1720(s), 1670(w), 1630(w), 1220(s) and 1180(s) cm.^{-1} ; $\nu_{\max}^{\text{CHCl}_3}$ 1760(s), 1740(s), 1630(w) and 1605(w) cm.^{-1} .

Anal. Calcd. for $\text{C}_{27}\text{H}_{34}\text{O}_8$: C, 66.65; H, 7.04; O, 26.31; Ac, 26.54. Found: C, 66.23; H, 7.05; O, 26.86; Ac, 25.12.

This triacetate gives a strong yellow color with tetranitromethane in chloroform, whereas the present diacetate (XII, *R* = Ac) gives no color under the same conditions.

Oximation of Monoacetate (XI, *R* = *R'* = H).—A solution of the monoacetate (250 mg.) and hydroxylamine hydrochloride (250 mg.) in pyridine (10 ml.) was kept at room temperature for 4 days. The mixture was extracted with tetrahydrofuran after the addition of aqueous sodium

chloride, the extract dried (MgSO_4) and evaporated. The partially crystalline residue was dissolved in tetrahydrofuran-methylene chloride and chromatographed on alumina (7.5 g.). The first 10 ml. to be eluted gave a gum. The next 20 ml. gave a solid which was recrystallized from tetrahydrofuran-methylene chloride to give the trioxime XIV previously obtained by the oximation of the unstable α -oximinoketone monoacetate VIII. Later fractions, eluted with methylene dichloride-methanol (20:1), yielded the trioxime XIII derived by oximation of the stable α -oximinoketone monoacetate IX (*R* = H).

Oxidation of the Diacetate (IX, *R* = Ac).—A solution of the diacetate (IX, *R* = Ac; 500 mg.) in pyridine (10 ml.) was added to the chromium trioxide-pyridine complex (prepared from chromium trioxide (1.05 g.) and pyridine (15 ml.)) and kept at 25° for 5 min. Addition of water and extraction with methylene chloride-ether (1:3) by crystallization of the product from ethyl acetate, gave the derived 11-ketone as needles (310 mg.), m.p. 183–186°, $[\alpha]_D +266^\circ$ (*c* 1.0 in CHCl_3), end absorption in methanol (ϵ at 214 $\mu\mu$ 3900) λ_{\max} (alkaline) 297 $\mu\mu$ (ϵ 4800); ν_{\max}^{KBr} 1780(s), 1750(s), 1720(s), 1705(s), 1590(m) and 1230(s); $\nu_{\max}^{\text{CHCl}_3}$ 1780(s), 1750(s), 1715(vs), 1590(m), 1220(s) and 1170(s) cm.^{-1} .

Anal. Calcd. for $\text{C}_{26}\text{H}_{31}\text{O}_7\text{N}$: C, 65.63; H, 6.83; O, 24.48; N, 3.06. Found: C, 65.06; H, 6.63; O, 24.87; N, 3.26.

Oxidation of the Triacetate (X).—A solution of the triacetate X (240 mg.) in pyridine (10 ml.) was added to the chromium trioxide-pyridine complex (from chromium trioxide (1.0 g.) and pyridine (15 ml.)) and kept at room temp. for 5 min. Addition of water and extraction with methylene chloride-ether (1:3), followed by crystallization from ethyl acetate gave needles (75 mg.). m.p. 160–175°, $[\alpha]_D +147^\circ$ (*c* 1.0 in CHCl_3). Recrystallization from ethyl acetate ether (charcoal) gave a sample (55 mg.) of the derived 11-ketone, m.p. 176–178°, $\lambda_{\max}^{\text{MeOH}}$ (neutral) 244 $\mu\mu$ (ϵ 12,200), λ_{\max} (alkaline) 278 $\mu\mu$ (ϵ 7,000); ν_{\max}^{KBr} 1770–1750(vs), 1720–1705(s), 1585(m), 1230(vs) and 1190(s) cm.^{-1} ; $\nu_{\max}^{\text{CHCl}_3}$ 1750(vs), 1720(s), 1650(w), 1585(m), 1220(s) and 1180(s) cm.^{-1} .

Anal. Calcd. for $\text{C}_{27}\text{H}_{33}\text{O}_8\text{N}$: C, 64.91; H, 6.66; O, 25.62; N, 2.80. Found: C, 65.14; H, 6.65; O, 25.41; N, 2.84.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY, AMES, IOWA]

Preparation and Characterization of Dodecaphenylcyclohexasilane

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The higher melting, perphenylated silicohydrocarbon isolated from the reaction of dichlorodiphenylsilane with sodium or lithium and designated compound B, has now been shown to be dodecaphenylcyclohexasilane and not octaphenylcyclohexasilane as proposed.

It has been reported in a preliminary communication¹ that the higher melting compound obtained from the reaction of dichlorodiphenylsilane with sodium or lithium was dodecaphenylcyclohexasilane. Kipping, who designated this substance as compound B,² assigned the structure octaphenylcyclohexasilane to it. We have assigned this structure to the lower melting material, compound A, on the basis of synthetic derivatives and ascribed the high reactivity of this compound in free radical type reactions to the ease of cleavage of the strained four-membered ring. The structure assigned to compound A by Kipping (. . . $\text{SiPh}_2\text{-SiPh}_2\text{-SiPh}_2\text{-SiPh}_2$. . .) contained two tervalent

silicon atoms, but electron spin resonance studies excluded this biradical structure.⁴ Their tervalent structure was altogether reasonable at that time in view of some uncommonly reactive transformations.

Since the structure octaphenylcyclohexasilane was assigned to compound A by us and since this structure had already been assigned to compound B by Kipping, it was felt necessary to investigate further the structure of compound B.

The analytical data obtained for compound B suggested that the compound was composed of diphenylsilylene units, and the hydrogen value^{2,3} showed that there was one silicon-silicon bond per diphenylsilylene unit. It was evident from this

(1) H. Gilman, D. J. Peterson, A. W. P. Jarvie and H. J. S. Winkler, *Tetrahedron Letters*, **23**, 5 (1960).

(2) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 930 and 948 (1921); F. S. Kipping, *ibid.*, 2719 and 2728 (1927).

(3) H. J. S. Winkler and H. Gilman, *J. Org. Chem.*, **26**, 1265 (1961).

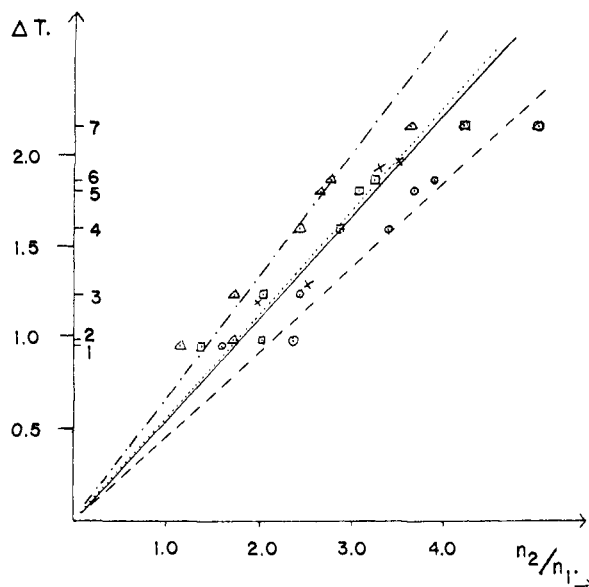


Fig. 1.—Melting point depressions of perylene by compound B at various concentrations. The mole fractions (n_2/n_1) were calculated under the assumption that compound B was: $(\text{Ph}_2\text{Si})_5$, ----○; $(\text{Ph}_2\text{Si})_6$, ———□ and $(\text{Ph}_2\text{Si})_7$, ———Δ. The theoretical depression, × was obtained using hexaphenyldisilane as a standard. The numbers on the ordinate refer to the entries in Table I.

that the compound consisted of a closed chain of diphenylsilylene units.

Compounds B and A were termed "saturated and unsaturated" by Kipping² because of their marked difference in reactivity. Thus, for example, compound B did not react with either iodine or oxygen whereas compound A reacted readily with these elements.⁴ The lower reactivity of compound B suggests a greater stability of the homocyclic silicon ring. It therefore seemed likely that the ring contained more than four silicon atoms.

Since a reliable molecular weight determination was imperative in establishing the structure of compound B, two different methods were used. One of these analytical procedures involved the use of perylene as the cryoscopic medium⁵; and the other was an isothermal distillation method.⁶ The molal depression constant was redetermined using hexaphenyldisilane as a reference. The value found, $K = 14.4$, was in agreement with the one previously determined using benzanilide as a reference compound.⁵ A series of molecular weights of compound B was determined in a range of mole fractions varying from 0.01–0.04. These are plotted in Fig. 1 against the depression observed. Each of the depressions was calculated as the average of at least ten double melting point determinations. In one case the mole fraction for a particular melting point depression was calculated on the basis of compound B being dodecaphenylcyclohexasilane. For reference, two other sets of points were calculated on the basis of com-

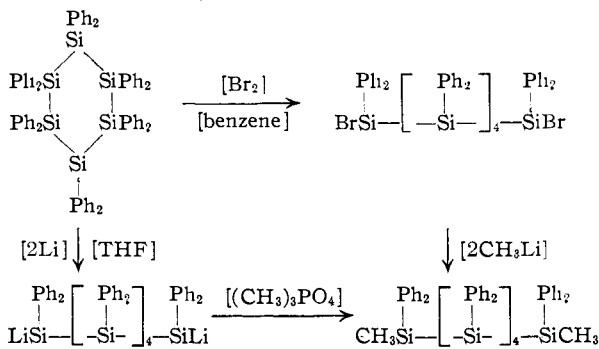
pound B containing five and seven diphenylsilylene groups. It may be seen that of the best fitting lines through the three sets of points, the one that coincides most closely with the "theoretical" line is that based on the calculations assuming compound B to be dodecaphenylcyclohexasilane. The best fitting lines through the two other sets of points have slopes different from the slope of the reference line.

The method of isothermal distillation was performed under reduced pressure in an apparatus originally described by Signer.⁷ Since Kipping had found that both compounds A and B had a molecular weight corresponding to four diphenylsilylene units, it was thought desirable to use compound A as a reference for determination of the molecular weight of compound B. It was found that the molecular weight of compound B corresponded to six diphenylsilylene units. This was found to agree with the determination by the same method but using azobenzene as a reference.

Chemical evidence for the structure of compound B was obtained by preparation of 1,6-dimethyldodecaphenylhexasilane from it. This compound was prepared by two different routes. One of these involved the cleavage of compound B with one equivalent of bromine in benzene at 0° followed by reaction with methyllithium. Kipping states that compound B reacts with bromine to give a mixture of products.² We have reconfirmed this finding if an excess of bromine is used at room temperature in either benzene or carbon tetrachloride. This mixture is thought to have arisen from multiple cleavage of the ring. However, if the reaction with bromine is carried out under the conditions now described, there is obtained a good yield of 1,6-dibromododecaphenylhexasilane. The analytical results for this compound were unsatisfactory, but those of its product of hydrolysis agree with the theoretical. The dibromo compound coupled readily with two mole equivalents of methyllithium to the 1,6-dimethyldodecaphenylhexasilane.

The alternate route to this compound involves a single cleavage of the six-membered ring by lithium followed by reaction with trimethyl phosphate. It was established that only single cleavage occurred by analyzing the solution of the disilyllithium compound for silyllithium content.

The identity of the two samples was confirmed by the method of mixture melting point and superimposability of their infrared spectra. Both



(4) H. Gilman, D. J. Peterson, A. W. P. Jarvie and H. J. S. Winkler, *J. Am. Chem. Soc.*, **83**, 1921 (1961).

(5) G. Wittig and G. Lehmann, *Ber.*, **90**, 875 (1957).

(6) G. Wittig and F. Bickelhaupt, *ibid.*, **91**, 883 (1958).

(7) R. Signer, *Ann.*, **478**, 246 (1930).

the molecular weight of this compound and its hydrogen value³ agree with the assigned structure.

Three different preparations of 1,6-dimethyldodecaphenylhexasilane, not directly dependent on the silicon skeleton of compound B, were attempted. These are summarized in the reaction schemes.

The only crystalline compound obtained from reaction 1 was the 2:1 reaction product 1,4-dimethyloctaphenyltetrasilane. The products from reactions 2 and 3 contained impurities with such solubilities that their separation from the desired compound could not conveniently be accomplished by either fractional crystallization or chromatography. The main reason for the presence of such impurities is that both reactions involve the use of silyllithium compounds which are known to cleave silicon-silicon bonds.⁸ The lower molecular weight dimethyl compounds thus resulting would be expected to have approximately the same physical properties as 1,6-dimethyldodecaphenylhexasilane and would hence be difficult to remove from it.

Reaction 4 appeared promising on the basis of good yields of pentaphenyldisilane isolated from the reaction of triphenylsilyllithium with compound B.⁹ Acid hydrolysis of part of the solution to be used for the coupling step of 4 yielded 1-methyl-1,1,2,2-tetraphenyldisilane for which the precursor must have been 1-methyl-1,1,2,2-tetraphenyl-2-lithiodisilane. The reaction of this disilyllithium compound with *sym*-dibromotetraphenyldisilane gave a compound which resembled 1,6-dimethyldodecaphenylhexasilane closely. The infrared spectra were superimposable and the mixed melting point was not depressed. However, the melt of the compound obtained from reaction 4 did not become clear until *ca.* 10° above the melting point.

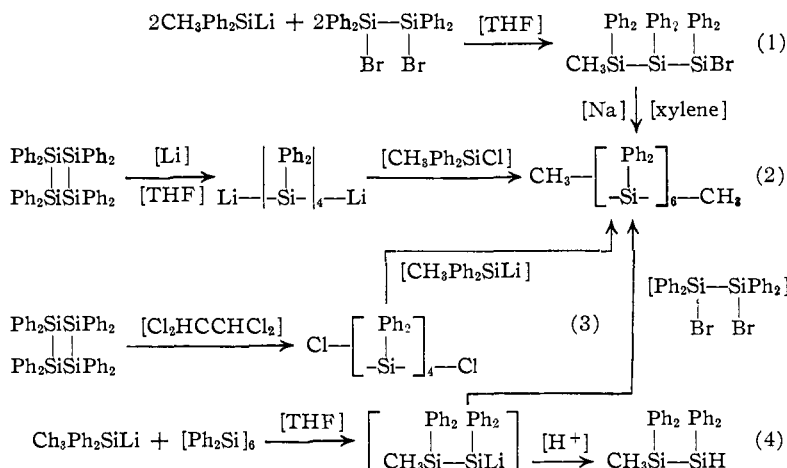
It is to be expected that the first step of reaction 4 led to the formation of some of the desired product in addition to a smaller amount of higher molecular weight silyllithium compounds, and some of the starting material, methyl-diphenylsilyllithium, was undoubtedly also present. This mixture of silyllithium compounds would react with *sym*-dibromotetraphenyldisilane to give a statistical distribution of perphenylated dimethylpolysilanes. One would expect the 1,4-, 1,5- and the 1,6-dimethyl compounds to possess solubility characteristics very similar to each other, which would render difficult the purification of any one of these in the presence of one or more of the other. The 1,4-dimethyloctaphenyltetrasilane is the most likely impurity in the 1,6-dimethyldodecaphenylhexasilane prepared by this method and the presence of this higher melting impurity could explain the melting point behavior.

Experimental¹⁰

Preparation of Compound B.—Compound B was obtained from the benzene washings of the precipitate ob-

(8) H. Gilman, G. D. Lichtenwalter and D. Wittenberg, *J. Am. Chem. Soc.*, **81**, 5320 (1959).

(9) A. W. P. Jarvie and H. Gilman, *J. Org. Chem.*, **26**, 1999 (1961).



tained from the reaction of dichlorodiphenylsilane with lithium in tetrahydrofuran.⁴ It was found convenient to evaporate the benzene and add acetone for the first precipitation of this compound and then recrystallize from either ethyl acetate or a mixture of benzene and petroleum ether (b.p. 60–70°). The melting point of the purified compound was 440–444° with some preshrinkage at 438°. The melt turned clear at 456°,¹¹ at which temperature an evolution of gas was observed.

Comparison of this compound with an original sample of compound B prepared by F. S. Kipping revealed that these were identical. The methods of mixture melting point and comparison of infrared spectra were used.

Anal. Calcd. for $[(\text{C}_6\text{H}_5)_2\text{Si}]_6$, $\text{C}_{72}\text{H}_{60}\text{Si}_6$: C, 79.07; H, 5.53; Si, 15.40. Hydrogen value (calcd. for one Si-Si bond per $(\text{C}_6\text{H}_5)_2\text{Si}$ unit), 123 [ml. at S.T.P./g.]. Found: C, 78.72, 78.91; H, 5.30, 5.45; Si, 15.37, 15.27; hydrogen value, 124, 125.

Molecular Weight Determination. Perylene Method.—The sample of compound B used for this determination had been recrystallized to a constant melting point from ethyl acetate and then dried for 10 hours at 0.001 mm. in a drying pistol heated by refluxing toluene. The method used was essentially that described by Wittig⁵ with certain alterations. The compound was weighed by difference into a "wig-lug",¹² and sufficient perylene¹³ was then weighed into the container to reach a mole fraction of the order corresponding to a depression of 1.0–2.5°. The compound and the perylene were mixed and ground to a fine powder in the type shaker used for preparing samples for potassium bromide pellets in infrared spectroscopy¹² (a 3-minute shaking time was used). The mixture was removed from the container and filled into six capillaries sealed to a fine point at the end. Six other capillaries were filled to the same height (*ca.* 3 mm.) with pure perylene ground similarly. One capillary containing pure perylene and one containing the mixture were placed close together in a ring-shaped capillary melting point apparatus filled with silicone fluid. A heating coil was placed directly in the silicone fluid in the part of the apparatus which did not contain the thermometer; a differential thermometer, graduated into $1/100^\circ$ over a 5° range (from *ca.* 269–274°) and a –20 to 300° thermometer were also placed in it. The ends of the capillaries containing the samples were in close proximity to the bulb of the differential thermometer and were observed through a microscope. The heating rate was adjusted so that the temperature increased 1° per two minutes. The melting points recorded for the purpose of this determina-

(10) All reactions involving organometallic compounds or organosilylmetallic compounds were performed in an atmosphere of dry, oxygen-free nitrogen.

(11) The melting point was observed in a Mel-Temp capillary melting point apparatus set at 110 v. This and other melting points described in the present study are uncorrected.

(12) This is a small container fitted with a plunger used in an amalgamator manufactured by the Crescent Dental Mfg. Co., Chicago, Ill.

(13) The perylene used was obtained from Rütgerswerke-Aktiengesellschaft, Castrop-Rauxel 2, Germany. It was purified by recrystallization from toluene and drying at 0.001 mm. (110°) for 10 hours.

TABLE I
 MOLECULAR WEIGHT OF COMPOUND B; PERYLENE METHOD

	1	2	3	4	5	6	7	8	9	10	11
Compound g_2 , mg. ^{a,b}	9.8	11.8	8.2	23.8	20.3	20.1	25.4	9.2	8.1	8.0	7.6
Perylene g_1 , mg.	168.9	130.7	93.2	193.3	152.5	143.0	139.1	235.4	157.1	110.2	107.8
$T = T_1 - T_m$	0.95	0.98	1.23	1.59	1.80	1.87	2.15	1.21	1.23	1.93	1.95
$n_2/n_1 10^2$ [(B)≡(Ph ₂ Si) ₆]	1.61	2.39	2.44	3.40	3.66	3.90	5.03				
$n_2'/n_1 10^2$ [(B)≡(Ph ₂ Si) ₄]	1.34	2.00	2.06	2.84	3.08	3.25	4.18				
$n_2''/n_1 10^2$ [(B)≡(Ph ₂ Si) ₂]	1.15	1.72	1.74	2.44	2.66	2.78	3.63				
Mol. wt. = $\frac{14.4 \times 1000 \times g_2}{T \times g_1}$	830	1190	1030	1115	1070	1085	1270				

^a Nos. 1-7 refer to compound B; see also the same numbers on Fig. 1. ^b Nos. 8-11 refer to hexaphenyldisilane the standard used.

tion were the temperatures at which the last trace of perylene or mixture disappeared with an eddying motion. After the pure perylene had melted the capillaries were removed and cooled to resolidify the melts. The process was repeated with the resolidified melts and for the other sets of capillaries. The melting point depressions ($\Delta T = T_1 - T_m$) were then found and averaged. The results given in Fig. 1 in graphical form as discussed earlier are listed in Table I: mol. wt. average of seven determinations, 1085; mol. wt. calcd. for (Ph₂Si)₆, 1092.

Isothermal Distillation Method.—The method and the apparatus used have been described in sufficient detail in the literature.^{6,7,14} The graduated part of the distillation apparatus consisted of 1-ml. pipets graduated in $\frac{1}{100}$ ml. The solvent was benzene and the following results were obtained: Experiment 1, compound B *vs.* compound A: compound B, initial volume 0.950 ml. containing 1.977 mg./ml., final volume 0.915 ml.; compound A, initial volume 0.950 ml. containing 1.375 mg./ml., final volume 0.970 ml.; mol. wt. found 1120.

Experiment 2, compound B *vs.* compound A, repeat: compound B, initial volume 0.911 ml. containing 40.8 mg./10 ml., final volume 0.929 ml.; compound A, initial volume 0.952 ml. containing 57.2 mg./25 ml., final volume 0.917 ml.; mol. wt. found 1225.

Experiment 3, compound B *vs.* azobenzene: compound B, initial volume 0.879 ml. containing 1.917 mg./ml., final volume 0.878 ml.; azobenzene, initial volume 0.625 ml. containing 0.354 mg./ml., final volume 0.650 ml.; mol. wt. found 1025; average molecular weight of compound B, experiment 1-3, 1130.

Reaction of Dodecaphenylcyclohexasilane with Bromine.—To 1.6 g. (0.02 g. atom) of bromine in 60 ml. of benzene (at ice-bath temperature) was added 11 g. (0.01 mole) of dodecaphenylcyclohexasilane. The reaction mixture was stirred at ice-bath temperature for 1 hour and then allowed to warm to room temperature. Removal of the benzene by distillation under reduced pressure (water aspirator) gave a yellow, oily solid. Treatment of the crude residue with 20 ml. of petroleum ether (b.p. 60-70°) gave 12.1 g. (96.6%) of a white solid, m.p. 196-198°. Recrystallization from benzene-petroleum ether (b.p. 60-70°) raised the melting point to 204-206°.

Anal. Calcd. for C₇₂H₆₀Si₆Br₂: C, 69.0; H, 4.79; Si, 13.4; Br, 12.8. Found: C, 67.66, 67.41; H, 5.06, 4.79; Si, 13.01, 12.98; Br, 18.2.

The analytical results for this compound indicate that considerable hydrolysis had taken place before the compound was analyzed. Hydrolysis on a preparative scale was hence undertaken.

Hydrolysis of 1,6-Dibromododecaphenylhexasilane.—To 4 g. (0.0036 mole) of 1,6-dibromododecaphenylhexasilane was added a mixture of 25 ml. of *t*-amyl alcohol, 20 ml. of toluene and 70 ml. of water. The reaction mixture was stirred for 26 hours at room temperature. The layers were separated and the aqueous layer was extracted with ether. The organic layers were combined and dried. Removal of the solvents gave 3 g. of a product, m.p. 100°. Recrystallization from benzene-petroleum ether (b.p. 60-70°) raised the melting point to 169-170°; yield of pure product 2 g. (56%).

Anal. Calcd. for C₇₂H₆₂Si₆O₂: C, 76.80; H, 5.51; Si, 14.93; hydrogen value (calcd. for five Si-Si bonds per C₇₂H₆₂Si₆O₂), 99.7 ml. at S.T.P./g. Found: C, 77.00,

77.03; H, 5.72, 5.63; Si, 14.86, 14.74; hydrogen value, 103, 99.8.

Reaction of 1,6-Dibromododecaphenylhexasilane with Methylolithium.—A solution of 0.018 mole of methylolithium in 21 ml. of ether was added to 8.0 g. (0.0064 mole) of 1,6-dibromododecaphenylhexasilane suspended in 20 ml. of tetrahydrofuran. The reaction mixture was stirred for 16 hours at ice-bath temperature and for 2 hours at room temperature before hydrolysis was performed by addition to 100 ml. of 0.1 *N* hydrochloric acid. The aqueous layer was extracted with ether and the organic layers combined and dried. Removal of the ether by distillation left 6 g. (84%) of a solid melting at 170-176° with pre-shrinkage at 155°. After recrystallization from benzene-petroleum ether (b.p. 60-70°), benzene-ethanol, and cyclohexane-petroleum ether (b.p. 60-70°) there was obtained a product, m.p. 181-182°. A mixed melting point with the sample prepared from reaction of trimethyl phosphate with 1,6-dilithiododecaphenylhexasilane (see the following experiments) was not depressed and the infrared spectra of the samples were identical.

Reaction of Compound B with Lithium Followed by Trimethyl Phosphate.—A total of 120 ml. of tetrahydrofuran was added dropwise to a mixture of 13 g. (0.012 mole) of dodecaphenylcyclohexasilane and an excess of lithium wire (1.4 g. or 0.2 g. atom) cut into short sections. The reaction mixture turned a yellow and then red soon after addition of the first milliliters of solvent. The reaction mixture was stirred for a total of 4 hours and a 10-ml. sample was removed for analysis of silyllithium content.¹⁵ The solution was 0.198 *N* in silyllithium, theoretical 0.200 *N*, calculated for a single cleavage of dodecaphenylcyclohexasilane. The remaining 110-ml. solution of 1,6-dilithiododecaphenylhexasilane containing 21.8 meq. of silyllithium groups was transferred through a glass-wool plug under nitrogen to a pressure-equalized addition funnel and added dropwise to 4 g. (0.0285 mole) of trimethyl phosphate. After complete addition the solution was allowed to stand at room temperature for 1 hour, and 100 ml. of water was added. The layers were separated and the aqueous layer was extracted once with 100 ml. of benzene and three times with 200 ml. of ether. The combined organic layers were dried over anhydrous calcium chloride and concentrated before petroleum ether (b.p. 60-70°) was added (25 ml.). The mixture obtained was chromatographed and there was obtained a total of 8.1 g. (56%) of pure 1,6-dimethyldodecaphenylhexasilane, m.p. 182-183°. Recrystallization from cyclohexane-petroleum ether (b.p. 60-70°) did not change the melting point.

Anal. Calcd. for C₇₄H₆₆Si₆: C, 79.10; H, 5.88; Si, 14.93; hydrogen value (calcd. for 5 Si-Si bonds per C₇₄H₆₆Si₆), 100. Found: C, 79.21, 79.39; H, 6.17, 5.81; Si, 14.93, 14.82; hydrogen value, 102, 100, 96.

The experiment was repeated, but the tetrahydrofuran solution was heated throughout the cleavage at such a temperature that gentle reflux of the solvent was maintained. By fractional crystallization there was obtained *sym*-dimethyltetraphenylidisilane (9%), 1,4-dimethyloctaphenyltetrasilane (6%) and 1,6-dimethyldodecaphenylhexasilane (52%). These compounds were identified by mixed melting points with authentic specimens and comparison of infrared spectra.

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Preparation of 1,6-Dimethyldodecaphenylhexasilane. 1. **From 1-Methyl-3-bromohexaphenyltrisilane (Attempted).**—A solution of methyldiphenylsilyllithium (0.368 *N*) in tetrahydrofuran was prepared from the cleavage of 10 g. (0.025 mole) of *sym*-dimethyltetraphenyldisilane in 100 ml. of tetrahydrofuran with excess lithium during a 10-hour period. The solution was filtered into an addition funnel under nitrogen through a glass-wool plug. In another addition funnel was placed 19 g. (0.038 mole) of *sym*-dibromotetraphenyldisilane in 100 ml. of tetrahydrofuran. The solutions were mixed by simultaneous addition of 5-ml. samples of each to a reaction flask equipped with a nitrogen inlet and a stirrer. Immediately after mixing (molar ratio 1:1) the reaction products were removed through a stopcock at the bottom of the flask. After complete reaction the solvents were removed and 50 ml. of benzene was added and evaporated once before the addition of another 50 ml. of benzene. This caused the precipitation of the lithium bromide which was removed by filtration. The filtrate was concentrated and petroleum ether (b.p. 60–70°) was added. After standing for 16 hours there was obtained 2.4 g. (17%) of a solid, m.p. 207–208°. This compound was identified after recrystallization from benzene-petroleum ether (b.p. 60–70°) as 1,4-dimethyloctaphenyltetrasilane, m.p. 218–219°, by mixed melting point and comparison of infrared spectra. The residues did not crystallize.

The reaction was repeated using more concentrated solutions, but the only crystalline product obtained was 1,4-dimethyloctaphenyltetrasilane even though the amount of lithium bromide obtained constituted 105% of the expected based on the amount of silyllithium which had been added.

2. **From 1,4-Dilithiooctaphenyltetrasilane and Methyl-diphenylchlorosilane.**—To a rapidly stirred mixture of 7.2 g. (0.01 mole) of octaphenylcyclotetrasilane and 0.55 g. (0.08 g. atom) of lithium was added sufficient tetrahydrofuran to form a thick slurry. After 10 minutes a yellow color developed which became more intense with time. A total of 50 ml. of tetrahydrofuran was added dropwise. After stirring for 5 hours at room temperature all the solid material had disappeared and the solution was analyzed for silyllithium content¹⁶ which indicated that the cleavage had proceeded to 80%. The solution was filtered into an addition funnel as usual and added to 1.9 g. (0.085 mole) of methyldiphenylchlorosilane in 20 ml. of tetrahydrofuran. The orange-brown color of the solution was discharged immediately on addition and the Color Test was negative. The reaction mixture was hydrolyzed and worked up as usual. The crude oil was chromatographed to yield two main fractions of crystalline materials, one melting at 198–200° and the other at 170–175°, both having infrared absorptions indicating the presence of methyl groups attached to silicon in addition to the normal silicon-phenyl absorptions.

The reaction was repeated using 22 g. of octaphenylcyclotetrasilane and 15 g. of methyldiphenylchlorosilane. There was obtained 23 g. of oils from the chromatogram. These oils yielded a small amount of a solid after treatment with a mixture of benzene and ethanol; m.p. 194–197°.

3. **From 1,4-Dichlorooctaphenyltetrasilane and Methyl-diphenylsilyllithium.**—A solution of methyldiphenylsilyllithium in tetrahydrofuran containing 0.014 mole was added dropwise over 45 minutes to 5.6 g. (0.007 mole) of 1,4-dichlorooctaphenyltetrasilane. The addition and subsequent reaction was carried out at ice-bath temperature to minimize Si-Si bond-cleavage by the silyllithium reagent. From the work-up there was obtained 4.5 g. (87%) of a compound melting at 228–230°. The infrared spectrum of this compound showed a strong absorption at 955 cm.⁻¹, characteristic of the "monoxide," octaphenyl-1-oxa-2,3,4,5-tetrasilacyclopentane. Isolation of this compound

indicated that only a very limited reaction took place under the conditions of the experiment since this siloxane may be obtained from 1,4-dichlorooctaphenyltetrasilane by passing it through a column of activated alumina.¹⁶

The above reaction was repeated at room temperature using a 24-hour reaction time. Two products were obtained in poor yields, one melting at *ca.* 270° and the other melting over a ten degree range, 165–175°. The latter compound is presumably an impure sample of the desired 1,6-dimethyldodecaphenylhexasilane.

4. **From Reaction of 1-Methyl-tetraphenyl-2-lithiodisilane with *sym*-Dibromotetraphenyldisilane.**—An 0.340 *M* solution of methyldiphenylsilyllithium in tetrahydrofuran was prepared from 10 g. of *sym*-dimethyltetraphenyldisilane and excess lithium. The solution (105 ml. containing 35.8 mmoles of silyllithium compound) was added to 6.5 g. of dodecaphenylcyclohexasilane (35.8 mmoles of Ph₂Si- units). The solution warmed up on mixing with the solid and was stirred for a total of 48 hours. A sample of the solution was removed for titration and was found to contain 0.240 mmole of silyllithium compound per ml., a 33% decrease in strength. All of the solution was added to 6.0 g. (0.0114 mole of dibromodisilane per 0.022 mole silyllithium compound) of *sym*-dibromotetraphenyldisilane. The reaction mixture was stirred for 1 hour at which time the Color Test was negative. The usual work-up including chromatography of the crude reaction mixture gave 2 major fractions weighing 1.2 and 10.1 g. (79%), respectively. The latter melted at 170–171°. Several recrystallizations from cyclohexane-petroleum ether (b.p. 60–70°) and ethyl alcohol-ethyl acetate raised the melting point to 182–184°, clear at 196°; a mixed melting point of this sample with 1,6-dimethyldodecaphenylhexasilane prepared from compound B by cleavage with lithium and reaction with trimethyl phosphate was not depressed and the infrared spectra were superimposable. The first fraction melted at 140–141° after recrystallization and was identified as *sym*-dimethyltetraphenyldisilane.

The reaction was repeated, but the solution of disilanyl-lithium compound (0.542 *N*, total volume 110 ml.) was divided in two. One half was hydrolyzed to give 10.8 g. (95%) of crude 1-methyl-1,1,2,2-tetraphenyldisilane, which after recrystallization gave one fraction melting 71–73° (85% yield) and another melting at 120–122° (5%). Both fractions contained Si-H and Si-methyl by infrared analysis and the former gave a hydrogen value of 119, 120 ml. at S.T.P./g. The calculated hydrogen value for two moles of hydrogen per C₂₅H₂₄Si₂ is 118.

The second half of the solution of the disilanyl-lithium compound was added to 8 g. (0.0148 mole) of *sym*-dibromotetraphenyldisilane (molar ratio 2:1) in 45 ml. of tetrahydrofuran. The normal work-up gave several fractions of eluates melting in ranges varying from 178–181° to 192–194°. These fractions probably contain increasing amounts of higher melting, lower molecular weight linear perphenylated polysilanes with terminal methyl groups.

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