of methanesulfonyl chloride boiling at 56° (12 mm.) and having n_D^{20} 1.4458. The product formed an anilide melting at 98–99° both alone and when mixed with an authentic sample.

Other sulfonyl chlorides from disulfides. In a similar manner 30.0 g. (0.25 mole) of ethyl disulfide upon treatment with 60.0 g. (1.0 mole) of glacial acetic acid and 92.5 g. (1.3 moles) of chlorine yielded 52.6 g. (82% yield) of ethanesulfonyl chloride boiling at 63–65° (14–15 mm.) and having n_D^{25} 1.4518. It formed a *p*-toluidide melting at 80–81° and at the same temperature when mixed with a known sample.

Likewise 10.9 g. (0.05 mole) of phenyl disulfide was dissolved in 30 ml. of methylene chloride and 12.2 g. (0.2 mole) of glacial acetic acid and treated with 19.0 g. (0.27 mole) of chlorine. After standing overnight the mixture was distilled and yielded 14.4 g. of colorless benzenesulfonyl chloride boiling at 115–116° (10 mm.). The product formed an anilide melting at 110° and unchanged when mixed with a pure sample of pure benzenesulfonanilide.

Sulfonyl chlorides from sulfinyl chlorides. A mixture of 29.6 g. (0.3 mole) of methanesulfinyl chloride and 20 g. (0.33 mole) of glacial acetic acid was treated with 22 g. (0.31 mole) of anhydrous chlorine at about −30° in the manner described. On distilling the mixture there was obtained 10.7 g. (47% yield) of acetyl chloride and 26.7 g. (78% yield) of methanesulfonyl chloride boiling at 52–55° (14 mm.) and having n_D^{25} 1.4450. The latter formed a *p*-toluidide melting at 103–104° and unchanged when mixed with a pure sample.

In the same way, ethanesulfinyl chloride (11.2 g., 0.1 mole) was treated with 0.1 mole of acetic acid and 0.1 mole of chlorine and yielded 10.4 g. (81% yield), of ethanesulfonyl chloride boiling at 80–81° (28 mm.) and having n_D^{25} 1.4514. Its *p*-toluidide was identical with that obtained from other preparations.

To shed light on the mechanism of the above reactions 29.3 g. (0.3 mole) of methanesulfinyl chloride and 20.0 g. (0.31 mole) of glacial acetic acid were mixed and allowed to stand overnight. Distillation of the mixture at reduced pressure gave 14.6 g. (73% recovery) of acetic acid and 26.8 g. (91% recovery) of methanesulfinyl chloride indicating that no appreciable chlorine interchange had occurred. A similar experiment with acetic acid and ethanesulfinyl chloride resulted in the recovery of 83 and 89%, respectively, of the starting materials.

To determine whether a chlorine-sulfinyl chloride complex might be formed as an intermediate, 10 g. of methanesulfinyl chloride in 25 ml. of methylene chloride was cooled to −70° in a Dry Ice–ether bath and treated with anhydrous chlorine for 30 min. When no change other than the condensation of liquid chlorine appeared to take place, the chlorination was discontinued and the reaction mixture was allowed to warm to room temperature under continuous observation. No change was observed and distillation of the mixture gave a nearly quantitative recovery of the methanesulfinyl chloride.

The chlorination of benzyl disulfide. Benzyl disulfide was chlorinated in methylene chloride to form α-toluenesulfenyl chloride which reacted with ethylene to form an 80% yield of 2-chloroethyl benzyl sulfide (b.p. 137–140° at 6–7 mm.). The sulfide was oxidized by 30% hydrogen peroxide to the sulfone (m.p. 94–95°) and treated with aqueous Chloramine-T to form the sulfilimine (m.p. 133–134°), thus confirming the observations of Stirling.[9]

On treating a solution of 6.2 g. (0.025 mole) of benzyl disulfide in 25 ml. of methylene chloride at −70° with 5.5 g. (0.075 mole) of chlorine a white crystalline product, presumably benzylsulfur trichloride, precipitated. This product decomposed at too low a temperature to permit analysis. Benzyl chloride and sulfur dichloride were found in the decomposition products.

The white solid obtained as described above from 6.2 g. of benzyl disulfide was treated with 3.0 g. of glacial acetic acid. The resulting orange solution was treated with 10% sodium bicarbonate and extracted with ether. From the ether solution 3.0 g. of benzyl chloride was isolated. The alkaline aqueous layer was refluxed with benzyl chloride and yielded dibenzyl sulfone suggesting that α-toluenesulfinyl chloride had also been formed in the acetolysis.

A solution of 12.3 g. (0.05 mole) of benzyl disulfide in 6.0 g. of acetic acid and 25 ml. of methylene chloride was treated with 11.0 g. (0.15 mole) of chlorine at −40°. After warming to room temperature dry nitrogen was passed through the mixture for several hours. The resulting liquid showed strong infrared absorption at 1158 cm.$^{-1}$ indicating the presence of a sulfinyl chloride. Treatment of the liquid with 10% sodium bicarbonate led to the isolation of benzyl chloride and refluxing of the alkaline solution with benzyl chloride produced a 52% yield of dibenzyl sulfone.

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The Reactions of Two Homocyclic Organosilicon Compounds with Organometallic and Organosilylmetallic Reagents

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Octaphenylcyclotetrasilane and dodecaphenylcyclohexasilane were treated with phenyllithium, phenylmagnesium bromide, and triphenylsilyllithium. It was found that dodecaphenylcyclohexasilane was more resistant to the silicon-silicon cleavage attack by these reagents than was octaphenylcyclotetrasilane.

A considerable amount of work has been done on the cleavage by organometallic reagents of the silicon-silicon bond in open-chain polysilanes. The first reported study is that of Friedel and Ladenburg[1–3] who found that the reaction of diethylzinc with hexaiododisilane gave tetraethylsilane in addition to the expected hexaethyldisilane. Later, Schumb, *et. al.* showed[4] that hexasubstituted disilanes could not be prepared by

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(1) C. Friedel and A. Ladenburg, *Compt. rend.*, **68**, 923 (1869).

(2) C. Friedel and A. Ladenburg, *Ann.*, **203**, 251 (1880).

(3) C. Friedel and A. Ladenburg, *Ann. Chim. Phys.* [5], 19, 401 (1880).

(4) W. C. Schumb, J. Ackerman, and C. M. Saffer, *J. Am. Chem. Soc.*, **60**, 2486 (1938).

treatment of hexachlorodisilane with sodium and alkyl or aryl halides. In each case, only the tetrasubstituted monosilane was obtained. If the reactions were carried out using preformed organosodium compounds[5] with hexachlorodisilane, the hexa-substituted disilanes were isolated, the monosilanes occurring only as minor products.

Similar cleavage reactions were observed when organolithium compounds[6–8] or Grignard reagents[9,10] were treated with halogenated polysilanes.

In comparison with the halogenated disilanes, hexaphenyldisilane is fairly resistant to attack by organometallic reagents. No cleavage occurred when hexaphenyldisilane was treated with phenyllithium[11,12] or *n*-butyllithium[11] in a mixture of diethyl ether and xylene at reflux temperature. Similarly, the disilane was unaffected by treatment with *p*-tolyllithium[13] (at 0°) in tetrahydrofuran or with triphenylmethyllithium in tetrahydrofuran at room temperature.[13] Only minor cleavage was observed when hexaphenyldisilane was treated for five days with phenyllithium in diethyl ether.[14] When, however, tetrahydrofuran or a mixture of tetrahydrofuran and diethyl ether was used as solvent for the reaction of the disilane with phenyllithium, considerable scission of the silicon-silicon bond occurred and good yields of the cleavage products were isolated.[14]

Excellent yields of benzyltriphenylsilane have been obtained from the reaction of benzyllithium with hexaphenyldisilane in a mixture of diethyl ether and tetrahydrofuran.[15]

In recent years several publications[16–18] have appeared on the reaction of silylmetallic compounds with disilanes. When pentaphenyldisilane[16] is treated with triphenylsilyllithium in tetrahydrofuran the products of the reaction are hexaphenyldisilane and a diphenylsilylene polymer. Triphenylsilanol and 1,1,2,2-tetramethyl-1,2-diphenyldisilane were isolated from the reactions of hexaphenyldisilane with dimethylphenylsilyllithium.[17] Analogous cleavage products were obtained when hexaphenyldisilane was treated with methyldiphenylsilyllithium.[17] The results of these studies indicate that the reactivity of the silyllithium compound increases with an increasing number of alkyl groups on the silicon atom.

The purpose of the present work has been to determine the effect of organometallic and organosilylmetallic reagents on homocyclic polysilanes. The two cyclic compounds used in this investigation were octaphenylcyclotetrasilane[19,20] and dodecaphenylcyclohexasilane.[19,21]

We have found that octaphenylcyclotetrasilane is more easily cleaved than dodecaphenylcyclohexasilane. Using Stuart-Briegleb molecular models it is impossible to construct the molecule of octaphenylcyclotetrasilane. Although the tetrahedral bond angles of silicon are more easily deformed than those of carbon,[22] the strain in such a structure must be considerable. In the case of the six-membered ring, strain-free conformations are possible and one would expect ring opening to occur less readily.

The reaction of octaphenylcyclotetrasilane with an equimolar quantity of phenyllithium in a mixture of diethyl ether and tetrahydrofuran gave an 18.5% yield of dodecaphenylcyclohexasilane and a 55% recovery of starting material. One can account for the formation of dodecaphenylcyclohexasilane, one of the cyclic polysilanes so far isolated in this reaction, by assuming that the phenyllithium cleaves the octaphenylcyclotetrasilane (I) to form II which then reacts with another molecule of I to give the silylmetallic compound III. The conformation of this chain may be such that intramolecular cyclization occurs readily and dodecaphenylcyclohexasilane (IV) is formed. No pentaphenyldisilane (VI) was isolated from the reaction mixture. However, infrared examination of the oils, which occurred as side products, indicated that Si—H containing compounds were present.

When octaphenylcyclotetrasilane reacted with a 50% excess of triphenylsilyllithium[23] a 16.5% yield of starting material was recovered. A compound which was probably nonaphenyltetrasilane (XII), (13.5%) and dodecaphenylcyclohexasilane (IV),

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[5] W. C. Schumb and C. M. Saffer, *J. Am. Chem. Soc.*, **63,** 93 (1941).

[6] H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73,** 5077 (1951).

[7] H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75,** 3762 (1953).

[8] H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **80,** 3243 (1958).

[9] W. C. Schumb and C. M. Saffer, *J. Am. Chem. Soc.*, **61,** 363 (1939).

[10] H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, **24,** 1588 (1959).

[11] G. E. Dunn, doctoral dissertation, Iowa State University, Ames, Iowa, 1957.

[12] T. C. Wu, doctoral dissertation, Iowa State University, Ames, Iowa, 1952.

[13] G. D. Lichtenwalter, doctoral dissertation, Iowa State University, Ames, Iowa, 1958.

[14] B. J. Gaj and H. Gilman, *Chem. & Ind.*, 493 (1960).

[15] G. L. Schwebke, unpublished studies.

[16] D. Wittenberg, M. V. George, and H. Gilman, *J. Am. Chem. Soc.*, 81, 4812 (1959).

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

[18] D. Wittenberg and H. Gilman, *Quart. Revs.*, **13,** 116 (1959).

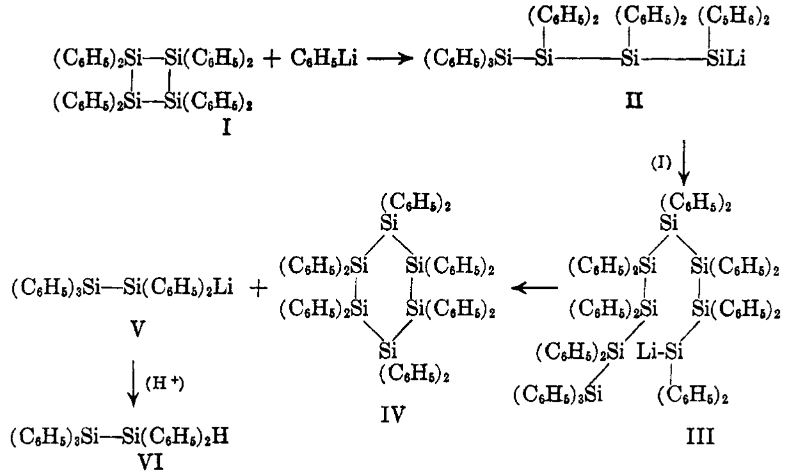
[19] F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119,** 830 and 848 (1921).

[20] H. Gilman, D. J. Peterson, A. W. Jarvie, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **82,** 2076 (1960).

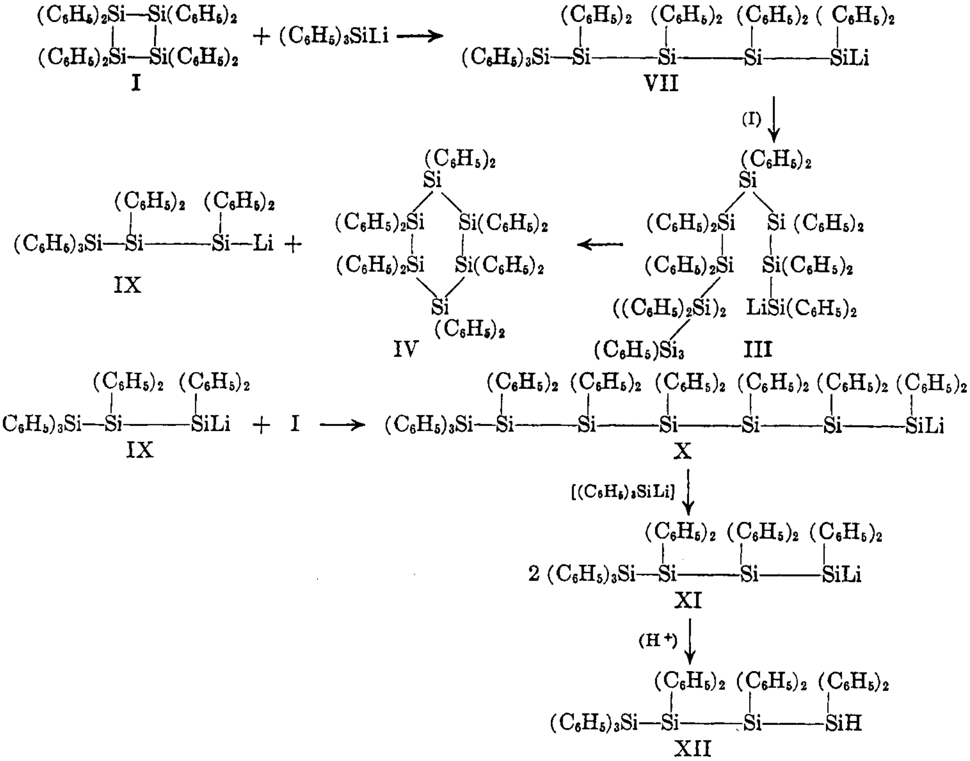
[21] H. Gilman, D. J. Peterson, A. W. Jarvie, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **83,** in press (1961), and *Tetrahedron Letters*, No. 26, 5 (1960).

[22] R. West, *J. Am. Chem. Soc.*, **77,** 2339 (1955).

[23] H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80,** 608 (1958).



(37.5%) are the products which so far have been isolated from the reaction mixture. A similar interpretation may be used to explain the formation of these products as well as other related compounds which have not yet been isolated:



Undoubtedly cleavage of these cyclic organosilicon compounds can take place in different ways to give a great variety of polysilanes. These linear polysilanes could, in turn, be cleaved in different parts of the chains by Si—Li units.

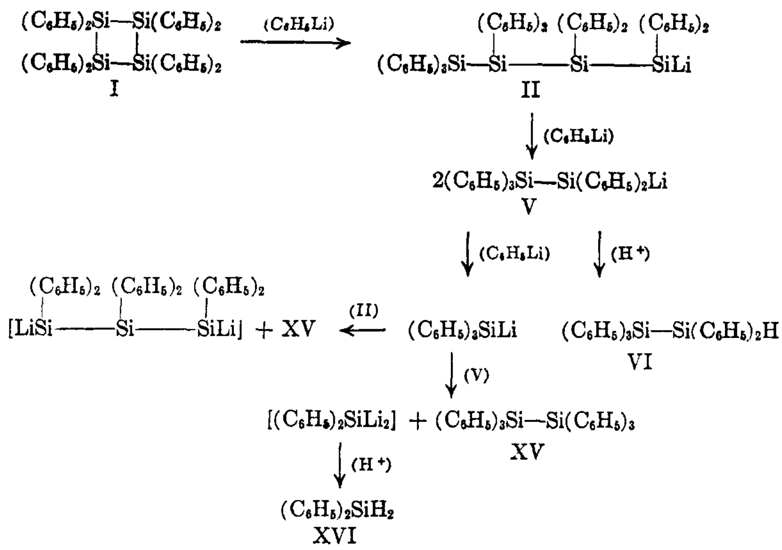
The greater stability of the six-membered silicon ring compared to the four-membered ring was revealed by the fact that dodecaphenylcyclohexasilane did not react with either phenyllithium or triphenylsilyllithium under the above conditions.

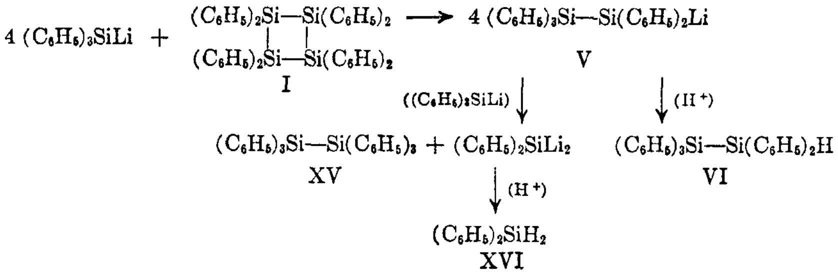
Octaphenylcyclotetrasilane failed to react with phenylmagnesium bromide in a mixture of tetrahydrofuran and diethyl ether. After stirring for two days the starting material was recovered quantitatively.

A different type of cleavage reaction was observed when a large excess of the organometallic reagent was used. From the reaction of octaphenylcyclotetrasilane with a fivefold excess of phenyllithium, no starting material was recovered and the main products of the reaction were hexaphenyldisilane (XV) (19.3%) and pentaphenyldisilane (VI) (36.5%).

No diphenylsilane (XVI) was isolated but infrared analysis showed the presence of Si—H containing compounds in the oily residues, which remained after evaporation of the solvents used for recrystallization of the pentaphenyldisilane.

Similarly, the reaction of octaphenylcyclotetra-





silane with a fivefold excess of triphenylsilyllithium gave hexaphenyldisilane (29%) and pentaphenyldisilane (20%).

It has been shown previously that pentaphenyldisilane is cleaved by triphenylsilyllithium[16] to form hexaphenyldisilane as the main reaction product. The formation of hexaphenyldisilane in the above reaction may hence be not surprising.

When dodecaphenylcyclohexasilane reacted with an eightfold excess of triphenylsilyllithium, again the products of the reaction were hexaphenyldisilane (16%) and pentaphenyldisilane (79%). The reaction of dodecaphenylcyclohexasilane with a ninefold excess of phenyllithium gave pentaphenyldisilane (62%) as the only identifiable product.

EXPERIMENTAL

Reaction of phenyllithium with octaphenylcyclotetrasilane (1:1 molar ratio). A solution of 0.01 mole of phenyllithium in 10 ml. of ether was added dropwise to 7.3 g. (0.01 mole) of octaphenylcyclotetrasilane suspended in 30 ml. of tetrahydrofuran. The reaction mixture was stirred for 5 hr. at room temperature then hydrolyzed by addition to 150 ml. of ice-cold 0.1*N* hydrochloric acid, ether was added and the layers were separated. Filtration of the organic layer gave 4.0 g. (55%) of octaphenylcyclotetrasilane, m.p. 312-315° (mixed melting point). Extraction of the aqueous layer with ether and removal of the solvents left 1.5 g. of a solid, m.p. 390-420°. After recrystallization from benzene-petroleum ether (b.p. 60-70°) there was obtained 1 g. (18.5%) of a product, m.p. 434-436°. A mixed melting point with an authentic sample of dodecaphenylcyclohexasilane was not depressed and the infrared spectra were identical. Evaporation of the crystallizing solvents gave a yellow oil. Infrared analysis showed that Si-H containing compounds were present in the oil.

Reaction of octaphenylcyclotetrasilane with triphenylsilyllithium (1:1.4 molar ratio). A solution of 0.02 mole of triphenylsilyllithium in 50 ml. of tetrahydrofuran was added dropwise to 10 g. (0.014 mole) of octaphenylcyclotetrasilane suspended in 50 ml. of tetrahydrofuran. After 16 hr. stirring at room temperature the reaction mixture was hydrolyzed under acid conditions. Filtration of the organic layer gave 1.6 g. (16%) of octaphenylcyclotetrasilane, m.p. 312-315° (mixed melting point). Extraction of the aqueous layer with ether and removal of the solvents left 4 g. of a white solid, m.p. 370-390°. After several recrystallizations from benzene-petroleum ether (b.p. 60-70°), 2.8 g. (37.5%) of a product, m.p. 434-436° were obtained. This was identified as dodecaphenylcyclohexasilane by mixed melting point and infrared spectra. Concentration of the benzene-petroleum ether (b.p. 60-70°) filtrates yielded 1 g. (13.5%) of a compound, m.p. 180-200°. Recrystallization from benzene-petroleum ether (b.p. 60-70°) and ethyl acetate-ethanol raised the melting point to 198-201°. This product showed a strong Si-H absorption band in the infrared. It was thought that this compound was probably nonaphenyltetrasilane.

Anal. Calcd. for $C_{54}H_{46}Si_4$: C, 80.45; H, 5.71; Si, 13.90. Found: C, 79.99, 80.24; H, 5.95, 5.96; Si, 13.76, 13.80.

Reaction of dodecaphenylcyclohexasilane with phenyllithium (1:1 molar ratio). A solution of 0.01 mole of phenyllithium in 10 ml. of ether was added dropwise to 11 g. (0.01 mole) of dodecaphenylcyclohexasilane suspended in 30 ml. of tetrahydrofuran. The reaction mixture was stirred for 5 hr. at room temperature. Work-up by the procedure described previously gave a 95% recovery of starting material.

Reaction of dodecaphenylcyclohexasilane with triphenylsilyllithium (1:1.4 molar ratio). To a suspension of 11 g. (0.01 mole) of dodecaphenylcyclohexasilane in 36 ml. of tetrahydrofuran was added dropwise a solution of triphenylsilyllithium (0.0143 mole) in 36 ml. of tetrahydrofuran. The reaction mixture was stirred for 16.5 hr. at room temperature then worked up by the normal procedure. A 92% yield of starting material was recovered.

Reaction of octaphenylcyclotetrasilane with phenylmagnesium bromide (1:2 molar ratio). A solution of 0.02 mole of phenylmagnesium bromide in 11 ml. of ether was added to 7.3 g. (0.01 mole) of octaphenylcyclotetrasilane suspended in 30 ml. of tetrahydrofuran. After 2 days stirring at room temperature, work-up of the reaction mixture gave a 98% recovery of starting material.

Reaction of octaphenylcyclotetrasilane with phenyllithium (1:5 molar ratio). To a suspension of 7.3 g. (0.01 mole) of octaphenylcyclotetrasilane in 20 ml. of tetrahydrofuran was added a solution of 40 ml. (0.048 mole) of phenyllithium in ether. The reaction mixture was stirred for 45 hr. at room temperature then hydrolyzed with 500 ml. of 0.1*N* hydrochloric acid. Filtration of the organic layer gave 1.0 g. (19.3%) of hexaphenyldisilane, m.p. 367–368° (mixed melting point). The aqueous layer was extracted with ether, the organic layers were combined and dried. Evaporation of the ether gave 3.2 g. (36.5%) of a solid, m.p. 115–120°. Several recrystallizations from benzene-petroleum ether (b.p. 60–70°) raised the melting point to 125–127°. A mixed melting point and comparison of the infrared spectra showed this compound to be pentaphenyldisilane. Concentration of the benzene/petroleum ether filtrates gave a yellow oil. Infrared analysis indicated that Si—H containing compounds were present in the oil.

Reaction of octaphenylcyclotetrasilane with triphenylsilyllithium (1:5 molar ratio). A tetrahydrofuran solution containing 0.027 mole of triphenylsilyllithium was added dropwise to 4 g. (0.0055 mole) of octaphenylcyclotetrasilane. After 48 hr. stirring at room temperature the reaction mixture was hydrolyzed by addition to 250 ml. of 0.1*N* hydrochloric acid. Filtration of the organic layer yielded 2.0 g. (29%) of an insoluble material, m.p. 365–369°. A mixed melting point with an authentic specimen of hexaphenyldisilane was not depressed. The aqueous layer was extracted with ether, the organic layers were combined and dried. Removal of the ether left a white oil which was dissolved in benzene and chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 1.8 g. (20%) of a product, m.p. 120–124°. Recrystallization from benzene-petroleum ether (b.p. 60–70°) raised the melting point to 125–127°. A mixed melting point determination with an authentic specimen of pentaphenyldisilane was not depressed and the infrared spectra were identical.

Reaction of dodecaphenylcyclohexasilane with triphenylsilyllithium (molar ratio, 1:8). A solution of 0.05 mole of triphenylsilyllithium in 140 ml. of tetrahydrofuran was added dropwise to 7.1 g. (0.0065 mole) of dodecaphenylcyclohexasilane suspended in 20 ml. of tetrahydrofuran. The mixture was stirred at room temperature for 44 hr., then worked up as described previously. There was obtained from the reaction 2 g. (16%) of hexaphenyldisilane and 13.5 g. (79%) of pentaphenyldisilane. Repetition of this reaction gave a 75% yield of pentaphenyldisilane and a 16% yield of hexaphenyldisilane.

Reaction of dodecaphenylcyclohexasilane with phenyllithium (1:9 molar ratio). An ethereal solution containing 0.08 mole of phenyllithium was added dropwise to a suspension of 10 g. (0.0092 mole) of dodecaphenylcyclohexasilane in 60 ml. of tetrahydrofuran. The mixture was stirred for 48 hr., then hydrolyzed under acid conditions. Work-up by the normal procedure gave 9.5 g. (62%) of a compound, **m.p.** 118–121°. Recrystallization from benzene–petroleum ether (b.p. 60-70°) raised the melting point to 125–127°. This compound was identified as pentaphenyldisilane by mixed melting point and infrared analysis.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAN JOSE STATE COLLEGE]

The Chlorination of 1,1-Dimethylsilacyclopentane and 1,1-Dimethylsilacyclohexane[1]

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The monochlorination of 1,1-dimethylsilacyclopentane and 1,1-dimethylsilacyclohexane results primarily in the formation of the chloromethyl derivatives. The addition of free radical catalysts does not substantially alter the extent of methyl chlorination, but does result in increased attack on the ring carbon β to the silicon and decreased attack on the ring carbon α to the silicon. The chemistry leading to the assignment of structures for the monochloro isomers of 1,1-dimethylsilacyclopentane is discussed.

Studies concerned with the chlorination of alkyl- and alkylchlorosilanes have shown that these reactions provide an excellent route for the introduction of a functional group into the alkyl portion of a silane.[3] Generally these reactions are carried out using sulfuryl chloride as the chlorinating agent and benzoyl peroxide as the catalyst.[4] Chlorine gas with ultraviolet light and phosphorus pentachloride have also been used.[5]

In the silacycloalkane series, Mironov and Nepomnia[6] have reported that 1,1-dichlorosilacylclopentane undergoes chlorination with sulfuryl chloride and benzoyl peroxide to yield the 3-chloro derivative, which, in turn, yields 1,1-dichlorosila-cyclo-2-pentene upon pyrolysis with quinoline.

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[2] Participant in the National Science Foundation Undergraduate Research Participation Program (G11923), summer, 1960.