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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AMES, IOWA

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

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

RALPH FESSENDEN AND FRANCIS J. FREENOR[2]

Received September 12, 1960

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-dichlorosilacyclopentane undergoes chlorination with sulfuryl chloride and benzoyl peroxide to yield the 3-chloro derivative, which, in turn, yields 1,1-dichlorosilacyclo-2-pentene upon pyrolysis with quinoline.

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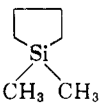
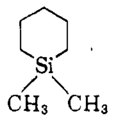
[1] This work was supported in part by a Frederick Gardner Cottrell grant from Research Corporation.

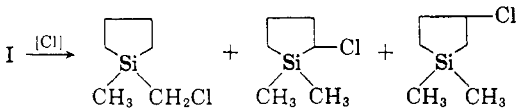
[2] Participant in the National Science Foundation Undergraduate Research Participation Program (G11923), summer, 1960.

The attempt to convert the dichlorosilacyclopentene to the dimethylsilacyclopentene with methylmagnesium chloride, however, resulted in both 1,1-dimethylsilacyclo-2-pentene (VII) and 1-trimethylsilyl-3-butene (VI).

In this investigation, 1,1-dimethylsilacyclopentane (I) and 1,1-dimethylsilacyclohexane (II) have been observed to undergo chlorination both with chlorine gas and with sulfuryl chloride, in the presence or absence of free radical catalysts, to yield predominantly 1-chloromethyl-1-methylsilacyclopentane (III) and 1-chloromethyl-1-methylsilacyclohexane. These observations are quite surprising in light of the reported resistance of silylmethyl groups to chlorination reactions of this type.[7]







III IV V

The use of free radical catalysts accelerated the reaction to some extent, but the chloromethyl isomer was still observed to be the major product. On the other hand, distribution between the 2-chlorosilacyclopentane (IV) and the 3-chloro isomer (V) was affected. Without catalyst, IV was observed in the higher yield; but with catalyst, V was predominant (See Table I). In the chlorination of 1,1-dimethylsilacyclohexane, a similar effect was observed in that the extent of β-chlorination increased with the addition of a catalyst.

The structure assignments of the monochlorosilacyclopentanes are based upon the facts that a chlorine on a carbon β to a silicon is highly reactive[8] and that pyrolysis of a chloroalkylsilane with quinoline results in the introduction of a double bond into the alkylsilane.[9]

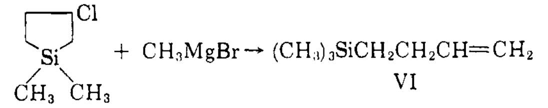
TABLE I

THE EFFECTS OF FREE RADICAL CATALYSTS ON THE DISTRIBUTION OF MONOCHLORO ISOMERS IN THE CHLORINATION OF 1,1-DIMETHYLSILACYCLOPENTANE[a]

	Monochloro Isomers, % Yield		
Reagent	Chloromethyl- (III)	2-Chloro- (IV)	3-Chloro- (V)
Cl_2	63	20	17
Cl_2/U.V. light	52	18	30
SO_2Cl_2	74	23	2
SO_2Cl_2/Bz_2O_2	62	11	27

[a] Ref. 12.

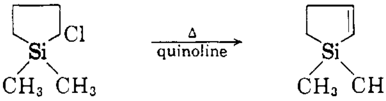
The 3-chloro derivative was easily identified by its high reactivity. Its peak in the gas chromatogram disappeared after the mixture of chlorination products was treated with water, ethanol or sodium hydroxide solution. Confirmation of this identification was accomplished by reaction of V with methylmagnesium bromide, resulting in the formation of 1-trimethylsilyl-3-butene (VI), which was identified by comparison with an authentic sample. Compounds III and IV were unaffected by these reactions.



$+ CH_3MgBr \rightarrow (CH_3)_3SiCH_2CH_2CH{=}CH_2$

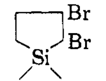
V VI

The structure assignments for III and IV were accomplished by comparison of their behaviors in the pyrolysis of the mixture of these two compounds with quinoline. The 2-chloro isomer (IV) would be expected to undergo elimination to form 1,1-dimethylsilacyclo-2-pentene (VII), while the chloromethyl compound (III) should survive the reaction conditions unless rearrangement occurs.

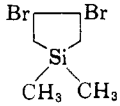


IV VII

Both the unsaturated compound (VII) and the chloromethyl compound (III) were isolated from the pyrolysis. The position of the double bond was shown by reaction with bromine followed by treatment of the dibromo derivative with silver nitrate. The dibromo derivative XI would exhibit only one reactive bromine while the dibromo deriv-



XI



XII

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(3) (a) S. N. Ushakov and A. M. Itenberg, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 2495 (1937); *Chem. Abstr.*, **32**, 2083 (1938); (b) F C. Whitmore and L. H. Sommer, *J. Am. Chem. Soc.*, **68**, 481 (1946); (c) L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 485 (1946); (d) L. H. Sommer, E. Dorfman, G. M. Goldberg, and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 488 (1946); (e) V. F. Mironov and V. A. Ponomarenko, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel. Khim. Nauk*, 199 (1957); *Chem. Abstr.*, **51**, 11272 (1957).

(4) Ref. 3(c) and 3(d).

(5) R. H. Krieble and J. R. Elliott, *J. Am. Chem. Soc.*, **67**, 1810 (1945); also Ref. 2(a).

(6) V. F. Mironov and V. V. Nepomnia, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel. Khim. Nauk*, 1231 (1959); *Chem. Abstr.*, **54**, 1268 (1960).

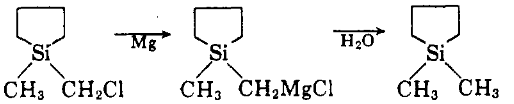
(7) J. J. McBride and H. C. Beachell, *J. Am. Chem. Soc.*, **70**, 2532 (1948) and ref. 3 (c).

(8) For a discussion of the reactivities of halogens on the α and β positions relative to a silicon, see P. D. George, M. Prober, and J. R. Elliott, *Chem. Revs.*, **56**, 1065 (1956).

(9) (a) D. T. Hurd, *J. Am. Chem. Soc.*, **67**, 1813 (1945); (b) C. L. Agre and W. Hilling, *J. Am. Chem. Soc.*, **74**, 3895 (1952).

ative XII would exhibit two reactive bromines. The weight of silver bromide obtained from the reaction indicated that most of the unsaturated compound was indeed VII.

To provide assurance that the ring structures had remained intact during the quinoline pyrolysis, it was desired to reconvert the chloromethyl isomer (III) to the starting 1,1-dimethylsilacyclopentane (I). Reaction of III (isolated from the pyrolysis and purified) with sodium iodide in acetone for three and a half days produced only 2% of the iodo compound. The mixture of III and the iodo derivative was converted to the Grignard reagents, then treated with water to yield I.



The predominance of methyl chlorination of the silacyclohexane (II) was shown in a similar fashion.

EXPERIMENTAL[10]

Chlorination of 1,1-dimethylsilacyclopentane. A. *With chlorine gas without ultraviolet light.* Chlorine gas (*ca.* 0.028 mole/min.) was bubbled for 38 min. through 19.6 g. (0.172 mole) of 1,1-dimethylsilacyclopentane[11] kept at a moderate temperature (under 40°) by a water bath. At the end of the reaction period, the weight of the reaction mixture had increased 4.4 g. Gas phase analysis of the mixture showed three peaks corresponding to the monochloro isomers[12]: peak 1 (shown to be the 3-chloro isomer), retention time 2.8 min., 17%; peak 2 (shown to be the chloromethyl isomer), retention time 4.9 min., 63%; peak 3 (shown to be the 2-chloro isomer), retention time 5.9 min., 20%.

Fractional distillation of the reaction mixture resulted in two major fractions: recovered starting material, b.p. 104–5°, 6.3 g (32%), and a series of fractions containing mixtures of the monchloro isomers, b.p. 145–165°, 13.3 g. (52%). A residue of 7.9 g. remained. Gas phase analysis of each of the fractions boiling between 145 and 165° showed incomplete separation of the mixture; consequently, these fractions were recombined and assignment of the structures was accomplished using this mixture.

1. *Structure assignment of. 1,1-dimethyl-3-chlorosilacyclopentane.* a. *Reaction with base.* Treatment of the mixture of monochloro isomers with water, ethanol or 0.1*N* sodium hydroxide solution resulted in the disappearance of peak 1[13] from the gas chromatogram.

b. *Reaction with methylmagnesium bromide.* In a 100-ml. round bottom flask were placed 10 g. of the isomer mixture and 50 ml. of 3*M* methylmagnesium bromide in ether (obtained from Arapahoe Chemicals, Inc.). A violent reaction ensued, after which the mixture was heated under reflux for 2 hr. After water workup and concentration of the ether solution by distillation, the gas chromatogram showed no peak corresponding to peak 1; however, peaks 2 and 3 were unaffected and there was a new peak at 1.7 min., which had the same retention time as that of 1-trimethylsilyl-3-butene, prepared by the method of Hauser and Hance[14], b.p. 112–113°, n_D^{25} 1.4112, 66% (lit.,[14] b.p. 112–113°, n_D^{27} 1.4102). The two butenes were compared at 140° and 60 ml. helium/min. and at 75° and 25 ml. helium/min. The same retention times for the two were observed in each case, 1.7 min. and 7.5 min., respectively. When the known sample was mixed with the product, no change in the symmetry of the peak in the gas chromatogram could be detected at either temperature.

No attempt was made to obtain a pure sample of the 3-chloro isomer, estimated b.p. 145–150° (based upon gas phase analysis of the distillation fractions boiling in this range).

2. *Structure assignments of 1,1-dimethyl-2-chlorosilacyclopentane and 1-chloromethyl-1-methylsilacyclopentane.* a. *Reaction with quinoline.* A 10-g. sample of the mixture of monochloro isomers was washed with water to remove the 3-chloro isomer, then heated under reflux for 20 min. with 12 g. of quinoline. The reaction flask was arranged for distillation, and all material boiling up to 195° was collected. The milky white distillate was dissolved in 25 ml. of ether, washed with water, and dried with magnesium sulfate. The ether solution was then concentrated to *ca.* 10 ml. by distillation and analyzed using gas chromatography. The gas chromatogram showed that peak 2 was unaffected while peak 3 was absent. A new peak was observed at 1.75 min.

In another run, the concentrated ether solution was fractionally distilled to yield 1.8 g. of 1,1-dimethylsilacyclo-2-pentene, b.p. 98–99°, n_D^{24} 1.4425 (lit.,[6] b.p. 100–106°), and 6.0 g. of 1-chloromethyl-1-methylsilacyclopentane, b.p. 156–157°, n_D^{24} 1.4647. A center cut of the latter compound was taken for analysis.

Anal. Calcd. for $C_6H_{13}SiCl$: C, 48.4; H, 8.8. Found: C, 48.2; H, 9.0.

The infrared spectrum (thin film) of the silacyclopentene showed characteristic double bond (6.40 μ) and Si—CH$_3$ (8.0μ) bands. No Si—O bands were observed in the spectrum. The infrared spectrum of the chloromethyl isomer also showed a characteristic Si—CH$_3$ band.

The 2-chloro isomer (estimated b.p. 157–165°) was the highest boiling of the three monochloro isomers, based upon gas phase analysis of the distillation fractions boiling in this range.

b. *Reaction of 1,1-dimethylsilacyclo-2-pentene with bromine.* To 0.2329 g. (0.00208 mole) of 1,1-dimethylsilacyclo-2-pentene, b.p. 98–99°, was added 0.3327 g. (0.00208 mole) of bromine in 7 ml. of ethanol. The solution immediately became colorless. Excess silver nitrate solution was added to the alcoholic solution. The resultant silver bromide precipitate was filtered and dried. There was obtained 0.4383 g. of silver bromide. Active bromine calculated for 0.00208 mole of 1,1-dimethyl-2,3-dibromosilacyclopentane is 0.3910 g. (one active bromine); for 1,1-dimethyl-3,4-dibromosilacyclopentane, 0.7820 g. (two active bromines).

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(10) All boiling points are uncorrected. Distillations were made at atmospheric pressure using a 2-ft. modified Podbeilniak column (*cf.* J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall, New York, 1950, p. 237). The infrared spectra were recorded using a Beckman IR-4 instrument. The carbon and hydrogen analysis was performed by the Berkeley Micro-analytical Laboratory. Gas phase analyses were accomplished using an Aerograph gas phase chromatography unit (Wilkens Instrument Co.) equipped with a 5′ Silicone column. The temperature (usually 135°) and the helium gas flow (usually 60 ml./min.) were held constant for a given run.

(11) The preparation of this compound is the subject of another investigation now being prepared for publication.

(12) The percentage of each of the monochloro isomers quoted refers only to its percentage of the total area under the peaks of the three isomers. These values are given for evaluation of the isomer distribution and are not intended to indicate the percentage of an isomer in the reaction mixture.

(13) For ease of comparison, the terms peak 1, peak 2, and peak 3, referring to peaks observed in the gas chromatogram of the chlorination products, will continue to be used instead of retention times.

(14) C. R. Hauser and C. R. Hance, *J. Am. Chem. Soc.*, **74,** 5091 (1952).

c. *Conversion of 1-chloromethyl-1-methylsilacyclopentane to 1,1-dimethylsilacyclopentane.* To 1.70 g. (0.0114 mole) of the chloromethyl isomer was added 3.40 g. (0.22 mole) of sodium iodide in 15 ml. of dried acetone. After 3.5 days at reflux, only a small amount of precipitated sodium chloride was observed. The gas chromatogram of the reaction mixture showed only a small peak (*ca.* 2%) which might correspond to the iodo compound and also showed that the chloromethyl isomer was essentially unaffected by the reaction conditions. The bulk of the acetone was removed by distillation. Ether (10 ml.) was added to the residue and the mixture was washed with water to remove the remaining acetone and sodium salts. The ether solution was then dried with magnesium sulfate.

This ether solution of the chloromethyl isomer (containing *ca.* 2% of its iodo derivative) was added to a mixture of 3.5 g. (0.144 mole) of magnesium turnings, 9.0 ml. of 3*M* methylmagnesium bromide (to consume any acetone or water) and 30 ml. of anhydrous ether. The mixture was heated under reflux for 14 hr. and was then worked up in the standard fashion.

Gas phase analysis of the product exhibited only one major peak, which had a retention time the same as that observed in the chromatogram of 1,1-dimethylsilacyclopentane. The same technique for comparison (at two temperatures and flow rates) was used here as was used with 1-trimethylsilyl-3-butene.

B. *With chlorine gas and ultraviolet light.* Using the same conditions as described in part A, 1.2 g. (0.01 mole) of I was chlorinated for 10 min. while being irradiated with ultraviolet light. The distribution of the monochloro isomers is summarized in Table I. Unchanged starting material was estimated to be 45% of the total reaction mixture.

C. *With sulfuryl chloride without catalyst.* One gram (0.0088 mole) of I and 0.2 g. (0.0088 mole) of sulfuryl chloride (b.p. 69–70°) were heated under reflux for 2.5 hr. The distribution of the monochloro isomers is summarized in Table I. Unreacted starting material was estimated at 87%.

D. *With sulfuryl chloride with benzoyl peroxide.* Using the same conditions as described in part C, with the exception of a 30 min. reflux and the addition of 0.2 g. of benzoyl peroxide, the unchanged starting material was estimated to be 61%. The distribution of the monochloro isomers is summarized in Table I.

Chlorination of 1,1-dimethylsilacyclohexane. A. *With chlorine gas.* Dimethylsilacyclohexane[11] (13.5 g., 0.105 mole) was chlorinated as described in part A. Gas phase analysis showed three peaks: peak 1, retention time 2.8 min., 9%; peak 2, retention time 4.2 min., 69%; peak 3, retention time 5.1 min., 23%. When the reaction mixture was treated with water, peak 1 disappeared from the gas chromatogram and therefore corresponded to the 3-chloro isomer.

The reaction mixture from the treatment with water was pyrolyzed with quinoline in the same manner as described for the monochlorosilacyclopentanes. The gas chromatogram of the distilled mixture showed the absence of peak 3 (therefore corresponding to the 2- or 4-chloro isomer, while peak 2 was the same as before reaction (therefore corresponding to the chloromethyl isomer).

B. *With sulfuryl chloride.* Treatment of 61 g. (0.48 mole of 1,1-dimethylsilacyclohexane with 64.3 g. (0.48 mole) of sulfuryl chloride and 0.1 g. of benzoyl peroxide resulted in the following percentages of monochloro isomers: 3-chloro isomer, 20%; 2- or 4-chloro isomer, 16%; chloromethyl isomer, 64%.

SAN JOSE, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Benzylhalosilanes and α-Bromobenzylhalosilanes

HERBERT H. ANDERSON[1] AND LEWIS R. GREBE

Received September 16, 1960

Bromination of benzylsilane proves somewhat complicated: A deficiency of mercuric bromide furnishes benzylbromosilane; in the dark at 0° two moles of bromine per mole of benzylsilane produces benzyldibromosilane; excess bromine in daylight without a catalyst gives α-bromobenzyltribromosilane; more bromine upon heating yields α,α-dibromobenzyltribromosilane. Reduction of α-bromobenzyltribromosilane with lithium aluminum hydride in ether produces a partial yield of α-bromobenzylsilane, isomeric with the benzylbromosilane already mentioned. Table I lists the properties of these seven new compounds and five others—benzylchlorosilane, benzyliodosilane, *sym*-bis(benzyl)disiloxane, benzyltrifluorosilane, and benzyltriiodosilane.

Seven earlier publications establish the use of halides and halogenoids of certain transitional elements and elements in regular groups in the total replacement of hydrogen attached to germanium in triethylgermanium hydride,[2] to tin in triethyltin hydride,[2] or to silicon in triethylsilane[2]; or in the partial replacement of hydrogen attached to silicon in diethylsilane,[2] *n*-heptylsilane,[3] cyclohexylsilane,[4] or *n*-butylsilane ; or to germanium in *n*-butylgermanium trihydride or di-*n*-butylgermanium dihydride.[4] Reaction of the appropriate alkylsilane or alkylgermane with a deficiency of mercuric chloride, bromide or thiocyanate or of silver cyanate or thiocyanate or of iodine furnishes partially substituted compounds such as *n*-heptylchlorosilane,[3] diethylbromosilane,[2] cyclohexylisocyanatosilane,[4] cyclohexylisothiocyanatosilane[4] or *n*-butyliodogermane.[4]

This paper, in turn, demonstrates the progressive uncatalyzed bromination of benzylsilane, in which there are two kinds of reactive hydrogen; silane hydrogen (Si-H) is more reactive than methylene hydrogen (CH_2). Silane hydrogen reacts with bromine in the dark to produce either benzylbromosilane or benzyldibromosilane, and should react

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[1] Kindly address communications to this author. Experiments by both authors.

(2) H. H. Anderson, *J. Am. Chem. Soc.*, **79**, 326, 4913 (1957); **80**, 5083 (1958).

(3) H. H. Anderson and A. Hendifar, *J. Am. Chem. Soc.*, **81**, 1027 (1959).

(4) H. H. Anderson, *J. Am. Chem. Soc.*, **81**, 4785 (1959); **82**, 1323, 3016 (1960).