[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

Polysilanes Containing One or More Si—H Groups

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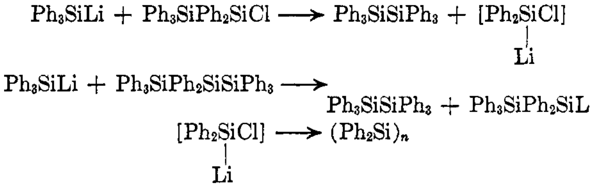
A perphenylated polysilane containing two Si—H groups has been isolated from the reaction of dichlorodiphenylsilane with sodium dispersion in ether. The structure of this compound has been established from its formation from octaphenylcyclotetrasilane by cleavage with lithium followed by acid hydrolysis. A similar reaction of dodecaphenylcyclohexasilane gave a linear hexasilane with Si—H groups in the terminal positions; an independent synthesis of this compound was realized but the yield was very low. Various other polysilanes containing the Si—H group have been prepared, and routes to homologous series of polysilanes have now become available and are discussed in relation to their practicability.

A review of the literature revealed that only a few organosilicon compounds are known containing one or more silicon-functional groups in addition to silicon-silicon bonds. The ones substituted with aliphatic groups were obtained incidental to the preparation of halogenated alkylsilanes.[1] During the early investigations in these laboratories of organosilylmetallic chemistry, pentaphenyldisilane was prepared from the reaction of triphenylsilylpotassium and dichlorodiphenylsilane followed by reduction with lithium aluminum hydride.[2]

$$\mathrm{Ph_3SiK + Ph_2SiCl_2 \longrightarrow Ph_3SiPh_2SiCl \xrightarrow{[LiAlH_4]} Ph_3SiPh_2SiH}$$

This preparation was repeated using triphenylsilyllithium instead of triphenylsilylpotassium.[3] In addition to a somewhat lower yield of pentaphenyldisilane (24.5%), there was isolated a small amount of octaphenyltrisilane (9.6%); the major product of the reaction was hexaphenyldisilane (45%), resulting from cleavage of a silicon-silicon bond either in chloropentaphenyldisilane or octaphenyltrisilane.[3,4]



$$\mathrm{Ph_3SiLi + Ph_3SiPh_2SiCl \longrightarrow Ph_3SiSiPh_3 + [Ph_2\underset{\displaystyle Li}{\underset{|}{Si}}Cl]}$$

$$\mathrm{Ph_3SiLi + Ph_3SiPh_2SiSiPh_3 \longrightarrow Ph_3SiSiPh_3 + Ph_3SiPh_2SiL}$$

$$\mathrm{[Ph_2\underset{\displaystyle Li}{\underset{|}{Si}}Cl] \longrightarrow (Ph_2Si)_{\mathit{n}}}$$

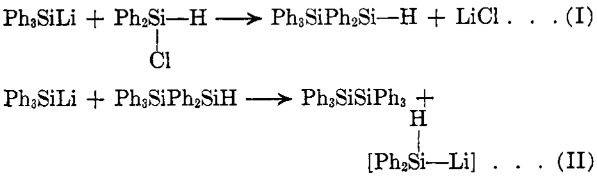
A less likely route to hexaphenyldisilane could involve halogen-metal interconversion between chloropentaphenyldisilane and triphenylsilyllithium.

Halogen-metal interconversion has been observed between alkyl halides and organosilylmetallic compounds.[5] Thus, triphenylchloromethane reacts with triphenylsilylpotassium to yield hexaphenyldisilane (45%) and hexaphenylethane (63% isolated as bis-triphenylmethyl peroxide), but no triphenylmethyltriphenylsilane.[5] Halogen-metal interconversion between a halosilane and an organosilylmetallic compound, although temporarily considered a possibility,[6] was soon thought to be of minor importance compared to cleavage of silicon-silicon bonds by organosilyllithium compounds in particular.[4]

$$\mathrm{Ph_3SiPh_2SiCl + Ph_3SiLi \longrightarrow Ph_3SiPh_2SiLi + Ph_3SiCl}$$

$$\mathrm{Ph_3SiLi + Ph_3SiCl \longrightarrow Ph_3SiSiPh_3 + LiCl}$$

We now wish to report the preparation of pentaphenyldisilane in a 42% yield by the reaction of triphenylsilyllithium with chlorodiphenylsilane. From this reaction there was also isolated a large amount of hexaphenyldisilane (41%). Since the triphenylsilyllithium solution was added to an excess of chlorodiphenylsilane it may be concluded that the rate of these competitive reactions, coupling (I) or cleavage (II), are similar and both are very rapid.



$$\mathrm{Ph_3SiLi + Ph_2\underset{\displaystyle Cl}{\underset{|}{Si}}{-}H \longrightarrow Ph_3SiPh_2Si{-}H + LiCl} \quad \ldots \text{(I)}$$

$$\mathrm{Ph_3SiLi + Ph_3SiPh_2SiH \longrightarrow Ph_3SiSiPh_3 + [Ph_2\overset{\displaystyle H}{\overset{|}{Si}}{-}Li]} \quad \ldots \text{(II)}$$

This reaction was carried out in order to establish whether at least some coupling takes place between a silyllithium compound and a chlorosilane containing a hydrogen on the same silicon atom. With this preparation at hand it should be possible to prepare homologous series of perphenylated polysilanes with Si—H groups in the terminal positions, $\mathrm{H{-}(SiPh_2)_{\mathit{n}}{-}H}$ ($n \geqq 2$). The suggestions given below for the preparation of such homologous series are practicable routes to compounds significant in future comparisons with

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[1] M. Kumada and M. Kuriyagawa, Japanese Patent **7223** (1954), *Chem. Abstr.*, **50**, 10125 (1956); M. Kumada and M. Yamaguchi, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, **57**, 175 (1954), *Chem. Abstr.*, **49**, 11542 (1955).

[2] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman, and S. H. Eidt, *J. Am. Chem. Soc.*, **74**, 561 (1952); see also H. Gilman and J. J. Goodman, *J. Am. Chem. Soc.*, **75**, 1250 (1953).

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

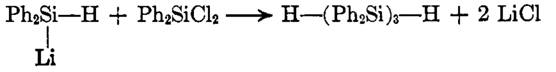
[4] H. Gilman, G. D. Lichtenwalter, and D. Wittenberg, *J. Am. Chem. Soc.*, **81**, 5320 (1959).

[5] A. G. Brook, G. Gilman, and L. S. Miller, *J. Am. Chem. Soc.*, **75**, 459 (1953); for some general references see D. Wittenberg and H. Gilman, *Quart. Revs. (London)*, **13**, 116 (1959).

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

carbon analogs. Such comparisons have been markedly restricted hitherto because of a paucity of procedures for the stepwise synthesis of such molecules. From these Si—H compounds, prepared by the suggested routes, it should be possible to synthesize other homologous series with different end-groups by reaction of the terminal Si—H or Si—X groups with organometallic or organosilylmetallic compounds.

The first member of the series, *sym*-tetraphenyldisilane, has been prepared from the coupling of chlorodiphenylsilane with magnesium.[7,8] Diphenylsilyllithium may be prepared from cleavage of *sym*-tetraphenyldisilane with lithium or directly from chlorodiphenylsilane.[7] Reactions of two mole equivalents of this silyllithium compound with dichlorodiphenylsilane should produce the trisilane, $\mathrm{H—(SiPh_2)_3—H}$.

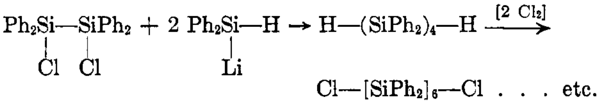


$$\mathrm{Ph_2}\underset{\mathrm{Li}}{\mathrm{Si}}\mathrm{—H} + \mathrm{Ph_2SiCl_2} \longrightarrow \mathrm{H—(Ph_2Si)_3—H} + 2\ \mathrm{LiCl}$$

A combination of chlorinations and couplings with diphenylsilyllithium should give the uneven-numbered members of this homologous series.

$$\mathrm{H—(SiPh_2)_3—H} + 2\ \mathrm{Cl_2} \longrightarrow \mathrm{Cl—(SiPh_2)_3—Cl} \xrightarrow{[2\ \mathrm{Ph_2SiHLi}]} \mathrm{H—(SiPh_2)_5—H}\ \ .\ .\ .\ \text{etc}$$

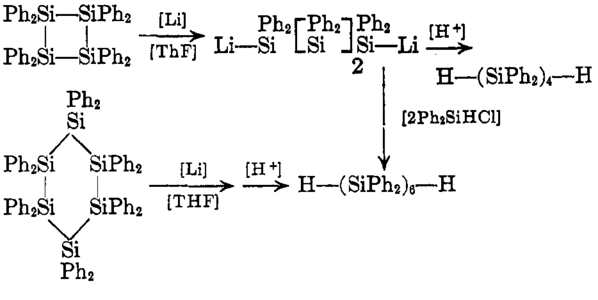
Similarly, the even-numbered members of this series might be synthesized from *sym*-dichlortetraphenyldisilane and diphenylsilyllithium.



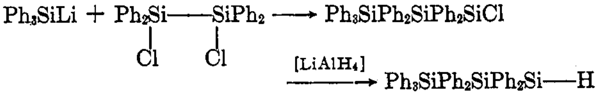
$$\mathrm{Ph_2}\underset{\mathrm{Cl}}{\mathrm{Si}}—\underset{\mathrm{Cl}}{\mathrm{Si}}\mathrm{Ph_2} + 2\ \mathrm{Ph_2}\underset{\mathrm{Li}}{\mathrm{Si}}\mathrm{—H} \rightarrow \mathrm{H—(SiPh_2)_4—H} \xrightarrow{[2\ \mathrm{Cl_2}]} \mathrm{Cl—[SiPh_2]_6—Cl}\ .\ .\ .\ \text{etc.}$$

However, since diphenylsilyllithium is formed in only moderate yields,[7] a more likely route to the even-numbered members of this series ($n \geqq 4$) was realized from octaphenylcyclotetrasilane.[9] Cleavage of this compound by lithium and subsequent acid hydrolysis yielded a tetrasilane.[10] However, if the 1,4-dilithio-octaphenyltetrasilane were to react with two mole equivalents of chlorodiphenylsilane one would expect to obtain the next higher even-numbered member of the series, a compound which was also obtained from cleavage of dodecaphenylcyclohexasilane[11] with lithium followed by acid hydrolysis.

Another possible route to these compounds may have been possible through lithium aluminum hydride reduction of 1,4-dichloro-octaphenyltetrasilane or 1,6-dibromododecaphenylhexasilane[12] which are readily obtainable from octaphenylcyclotetrasilane and dodecaphenylcyclohexasilane. However, it has been demonstrated in these laboratories that the silicon-silicon bonds in polysilanes are susceptible to reductive cleavage by lithium aluminum hydride.[13]



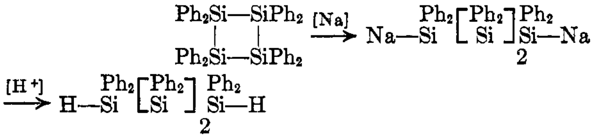
This cleavage was demonstrated in the reaction of one mole equivalent of triphenylsilyllithium with *sym*-dichlorotetraphenyldisilane[8] followed by reduction with lithium aluminum hydride.



$$\mathrm{Ph_3SiLi} + \mathrm{Ph_2}\underset{\mathrm{Cl}}{\mathrm{Si}}—\underset{\mathrm{Cl}}{\mathrm{Si}}\mathrm{Ph_2} \longrightarrow \mathrm{Ph_3SiPh_2SiPh_2SiCl} \xrightarrow{[\mathrm{LiAlH_4}]} \mathrm{Ph_3SiPh_2SiPh_2Si—H}$$

From the reaction there was isolated some of the expected heptaphenyltrisilane and a small amount of decaphenyltetrasilane in addition to triphenylsilane and hydrolysis products of unreacted 1-chloroheptaphenyltrisilane. The triphenylsilane did not result from hydrolysis of unreacted triphenylsilyllithium since Color Test I[14] was negative at the end of the coupling step. The physical properties and the infrared spectrum agreed with those of a sample prepared previously by the cleavage of octaphenylcyclotetrasilane with lithium followed by acid hydrolysis.[3]

The tetrasilane, 1,1,2,2,3,3,4,4-octaphenyltetrasilane, was obtained from dichlorodiphenylsilane directly by reaction with sodium dispersion. This very vigorous reaction appears to involve the formation of octaphenylcyclotetrasilane and this compound is subsequently cleaved to 1,4-disodio-octaphenyltetrasilane:



$$\mathrm{Ph_2SiCl_2} + \mathrm{Na\ (dispersed)} \xrightarrow{[\text{ether}]} \begin{matrix}\mathrm{Ph_2Si—SiPh_2}\\ |\qquad\quad |\\ \mathrm{Ph_2Si—SiPh_2}\end{matrix} \xrightarrow{[\mathrm{Na}]} \mathrm{Na—}\overset{\mathrm{Ph_2}}{\mathrm{Si}}\left[\overset{\mathrm{Ph_2}}{\mathrm{Si}}\right]_2\overset{\mathrm{Ph_2}}{\mathrm{Si}}\mathrm{—Na} \xrightarrow{[\mathrm{H^+}]} \mathrm{H—}\overset{\mathrm{Ph_2}}{\mathrm{Si}}\left[\overset{\mathrm{Ph_2}}{\mathrm{Si}}\right]_2\overset{\mathrm{Ph_2}}{\mathrm{Si}}\mathrm{—H}$$

Cleavage of the silicon-silicon bond by sodium dispersion has previously been attempted without success in solvents such as dioxane, ether, and tetralin,[15] however, hexaphenyldisilane was cleaved

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[7] H. Gilman and W. Steudel, *Chem. & Ind.* (*London*), 1094 (1959).

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

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

[10] Unpublished studies by D. J. Peterson.

[11] H. Gilman, D. J. Peterson, A. W. P. Jarvie, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **83**, 4089 (1961).

[12] A. W. P. Jarvie and H. Gilman, unpublished studies.

[13] Unpublished studies by R. A. Tomasi.

[14] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[15] H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **73**, 4031 (1951), also unpublished studies by T. C. Wu.

in ethylene glycol dimethyl ether by sodium to triphenylsilylsodium.[16] The observation that octaphenylcyclotetrasilane apparently did cleave in ether is further evidence for its strained structure and accompanying high reactivity. The alternate formation of 1,4-disodioöctaphenyltetrasilane directly from dichlorodiphenylsilane cannot be excluded on basis of the present evidence.

The normal absorptions in the infrared region for a tri-aryl-substituted silane are 2127, 805, and 731 cm.$^{-1}$ [17] These absorptions were found among others in all the silanes mentioned in this work. It is of particular interest in identification of these compounds to observe the region 900–700 cm.$^{-1}$, which is characteristically different for the various members of the homologous series, provided sufficiently dilute solutions in carbon disulfide are used. The absorption pattern in this region is due to the presence of both silicon-hydrogen bending modes and aromatic carbon-hydrogen out-of-plane bending vibrations. The differences which occur between two members of this series are due to variations in relative intensities of these bands as the silicon-hydrogen groups (and hence also absorptions due to this group) become more dilute as the number of phenyl groups in the molecule increases. This effect may also readily be demonstrated, for more concentrated solutions in carbon disulfide, in the silicon-hydrogen stretching region if the intensity of this absorption is compared with the intensity of the aromatic over-tone bands.

EXPERIMENTAL[18]

Preparation of pentaphenyldisilane. Triphenylsilyllithium was prepared from 20 g. (0.037 mole) of hexaphenyldisilane and an excess of lithium in 100 ml. of tetrahydrofuran. The solution was analyzed for silyllithium content.[19] The solution was found to be 0.63*N* in silyllithium groups which corresponds to 82% of the theoretical. This solution (110 ml.) containing 0.069 mole of triphenylsilyllithium was added to 16.2 g. (0.074 mole) of diphenylchlorosilane in 50 ml. of ether. The reaction mixture was stirred for two hours at the end of which time the Color Test[14] was negative. Hydrolysis was performed by pouring the reaction mixture into 300 ml. of ice-cooled 1.0*N* hydrochloric acid. The organic layer was washed with two 200 ml.-portions of water and then filtered. There was obtained 7.5 g. (41%) of hexaphenyldisilane which was recrystallized from xylene to give a m.p. of 370–372° (mixed melting point). The organic layer was dried, concentrated, and chromatographed to give 12.8 g. (42%) of pentaphenyldisilane, m.p. 124–126° after recrystallization from benzene-petroleum ether (b.p. 60–70°). A mixed melting point with an authentic sample was not depressed and the infrared spectra of the samples were superimposable.

Reaction of 1,4-dilithio-octaphenyltetrasilane with chlorodiphenylsilane. Octaphenylcyclotetrasilane (6.5 g., 0.0089 mole) was cleaved with an excess of lithium (0.5 g., 0.072 g. atom) in 50 ml. of tetrahydrofuran by adding the solvent slowly to a mixture of the solids. Initiation of the reaction was effected by heating a thick paste containing only a small amount of tetrahydrofuran until a yellow color developed. The reaction mixture was stirred for a total of five hours and an aliquot was withdrawn and analyzed to be 0.316*N* in silyllithium. This assay indicated that the cleavage had proceeded to 89% of the theoretical. The lithium was filtered off by pouring the solution under nitrogen through a glass-wool plug into an addition funnel. From this, the solution was added dropwise to 4.65 g. (0.0212 mole) of chlorodiphenylsilane in 50 ml. of ether cooled to −20°. The solution was left overnight and then hydrolyzed by pouring into 1.0*N* hydrochloric acid. The organic layer was washed with two 200 ml.-portions of water and then with 200 ml. of saturated brine solution. The organic layer was dried over anhydrous calcium chloride, concentrated, and chromatographed to yield various solids, m.p. 112–115°, 78–85° and 120–130°, respectively. These fractions were recrystallized to raise the melting points somewhat, but the fractions were not sufficiently pure for isolation of the desired 1,6-di-Si—H compound.

The reaction was repeated using 55 ml. of an 0.450*N* silyllithium solution of 1,4-dilithio-octaphenyltetrasilane prepared from the cleavage of 20 g. (0.0275 mole) of octaphenylcyclotetrasilane in 110 ml. of tetrahydrofuran. This solution was added to 6.0 g. (0.0275 mole) of chlorodiphenylsilane. The addition was performed in a flask equipped with a stop-cock at the bottom permitting the removal of the reaction mixture immediately after the simultaneous addition of equimolar quantities of the reactants (molar ratio 2:1, chlorodiphenylsilane to disilyllithium compound). The tetrahydrofuran was evaporated and 50 ml. of benzene was added causing the precipitation of lithium chloride which was filtered off and dissolved in 50 ml. of water. The water solution was analyzed for chloride revealing the presence of 24.8 meq. or 100% of the theoretical based on the amount of silyllithium compound added. The organic layer was concentrated and petroleum ether (b.p. 60–70°) was added. On prolonged standing there separated a crystalline solid which was recrystallized from cyclohexane-petroleum ether (b.p. 60–70°), m.p. 205–208°. Various other solids separated from the mother liquors; one of these was recrystallized to give 0.8 g. (5.4%) of a compound which melted at 146–148° after recrystallization from cyclohexane-petroleum ether (b.p. 60–70°). This compound had an infrared spectrum superimposable on that of the 1,6-di-Si—H compound obtained from the following experiment, and the melting point of the latter was not depressed by the presence of the former.

Reaction of dodecaphenylcyclohexasilane (B) with lithium followed by acid hydrolysis. Compound (*B*) was recrystallized from benzene-petroleum ether (b.p. 60–70°) and dried. A slurry of 10 g. (0.0095 mole) of this solid and 20 ml. of tetrahydrofuran was stirred with an excess of lithium wire cut into short sections. Heat was applied for *ca.* 10 minutes before a yellow color indicative of the initiation of the cleavage was noticed. A total of 150 ml. of tetrahydrofuran was added during a 30-min. period and the reaction mixture was stirred for 3 hours at room temperature before it was analyzed for silyllithium content.[19] The analysis indicated the presence of 109% of the theoretical amount of silyllithium expected from a single cleavage of Compound (*B*). Hydrolysis was performed by pouring the reaction mixture through a glass-wool plug into 400 ml. of ice cooled 1.0*N* hydrochloric acid. The aqueous layer was extracted

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[16] A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 278 (1954); a possible intermediate (triphenylsilylsodium) has been postulated in the reaction of a mixture of chlorotrimethylsilane and chlorotriphenylsilane with sodium in refluxing xylene, from which was isolated hexaphenyldisilane and 1,1,1-trimethyl-2,2,2-triphenyldisilane (unpublished work by W. J. Trepka).

[17] R. N. Kniseley, V. A. Fassel, and E. E. Conrad, *Spectrochim. Acta*, 651 (1959).

[18] All reactions involving organometallic or organosilylmetallic compounds were performed in an atmosphere of dry, oxygen-free nitrogen. The melting points reported in this study are uncorrected.

[19] H. Gilman, R. A. Klein, and H. J. S. Winkler, *J. Org. Chem.*, **26**, 2474 (1961).

with two 200-ml. portions of ether and the organic layers were combined and dried over anhydrous calcium chloride before evaporation and addition of petroleum ether which caused the precipitation of 7.3 g. (73%) of a compound melting at 124–125°. This solid was recrystallized from ethyl alcohol–ethyl acetate and cyclohexane–petroleum ether (b.p. 60–70°) to yield a solid melting at 147–148°.

Anal. Calcd. for $C_{72}H_{62}Si_6$: C, 79.00; H, 5.71; Si, 15.30. Found: C, 79.15, 79.23; H, 6.28, 6.03; Si, 15.50. Hydrogen value: calcd. for seven moles of hydrogen per $C_{72}H_{62}Si_6$, 143.5 [ml. at S.T.P./g. of compound]. Found: 144.5, 147. Molecular Weight (perylene method). Calcd.: 1096. Found: 1105, 1044.

Preparation of 1,1,1,2,2,3,3-heptaphenyltrisilane. A solution of triphenylsilyllithium was prepared from 20 g. of hexaphenyldisilane, excess lithium, and tetrahydrofuran (200 ml.). The solution was assayed to contain 98% of the theoretical amount of triphenylsilyllithium (0.377*N*). To a solution of 8.8 g. (0.020 mole) of *sym*-dichlorotetraphenyldisilane[8] in 50 ml. of tetrahydrofuran was added 55 ml. of the above prepared solution of triphenylsilyllithium (containing 0.020 mole of silyllithium compound). The color of the silyllithium solution disappeared immediately on addition to the dichlorodisilane. A Color Test[14] revealed there was no organosilylmetallic compound present in the solution. To this solution was then added 0.19 g. (0.05 mole) of lithium aluminum hydride and the solution was refluxed for a total of 14 hours. Hydrolysis was accomplished by pouring the solution into 400 ml. of 1.0*N* hydrochloric acid stirred rapidly by a counter-rotating stirrer (1500 r.p.m.). The aqueous layer was extracted with 500 ml. of benzene and the organic extracts combined and dried over anhydrous calcium chloride before concentration and chromatography. There was obtained 1.8 g. (35%) triphenylsilane identified by its infrared spectrum and by mixed melting point with an authentic sample; 2.4 g. (19%) of heptaphenyltrisilane melting at 157–158° after recrystallization from benzene–petroleum ether (b.p. 60–70°), a mixed melting point with an authentic sample[3] was not depressed; 3.4 g. (27%) heptaphenyltrisilanol-1, m.p. 165–166° after recrystallization from benzene–petroleum ether (b.p. 60–70°); 0.5 g. (5%) decaphenyltetrasilane, m.p. 350–352°; and various other minor quantities of pentaphenyldisilane, m.p. 122–123°, *sym*-tetraphenyldisilanediol, and *sym*-tetraphenyldisilane were identified.

Anal. Calcd. for heptaphenyltrisilanol-1 $C_{42}H_{36}Si_3O$: C, 78.70; H, 5.66; Si, 13.22. Found: C, 79.05, 79.12; H, 5.75, 5.60; Si, 13.05, 13.09.

Reaction of dichlorodiphenylsilane with sodium dispersion. A 500-ml. flask was equipped with an efficient stirrer, a condenser topped by a nitrogen inlet, and an addition funnel constructed in such a manner that its content could be stirred by a magnetic stirrer before addition to the flask. The reaction flask was charged with 21.2 g. (0.082 mole) of dichlorodiphenylsilane and 100 ml. of ether. Sodium dispersion (22.6% sodium in alkylate) was added dropwise until a total of 20 ml. (16 g., 0.158 mole) had been added. After 1 min. stirring, a considerable amount of heat was generated and the solution refluxed rapidly while the reaction mixture turned dark brown with a purple precipitate. Sufficient heat was generated during the following 30 min. to maintain reflux. The mixture was stirred for an additional 24 hours while heat was supplied to keep the solvent refluxing. The suspended material was allowed to settle and a Color Test[14] revealed the presence of an organosilylmetallic species. An aliquot was removed for analysis of base content after hydrolysis. The solution was found to be 1.4*N* in base.

To the reaction mixture was added a mixture of 40 ml. of glacial acetic acid, 60 ml. of absolute ethanol, and 100 ml. of petroleum ether (b.p. 60–70°). Heat was evolved and the brown color of the solution changed to light purple. The suspension was then added to 400 ml. of water and the precipitate filtered off and washed thoroughly on the filter with water. The solid was dried in air to give 12.5 g. (70%) of a compound melting at 155–160°. Recrystallization from benzene–petroleum ether (b.p. 60–70°) yielded 1,1,2,2,3,3,4,4-octaphenyltetrasilane[10] as the major fraction, m.p. 161–162°, mixed m.p. with an authentic sample was not depressed and the infrared spectra were superimposable.

Anal. Calcd. for $C_{48}H_{42}Si_4$: C, 78.84; H, 5.79; Si, 15.37. Found: C, 78.54, 78.54; H, 5.68, 5.73; Si, 15.10, 15.42. Hydrogen value: calcd. for 5 mole of hydrogen per mole of compound: 153 [ml. at S.T.P./g.]. Found: 150, 158.

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AMES, IOWA

[CONTRIBUTION FROM MIDWEST RESEARCH INSTITUTE]

Triorganosilyl Derivatives of Chelated Titanates[1]

L. W. BREED AND W. J. HAGGERTY, JR.

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Silyl titanates of titanium (IV), with two normal valences and two coordinating valences forming chelate rings with 8-quinolinol, dibenzoylmethane, and acetylacetone, are prepared by a variety of procedures. The methods involve displacements of functional groups on titanium chelates without disturbing the chelate rings.

Because compounds of titanium(IV) are tetrafunctional and do not form stable bonds with carbon except in the cyclopentadienyl series, they are not considered suitable for the preparation of linear polymers similar to siloxanes derived from difunctional silicon compounds. However, titanium derivatives may be partially substituted with groups capable of forming very stable chelate rings by coordination with the titanium atom. If a titanium compound is substituted with two chelating groups and if the remaining two groups may be preferentially displaced in condensation reactions, the compound is effectively difunctional in polymerization reactions.

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[1] This research was supported by the United States Air Force, Air Research and Development Command, under Contract AF 33(616)-6916 and monitored by Materials Central, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.