ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

An Intramolecular Cleavage–Cyclization Reaction of Silicon-containing Organolithium Compounds

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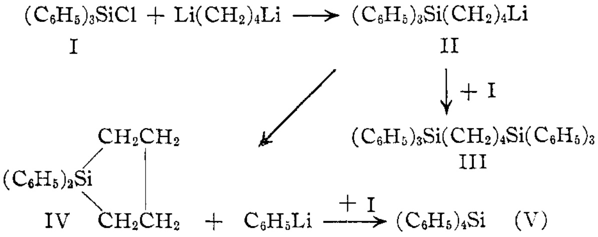
RECEIVED DECEMBER 23, 1957

The reaction of chlorotriphenylsilane with tetramethylenedilithium gave the expected tetramethylene-bis-(triphenylsilane) only in very low yields, while as the main products 1,1-diphenylsilacyclopentane and tetraphenylsilane were obtained. The formation of these compounds by an intramolecular cleavage–cyclization reaction of the reaction intermediate 4-triphenylsilyl-butyllithium is discussed. 4-Bromobutyltriphenylsilane was prepared in a three-step synthesis and allowed to react with lithium and magnesium. The stability of these organometallic compounds was studied. The investigation was further extended to the reaction of chlorotriphenylsilane and pentamethylenedilithium.

A number of studies concerned with the preparation of silicon-containing ring systems, in which silicon is bonded only to carbon, have been reported.[1a–m] The reaction of difunctional Grignard reagents with silicon tetrachloride has been applied in the syntheses of 1,1-dichlorosilacycloalkanes.[1a–f] As an example 1,1-dichlorosilacyclohexane was formed in a 70% yield from the reaction of 1,5-pentamethylenedimagnesium dibromide and silicon tetrachloride.[1c,d] Difunctional lithium compounds similarly yielded spirans with silicon as the spiro atom.[1d,g,k,l] Treatment of appropriately substituted trichlorosilanes with difunctional Grignard reagents provided a useful route to the synthesis of monofunctional cyclic organosilicon compounds. By this procedure, for instance, 1-chloro-1-methyl- and 1-chloro-1-phenylsilacyclopentane were obtained in yields of 47 and 36%, respectively, from the reaction of 1,4-tetramethylenedimagnesium dibromide and trichloromethylsilane and trichlorophenylsilane, respectively.[2] Several "non-functional" cyclic organosilicon compounds were obtained from a difunctional Grignard reagent and a disubstituted dichlorosilane[1e] under forced conditions, but difunctional lithium compounds apparently give much better results[1c,d,g,k,l,m] and react more readily.

The reaction of difunctional organolithium compounds with trisubstituted chlorosilanes has been reported to yield "non-functional" disilanes. Thus tetra-, penta-, hexa- and octamethylene-bis-(trimethylsilane) were obtained from the corresponding dilithium compounds and chlorotrimethylsilane in 63, 68, 42 and 71% yields, respectively.[3]

In attempts to prepare tetramethylene-bis-(triphenylsilane) (III) from the analogous reaction of tetramethylenedilithium and chlorotriphenylsilane in diethyl ether, we found the desired product to be formed only in a 4.4% yield. The unexpected main products were 1,1-diphenylsilacyclopentane (IV) and tetraphenylsilane (V), which were isolated in 38.7 and 48% yields, respectively.



Apparently tetramethylenedilithium first displaces the chlorine atom in chlorotriphenylsilane to form 4-triphenylsilyl-butyllithium (II). The latter in a slow reaction couples with a second molecule of chlorotriphenylsilane to give III. But in a more rapid intramolecular cleavage–cyclization reaction II splits off phenyllithium[4] to form IV. Phenyllithium thereafter couples with chlorotriphenylsilane to give tetraphenylsilane.

The two compounds III and IV, which have not been reported previously, were both synthesized by independent methods. Tetramethylene-bis-(triphenylsilane) was formed in a 3% yield from the reaction of 1,4-dibromobutane with triphenylsilyllithium in tetrahydrofuran. As a main product hexaphenyldisilane was isolated in a 74% yield, formed apparently by a halogen–metal interconversion reaction.[5] 1,1-Diphenylsilacyclopentane was obtained in a 46% yield from the reaction of dichlorodiphenylsilane with tetramethylenedilithium.

In order to throw light on the abnormal cleavage–cyclization reaction, 4-bromobutyl-triphenylsilane was synthesized, allowed to react with lithium and magnesium, and the stability of the organometallic compounds of type II was investigated.

Wittig and Rueckert[6] reported the cleavage of tetrahydrofuran by triphenylmethylsodium at room

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[1] (a) A. Bygden, *Ber.*, **48**, 1236 (1915); (b) J. M. Hersch, U. S. Patent 2,464,231 [*C. A.*, **43**, 8210 (1949)]; (c) R. West and E. G. Rochow, *Naturwissenschaften*, **40**, 142 (1953); (d) R. West, THIS JOURNAL, **76**, 6012 (1954); (e) M. Kumada, *J. Inst. Polytech. Osaka City Univ., Ser. C*, **2**, 11 (1951) [*C. A.*, **46**, 6082 (1952)]; (f) A. F. Plate, N. A. Monna and Yu. P. Egorov, *Doklady. Akad. Nauk S.S.S.R.*, **97**, 847 (1954) [*C. A.*, **49**, 10169 (1955)]; (g) A. F. Plate, N. A. Belikova and Yu. P. Egorov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1085 (1956) [*C. A.*, **51**, 5085 (1957)]; (h) L. H. Sommer and O. F. Bennett, THIS JOURNAL, **79**, 1008 (1957); (i) L. H. Sommer and G. A. Baum, *ibid.*, **76**, 5002 (1954); (j) R. West, *ibid.*, **77**, 2339 (1955); (k) K. Oita and H. Gilman, *ibid.*, **79**, 339 (1957); (l) K. Oita and H. Gilman, *J. Or . Chem.*, **22**, 336 (1957); (m) H. Gilman and R. D. Gorsich, THIS JOURNAL, **77**, 6380 (1955).

[2] H. Gilman and G. D. Lichtenwalter, unpublished studies on alicyclic silicon compounds.

[3] R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).

[4] Apparently no phenyllithium is split off, however, when *n*-butyltriphenylsilane is treated with *n*-butyllithium; see H. Gilman, R. A. Benkeser and G. E. Dunn, THIS JOURNAL, **72**, 5878 (1950).

[5] For halogen–metal interconversion in silicon chemistry see A. G. Brook, H. Gilman and L. S. Miller, *ibid.*, **75**, 4759 (1953); A. G, Brook and S. Wolfe, *ibid.*, **79**, 1431 (1957); H. Gilman and D. H. Miles, *ibid.*, **80**, 611 (1958).

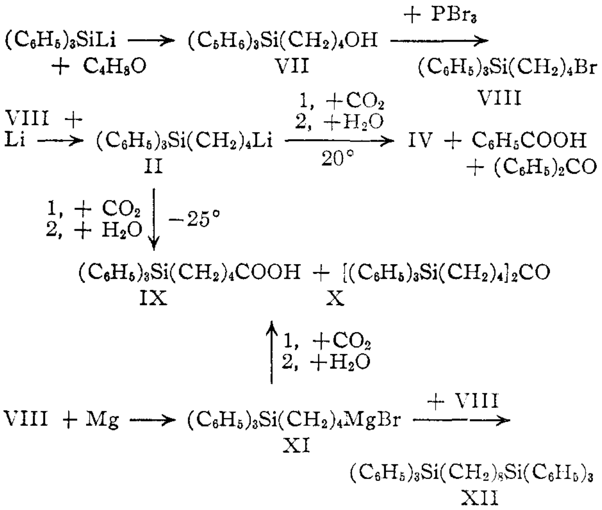
[6] G. Wittig and A. Rueckert, *Liebigs Ann. Chem.*, **566**, 104 (1950).

temperature in the presence of triphenylboron to give a boron complex salt, the hydrolysis of which yielded 5,5,5-triphenyl-1-pentanol (VI). They also reported that triphenylmethylsodium itself did not cleave the cyclic ether, even after prolonged heating at 100°.

$$(C_6H_5)_3CNa + C_4H_8O + (C_6H_5)_3B \longrightarrow$$

$$[(C_6H_5)_3C(CH_2)_4O{\rightarrow}B(C_6H_5)_3]^-Na^+ \xrightarrow{+\text{ acid}} \underset{\text{VI}}{(C_6H_5)_3C(CH_2)_4OH}$$

Normant[7] found that Grignard reagents cleave tetrahydrofuran at 200° to give primary alcohols of the type R–$(CH_2)_4OH$. Gorsich[8] has obtained 4-hydroxybutyltriphenylsilane (VII), the silicon analog of VI, in an 18% yield on refluxing triphenylsilyllithium in tetrahydrofuran for 2.7 days. To improve the yield the cleavage reaction was carried out in a sealed tube, which was heated for 3 hours at 125°. Color Test I[9] was found to be negative and from the reaction mixture VII was isolated in a 71% yield. The alcohol VII was converted to the bromide VIII with phosphorus tribromide[10] in a 54.5% yield.



$$\underset{+\ C_4H_8O}{(C_6H_5)_3SiLi} \longrightarrow \underset{\text{VII}}{(C_5H_6)_3Si(CH_2)_4OH} \xrightarrow{+\ PBr_3} \underset{\text{VIII}}{(C_6H_5)_3Si(CH_2)_4Br}$$

$$\text{VIII} + \text{Li} \longrightarrow \underset{\text{II}}{(C_6H_5)_3Si(CH_2)_4Li} \xrightarrow[20^\circ]{1,\ +CO_2;\ 2,\ +H_2O} \text{IV} + C_6H_5COOH + (C_6H_5)_2CO$$

$$\text{II} \xrightarrow[-25^\circ]{1,\ +\ CO_2;\ 2,\ +\ H_2O} \underset{\text{IX}}{(C_6H_5)_3Si(CH_2)_4COOH} + \underset{\text{X}}{[(C_6H_5)_3Si(CH_2)_4]_2CO}$$

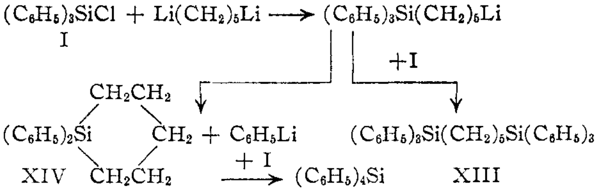
$$\text{VIII} + \text{Mg} \longrightarrow \underset{\text{XI}}{(C_6H_5)_3Si(CH_2)_4MgBr} \xrightarrow{+\ \text{VIII}} \underset{\text{XII}}{(C_6H_5)_3Si(CH_2)_8Si(C_6H_5)_3}$$

$$\text{XI} \xrightarrow{1,\ +CO_2;\ 2,\ +H_2O} \text{IX}$$

When 4-bromobutyltriphenylsilane was treated with lithium in ethyl ether at −25° and the mixture carbonated as soon as it had warmed to room temperature, benzoic acid, benzophenone and 1,1-diphenylsilacyclopentane (IV) were isolated in 56.5, 20 and 50.6% yields, respectively. 4-Carboxybutyltriphenylsilane (IX) was not formed under these conditions. When 4-triphenylsilyl-butyllithium (II) prepared at −25° was carbonated at low temperatures, however, IX was isolated in a 56% yield, together with a small amount of 1,9-bis-(triphenylsilyl)-5-nonanone (X). Benzoic acid and the cyclic compound IV were found only in trace amounts.

The reaction of 4-bromobutyl-triphenylsilane (IX) with magnesium in ether at reflux temperature gave after carbonation the normal acid IX in a 60% yield, together with 20% of coupling product, octamethylene-bis-(triphenylsilane) (XII).

The investigation was further extended to the reaction of chlorotriphenylsilane and pentamethylenedilithium. In this case, however, the normal coupling product pentamethylene-bis-(triphenylsilane) (XIII) was obtained in a 75% yield. As a by-product 0.65% of tetraphenylsilane and some impure 1,1-diphenylsilacyclohexane (XIV) was isolated.

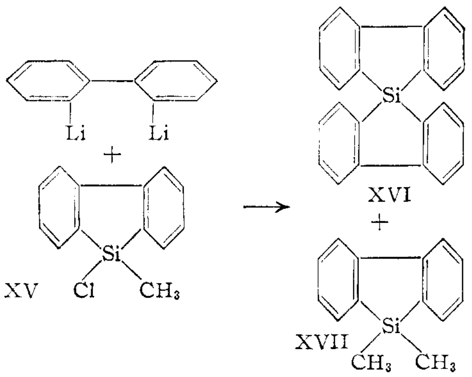


$$\underset{\text{I}}{(C_6H_5)_3SiCl} + Li(CH_2)_5Li \longrightarrow (C_6H_5)_3Si(CH_2)_5Li$$

$$(C_6H_5)_3Si(CH_2)_5Li \longrightarrow \text{XIV} + C_6H_5Li \xrightarrow{+\ \text{I}} (C_6H_5)_4Si$$

$$(C_6H_5)_3Si(CH_2)_5Li \xrightarrow{+\text{I}} \underset{\text{XIII}}{(C_6H_5)_3Si(CH_2)_5Si(C_6H_5)_3}$$

While other ring closure reactions[1c,d] show maximum yields in the preparation of six-membered cyclic silanes, slightly lower yields with five-membered rings and very low yields with the seven-membered rings, the cleavage–cyclization reaction seems to occur preferably when a five-membered cyclic silane is formed as a reaction product. A similar abnormal cyclization was observed recently in the dibenzosilole series.[11] On treatment of 5-chloro-5-methyldibenzosilole (XV) with an equimolar quantity of 2,2′-dilithiobiphenyl in diethyl ether almost equimolar amounts of 5,5′-spirobi-(dibenzosilole) (XVI) and 5,5-dimethyldibenzosilole (XVII) were obtained.



Experimental[12]

Tetramethylenedilithium and Chlorotriphenylsilane.—Tetramethylenedilithium was prepared according to the directions of West and Rochow.[3] Twenty-one and six-tenths grams (0.1 mole) of 1,4-dibromobutane in 150 ml. of anhydrous ether was added slowly with vigorous stirring to 5.0 g. (0.72 g. atom) of lithium sand, suspended in 50 ml. of ether. The reaction was started by stirring for a few minutes at room temperature; the mixture thereafter was kept at −10 to −20°. After the addition was completed, the run was stirred for 1 hr. at −10° and 0.5 hr. at 10°. The solution was filtered through glass wool into an addition funnel. The tetramethylenedilithium solution was then slowly added with stirring to 55 g. (0.187 mole) of chlorotriphenylsilane in 50 ml. of anhydrous ether. The reaction mixture was stirred for one hr. at −10°, then allowed to warm to room temperature. Three hours later Color Test I[9] was negative. The white precipitate was filtered and

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(7) H. Normant, *Compt. rend.*, **239**, 1510 (1954).

(8) R. D. Gorsich, unpublished studies.

(9) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925); G. Wittig, *Angew. Chem.*, **53**, 243 (1940).

(10) Modification of the method of L. H. Sommer, R. E. Van Strien and F. C. Whitmore, THIS JOURNAL, **71**, 3056 (1949).

(11) H. Gilman and R. D. Gorsich, *ibid.*, **80**, 1883 (1958).

(12) All melting points and boiling points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen. Silicon analyses were carried out according to the directions of H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950).

washed with ether and water, leaving 18 g. of residue (A). The layers of the filtrate were separated, the organic layer was washed twice with water and the solvent removed by distillation. In order to remove triphenylsilanol and hexaphenyldisiloxane, the hydrolysis products of unreacted chlorotriphenylsilane, the residue from the distillation (B) was chromatographed on alumina. The products eluted with petroleum ether (b.p. 60–70°) and benzene were combined with residue A and distilled at reduced pressure. At 159–165° (5 mm.), 9.2 g. (38.7%) of 1,1-diphenylsilacyclopentane, n^{20}D 1.5855, was obtained. The second fraction, boiling at 210–230° (5 mm.), an oil which partially solidified, was recrystallized twice from methanol to give 1.3 g. (5.4%) of *n*-butyltriphenylsilane, m.p. 85–86°, identified by mixed melting point with an authentic sample. Further distillation gave 16 g. of a fraction, boiling at 180–200° (0.05 mm.), which was recrystallized three times from a mixture of benzene and ethanol. There was obtained 6.5 g. of tetraphenylsilane, m.p. 232–234°, identified by mixed melting point with an authentic sample. The yield of crude product was 48%, and the yield of pure product was 19.4%.

The distillation residue was dissolved in benzene, filtered and precipitated with petroleum ether (b.p. 60–70°) to give 2.5 g. (4.4%) of tetramethylene-bis-(triphenylsilane), m.p. 209–213°. After recrystallization from cyclohexane the compound melted at 215–216°.

Tetramethylenedilithium and Dichlorodiphenylsilane.—A solution of tetramethylenedilithium in ether, prepared from 21.6 g. (0.1 mole) of 1,4-dibromobutane as described above, was added slowly at −20° with stirring to 25.3 g. (0.1 mole) of dichlorodiphenylsilane. The mixture was stirred for one hr. at −20° and then warmed to room temperature. One hour later Color Test I was negative. After hydrolysis, the organic layer was washed several times with water, dried with sodium sulfate, and the solvent removed by distillation. The residue was chromatographed on alumina, and the product, eluted with petroleum ether (b.p. 60–70°), was distilled at reduced pressure. There was obtained 10.8 g. (46%) of 1,1-diphenylsilacyclopentane, b.p. 159–162° (5 mm.), n^{20}D 1.5853.

Anal. Calcd. for $C_{16}H_{18}Si$: Si, 11.77; *MR*, 77.05. Found: Si, 11.63; *MR*, 77.21.

1,4-Dibromobutane and Triphenylsilyllithium.—Triphenylsilyllithium was prepared by cleavage of hexaphenyldisilane with lithium at room temperature in tetrahydrofuran.[13] Thirty-five millimoles of the reagent was slowly added with stirring to 3.8 g. (0.0175 mole) of 1,4-dibromobutane. A white precipitate was formed immediately. Color Test I[9] was negative. The reaction mixture was filtered and the residue carefully washed with ether and water. There was obtained 6.65 g. (74%) of hexaphenyldisilane, m.p. 363–366°, identified by mixed melting point with an authentic sample. The layers of the filtrate were separated, the organic layer was washed twice with water and the solvent evaporated. The residue, oily crystals, was washed with cold ethanol and petroleum ether (b.p. 60–70°), leaving 0.30 g. (3%) of tetramethylene-bis-(triphenylsilane), m.p. 207–210°. Recrystallization twice from cyclohexane raised the m.p. to 215–216°.

Anal. Calcd. for $C_{40}H_{38}Si_2$: Si, 9.77. Found: Si, 9.69, 9.80.

4-Hydroxybutyltriphenylsilane.—Thirty grams (0.058 mole) of hexaphenyldisilane was cleaved in 100 ml. of tetrahydrofuran by stirring with 5.0 g. (0.84 g. atom) of finely cut lithium wire for 6 hr. at room temperature. The light brown solution was filtered through glass wool into a Schlenk tube, previously filled with nitrogen. The tube was sealed and placed in an oil-bath. The bath was slowly heated to 125° and kept at this temperature for 3 hr. After cooling the tube was opened under nitrogen. Color Test I[9] was negative. After hydrolysis with dilute acid and addition of some ether the layers were separated, the organic layer dried with sodium sulfate, and the solvent removed by distillation. The residue was recrystallized from petroleum ether (b.p. 110–120°) to give 27.3 g. (71%) of 4-hydroxybutyltriphenylsilane, m.p. 107–109°. Recrystallization twice from petroleum ether (b.p. 60–70°) raised the m.p. to 110–111°. The infrared spectrum of the compound in carbon tetrachloride solution showed strong absorption bands at 2.75, 3.3, 3.4 and 9.0 μ, indicative of O–H, aromatic C–H, aliphatic C–H stretching frequencies and phenyl–silicon linkage, respectively.

Anal. Calcd. for $C_{22}H_{24}OSi$: C, 79.45; H, 7.28; Si, 8.46. Found: C, 79.56, 79.42; H, 7.03, 7.28; Si, 8.65.

4-Bromobutyltriphenylsilane.—To 12.4 g. (0.0374 mole) of 4-hydroxybutyltriphenylsilane, placed in a Schlenk tube, 5.4 g. (0.020 mole) of phosphorus tribromide was added dropwise. Heat was evolved and some HBr. The tube was heated thereafter for 10 hr. in a steam-bath. After cooling again to room temperature, ether was added and the mixture hydrolyzed. After washing twice with water and dilute ammonium hydroxide the organic layer was dried with sodium sulfate and the solvent evaporated. The residue was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina, using petroleum ether as an eluent. Recrystallization of the resulting material from methanol gave 8.05 g. (54.5%) of 4-bromobutyltriphenylsilane, m.p. 86.5–87.5°. A second recrystallization from methanol raised the melting point to 87.5–88.5°.

Anal. Calcd. for $C_{22}H_{23}BrSi$: Si, 7.10. Found: Si, 7.13, 7.24.

A second run, using a 1:1 molar ratio mixture of 4-hydroxybutyltriphenylsilane and phosphorus tribromide was heated for one hour in a steam-bath and worked up in the same manner to give 4-bromobutyltriphenylsilane in a 48% yield.

In a third run the reagents (1:1 ratio) were refluxed for 100 min. in benzene. The work-up in the manner described above gave the bromo compound in a 43% yield.

4-Bromobutyltriphenylsilane and Lithium. First Experiment.—To 7.9 g. (0.020 mole) of 4-bromobutyltriphenylsilane and 1.0 g. (0.14 g. atom) of finely cut lithium wire, 35 ml. of anhydrous ether was added and the mixture cooled to −10°. The reaction was started by stirring at this temperature until the lithium became shiny and Color Test I was positive. The mixture was then cooled to −25° and stirred at this temperature until the halide had completely gone into solution. The mixture was stirred for another half hr., warmed to room temperature and carbonated immediately thereafter. After hydrolysis the organic layer was extracted twice with aqueous alkali. The combined water layers were acidified and extracted twice with ether. After drying with sodium sulfate and removal of the solvent, 1.37 g. (56.6%) of benzoic acid, m.p. 120–121°, was obtained. A mixed melting point with an authentic sample gave no depression.

The neutral organic layer, after drying and removal of the solvent, was distilled at reduced pressure to give 4.05 g. of a liquid, b.p. 170–185° (15 mm.). On redistillation 2.4 g. (50.4%) of 1,1-diphenylsilacyclopentane was obtained, b.p. 191–193° (18 mm.), n^{20}D 1.5878. The infrared spectrum was identical with that of a sample obtained previously. As a distillation forerun 0.95 g. of a liquid was obtained, b.p. 179–191° (18 mm.), the infrared spectrum of which indicated a mixture of 1,1-diphenylsilacylopentane and benzophenone (approx. 20% yield). Recrystallization of the distillation residue twice from a mixture of benzene and petroleum ether gave 0.15 g. (2.2%) of tetraphenylsilane, m.p. 229–230°.

Second Experiment.—Five and five-tenths grams (0.0139 mole) of 4-bromobutyl-triphenylsilane and 1.0 g. (0.14 g. atom) of lithium in 40 ml. of anhydrous ether were allowed to react at −25° as described above. After the reaction was completed, the solution was cooled to −70° and Dry Ice added. The excess of unreacted lithium was removed mechanically, the mixture hydrolyzed, and the organic layer extracted twice with aqueous alkali. The combined water layers were acidified and extracted twice with ether. The removal of the solvent left 2.9 g. of crude acid, m.p. 117–125°. Extraction of the crude product with 200 ml. of boiling water left 2.8 g. (56%) of 4-carboxybutyltriphenylsilane, m.p. 127–129°, identified by mixed melting point with an analyzed sample. The aqueous solution was extracted twice with ether to give 70 mg. (4.1%) of benzoic acid, m.p. 115–118°, identified by mixed melting point and infrared spectra.

The neutral organic layer was dried with sodium sulfate and the solvent evaporated. The residue was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Extraction with petroleum ether gave 0.35 g. of a colorless liquid, the infrared spectrum of which indicated the presence of 1,1-diphenylsilacyclopentane as the main

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[13] H. Gilman and G. D. Lichtenwalter, THIS JOURNAL, **80**, 608 (1958); see also A. G. Brook and H. Gilman, *ibid.*, **76**, 278 (1954).

product (approx. yield 8%), and 0.05 g. (1.1%) of tetraphenylsilane, m.p. 230–232°. Using benzene as an eluent thereafter a product was obtained which on recrystallization twice from ethanol gave 0.12 g. (2.6%) of 1,9-bis-(triphenylsilyl)-5-nonanone, m.p. 162–163°. The infrared spectrum of the compound in carbon tetrachloride solution showed strong absorption bands at 3.3, 3.4, 5.9 and 9.0 μ, indicative of aromatic C–H and aliphatic C–H stretching frequencies, the carbonyl group and the phenyl-silicon linkage, respectively.

Anal. Calcd. for $C_{45}H_{46}OSi_2$: C, 82.01; H, 7.04; Si, 8.52. Found: C, 81.83; H, 7.24; Si, 8.35.

Extracting the alumina finally with acetone gave a product from which, after recrystallization from petroleum ether (b.p. 60–70°), 0.26 g. (5.6%) of 4-hydroxybutyltriphenylsilane, m.p. 110–111°, was obtained, identified by mixed melting point with an authentic sample.

4-Bromobutyltriphenylsilane and Magnesium.—A solution of 5.7 g. (0.0144 mole) of 4-bromobutyltriphenylsilane in 30 ml. of anhydrous ether was added dropwise with stirring to 4.5 g. (0.185 g. atom) of magnesium turnings. Heat was evolved, and the ether started refluxing. After the addition was completed, the mixture was refluxed for one hr. with stirring and carbonated. After hydrolysis the organic layer was extracted twice with aqueous alkali. The acidified water layer was extracted with ether, the ether dried with sodium sulfate, and the solvent removed. There was obtained 3.1 g. (60%) of 4-carboxybutyltriphenylsilane, m.p. 124–127°. By extraction with boiling water no water-soluble acid was isolated, which indicates that no benzoic acid was formed in the reaction. Recrystallization of a sample from a mixture of ethyl acetate and petroleum ether (b.p. 60–70°) raised the m.p. to 128–129°.

Anal. Calcd. for $C_{23}H_{24}O_2Si$: Si, 7.79; neut. equiv., 360.5. Found: Si, 7.81, 7.82; neut. equiv., 337.

The neutral organic layer was distilled and the residue chromatographed on alumina. Using petroleum ether as an eluent, oily crystals were obtained, which after recrystallization gave 0.12 g. (2%) of tetraphenylsilane, m.p. 228–230°, identified by mixed melting point with an authentic sample and by infrared spectra. Extraction with carbon tetrachloride gave a product, which on recrystallization from ethanol yielded 0.8 g. (20%) of octamethylene-bis-(triphenylsilane), m.p. 132–133°.

Anal. Calcd. for $C_{44}H_{46}Si_2$: Si, 8.90. Found: Si, 8.90, 9.01.

Pentamethylenedilithium and Chlorotriphenylsilane.—Pentamethylenedilithium was prepared according to the directions of West and Rochow.[3] At −10 to −15°, 23.0 g. (0.10 mole) of 1,5-dibromopentane in 150 ml. of anhydrous ether was added dropwise with stirring to 4.0 g. (0.57 g. atom) of lithium sand, suspended in 50 ml. of ether. After the addition was completed, the mixture was stirred for one hour at −10° and half an hour more at 0°. The solution was filtered through glass wool into an addition funnel, and the reagent slowly added with stirring to 53 g. (0.18 mole) of chlorotriphenylsilane suspended in 50 ml. of ether. The mixture was stirred at −10° for half an hour, warmed to room temperature and stirred for two more hr., at which time Color Test I had become negative. Water was added to dissolve the lithium salts and to convert the unreacted chlorosilane to triphenylsilanol. The mixture was filtered, the precipitate carefully washed with ether and water and then extracted with hot ethanol. There was obtained 44.0 g. of pentamethylene-bis-(triphenylsilane), m.p. 144–146.5°. The yield, based on dibromopentane, was 75%. Recrystallization of a sample from cyclohexane raised the melting point to 146–146.5°.

Anal. Calcd. for $C_{41}H_{40}Si_2$: Si, 9.53. Found: Si, 9.70, 9.48.

The ethanolic mother liquor and the ether filtrate of the run were combined and the solvent removed by distillation. The residue was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Using petroleum ether as an eluent a small amount of oil was obtained, which on distillation gave 0.25 g. (1%) of a colorless liquid, b.p. 193–198° (5 mm.), $n^{20}D$ 1.5779. The liquid is thought to contain mainly 1,1-diphenylsilacyclohexane, as indicated by comparing the spectrum of the liquid with that of the pure compound.[14]

Further work-up in the chromatography gave, with petroleum ether as an eluent, 220 mg. (0.65%) of tetraphenylsilane, m.p. 233–235°, identified by mixed melting point with an authentic sample.

Acknowledgment.—This research was supported by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. The authors are grateful to D. J. Peterson for the preparation of starting materials. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State College, and special acknowledgment is made to E. Miller Layton and Miss M. Powers for the spectra.

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AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Syntheses and Some Reactions of α-Silylcarbinols

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RECEIVED JANUARY 11, 1958

Compounds of the type $R_3SiC(OH)R'_2$ have been synthesized by the interaction of organosilyllithium compounds with aliphatic ketones. Some of the chemical properties of these α-silylcarbinols are discussed.

Trimethylsilylmethanol,[1] the first α-silylcarbinol to appear in the literature, was prepared by the acid-catalyzed methanolysis of acetoxymethyltrimethylsilane. More recently, this method of preparation of α-silylcarbinols has been extended to include compounds of the type $R_nSi(CH_2OH)_{4-n}$.[2–6]

Suspensions of triphenylsilylpotassium in diethyl ether have been reported to react with formaldehyde[7] to give triphenylsilylmethanol (I) and with benzophenone[8] to give benzhydryloxytriphenylsilane (II).

$(C_6H_5)_3SiCH_2OH$ I $(C_6H_5)_3SiOCH(C_6H_5)_2$ II

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