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Some Reactions of Silyllithium Compounds with Ethers

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Silyllithium compounds were found to react with trimethylene oxide and tetrahydrofuran, giving rise to 3- and 4-silyl-substituted carbinols. Tetrahydropyran was polymerized by triphenylsilyllithium(III) at elevated temperatures. Methyltriphenylsilane resulted from the reaction of III with 1,2-dimethoxyethane, whereas with dioxane, ethylene-bis-(triphenylsilane) was formed. With diphenyl ether and benzyl methyl ether, apparently metalation occurred and secondary products resulted. 2-Naphthyltriphenylsilane was obtained from the reaction of III with 1,4-dihydronaphthalene-1,4-endoxide. N-(Triphenylsilylmethyl)-piperidine was isolated when III was allowed to react with N-(*n*-butoxymethyl)-piperidine.

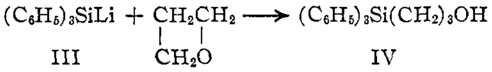
For the preparation of certain functional silanes, silylmetallic compounds have proved to be useful intermediates. Thus, a variety of α-silylcarbinols have been obtained from the reaction of silyllithium compounds with aliphatic ketones.[1] Triphenylsilylmethanol resulted from triphenylsilylpotassium and formaldehyde,[2] whereas 1-(triphenylsilyl)-ethanol was formed from acetaldehyde and the corresponding silyllithium reagent.[3] Acetyltriphenylsilane and 1,1-bis-(triphenylsilyl)-ethanol have been synthesized from triphenylsillyllithium and acetyl chloride.[3]

Cleavage of hexaphenyldisilane with lithium in pyridine has been reported[4] to give 4-(triphenylsilyl)-pyridine after hydrolysis and oxidation. Triphenylsilyllithium, prepared in tetrahydrofuran, cleaved this solvent at elevated temperatures with the formation of 4-(triphenylsilyl)-butanol.[5] It seemed desirable to investigate further the reaction of silylmetallic compounds with the media used for their preparation and with various ethers in general, with a view to their possible value in the synthesis of functional silanes.

Lithium cleavage of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane in tetrahydrofuran has been recently reported[6] to give methyldiphenylsilyllithium (I). A solution of the reagent, prepared in this manner, gave a negative Color Test I[7] after heating for 4 hours at 135° in a sealed tube. In the subsequent work-up, 4-(methyldiphenylsilyl)-butanol (II) was isolated in a 52% yield. Analogous cleavages of tetrahydrofuran by Grignard reagents[8] and by triphenylmethylsodium[9] have been reported previously.

$$\underset{\text{I}}{(C_6H_5)_2(CH_3)SiLi} + C_4H_8O \longrightarrow \underset{\text{II}}{(C_6H_5)_2(CH_3)Si(CH_2)_4OH}$$

The reaction of Grignard reagents and organolithium compounds with trimethylene oxide had been shown to give good yields of 3-substituted carbinols.[10] Similarly with triphenylgermyllithium, 3-(triphenylgermyl)-propanol was obtained in a 20.7% yield.[11] Triphenylsilyllithium (III) produced the corresponding 3-(triphenylsilyl)-propanol (IV) in a 77% yield.[12]



$$\underset{\text{III}}{(C_6H_5)_3SiLi} + \begin{array}{c} CH_2CH_2 \\ |\quad\;\; | \\ CH_2O \end{array} \longrightarrow \underset{\text{IV}}{(C_6H_5)_3Si(CH_2)_3OH}$$

When the silyllithium reagent III was prepared by lithium cleavage of hexaphenyldisilane in tetrahydropyran and allowed to react with the solvent at elevated temperatures, Color Test I was still strongly positive after 10 hours at 125° and one hour at 200–220°. Reaction with the solvent occurred after 40 hours at 200–220°. The work-up, however, did not give the desired 5-(triphenylsilyl)-pentanol. Instead, a polymer was obtained which did not melt below 375°. In this connection it is interesting to note that triphenylgermyllithium when heated with tetrahydrofuran, was found to give a polymer rather than the expected 4-(triphenylgermyl)-butanol.[11]

1,2-Dimethoxyethane has been used as a solvent for the preparation of triphenylsilylpotassium, -sodium and -lithium.[13] It was found, however, that these solutions are not stable with time. Especially when refluxed, the yield of the silylmetallic compound decreased rapidly.[13] No effort had been made, however, to identify the decomposition products. We found that triphenylsilyllithium was consumed completely after one hour of reflux in 1,2-dimethoxyethane, as indicated by a negative Color Test I. In the subsequent work-up, methyltriphenylsilane was isolated in an 84.5% yield.

$$\text{III} + CH_3OCH_2CH_2OCH_3 \longrightarrow (C_6H_5)_3SiCH_3$$

In contrast to this apparent cleavage of a CH_3–O– bond in 1,2-dimethoxyethane by the silyllithium reagent III, Scott and co-workers[14] had noticed metalation of this ether in its reaction with the naphthalene–disodium adduct to form dihydronaphthalene, sodium methoxide and methyl vinyl ether.

$$C_{10}H_8Na_2 + 2CH_3OCH_2CH_2OCH_3 \longrightarrow C_{10}H_{10} + 2CH_3ONa + 2CH_3OCH{=}CH_2$$

Treatment of hexaphenyldisilane with excess

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[1] H. Gilman and G. D. Lichtenwalter, THIS JOURNAL, **80**, 2680 (1958).

[2] H. Gilman and T. C. Wu, *ibid.*, **76**, 2502 (1954).

[3] D. Wittenberg and H. Gilman, *ibid.*, **80**, 4529 (1958).

[4] D. Wittenberg and H. Gilman, *Chemistry & Industry*, 390 (1958).

[5] D. Wittenberg and H. Gilman, THIS JOURNAL, **80**, 2677 (1958).

[6] H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 608 (1958).

[7] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

[8] H. Normant, *Compt. rend.*, **239**, 1510 (1954).

[9] G. Wittig and A. Rückert, *Ann.*, **566**, 104 (1950).

[10] S. Searles, THIS JOURNAL, **73**, 124 (1951).

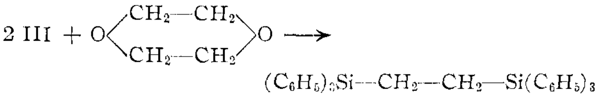
[11] H. Gilman, C. W. Gerow and M. B. Hughes, *J. Org. Chem.*, **23**, in press (1958).

[12] Related reactions of silyllithium compounds with a variety of epoxides will be reported later.

[13] A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 278 (1954).

[14] N. D. Scott, J. F. Walker and V. L. Hansley, *ibid.*, **58**, 2442 (1936).

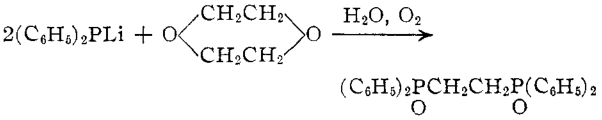
lithium in refluxing dioxane produced a 10% yield of ethylene-bis-(triphenylsilane) (V).



V

The compound was shown to be identical with an authentic specimen, obtained from the reaction of ethylene-bis-(trichlorosilane) with phenyllithium.[15] In addition, small amounts of ethyltriphenylsilane, tetraphenylsilane and of an unidentified compound with the formula $C_{32}H_{30}Si_2$ were isolated. The latter compound was shown to be unlike ethylpentaphenyldisilane, obtained from chloropentaphenyldisilane[16] and ethyllithium. Triphenylsilyllithium also was prepared in tetrahydrofuran,[6] and, after removal of the solvent, refluxed for 48 hours in dioxane, at which time Color Test I was negative. Under these conditions, a mixture of hexaphenyldisilane and ethylene-bis-(triphenylsilane) (V) was isolated, in addition to a small amount of 4-(triphenylsilyl)-butanol, the cleavage product of III and tetrahydrofuran.[5]

The formation of V from dioxane and III has its analog in the recent observation that ethylene-bis-(diphenylphosphine oxide) (VI) results from diphenylphosphinolithium and dioxane.[17]



VI

When III was allowed to react with benzyl methyl ether in tetrahydrofuran at reflux temperature, 1-phenylethanol and tetraphenylsilane were isolated, in addition to small amounts of triphenylsilane, benzyltriphenylsilane and 4-(triphenylsilyl)-butanol. 1-Phenylethanol was obtained by Wittig and Löhmann[18] after treatment of benzyl methyl ether with phenyllithium, the process involving metalation of the ether, followed by rearrangement of the metalation product. Tetraphenylsilane was found to be the main product from the reaction of triphenylsilylmetallic compounds with triphenylsilane,[19] as well as with compounds which are metalated by these reagents with the formation of triphenylsilane.[19] A metalation of benzyl methyl ether by III, followed by rearrangement of the metalation product, and by the formation of tetraphenylsilane from triphenylsilane and excess of III, might therefore be assumed to have taken place.

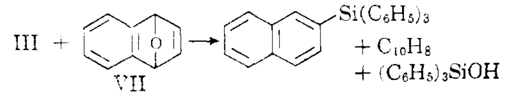
s-Trioxane was allowed to react with III in refluxing tetrahydrofuran, but none of the expected ether cleavage products was found. Instead, 4-(triphenylsilyl)-butanol and a small amount of tetraphenylsilane were isolated.

$$\begin{tikzcd}
\text{III} + C_6H_5CH_2OCH_3 \arrow[r] & (C_6H_5)_3SiH \arrow[d, "+\text{ III}"] & + & C_6H_5CH(Li)OCH_3 \arrow[d] \\
& (C_6H_5)_4Si & & C_6H_5CH(CH_3)OLi
\end{tikzcd}$$

(+ other products)

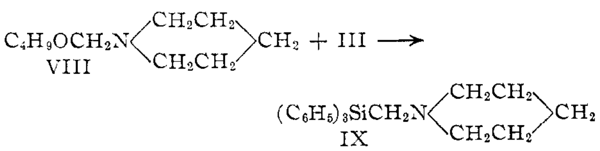
Whereas diphenyl sulfide was cleaved by triphenylsilyllithium to form phenyllithium, lithium thiophenoxide and hexaphenyldisilane,[20] no corresponding cleavage occurred in the reaction of III with diphenyl ether. After stirring for 24 hours at room temperature, carbonation yielded a trace of 2,2′-dicarboxydiphenyl ether, whereas most of the reagent III was recovered as triphenylsilanol and hexaphenyldisiloxane.[21]

1,4-Dihydronaphthalene-1,4-endoxide (VII), a highly strained cyclic ether, also was treated with III. The reaction of phenyllithium with VII has been reported to yield 2-phenylnaphthalene,[22] subsequent to treatment with methanolic hydrochloric acid. However, the corresponding silicon compound, 2-naphthyltriphenylsilane, was isolated in only a 10% yield from the reaction of VII with III. As the main products, naphthalene and triphenylsilanol were isolated, possibly formed during the aromatization of an intermediately formed carbinol.



VII

The cleavage of alkyl dialkylaminomethyl ethers with Grignard reagents[23,24] and with organolithium compounds[25] has been described as a convenient synthesis of certain tertiary amines. It seemed desirable to investigate the reaction of these aminoethers with silylmetallic compounds as a possible route for the preparation of certain aminomethylsilanes. N-(*n*-Butoxymethyl)-piperidine (VIII), prepared from 1-butanol, piperidine and formaldehyde,[23] was allowed to react with triphenylsilyllithium. The reaction product, N-(triphenylsilylmethyl)-piperidine (IX), was isolated in a 55% yield.



VIII

IX

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(15) H. Gilman and H. G. Brooks, unpublished results.

(16) H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, THIS JOURNAL, **74**, 561 (1952); H. Gilman and J. J. Goodman, *ibid.*, **75**, 1250 (1953).

(17) M. V. George, unpublished studies.

(18) G. Wittig and L. Löhmann, *Ann.*, **550**, 260 (1942); see also, G. Wittig and W. Happe, *ibid.*, **557**, 205 (1947); G. Wittig and R. Clausnizer, *ibid.*, **588**, 145 (1954); G. Wittig and E. Stahnecker, *ibid.*, **605**, 69 (1957); K. Ziegler and H. G. Gellert, *ibid.*, **567**, 185 (1950).

(19) H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 2509 (1953); A. G. Brook and H. Gilman, *ibid.*, **76**, 2333, 2338 (1954).

(20) D. Wittenberg, T. C. Wu and H. Gilman, *J. Org. Chem.*, **23**, in press (1958).

(21) A. G. Brook and H. Gilman, THIS JOURNAL, **77**, 2322 (1955).

(22) G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956); see also G. Wittig, *Angew. Chem.*, **69**, 245 (1957).

(23) G. M. Robinson and R. Robinson, *J. Chem. Soc.*, **123**, 532 (1923).

(24) S. P. Massie, *Iowa State Coll. J. Sci.*, **21**, 41 (1946) [*C. A.*, **41**, 3044 (1947)].

(25) A. H. Haubein, unpublished studies; see *Iowa State Coll. J. Sci.*, **18**, 48 (1943) [*C. A.*, **38**, 716 (1944)].

Experimental[26]

4-(Methyldiphenylsilyl)-butanol.—A solution of 0.04 mole of methyldiphenylsilyllithium was prepared in 50 ml. of tetrahydrofuran by lithium cleavage of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane according to a reported procedure.[6] The solution was placed in a Schlenk tube, previously filled with nitrogen. The sealed tube was heated for 3 hr. in an oil-bath at 110°. Since the solution still gave a positive Color Test I,[7] the tube was subsequently heated for an additional 4 hr. at 135°. Color Test I was then negative. The work-up by hydrolysis, addition of some ether, extraction of the organic layer with water, drying with sodium sulfate, and removal of the solvents left an oil. Distillation at reduced pressure yielded 5.64 g. (52.1%) of 4-(methyldiphenylsilyl)-butanol, b.p. 147–149° (0.1 mm.), n^{20}_{D} 1.5693, d^{20}_{4} 1.0392.

Anal. Calcd. for $C_{17}H_{22}OSi$: Si, 10.38; *MR*D, 85.46. Found: Si, 10.28, 10.30; *MR*D, 85.31.

In a second experiment, 19.2 g. (0.083 mole) of chloromethyldiphenylsilane (technical grade, b.p. 160–170° (11 mm.)) was dissolved in 100 ml. of tetrahydrofuran and added slowly with continuous stirring to 4.0 g. (0.58 g. atom) of lithium wire. Heat was evolved and the solution turned deep green. After the addition was complete, stirring was continued for one hour. The filtered solution was placed in a Schlenk tube and the sealed tube heated for 2 hr. in an oil-bath at 125°. Color Test I was negative. Work-up in the same manner as in the previous experiment yielded 6.1 g. (27.2%) of 4-(methyldiphenylsilyl)-butanol, b.p. 139–142° (0.05 mm.), n^{20}_{D} 1.5688.

3-(Triphenylsilyl)-propanol.—A solution of 0.13 mole of triphenylsilyllithium in tetrahydrofuran[6] was added with stirring to 9.65 g. (0.17 mole) of trimethylene oxide. During the addition, the flask was cooled with ice. Color Test I[7] was negative immediately after the addition was complete. The work-up by hydrolysis, addition of some ether, extraction with water, drying of the organic layer with sodium sulfate, and removal of the solvents left an oil which partially crystallized. Recrystallization from ethanol gave 31.8 g. (77%) of 3-(triphenylsilyl)-propanol, m.p. 135–137°. Two recrystallizations of a sample from a mixture of benzene and petroleum ether (b.p. 60–70°) raised the melting point to 139.5–140.5°.

Anal. Calcd. for $C_{21}H_{22}OSi$: Si, 8.82. Found: Si, 8.90, 8.97.

Lithium Cleavage of Hexaphenyldisilane in Tetrahydropyran.—Immediately before use, tetrahydropyran (Matheson practical grade) was refluxed for one hour with lithium aluminum hydride and subsequently distilled under nitrogen. The fraction boiling at 86.5–87.5° was used in the following experiment.

Thirty-five grams (0.077 mole) of hexaphenyldisilane and 4.0 g. (0.58 g. atom) of lithium sand were placed in a three-necked flask equipped with nitrogen inlet, stirrer, reflux condenser and addition funnel. A small amount of tetrahydropyran was added and the resulting paste stirred under reflux until a yellow color had occurred. Then the rest of the solvent (100 ml.) was added and the mixture stirred at reflux temperature for 12 hr., at which time all the hexaphenyldisilane had gone into solution. The hot brown solution was filtered through glass wool into a Schlenk tube, previously filled with nitrogen. The sealed tube was immersed in an oil-bath and heated for 10 hr. at 125°. After cooling and opening the tube, Color Test I was found to be strongly positive. Subsequent to heating for one hour at 200–220°, the Color Test was still positive. The solution was then heated for 40 hr. at 200–220°. Half of the contents of the tube were found to be converted to a glass-like resin. The supernatant liquid gave a negative Color Test. No pure crystalline compound was isolated from the organic solution. The solid residue was insoluble in common solvents and did not melt below 375°.

Methyltriphenylsilane.—A mixture of 20 g. (0.0386 mole) of hexaphenyldisilane and 2.0 g. (0.29 g. atom) of finely cut lithium wire was stirred at room temperature with 100 ml. of dry 1,2-dimethoxyethane for 6 hr., at which time the disilane had completely gone into solution. The dark brown solution was filtered through glass wool into another flask and refluxed under nitrogen for one hour, at which time Color Test I was negative. Work-up by hydrolysis, addition of some ether, extraction with water, drying of the organic layer with sodium sulfate, and removal of the solvent gave a colorless oil, which partially solidified. It was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Using the same solvent as an eluent, a product was obtained which, after recrystallization from methanol, yielded 17.8 g. (84.5%) of methyltriphenylsilane, m.p. 68–68.5°, identified by a mixed melting point determination.

Lithium Cleavage of Hexaphenyldisilane in Dioxane.—A small amount of dry dioxane was added to a mixture of 20 g. (0.0385 mole) of hexaphenyldisilane and 2.1 g. (0.3 g. atom) of finely cut lithium wire. The resulting paste was stirred for 2 hr. at reflux temperature, at which time a brown color resulted. The rest of the solvent (100 ml.) was added and the mixture refluxed with stirring for 48 hr. Filtration through glass wool under nitrogen, hydrolysis with dilute acid, addition of some ether, and filtration gave 2.1 g. (10%) of ethylene-bis-(triphenylsilane), m.p. 205–210°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) raised the melting point to 210–211°. A mixed melting point with an authentic sample, obtained from the reaction of ethylene-bis-(trichlorosilane) with phenyllithium,[15] was not depressed.

The organic layer of the filtrate was dried and the solvents removed. The residue was distilled at reduced pressure. The first fraction, 0.4 g. of a colorless oil, b.p. 130–140° (0.04 mm.), solidified gradually. Recrystallization from methanol gave 0.3 g. (1.35%) of ethyltriphenylsilane, m.p. 74–76° (mixed m.p.). The next fraction, 2.0 g. of crystalline material, boiling over the range 215–230° (0.04 mm.), was recrystallized twice from benzene and yielded 1.1 g. (4.2%) of tetraphenylsilane, m.p. 228–230° (mixed m.p.).

The fraction boiling over the range 240–265° (0.04 mm.), 4.5 g. of a crystalline material, was recrystallized twice from acetone and from ethyl acetate to give 3.2 g. of a product, melting over the range 169–173°. Two more recrystallizations from ethyl acetate raised the melting point to 172.5–173°. The infrared spectrum showed strong absorption bands at 3.3, 3.5 and 9.0 μ, indicative of aromatic C–H, of aliphatic C–H, and of the phenyl–silicon linkage, respectively. A mixed melting point with ethylpentaphenyldisilane was depressed. The structure of the compound has not yet been determined.

Anal. Calcd. for $C_{32}H_{30}SiO_2$: C, 81.64; H, 6.43; Si, 11.94. Found: C, 82.08, 82.14; H, 6.12, 5.95; Si, 11.79, 11.88.

No crystalline compound was isolated from the distillation residue.

In a second experiment, when hexaphenyldisilane was refluxed with equimolar amounts of lithium in dioxane for 7 days, 73.5% of hexaphenyldisilane was recovered unchanged. In addition, a 1% yield of impure ethylene-bis-(triphenylsilane), m.p. 203–207°, was isolated.

Reaction of Triphenylsilyllithium with Dioxane.—A solution of 0.1 mole of triphenylsilyllithium was prepared in tetrahydrofuran.[6] The solvent was removed by distillation under nitrogen and replaced by 100 ml. of dioxane. The red-brown solution was refluxed with stirring for 2 days, at which time Color Test I[7] was negative. Subsequent to hydrolysis, 7.2 g. of insoluble material was removed by filtration. The purification of the product, containing a mixture of hexaphenyldisilane and ethylene-bis-(triphenylsilane), was accompanied by much loss of material. Extraction and fractional crystallization from benzene and ethyl acetate yielded 2.47 g. (9.6%) of pure hexaphenylsilane, m.p. 354–358°, and 1.12 g. (4%) of ethylene-bis-(triphenylsilane), m.p. 209–211°.

In the work-up of the organic layer of the filtrate, 2.7 g. (10%) of impure ethylene-bis-(triphenylsilane), 1.85 g. (5%) of 4-(triphenylsilyl)-butanol, m.p. 103–106°, and 0.7 g. (4%) of crude tetraphenylsilane were isolated.

Ethylpentaphenyldisilane.—Ethyllithium was prepared from ethyl bromide and lithium in ether at −10 to −20°,

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[26] Melting points and boiling points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran used was refluxed over sodium metal for at least 24 hr., and finally distilled immediately before use from lithium aluminum hydride. Silicon analyses were carried out according to the procedure of H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, This Journal, **72**, 5767 (1950).

according to a reported procedure.[27] The yield based on titration was 96%. A solution containing 0.01 mole of ethyllithium was added to 4.76 g. (0.01 mole) of chloropentaphenyldisilane. After stirring for 2 hr. at room temperature and one additional hour at ether reflux temperature, Color Test I was negative. The work-up by hydrolysis, extraction of the organic layer with water, drying with sodium sulfate, and removal of the solvent gave oily crystals. The product was dissolved in petroleum ether and chromatographed on alumina. The material, which was eluted with the same solvent, was recrystallized from petroleum ether to give 2.3 g. (51%) of ethylpentaphenyldisilane, m.p. 148–149°.

Anal. Calcd. for $C_{32}H_{30}Si_2$: Si, 11.93. Found: Si, 11.85, 11.86.

Reaction of Triphenylsilyllithium with *s*-Trioxane.—A solution of 0.1 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 9.0 g. (0.1 mole) of *s*-trioxane. No heat was evolved, nor was any color change observed. The mixture was stirred at reflux temperature for 60 hours, at which time Color Test I[7] was found to be negative. The work-up by hydrolysis, addition of some ether, drying of the organic layer with sodium sulfate, evaporation of the solvents, and chromatography of the residue gave 1.3 g. (8%) of tetraphenylsilane and 7.4 g. (21%) of a compound, m.p. 92–93°, the infrared spectrum of which was identical with that of 4-(triphenylsilyl)-butanol. A mixed melting point with triphenylsilylmethanol was depressed.

Reaction of Triphenylsilyllithium with Diphenyl Ether.—A solution of 0.025 mole of triphenylsilyllithium was added to 4.3 g. (0.025 mole) of diphenyl ether and the mixture stirred for 24 hr. at room temperature. Carbonation, followed by hydrolysis, addition of some ether, extraction of the organic layer with aqueous alkali, and acidification of the combined water layers gave 0.2 g. of acidic material. Two recrystallizations from acetic acid yielded a trace of crystals, m.p 226–228°. The compound was identified as 2,2′-dicarboxydiphenyl ether by a mixed melting point determination.

From the organic layer, 4.5 g. (67%) of triphenylsilanol, m.p. 148–150°, and 0.5 g. (7.5%) of hexaphenyldisiloxane, m.p. 220–224°, were isolated.

Reaction of Triphenylsilyllithium with Benzyl Methyl Ether.—A solution of 0.1 mole of triphenylsilyllithium in tetrahydrofuran was added to 12.2 g. (0.1 mole) of benzyl methyl ether and the mixture refluxed for 66 hr., at which time Color Test I was negative. Subsequent to hydrolysis with dilute acid, 6.4 g. of tetraphenylsilane, m.p. 218–225°, was separated by filtration. The organic layer of the filtrate was dried and the solvent removed. Addition of some petroleum ether (b.p. 60–70°) to the distillation residue separated an additional 0.75 g. of tetraphenylsilane. Distillation of the filtrate at reduced pressure yielded 0.97 g. (7.9%) of 1-phenylethanol, b.p. 47–50° (0.1 mm.), n^{20}_D 1.5298, identified by its infrared spectrum and by its 3,5-dinitrobenzoate, m.p. 94–95° (mixed m.p.). In addition, there was obtained 4.78 g. (18.4%) of triphenylsilane, b.p. 145–146° (0.1 mm.), identified by its infrared spectrum. The highest boiling fraction solidified on standing and was fractionally crystallized to yield 0.1 g. of tetraphenylsilane and 0.65 g. (2%) of benzyltriphenylsilane, m.p. 98–99°, identified by infrared spectra and mixed melting point determinations. The total yield of tetraphenylsilane was 42%. In addition, a trace of 4-(triphenylsilyl)-butanol was obtained.

Reaction of Triphenylsilyllithium with 1,4-Dihydronaphthalene-1,4-endoxide.—A solution of 0.035 mole of triphenylsilyllithium in tetrahydrofuran was added dropwise to 5.0 g. (0.035 mole) of 1,4-dihydronaphthalene-1,4-endoxide. Heat was evolved during the addition; the mixture, however, was not cooled. Color Test I was negative throughout the reaction. Subsequent to hydrolysis with dilute sulfuric acid, the mixture was filtered to separate 0.65 g. (3.5%) of hexaphenyldisilane. The organic layer of the filtrate was dried and the solvent removed. The oily residue was chromatographed on alumina. Three products were isolated and identified by mixed melting point determinations: 1.85 g. (41.2%) of naphthalene, m.p. 78–80°; 1.40 g. (10.3%) of 2-naphthyltriphenylsilane, m.p. 145–147°; and 1.75 g. (18.1%) of triphenylsilanol, m.p. 148–151°.

N-(Triphenylsilylmethyl)-piperidine.—N-(*n*-Butoxymethyl)-piperidine was prepared according to a reported procedure.[23] The yield of product, boiling at 90–92° (9 mm.), was 68%.

A solution of 0.039 mole of triphenylsilyllithium in tetrahydrofuran was added to 8.5 g. (0.050 mole) of N-(*n*-butoxymethyl)-piperidine and the mixture stirred at reflux temperature for 10 hr., at which time Color Test I was only slightly positive. The work-up by hydrolysis, addition of some ether, extraction of the organic layer with water, drying with sodium sulfate, filtration and removal of the solvents gave an oil, which was subsequently chromatographed on alumina. With petroleum ether (b.p. 60–70°) a product was eluted which, after recrystallization from methanol and from petroleum ether, gave 3.5 g. (32%) of N-(triphenylsilylmethyl)-piperidine, m.p. 81.5–83°.

Anal. Calcd. for $C_{24}H_{27}NSi$: N, 3.92; Si, 7.86. Found: N, 4.09, 4.15; Si, 7.97, 7.80.

In a second experiment, a mixture of 8.0 g. (0.047 mole) of N-(*n*-butoxymethyl)-piperidine and 0.035 mole of triphenylsilyllithium in tetrahydrofuran was heated at 135° for 5 hr. in a sealed tube. Color Test I was then negative. The work-up in the manner described in the previous experiment gave 6.9 g. (55%) of N-(triphenylsilylmethyl)-piperidine, m.p. 82–83°.

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