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 $\mu$, 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.), $n^{20}\text{D}$ 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.

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[14] G. D. Oshesky and F. F. Bentley, THIS JOURNAL, **79**, 2057 (1957). The authors are grateful to Dr. H. Rosenberg for helping provide additional information on the physical constants of 1,1-diphenylsilacyclohexane, prepared by G. D. Oshesky and F. F. Bentley (b. p. 122° (0.12 mm.), $n^{25}\text{D}$ 1.5820, $d^{25}$ 1.0319).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# The Syntheses and Some Reactions of α-Silylcarbinols

BY HENRY GILMAN AND GLEN D. LICHTENWALTER

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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 $\qquad$ $(C_6H_5)_3SiOCH(C_6H_5)_2$ II

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[1] J. L. Speier, B. F. Daubert and R. R. McGregor, THIS JOURNAL, **70**, 1117 (1948).

[2] J. L. Speier and B. F. Daubert, *ibid.*, **70**, 1400 (1948).

[3] J. L. Speier, B. F. Daubert and R. R. McGregor, *ibid.*, **71**, 1474 (1949).

[4] J. L. Speier, U. S. Patent 2,550,205 (1951); Dow Corning Corporation, British Patent 635,733 (1950) [*C. A.*, **44**, 6876 (1950)].

[5] J. L. Speier, U. S. Patent 2,582,568 (1952); Dow Corning Corporation, British Patent 630,951 (1949) [*C. A.*, **44**, 4491 (1950)].

[6] J. L. Speier, U. S. Patent 2,582,569 (1952); Dow Corning Corporation, British Patent 630,952 (1949) [*C. A.*, **44**, 4491 (1950)].

[7] H. Gilman and T. C. Wu, THIS JOURNAL, **76**, 2502 (1954).

[8] H. Gilman and T. C. Wu, *ibid.*, **75**, 2935 (1953).

TABLE I

PHYSICAL CONSTANTS AND RELATED DATA FOR $\alpha$-SILYLCARBINOLS

| $\alpha$-Silylcarbinol | Yield, % | B.p. °C. | B.p. Mm. | M.p., °C. | $n^{20}$D | $d^{20}_{20}$ | $MR$D[c] Calcd. | $MR$D[c] Found | Silicon, % Calcd. | Silicon, % Found | Yield[h], $R_3SiH$ % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $(C_6H_5)_3SiC(OH)(CH_3)_2$ | 52 | | | 158–159 | | | | | 8.83 | 8.57, 8.64 | [g] |
| $(C_6H_5)_3SiC(OH)C_5H_{10}$[a] | 7 | | | 157–159 | | | | | 7.84 | 7.93[d] | 30 |
| $CH_3(C_6H_5)_2SiC(OH)(CH_3)_2$ | 44 | 117–118 | 0.005 | | 1.5713 | 1.047 | 80.5 | 80.8 | 10.95 | 11.01, 10.94 | 20 |
| $(CH_3)_2C_6H_6SiC(OH)(CH_3)_2$ | 45 | 60 | .005 | | 1.5108 | 0.9714 | 60.9 | 59.9 | [e] | | [g] |
| $(CH_3)_2C_6H_5SiC(OH)C_5H_{10}$[a] | 29 | 92–93 | .003 | | 1.5365 | 1.016 | 72.8 | 72.3 | [f] | | [g] |
| $(C_6H_5)_3SiC(OH)(CH_3)(n\text{-}C_{17}H_{35})$ | 33 | | | 85–86[b] | | | | | 5.17 | 5.15, 5.10 | 34 |
| $(C_6H_5)_3SiC(OH)(C_2H_6)(n\text{-}C_{15}H_{31})$ | 34 | | | 49.5–50.5[b] | | | | | 5.32 | 5.27, 5.12 | [g] |
| $(C_6H_5)_3SiC(OH)(n\text{-}C_8H_{17})(n\text{-}C_{10}H_{21})$ | 25 | 204–205 | .01 | | 1.5520 | 0.9995 | 175.1 | 174.0 | 5.17 | 5.37, 5.38 | [g] |
| $(C_6H_5)_3SiC(OH)(n\text{-}C_{11}H_{23})_2$ | 10 | 223–225 | .01 | | 1.5373 | 0.9721 | 193.7 | 192.5 | 4.68 | 4.46, 4.48 | [g] |
| $(C_6H_5)_3SiC(OH)(C_7H_{15})_2$ | 26 | 196–197 | .01 | | 1.5572 | 1.006 | 156.5 | 155.8 | 5.78 | 5.48, 5.83 | 34 |

[a] $\alpha$-Silylcarbinol derived from cyclohexanone. [b] Recrystallized from methanol. [c] The values used for the calcd. $MR$D are those of Vogel, *et al.*, *Chemistry & Industry*, 358 (1950), and Vogel, *et al.*, *Chemistry & Industry*, 19 (1953). [d] In order to conserve the small amount of product, only one analysis was made. [e] Calcd. for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 67.91, 67.88; H, 8.79, 8.88. [f] Calcd. for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46. Found: C, 71.65, 71.92; H, 9.15, 9.18. [g] The $R_3SiH$ compound was not obtained pure, but was shown to be present by an infrared spectrum. The Si–H bond gives a strong band at 4.8 μ. [h] Derived from the corresponding $R_3SiLi$ compound.

Attempts to isolate $\alpha$-silylcarbinols from the reactions of triphenylsilylpotassium with acetone or hexamethylacetone in diethyl ether were unsuccessful.[9]

It was postulated[8] that II may have formed as the result of a normal addition of triphenylsilylpotassium to benzophenone followed by a rearrangement. In line with this postulate, Brook,[10] in some splendid studies, has succeeded in preparing diphenyltriphenylsilylcarbinol and found that it rearranges to II in the presence of catalytic amounts of base.

As an extension of previous work[11,12] in this Laboratory concerned with the chemistry of organosilylmetallic compounds, we have investigated the addition of organosilyllithium compounds in tetrahydrofuran (THF) to a variety of aliphatic ketones. Triphenylsilyllithium[11] reacts with acetone to give the normal addition product 2-(triphenylsilyl)-2-propanol (III).

$$\begin{tikzcd}[column sep=large] (C_6H_5)_3SiLi + CH_3COCH_3 \arrow[r, "52\%"] & (C_6H_5)_3SiC(OH)(CH_3)_2 \quad \text{III} \\ (C_6H_5)_3SiCO_2CH_3 + 2CH_3MgI \arrow[ur, "72\%"'] & \end{tikzcd}$$

Compound III also was obtained by the reaction of methyl triphenylsilanecarboxylate[13] with methylmagnesium iodide, thus proving the structure.

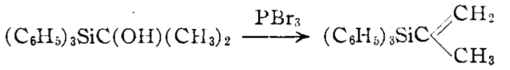
Similarly, methyldiphenylsilyllithium[11] and dimethylphenylsilyllithium react with acetone to give the corresponding $\alpha$-silylcarbinols. Triphenylsilyllithium added normally to cyclohexanone, 2-nonadecanone, 3-octadecanone, 9-nonadecanone, 8-pentadecanone and 12-tricosanone.

Abstraction of the acidic hydrogen from the ketone was an important side reaction. The silicon hydride corresponding to the silyllithium compound employed usually was obtained. In an extreme case, triphenylsilane resulted in 78% yield from the reaction of triphenylsilyllithium with dibenzyl ketone, and none of the $\alpha$-silylcarbinol was isolated.

The reactions were carried out, and the $\alpha$-silylcarbinols were isolated under conditions similar to those employed when II was obtained from the reactions of either triphenylsilylpotassium or triphenylsilyllithium with benzophenone. Hence, it was apparent that $\alpha$-silylcarbinols derived from aliphatic ketones do not rearrange under the conditions which convert diphenyltriphenylsilylcarbinol to compound II. It was of interest, however, to determine the effect of various basic conditions on $\alpha$-silylcarbinols. For this purpose, compound III, the most easily prepared of this series, was selected as a representative compound for study.

Catalytic amounts of potassium hydroxide in refluxing ethanol had no effect on III. A 2 *N* solution of potassium hydroxide in 95% ethanol converted III to triphenylsilanol in 48% yield. Only ethoxytriphenylsilane (10%) was isolated when a solution of III in ethanol containing a catalytic amount of potassium hydroxide was heated in a sealed tube for 20 hr. at 200°.

Attempted conversion of III to the bromide with phosphorus tribromide at 0° resulted in no observable reaction. In refluxing benzene, dehydration to the olefin occurred.



$$(C_6H_5)_3SiC(OH)(CH_3)_2 \xrightarrow{PBr_3} (C_6H_5)_3SiC\begin{matrix}\diagup CH_2 \\ \diagdown CH_3\end{matrix}$$

The same olefin was obtained by treatment of III with phosphorus pentoxide. Unlike the recently reported[14] $\alpha$-silyl ketones, III was not cleaved by phenyllithium, even under forcing conditions. Attempted esterification of III with either acetic anhydride in benzene or benzoyl chloride in pyridine failed.

Physical constants and related data for the $\alpha$-silylcarbinols prepared are presented in Table I.

## Experimental[15]

**Materials.**—Triphenylsilyllithium, methyldiphenylsilyllithium and dimethylphenylsilyllithium were prepared according to published directions.[11] 2-Nonadecanone, 3-octadecanone, 9-nonadecanone, 8-pentadecanone and 12-tricosanone were kindly supplied by Richard A. Reck and Dr. H. J. Harwood of the Armour Research Division. Tetrahydrofuran (THF) was distilled immediately before use, first from sodium wire and then from lithium aluminum hydride.

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[9] T. C. Wu, unpublished studies, Iowa State College.

[10] A. G. Brook, private communication.

[11] H. Gilman and G. D. Lichtenwalter, THIS JOURNAL, **80**, 608 (1957).

[12] H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 607 (1958).

[13] For the preparation see A. G. Brook and H. Gilman, *ibid.*, **77**, 2322 (1955).

[14] A. G. Brook, *ibid.*, **79**, 4373 (1957).

[15] Organometallic reactions were carried out under an atmosphere of dry nitrogen. Melting points are uncorrected. The nomenclature used was that recommended by "Chemical Abstracts."

**2-(Triphenylsilyl)-2-propanol (III) from Triphenylsilyllithium and Acetone.**—To a stirred solution of 11.9 g. (15.0 ml., 0.205 mole) of acetone in 100 ml. of THF was added 200 ml. of a THF solution of triphenylsilyllithium prepared from 20.0 g. (0.0386 mole) of hexaphenyldisilane and excess lithium. After the addition was complete, Color Test I[16] was negative. The reaction mixture was hydrolyzed with aqueous ammonium chloride, and the organic layer was dried over sodium sulfate. Evaporation of the THF left a white solid which was recrystallized from petroleum ether (b.p. 60–70°) to give 12.8 g. (52%) of III, m.p. 156–159°. One further recrystallization from the same solvent raised the melting point to 158–159°.

**Experimental Variations for Other $\alpha$-Silylcarbinols.**—A method similar to the above was used for the preparation of the other $\alpha$-silylcarbinols presented in Table I. The liquid $\alpha$-silylcarbinols derived from acetone and cyclohexanone were isolated by a simple distillation under reduced pressure. Those derived from 2-nonadecanone, 3-octadecanone, 9-nonadecanone, 8-pentadecanone and 12-tricosanone were purified by a more involved procedure. The crude product from the reaction mixture was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on an alumina column. The $\alpha$-silylcarbinol was adsorbed by the column, while triphenylsilane and some unchanged ketone passed through the column. The $\alpha$-silylcarbinol was eluted from the column with benzene and was purified either by distillation or, in the case of solids, by recrystallization. All of the $\alpha$-silylcarbinols showed characteristic infrared absorption peaks at 2.8 (O–H), 3.3 ($C_{ar}$–H), 3.5 ($C_{al}$–H) and 9.1 $\mu$ (Si–$C_6H_5$). Those containing the Si–$CH_3$ group showed a peak at 8.0 $\mu$. For the physical properties and analyses of these compounds, see Table I.

**2-(Triphenylsilyl)-2-propanol (III) from Methyl Triphenylsilanecarboxylate and Methylmagnesium Iodide.**—To a solution of 1.0 g. (0.00314 mole) of methyl triphenylsilanecarboxylate in 20 ml. of ether was added excess ethereal methylmagnesium iodide. The reaction mixture was stirred overnight. Hydrolysis with aqueous ammonium chloride, followed by work-up in the manner described for the first preparation of III, gave 0.72 g. (72%) of III, m.p. 158–159°. A mixed melting point with the product from triphenylsilyllithium and acetone was not depressed. The infrared spectra were identical.

**Behavior of 2-(Triphenylsilyl)-2-propanol (III) in the Presence of Base. A. Catalytic Amounts of Potassium Hydroxide.**—A solution of 1.0 g. (0.00314 mole) of III in 50 ml. of ethanol containing $10^{-5}$ mole of potassium hydroxide was refluxed for 16 hr. Cooling gave 0.56 g. of crystals, m.p. 158–160°. Concentration gave another 0.33 g., m.p. 153–157°. Both fractions were identified as III by the method of mixed melting points. Total recovery was 89%.

**B. Concentrated Potassium Hydroxide.**—A solution of 1.0 g. (0.00314 mole) of III in 50 ml. of 95% ethanol, 2 *N* in potassium hydroxide, was refluxed overnight. The ethanol was evaporated, and the resulting solid was extracted with benzene and filtered. The benzene was distilled, and the resulting solid was recrystallized from petroleum ether (b.p. 60–70°) to give 0.42 g. (48%) of triphenylsilanol, m.p. 153–154°, identified by a mixed melting point and an infrared spectrum. A mixed melting point with III was depressed.

**C. Catalytic Amounts of Potassium Hydroxide at 200°.**—A solution of 3.0 g. (0.00942 mole) of III in 50 ml. of ethanol containing $10^{-4}$ mole of potassium hydroxide was heated at 200° in a sealed tube for 24 hr. The tube was cooled in an ice-bath, but no starting material crystallized. The ethanol was removed *in vacuo*. The resulting paste was dissolved in cold petroleum ether (b.p. 60–70°), showing III to be definitely absent or present in only trace amounts. The solution was chromatographed on an alumina column. The white solid obtained from the eluent was recrystallized from methanol to give 0.28 g. (10%) of ethoxytriphenylsilane, m.p. 65–66°, identified by a mixed melting point and by the infrared spectrum.

**Conversion of 2-(Triphenylsilyl)-2-propanol (III) to Isopropenyltriphenylsilane. A. With Phosphorus Tribromide.**—To a solution of 5.0 g. (0.0157 mole) of III in 50 ml. of benzene was added 5.7 g. (2.0 ml., 0.021 mole) of phosphorus tribromide. The solution was refluxed for 24 hr., during which time the evolution of hydrogen bromide gradually subsided. The solution was cooled and hydrolyzed with water. The benzene layer was diluted with ether and dried over sodium sulfate. Evaporation of solvents left 4.0 g. (85%) of crude product, m.p. 95–97°. This was recrystallized from methanol to give 3.32 g. (70%) of isopropenyltriphenylsilane, m.p. 100°.

*Anal.* Calcd. for $C_{21}H_{20}Si$: Si, 9.35. Found: Si, 9.22, 9.24.

The infrared spectrum was consistent with the structure of isopropenyltriphenylsilane. It was observed that the characteristic olefinic double bond peak at 6.1 $\mu$ was missing. Examination of the spectra of several known vinylsilanes revealed that this peak was absent in each case. The spectrum of the compound isolated was almost identical to that of triphenylvinylsilane.

**B. With Phosphorus Pentoxide.**—A mixture of 3.0 g. (0.00943 mole) of III and 1.5 g. (0.0105 mole) of phosphorus pentoxide was stirred for 1 hr. at room temperature and refluxed for 30 min. The reaction mixture, containing a sirupy phosphoric acid layer, was hydrolyzed with water. The benzene layer was diluted with ether and dried over sodium sulfate. The solid left by evaporation of solvents was dissolved in hot petroleum ether (b.p. 60–70°) and chromatographed on an alumina column. From the eluent was obtained 1.6 g. (56%) of isopropenyltriphenylsilane, m.p. 100–101°. This compound was identical to the product from the preceding reaction, as shown by a mixed melting point and a comparison of the infrared spectra. The column was eluted with benzene to give 0.52 g. (17%) of III, m.p. 158–159° (mixed m.p.).

**2-(Triphenylsilyl)-2-propanol (III) and Phenyllithium.**—To a solution of 1.0 g. (0.00314 mole) of III in 20 ml. of ether was added 30 ml. of an ethereal solution containing 0.0095 mole of phenyllithium. There was no visible evidence of reaction. The ether was distilled and replaced by dry benzene. This solution was refluxed for several hours, Color Test I[16] remaining strongly positive. The benzene was distilled, and the resulting paste was heated for 3 hr. Ether was added, and the reaction mixture was hydrolyzed with water. From the ether layer was obtained 0.9 g. (90%) of III, m.p. 153–156° (mixed m.p.).

**Triphenylsilyllithium and Dibenzyl Ketone.**—To a solution of 8.1 g. (0.0386 mole) of dibenzyl ketone in 50 ml. of THF was added 100 ml. of a THF solution of triphenylsilyllithium prepared from 10.0 g. (0.0193 mole) of hexaphenyldisilane and excess lithium. Color Test I[16] was negative after the addition was complete. The reaction mixture was hydrolyzed with aqueous ammonium chloride. The organic layer was dried over sodium sulfate. The oil left by evaporation of the solvent was distilled to give 7.81 g. (78%) of triphenylsilane, b.p. 119–122° (0.01 mm.), which crystallized on standing, m.p. 43–45° (mixed m.p., infrared spectrum).

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(16) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).