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Reactions of Silyllithium Compounds with Derivatives of Carboxylic Acids. I. Triphenylsilyllithium and Acetyl Chloride

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From the reaction of triphenylsilyllithium with acetyl chloride three main products have been obtained: acetyltriphenylsilane, 1,1-bis-(triphenylsilyl)-ethanol and triphenyl-(1-triphenylsiloxyethyl)-silane. The formation of these compounds is discussed, proof for their structure is given, and some of their reactions are described.

In many reactions, silylmetallic compounds apparently behave differently from their carbon analogs. While triphenylmethylsodium (I) enolizes aliphatic ketones,[1] triphenylsilyllithium (II) has been reported to give α-silylcarbinols.[2] Sodium benzophenone ketyl and hexaphenylethane[3] are formed from benzophenone and I, but both triphenylsilylpotassium and -lithium yield the "abnormal" addition product triphenyl-(diphenylmethoxy)-silane.[4,5] Whereas compound I and even the more reactive diphenylmethylsodium do not react with pyridine,[6] and organolithium compounds generally show 1,2-addition,[7] II was found to undergo 1,4-addition to the heterocycle.[8] Tetrahydrofuran was cleaved by I only in the presence of complex-forming agents such as triphenylboron[9] or triphenylaluminum.[10] The Si–Li analog II cleaved the solvent without any added catalyst to form 4-(triphenylsilyl)-butan-1-ol.[11]

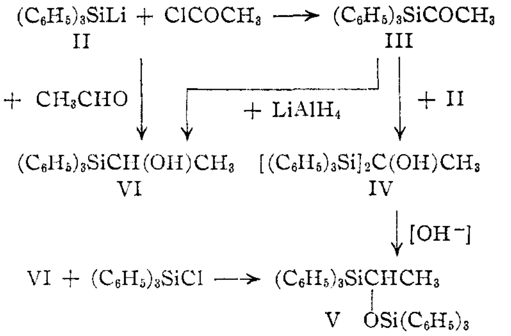
β-Benzopinacolone was obtained in excellent yield from I and benzoyl chloride,[12] and Brook[13] obtained the silicon analog, benzoyltriphenylsilane, in a low yield from the corresponding reaction with triphenylsilylpotassium.

Since only enolization had occurred in the reaction of aliphatic acid chlorides with I,[14] it seemed of interest to study their reaction with silyllithium compounds. The reaction promised some value as a method of preparing aliphatic α-silyl ketones, which have not been reported previously.[15]

When a solution of II in tetrahydrofuran[16] was added slowly at -10 to $-20°$ to acetyl chloride, Color Test I[17] was found negative immediately after the addition. The expected acetyltriphenylsilane[18] (III), however, could only be isolated in a low yield as the 2,4-dinitrophenylhydrazone. As the chief products, triphenylsilane in a 31% yield and 1,2-bis-(triphenylsilyl)-ethanol[18] (IV) in a 22% yield were obtained. It is assumed that IV is formed by addition of II to the ketone III.

In order to improve the yield of the ketone, low operating temperatures and the use of an excess of the acid chloride were obviously indicated. Working at -40 to $-50°$ with an 8.5-fold excess of acetyl chloride gave rise to an 8.5% yield of III. In addition, there was obtained triphenylsilane (29%), 1,1-bis-(triphenylsilyl)-ethanol (26%), and a compound (1.9%), m.p. 158–159°, which showed the same silicon analysis as IV, and was later proved to be compound V.

When in a third experiment the reverse addition (*i.e.*, addition of the acid chloride to the silyllithium reagent) was applied at room temperature, the work-up gave only a very poor yield of the ketone, no carbinol IV, but its isomer V in a 16.5% yield.



$$\begin{tikzcd}
\underset{\text{II}}{(C_6H_5)_3SiLi} + ClCOCH_3 \arrow[r] \arrow[d, "+\ CH_3CHO"'] & \underset{\text{III}}{(C_6H_5)_3SiCOCH_3} \arrow[dl, "+\ LiAlH_4"] \arrow[d, "+\ II"] \\
\underset{\text{VI}}{(C_6H_5)_3SiCH(OH)CH_3} & \underset{\text{IV}}{[(C_6H_5)_3Si]_2C(OH)CH_3} \arrow[d, "{[OH^-]}"] \\
VI + (C_6H_5)_3SiCl \arrow[r] & \text{V}\quad (C_6H_5)_3Si\underset{\displaystyle OSi(C_6H_5)_3}{\underset{|}{C}}HCH_3
\end{tikzcd}$$

While the carbinol IV was recovered unchanged after refluxing with pyridine, ethanolic potassium hydroxide caused almost quantitative conversion to the isomer V.[19] The infrared spectrum of the latter compound indicated the absence of OH grouping, but the presence of a Si–O linkage. Its structure as triphenyl-(1-triphenylsiloxyethyl)-silane (V) was established by an independent synthesis. Acetyltriphenylsilane gave on reduction with lithium aluminum hydride 1-(triphenylsilyl)-ethanol (VI)

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[1] See, F. Runge, "Organometallverbindungen," Wissenschaftliche Verlags-G.m.b.H., Stuttgart, 1944, p. 51, for general references.

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

[3] W. Schlenk and R. Ochs, *Ber.*, **49**, 612 (1916).

[4] H. Gilman and T. C. Wu, THIS JOURNAL, **75**, 2935 (1953).

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

[6] E. Bergmann and W. Rosenthal, *J. prakt. Chem.*, **135**, 267 (1932).

[7] K. Ziegler and H. Zeiser, *Ber.*, **63**, 1847 (1930); *Ann.*, **485**, 174 (1931).

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

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

[10] G. Wittig and O. Bub, *ibid.*, **566**, 113 (1950).

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

[12] W. Schlenk and E. Markus, *Ber.*, **47**, 1667 (1914).

[13] A. G. Brook, THIS JOURNAL, **79**, 4373 (1957).

[14] W. Schlenk and E. Bergmann, *Ann.*, **464**, 1 (1928).

[15] Only indirect evidence for the formation of an α-silylaldehyde has been reported; see L. H. Sommer, D. L. Baily, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans and F. C. Whitmore, THIS JOURNAL, **76**, 1613 (1954).

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

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

[18] The names used herein were recommended by the editorial staff of "Chemical Abstracts."

[19] The rearrangement of phenyl-substituted α-silylcarbinols to the corresponding alkoxysilanes in the presence of catalytic amounts of base has been studied recently; see A. G. Brook, THIS JOURNAL, **80**, 1886 (1958).

in high yield. The same compound was obtained from the reaction of triphenylsilyllithium with acetaldehyde in a 39% yield. Refluxing VI with chlorotriphenylsilane in pyridine gave a 62% yield of a compound, which was shown to be identical with V by mixed melting point and infrared spectra.

Attempts to dehydrate 1,1-bis-(triphenylsilyl)-ethanol (IV) to form vinylidene-bis-(triphenylsilane) (VII) have so far been unsuccessful.

$$\underset{\text{IV}}{[(C_6H_5)_3Si]_2C(OH)CH_3} \xrightarrow{-H_2O} \underset{\text{VII}}{[(C_6H_5)_3Si]_2C{=}CH_2}$$

The carbinol was recovered unchanged after treatment with phosphorus pentoxide in refluxing benzene, while the same reagent in refluxing xylene caused rupture of the silicon–carbon bonds. The compound was stable toward refluxing acetic anhydride. Treatment with hot acetic anhydride and one drop of concentrated sulfuric acid converted it in a 44% yield to 1,1-bis-(triphenylsilyl)-ethyl acetate. The application of a larger amount of sulfuric acid in the latter reaction again caused cleavage of the silicon–carbon bonds.

Acetyltriphenylsilane was found stable toward refluxing pyridine, but treatment with sodium hydroxide in aqueous ethanol at reflux temperature caused cleavage with the formation of triphenylsilanol.

$$(C_6H_5)_3SiCOCH_3 + H_2O \xrightarrow{[OH^-]} (C_6H_5)_3SiOH + [CH_3CHO]$$

Similarly, in an excellent study, Brook[13] recently reported the base-catalyzed cleavage of benzoyltriphenylsilane to triphenylsilanol and benzaldehyde.

Experimental[20]

Triphenylsilyllithium and Acetyl Chloride. First Experiment.—A solution of 0.1 mole of triphenylsilyllithium in tetrahydrofuran[15] was added slowly to 66 g. (0.85 mole) of acetyl chloride, cooled to −50°. During the addition the temperature was maintained at −40° to −50°. Color Test I[17] was found to be negative throughout the addition. The cold reaction mixture was poured on ice. After warming to room temperature, 150 ml. of ether was added and the layers separated. The organic layer was washed several times with water and filtered to give 5.75 g. (20.4%) of 1,1-bis-(triphenylsilyl)-ethanol (IV), m.p. 205–211°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) raised the melting point to 216–217°. A solution of the compound in carbon disulfide showed typical infrared absorption bands at 2.87, 3.3, 3.45 and 9.05 μ, indicative of OH, of aromatic CH, of aliphatic CH, and of the phenylsilicon linkage, respectively.

Anal. Calcd. for $C_{38}H_{34}OSi_2$: Si, 9.98. Found: Si, 9.92, 9.90.

The filtrate was dried with sodium sulfate and the solvent removed by distillation. The residue was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Elution with the same solvent gave 7.5 g. (29%) of triphenylsilane, m.p. 42–45°, which was identified by a mixture melting point determination. Using cyclohexane as an eluent, a product was obtained which after recrystallization from the same solvent gave 0.5 g. (1.9%) of triphenyl-(1-triphenylsiloxyethyl)-silane (V), m.p. 157–158°. The product gave no melting point depression with an authentic specimen, m.p. 158–159°.

Further elution with carbon tetrachloride gave a yellow product, which partially crystallized. It was treated with hot petroleum ether (b.p. 60–70°) and filtered to yield 1.5 g. (5.6%) of undissolved, crude 1,1-bis-(triphenylsilyl)-ethanol, m.p. 201–209°. Recrystallization from a mixture of benzene and petroleum ether raised the m.p. to 214–216°.

The petroleum ether filtrate was concentrated. On cooling it deposited 2.5 g. (8.3%) of crude acetyltriphenylsilane (III), m.p. 109–115°. Recrystallization from ethanol raised the m.p. to 126–127°. The yield of pure product was 1.3 g. (4%). A solution of the ketone in carbon disulfide showed typical infrared absorption bands at 3.3, 3.45, 6.1 and 9.1 μ, indicative of aromatic CH, of aliphatic CH, of the carbonyl group, and of the phenol–silicon linkage, respectively.

Anal. Calcd. for $C_{20}H_{18}OSi$: Si, 9.29. Found: Si, 9.19, 9.24.

To 0.15 g. of acetyltriphenylsilane, dissolved in ethanol, was added a freshly prepared solution of 0.1 g. of 2,4-dinitrophenylhydrazine.[21] After 30 min. the yellow precipitate was filtered off and recrystallized from a mixture of ethyl acetate and ethanol to give 0.2 g. (79%) of the 2,4-dinitrophenylhydrazone of acetyltriphenylsilane, m.p. 194–195°.

Anal. Calcd. for $C_{26}H_{22}N_4O_4Si$: Si, 5.82. Found: Si, 5.73.

Second Experiment.—To 5.0 g. (0.064 mole) of acetyl chloride was added slowly with stirring, and cooling at −10 to −20°, a solution of 0.050 mole of triphenylsilyllithium in tetrahydrofuran. The mixture was worked up by hydrolysis, addition of some ether, extraction twice with water, drying with sodium sulfate and removal of the solvents. When the residue was treated with petroleum ether (b.p. 60–70°), 3.0 g. of a solid precipitated, m.p. 207–209°. Recrystallization from carbon tetrachloride gave 2.29 g. (16.3%) of 1,1-bis-(triphenylsilyl)-ethanol, m.p. 216–217°, identified by mixed m.p. with an analyzed sample.

The mother liquor was concentrated and chromatographed on alumina. Using petroleum ether (b.p. 60–70°) as an eluent, 4.0 g. (31%) of triphenylsilane, m.p. 43–46°, was obtained. Carbon tetrachloride as an eluent gave a yellow oil, from which, on standing with petroleum ether, 0.8 g. (5.7%) of crude 1,1-bis-(triphenylsilyl)-ethanol, m.p. 200–209°, separated. Since no crystalline, pure product could be isolated from the filtrate, the solvent was removed and the oily residue distilled under reduced pressure. There was obtained 1.63 g. of a pale yellow liquid, b. 156–170° (0.05 mm.). The infrared spectrum indicated the presence of acetyltriphenylsilane, and also showed additional absorption bands at 5.75 and 8.10 μ, indicative of an CH_3COO– grouping. Since attempts to separate the mixture by crystallization were unsuccessful, an ethanolic solution of the oil was treated with an excess of 2,4-dinitrophenylhydrazine solution.[21] The precipitate formed was recrystallized from a mixture of ethyl acetate and ethanol to give 0.8 g. (3.3%) of the 2,4-dinitrophenylhydrazone of III, m.p. 194–195°, identified by mixed melting point with an analyzed sample.

Third Experiment.—To a solution of 0.045 mole of triphenylsilyllithium in tetrahydrofuran was added slowly, without cooling but with vigorous stirring, 8.0 g. (0.1 mole) of acetyl chloride. Heat was evolved and the mixture almost reached the reflux temperature. The reaction was worked up by hydrolysis, addition of some ether, extraction with water, drying of the organic layer with sodium sulfate, and removal of the solvents by distillation. The residue was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Elution with the same solvent gave 4.5 g. (39%) of triphenylsilane, m.p. 45–46.5°. Using cyclohexane as an eluent, a colorless oil was obtained, which crystallized on standing with petroleum ether (b.p. 60–70°) to give 2.3 g. (16.5%) of triphenyl-(1-triphenylsiloxyethyl)-silane, m.p. 157–158°, identified by a mixture melting point determination. Extraction with carbon tetrachloride gave a yellow oil, which could not be further purified. Its ethanolic solution gave 0.67 g. (3%) of a precipitate with 2,4-dinitrophenylhydrazine, which after recrystallization from a mixture of ethyl acetate and ethanol did not depress the melting point of the 2,4-dinitrophenylhydrazone of III.

The final extraction with benzene and acetone yielded 0.3 g. (0.25%) of triphenylsilanol, m.p. 150–152° (after re-

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(20) 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).

(21) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," third edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

crystallization from cyclohexane), identified by mixture melting point.

1-(Triphenylsilyl)-ethanol (VI). A. From Triphenylsilyllithium and Acetaldehyde.—A solution of 0.05 mole of triphenylsilyllithium in 80 ml. of tetrahydrofuran was added slowly with stirring to 10 g. (0.23 mole) of acetaldehyde. During the addition the reaction mixture was cooled to −20°. Color Test I[17] was negative immediately after the addition. The work-up by hydrolysis, addition of some ether, extraction with dilute acid and water, drying of the organic layer with sodium sulfate and evaporation of the solvents, left an oil, which was purified by chromatography on alumina. Elution with petroleum ether (b.p. 60–70°) gave 4.8 g. (38%) of triphenylsilane, m.p. 45–46.5°. Using benzene as an eluent, there was obtained a product, which after recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) yielded 5.95 g. (39%) of 1-(triphenylsilyl)-ethanol, m.p. 100–101°.

Anal. Calcd. for $C_{20}H_{20}OSi$: Si, 9.22. Found: Si, 9.10, 9.15.

B. **By Reduction of Acetyltriphenylsilane.**—One-tenth gram (0.00033 mole) of acetyltriphenylsilane was added to a solution of 0.04 g. (0.001 mole) of lithium aluminum hydride in 5 ml. of tetrahydrofuran. After 10 min. the excess of hydride was destroyed with ethyl acetate, and the mixture hydrolyzed. Subsequent to the addition of some ether, the organic layer was washed twice with dilute sulfuric acid, dried with sodium sulfate, and the solvents removed by distillation. The crystalline residue melted at 98–100°. Recrystallization from petroleum ether (b.p. 60–70°) raised the melting point to 100–101°. A mixture melting point with a sample of VI, obtained in the previous experiment, was not depressed. The yield was almost quantitative.

Triphenyl-(1-triphenylsiloxyethyl)-silane (V). A. From 1-(Triphenylsilyl)-ethanol and Chlorotriphenylsilane.—A solution of 0.59 g. (0.002 mole) of chlorotriphenylsilane and 0.61 g. (0.002 mole) of 1-(triphenylsilyl)-ethanol in 10 ml. of dry pyridine was refluxed for one hour. The reaction mixture was poured into water. The oily precipitate was refluxed with 10 ml. of methanol, filtered and the insoluble part recrystallized from a mixture of benzene and ethanol. There was obtained 0.7 g. (62%) of triphenyl-(1-triphenylsiloxyethyl)-silane, m.p. 158–159°. A solution of the compound in carbon disulfide showed typical infrared absorption bands at 3.3, 3.45, 9.05 and 9.5 μ, indicative of aromatic CH, of aliphatic CH, of the phenyl–silicon linkage, and of the Si–O linkage, respectively.

Anal. Calcd. for $C_{38}H_{34}OSi_2$: Si, 9.98. Found: Si, 9.95, 10.19, 9.96.

B. **By Rearrangement of 1,1-Bis-(triphenylsilyl)-ethanol.**—To a solution of 0.5 g. (0.00089 mole) of 1,1-bis-(triphenylsilyl)-ethanol in benzene was added 10 ml. of 5% ethanolic potassium hydroxide. The mixture was refluxed for 15 min., then water was added slowly. Filtration gave 0.5 g. of a crystalline compound, m.p. 140–153°. Recrystallization from a mixture of benzene and ethanol raised the melting point to 158–159°. The compound did not depress the melting point of an authentic specimen of triphenyl-(1-triphenylsiloxyethyl)-silane, obtained in the previous experiment.

Further Reactions of Acetyltriphenylsilane (III). A. With Pyridine.—One-tenth gram of acetyltriphenylsilane (0.00033 mole) was refluxed for 15 min. in moist pyridine. After evaporation of the solvent, the starting material was recovered quantitatively.

B. **With Sodium Hydroxide in Ethanol.**—One-tenth gram (0.00033 mole) of acetyltriphenylsilane was refluxed for 10 min. with 0.5 g. of sodium hydroxide in 10 ml. of 90% ethanol. The reaction mixture was poured on ice and extracted with ether. After drying the organic layer with sodium sulfate, the solvent was removed by distillation, and the brown residue recrystallized from petroleum ether (b.p. 60–70°). There was obtained 0.06 g. (65%) of triphenylsilanol, m.p. 149–152°, identified by mixed melting point.

Further Reactions of 1,1-Bis-(triphenylsilyl)-ethanol (IV). A. With Phosphorus Pentoxide.—A mixture of 0.5 g. (0.00089 mole) of 1,1-bis-(triphenylsilyl)-ethanol and 2 g. (0.014 mole) of phosphorus pentoxide was refluxed, with stirring, in benzene for 30 min. After hydrolysis, separation of the layers and removal of the solvent, the starting material, m.p. 212–215°, was recovered unchanged.

In a second experiment, a mixture of 0.8 g. (0.0014 mole) of IV and 5 g. (0.035 mole) of phosphorus pentoxide was refluxed in xylene for 5 hr. The work-up as described above gave a pale yellow oil. Attempts to crystallize it from different solvents were unsuccessful.

B. **With Acetic Anhydride.**—One and five-tenths grams (0.0027 mole) of IV was refluxed for 30 min. with 20 ml. of acetic anhydride and one drop of concd. sulfuric acid. On slow cooling 0.95 g. of colorless crystals separated, m.p. 206–210°. Recrystallization from carbon tetrachloride gave 0.7 g. (44%) of 1,1-bis-(triphenylsilyl)-ethyl acetate, m.p. 210–210.5°.

Anal. Calcd. for $C_{40}H_{36}O_2Si_2$: Si, 9.29. Found: Si, 9.20, 9.24.

The starting material was recovered unchanged when 1 g. (0.0018 mole) of IV was refluxed with 20 ml. of acetic anhydride without added acidic catalyst.

Refluxing 1.0 g. (0.0018 mole) of the carbinol IV with 20 ml. of acetic anhydride and 0.5 ml. of concd. sulfuric acid for 15 min. gave in the work-up a brown oil, from which no crystalline compounds could be isolated.

C. **With Pyridine.**—When 1.0 g. (0.0018 mole) of IV was refluxed for 30 min. in moist pyridine and the solvent removed thereafter by distillation, the residue melted at 213–214° and showed no melting point depression with the starting material. The recovery was quantitative.

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