

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

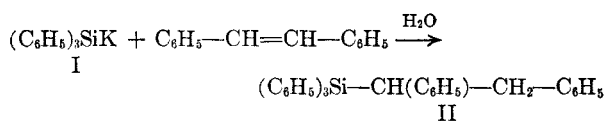
## Addition of Silylmetallic Compounds to Olefins

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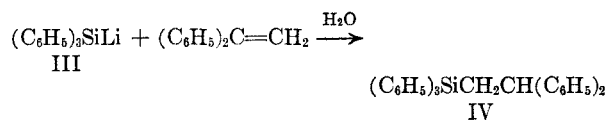
Triphenylsilylpotassium and triphenylsilyllithium have been found to add to the olefinic linkage of 1,1-diphenylethylene and of triphenylethylene. No addition occurred, under corresponding conditions, to tetraphenylethylene and to a variety of aliphatic and alicyclic olefins. For comparison purposes, triphenyl-(1,1-diphenylethyl)silane and triphenyl-(1,1,2-triphenylethyl)silane were synthesized by metalation of triphenyl(diphenylmethyl)silane with *n*-butyllithium and subsequent treatment with methyl sulfate and benzyl chloride, respectively.

It has been reported recently that triphenylsilylpotassium (I) adds to the carbon-carbon double bond of *trans*-stilbene<sup>1</sup> to give triphenyl-(1,2-diphenylethyl)silane (II). In addition to II, a



variety of other compounds of higher molecular weight was isolated from the reaction of *trans*-stilbene with triphenylsilyllithium<sup>2</sup> (III).

As an extension of these studies, the addition of triphenylsilyl-metallic compounds to other olefins has now been investigated. I and III were found to add to 1,1-diphenylethylene. In correspondence with the addition products of other organoalkalimetal compounds to this olefin,<sup>3</sup> the structure of triphenyl-(2,2-diphenylethyl)silane (IV) is assigned to the product obtained from both reactions in high yields.

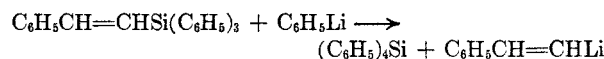


Compound IV was also obtained from the reaction of 1,1-diphenylethyl chloride with triphenylsilylpotassium. 1,1-Diphenylethyl chloride has been reported to dehydrohalogenate quite readily to form 1,1-diphenylethylene.<sup>4</sup> A similar course of reaction might have taken place in its reaction with I, as a result of which IV might have formed from the addition of excess I to the 1,1-diphenylethylene formed in this manner.

As I and III had been found to add to benzophenone in a reverse manner,<sup>5</sup> giving rise to a product in which the silicon atom is bonded to the

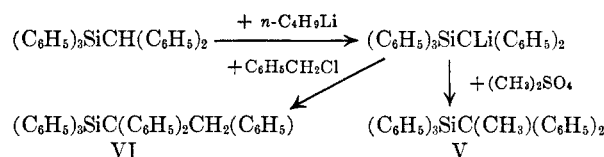
oxygen, a second possible mode of addition of I and III to 1,1-diphenylethylene has to be considered: namely, the formation of triphenyl-(1,1-diphenylethyl)silane (V) by the addition reaction. In order to throw light on these reactions, it seemed desirable to synthesize IV and V by independent methods.

Organolithium compounds have been reported to add to the olefinic linkage of triphenylvinylsilane.<sup>6</sup> The corresponding reaction of phenyllithium with triphenyl- $\beta$ -styrylsilane was investigated in the hope of synthesizing compound IV in this manner. However, no addition took place. Instead, tetraphenylsilane was isolated from the reaction mixture, apparently formed by a displacement reaction. An analogous transformation has



been reported in the reaction of *n*-butyllithium with triphenyl(phenylethynyl)silane.<sup>7</sup>

The metalation of benzyltriphenylsilane<sup>7</sup> by *n*-butyllithium had been reported to occur in the side chain. A similar reaction was expected with triphenyl(diphenylmethyl)silane. When the latter compound was metalated with *n*-butyllithium in a mixture of tetrahydrofuran and ether and subsequently treated with methyl sulfate, V was isolated in a 58% yield. The compound was shown to be unlike the addition compound IV.



Molecular rearrangements excluded, I and III might be expected to add to 1,1-diphenylethylene in a 1,2- or a 2,1-manner. As structure V has been excluded, the addition compound very probably has structure IV.

(6) L. F. Cason and H. G. Brooks, *J. Org. Chem.*, **19**, 1278 (1954); *J. Am. Chem. Soc.*, **74**, 4582 (1952).

(7) H. Gilman and H. Hartzfeld, *J. Am. Chem. Soc.*, **73**, 5878 (1951). See also, H. Gilman, R. A. Benkeser, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 1689 (1950); L. H. Sommer, L. J. Tyler, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2872 (1948).

(1) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75**, 234 (1953).

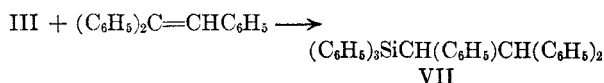
(2) A. G. Brook, K. M. Tai, and H. Gilman, *J. Am. Chem. Soc.*, **77**, 6219 (1955).

(3) K. Ziegler and K. Bähr, *Ber.*, **61**, 253 (1928).

(4) C. S. Schoepfle and J. D. Ryan, *J. Am. Chem. Soc.*, **52**, 4021 (1930).

(5) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75**, 2935 (1953); H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 607 (1958).

Triphenylsilyllithium also added smoothly to triphenylethylene. The addition may have taken place in a 1,2- or a 2,1-manner. Triphenyl-(1,1,2-triphenylethyl)silane (VI) was synthesized by metalation of triphenyl(diphenylmethyl)silane with *n*-butyllithium and subsequent treatment with benzyl chloride, and was shown to be unlike the addition compounds. In correspondence with the related addition of 2-phenyl-2-propylpotassium to 9-benzylidene-fluorene,<sup>8</sup> the structure of triphenyl-(1,2,2-triphenylethyl)silane (VII) is assigned to the addition product of III to triphenylethylene.



No addition product was isolated from the reaction of I or III, under corresponding conditions, with tetraphenylethylene. Triphenylsilylpotassium also did not add to a variety of aliphatic and alicyclic olefins (see Table I).

TABLE I  
REACTION OF TRIPHENYLSILYLPOTASSIUM WITH OLEFINS

Olefin	Reaction Time, hr.	Yield of Pure Triphenylsilanol, %	Other Products Isolated <sup>a</sup>
<i>n</i> -Octene-1	96 <sup>b</sup>	63	
<i>n</i> -Octene-1	48 <sup>c</sup>	25	R <sub>4</sub> Si, 24% (R <sub>3</sub> Si) <sub>2</sub> O, 22%
<i>n</i> -Dodecene-1	72 <sup>b</sup>	78	
<i>n</i> -Dodecene-1	48 <sup>c</sup>	21	R <sub>4</sub> Si, 36% (R <sub>3</sub> Si) <sub>2</sub> O, 20%
<i>n</i> -Hexadecene-1	24 <sup>b,e</sup>	86	
<i>n</i> -Octadecene-1	24 <sup>b,e</sup>	89	
Cyclohexene	48 <sup>d</sup>	87	
Cyclohexene	48 <sup>b</sup>	66	
1-Methylcyclopentene	48 <sup>b</sup>	72	
1,1-Diphenylethylene	2 <sup>b</sup>	—	Adduct, 42%
Tetraphenylethylene	48 <sup>d</sup>	74	R <sub>2</sub> C=CR <sub>2</sub> , 70%
Tetraphenylethylene	3 <sup>b</sup>	52	R <sub>2</sub> C=CR <sub>2</sub> , 74%
1,4-Diphenylbutadiene-1,3	5 <sup>d</sup>	42	R <sub>3</sub> SiSiR <sub>3</sub> , 12%
Δ <sup>9,9'</sup> -Bifluorene	3 <sup>b</sup>	—	Tars

<sup>a</sup> R represents a phenyl group. <sup>b</sup> The excess alloy present after the preparation of triphenylsilylpotassium was removed by the amalgamation procedure. See ref. 10. <sup>c</sup> 1,2-Dimethoxyethane was used as a solvent. <sup>d</sup> Excess alloy was present in the system. <sup>e</sup> Dr. K. M. Tai (unpublished studies) treated R<sub>3</sub>SiK with these olefins in a 1,2-dimethoxyethane and obtained 30% of R<sub>4</sub>Si, 28% of R<sub>3</sub>SiOH and 30% of (R<sub>3</sub>Si)<sub>2</sub>O from *n*-hexadecene-1, while *n*-octadecene-1 gave 32% of R<sub>4</sub>Si, 17% of R<sub>3</sub>SiOH and 42% of (R<sub>3</sub>Si)<sub>2</sub>O (R is a phenyl group).

(8) K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, *Ann.*, **473**, 1 (1929). 2-Phenyl-2-propylpotassium did not add to triphenylethylene.

EXPERIMENTAL<sup>9</sup>

*Triphenyl(2,2-diphenylethyl)silane. A. From triphenylsilylpotassium and 1,1-diphenylethylene.* A triphenylsilylpotassium suspension was prepared in ether by cleaving 0.01 mole of hexaphenyldisilane according to a described procedure.<sup>10</sup> The excess alloy was removed by the amalgamation method.<sup>10</sup> The triphenylsilylpotassium suspension so obtained was added to 3.6 g. (0.02 mole) of 1,1-diphenylethylene dissolved in 20 ml. of ether. Some heat was evolved, the reaction mixture became deep red and finally dark brown. After 2 hr. of stirring at room temperature, the mixture was hydrolyzed. The ethereal solution was dried over sodium sulfate and the solvent removed by distillation. The gummy residue gradually solidified on standing. Recrystallization three times from ethanol gave 3.5 g. (42%) of triphenyl(2,2-diphenylethyl)silane as lustrous plates, melting at 106–108°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>28</sub>Si: Si, 6.37. Found: Si, 6.43, 6.45.

*B. From triphenylsilyllithium and 1,1-diphenylethylene.* A solution of 0.0122 mole of triphenylsilyllithium<sup>11</sup> in tetrahydrofuran was added to 2.2 g. (0.0122 mole) of 1,1-diphenylethylene. A deep red color developed immediately and heat was evolved. After stirring for 30 minutes at room temperature, the mixture was hydrolyzed. From the organic layer, after drying with sodium sulfate and removal of the solvent by distillation, an oily residue was obtained which slowly solidified. Recrystallization from a mixture of ethanol and benzene gave two crops of triphenyl(2,2-diphenylethyl)silane, 3.5 g., m.p. 105–107°, and 0.8 g., m.p. 103–106°. Recrystallization from the same solvent pair raised the melting point to 107–108°. The yields was 80%.

*C. From triphenylsilylpotassium and 1,1-diphenylethyl chloride.* A solution of 4.3 g. (0.01 mole) of 1,1-diphenylethyl chloride (supplied by the Techniservice Co., New York, N. Y.) in 20 ml. of ether was added, within a period of 2 min., to an amalgamated suspension of 0.02 mole of triphenylsilylpotassium.<sup>10</sup> The reaction mixture became brownish-red and some heat was evolved. After 2 hr. of stirring, Color Test I<sup>12</sup> became negative. The reaction mixture was hydrolyzed and filtered to separate 1.1 g. of hexaphenyldisilane, m.p. 365–368°, identified by mixed melting point. The ethereal solution was dried and the solvent removed by distillation. The residue was recrystallized twice from ethanol to give 4.1 g. (47%) of shiny crystals, m.p. 106–107°. A mixed melting point with triphenyl(2,2-diphenylethyl)silane was not depressed. The infrared spectra of these two products were identical.

*D. From triphenyl-β-styrylsilane and phenyllithium.* (Attempted). A solution containing 0.002 mole of phenyllithium in tetrahydrofuran, prepared according to a reported procedure,<sup>13</sup> was added to 0.5 g. (0.00138 mole) of triphenyl-β-styrylsilane. The deep red solution soon turned brown. After stirring for 2 hr. at room temperature, the mixture was hydrolyzed, some ether was added, and the solvent removed from the dried organic layer. The pale yellow residue was chromatographed on alumina. The product eluted with petroleum ether (b.p. 60–70°) was recrystallized

(9) All melting 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 procedure of H. Gilman, H. W. Melvin, Jr., and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

(10) H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

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

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

(13) H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957).

from a mixture of benzene and ethanol to give 0.18 g. (39%) of tetraphenylsilane, m.p. 230–233°, identified by mixed melting point and infrared spectra. No other product was isolated from the mother liquor.

*Triphenyl(1,1-diphenylethyl)silane.* An ethereal solution of 0.015 mole of *n*-butyllithium<sup>14</sup> was added at once to a solution of 5.0 g. (0.012 mole) of triphenyl(diphenylmethyl)silane, dissolved in 25 ml. of tetrahydrofuran. Heat was evolved and the solution turned deep red immediately. After stirring for 40 min. at room temperature, an excess of methyl sulfate was added. The color of the solution was discharged immediately. Hydrolysis and the usual work-up of the organic layer gave an oily residue, which gradually solidified. Two recrystallizations from a mixture of benzene and ethanol gave 3.0 g. (58%) of triphenyl(1,1-diphenylethyl)silane, m.p. 193–195°.

*Anal.* Calcd. for C<sub>32</sub>H<sub>28</sub>Si: Si, 6.37. Found: Si, 6.34, 6.47.

*Triphenyl(1,2,2-triphenylethyl)silane.* A solution of 0.020 mole of triphenylsilyllithium<sup>11</sup> in tetrahydrofuran was added with stirring to 5.12 g. (0.020 mole) of triphenylethylene. A deep red color developed immediately and heat was evolved. After stirring for 1 hr. at room temperature, the mixture was hydrolyzed. Subsequent to the usual work-up of the organic layer, an oily residue was obtained, which partially solidified. Two recrystallizations from a mixture of benzene and ethanol gave 6.4 g. (62%) of triphenyl(1,2,2-triphenylethyl)silane, m.p. 171–172°.

*Anal.* Calcd. for C<sub>38</sub>H<sub>32</sub>Si: Si, 5.45. Found: Si, 5.42, 5.59.

*Triphenyl(1,1,2-triphenylethyl)silane.* An ethereal solution of 0.015 mole of *n*-butyllithium<sup>14</sup> was added at once to a solution of 5.0 g. (0.012 mole) of triphenyl(diphenylmethyl)silane, dissolved in 25 ml. of tetrahydrofuran. After stirring for 40 min. at room temperature, an excess of benzyl chloride was added. The color of the solution was discharged after a few minutes. Hydrolysis and the usual work-up of the organic layer gave a yellow oil, which partially solidified on standing with 10 ml. of petroleum ether (b.p. 60–70°). The crystalline product was recrystallized three times from a mixture of benzene and ethanol to give 1.5 g. (25%) of triphenyl(1,1,2-triphenylethyl)silane, m.p. 198–200°.

*Anal.* Calcd. for C<sub>38</sub>H<sub>32</sub>Si: Si, 5.45. Found: Si, 5.58, 5.60.

(14) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

*Reaction of triphenylsilyllithium with tetraphenylethylene.* A solution of 0.015 mole of triphenylsilyllithium in tetrahydrofuran was added to 5.0 g. (0.015 mole) of tetraphenylethylene. Apparently no reaction took place. The mixture was stirred for 6 hr. at room temperature, at which time the solution had turned deep brown. After stirring for one additional hour at 50°, the mixture was hydrolyzed with dilute acid. The work-up of the organic layer gave oily crystals, which were washed with 25 ml. of petroleum ether (b.p. 60–70°) and recrystallized from ethyl acetate to give 4.2 g. (84%) of tetraphenylethylene, m.p. 222–224° (mixed melting point). The filtrate was chromatographed on alumina. With petroleum ether as an eluent, 2.2 g. (56%) of triphenylsilane was obtained, m.p. 43–45° (after recrystallization from methanol).

*Attempted reactions of triphenylsilylpotassium with other olefins.* All reactions were carried out in the same manner. The triphenylsilylpotassium suspension was mixed with an equimolar amount of the olefinic compound and the mixture stirred for a certain period of time. Then water was added, the layers separated, the organic layer dried, and the solvent removed. The residue was recrystallized from petroleum ether (b.p. 60–70°) to give triphenylsilanol as the chief product. The results are given in Table I. In two experiments using 1,2-dimethoxyethane as the solvent in place of ether, a mixture of tetraphenylsilane and hexaphenyldisiloxane also was obtained.

In the reaction of  $\Delta^{9,9}$ -bifluorene with triphenylsilylpotassium in ether, heat was evolved and the reaction mixture became very dark. The work-up gave a tar-like material, from which no pure product has been isolated.

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AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAN JOSE STATE COLLEGE]

## Synthesis and Cleavage of *N*-Trimethylsilylpyrrole<sup>1</sup>

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*N*-Trimethylsilylpyrrole has been synthesized by the reaction of potassium pyrrole and trimethylchlorosilane and by an exchange reaction between hexamethyldisilazane and pyrrole. *N*-Trimethylsilylpyrrole has been found to be stable in ethanol; however, it undergoes cleavage to pyrrole and silicon derivatives (trimethylsilanol, hexamethyldisiloxane, or trimethylethoxysilane, depending upon the conditions of the reaction) in boiling water and in refluxing aqueous ethanol. The cleavage reaction is catalyzed by either acid or base. *N*-Trimethylsilylpyrrole undergoes decomposition when heated in a sealed tube at 225°. No evidence for the formation of 2-trimethylsilylpyrrole in this reaction could be obtained. Infrared spectra are given for *N*-trimethylsilylpyrrole and tetrapyrrolylsilane.

Although a number of compounds containing the silazane linkage are known, there appears to be no reported study of the stability of such a linkage in which the nitrogen of the silazane is in an aromatic

(1) This work was supported by a Frederick Gardner Cottrell grant from Research Corporation.

heterocyclic system. In view of the known susceptibility of the silazane linkage to cleavage by water, alcohols, and other reagents,<sup>2</sup> this investigation has been directed toward preparation of such a compound and a study of its cleavage reactions.

Silazane compounds undergo solvolysis and