TABLE I

PROPERTIES AND ANALYSES

Compound	B.p., °C./mm.	n_D^{25}	d^{25}	Silicon, % Calcd.	Silicon, % Found
$C_2H_5C_6H_4SiCl_3$	75–76/0.8	1.5200	1.245	11.72	11.97, 12.02
$C_2H_4ClC_6H_4SiCl_3$	87–88/0.4	1.5370	1.348	10.25	10.37, 10.52
$H_2C{=}\overset{H}{C}C_6H_4SiCl_3$	59–60/0.6	1.5534	1.282	11.82	11.99, 12.04
$H_2C{=}\overset{H}{C}C_6H_4Si(OCH_3)_3$	66.5/0.1	1.5038	1.057	12.52	12.52, 12.61
$H_2C{=}\overset{H}{C}C_6H_4Si(OCH_3)_2CH_3$	60/0.5	1.5111	1.005	13.48	13.33, 13.26
$H_2C{=}\overset{H}{C}C_6H_4Si(CH_3)_2OCH_3$	42–43/0.1	1.5179	0.953	14.60	14.50, 14.51
$H_2C{=}\overset{H}{C}C_6H_4Si(CH_3)_3$	53–54/1.2	1.5212	0.886	15.93	15.71, 16.09
$\left[H_2C{=}\overset{H}{C}C_6H_4Si(CH_3)_2\right]_2O$	115–116/0.05	1.5427	—	16.59	16.61, 16.75

Anal. Calcd. for $C_{11}H_{16}Si$: Si, 15.93. Found: Si, 15.71, 16.09.

Trimethoxy(p-styrenyl)silane. Four hundred and ninety g. (2.06 moles) of trichloro(*p*-styrenyl)silane, dissolved in an equal volume of dry benzene was added with stirring and cooling to 1.5 l. of anhydrous methanol which had been saturated with anhydrous ammonia. Ammonium chloride, which precipitated, was filtered from the mixture. As benzene and methanol were distilled from the filtrate, more NH_4Cl precipitated. This was filtered and the filtrate was distilled under vacuum. There was obtained 377 g. (1.68 moles) (82%) of trimethoxy(*p*-styrenyl)silane boiling at 66.5°/0.1 mm., n_D^{25} 1.5038; d^{25} 1.057.

Anal. Calcd. for $C_{11}H_{16}O_3Si$: Si, 12.52. Found: Si, 12.52, 12.61.

Dimethoxymethyl(p-styrenyl)silane. An ether solution of 1.66 moles of methylmagnesium bromide was added with stirring and cooling to 373 g. (1.66 moles) of trimethoxy(*p*-styrenyl)silane, dissolved in 500 ml. dry benzene. After addition was complete, the mixture was stirred at room temperature for 0.5 hour. Salts were filtered off and the filtrate was distilled, giving 171.5 g. (0.83 moles) (50%) of dimethoxymethyl(*p*-styrenyl)silane, b.p. 60°/0.5 mm. n_D^{25} 1.5111, d^{25} 1.005.

Anal. Calcd. for $C_{11}H_{16}O_2Si$: Si, 13.48. Found: Si, 13.33, 13.26.

Methoxydimethyl(p-styrenyl)silane. An ether solution of 0.5 mole of methylmagnesium bromide was added with stirring and cooling to 104 g. (0.5 mole) of dimethoxymethyl(*p*-styrenyl)silane, dissolved in 600 ml. dry benzene. Salts were filtered off. The filtrate was distilled giving 57 g. (60%) of the desired silane, b.p. 42–43°/0.1 mm., n_D^{25} 1.5179, d^{25} 0.953.

Anal. Calcd. for $C_{11}H_{16}OSi$: Si, 14.60. Found: Si, 14.50, 14.51.

Tetramethyl-1,3-bis(p-styrenyl)disiloxane. Seventy-eight g. of methoxydimethyl(*p*-styrenyl)silane, dissolved in 125 ml. ether was stirred for 3 hr. with 125 ml. of 5% H_2SO_4. The ether layer was separated, washed free of acid, and dried over anhydrous Na_2SO_4. Distillation of this reaction mixture gave 5 g. of unhydrolyzed silane, 20 g. of crude disiloxane and 40 g. of polymerized residue. On redistilling the crude material, a middle fraction (5.5 g.) of the disiloxane boiled at 115–116°/0.05 mm., n_D^{25} 1.5427.

Anal. Calcd. for $C_{20}H_{26}OSi_2$: Si, 16.59. Found: Si, 16.61, 16.75.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactions of Silyllithium Compounds with Derivatives of Carboxylic Acids. II

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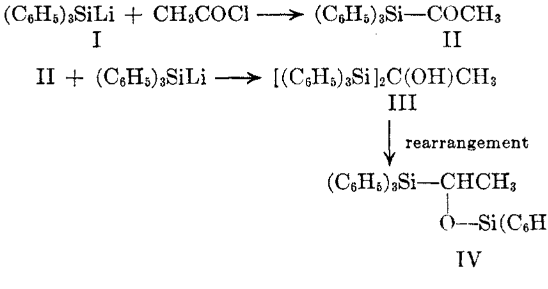
The reactions of triphenylsilyllithium with acetic anhydride, ethyl acetate, propionyl chloride, phenylacetyl chloride, acetonitrile, and benzonitrile were investigated. The formation of the reaction products is discussed and evidence for their structures is presented.

It has been reported recently[1] that triphenylsilyllithium (I) reacts with acetyl chloride to give low yields of acetyltriphenylsilane (II), whereas the chief products were triphenylsilane, 1,1-bis-(triphenylsilyl)ethanol (III), and triphenyl(1-triphenylsiloxyethyl)silane (IV).



$$\underset{\text{I}}{(C_6H_5)_3SiLi} + CH_3COCl \longrightarrow \underset{\text{II}}{(C_6H_5)_3Si{-}COCH_3}$$

$$\text{II} + (C_6H_5)_3SiLi \longrightarrow \underset{\text{III}}{[(C_6H_5)_3Si]_2C(OH)CH_3} \xrightarrow{\text{rearrangement}} \underset{\text{IV}}{(C_6H_5)_3Si{-}\underset{\displaystyle O{-}Si(C_6H_5)_3}{\underset{|}{C}}HCH_3}$$

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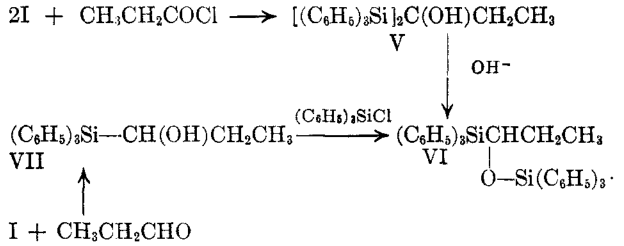
[1] For paper No. I of this series, see D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 4529 (1958).

It seemed desirable to extend these studies to other derivatives of carboxylic acids, especially with a view to develop a procedure by which acetyltriphenylsilane and related acylsilanes could be synthesized in better yield and with a minimal formation of secondary products. However, reactions of I with acetic anhydride and with ethyl acetate gave almost identical results as were observed in the acetyl chloride reaction. Compounds III and IV were isolated as the main products, in addition to triphenylsilane. The desired ketone II was identified only in trace amounts.

From the reaction of I with propionyl chloride, a 23% yield of a compound was obtained, the analysis of which agreed with a formula $C_{39}H_{36}OSi_2$. However, the infrared spectrum of the compound did not show any absorption bands characteristic for the OH group. Its possible structure as 1,1-bis(triphenylsilyl)propan-1-ol (V) was therefore excluded. The compound was shown to be identical with triphenyl-(1-triphenylsiloxypropyl)-silane (VI), synthesized by an independent method. 1-(Triphenylsilyl)propan-1-ol (VII) was obtained from I and propionaldehyde. The reaction of VII with chlorotriphenylsilane in pyridine gave a good yield of compound VI.



When phenylacetyl chloride was allowed to react with triphenylsilyllithium, triphenylsilane was formed in a 43% yield. This indicates that abstraction of the acidic hydrogen from the acid chloride is the predominant reaction. In this connection it is interesting to note that triphenylmethylsodium gave quantitative yields of triphenylmethane on treatment with acid halides containing acidic hydrogen atoms.[2a] Also it has been observed that triphenylsilane is formed as the main product (78%) when dibenzylketone was reacted with triphenylsilyllithium.[2b]

Acrylonitrile was polymerized by triphenylsilyllithium. Similarly, only polymeric products had been reported from the reaction of triphenylmethylsodium with acrylonitrile.[3]

From the reaction of I with acetonitrile, a small amount of a solid, m.p. 187–189°, was obtained. Analysis showed that this substance was different from the expected 1,1-bis(triphenylsilyl)ethylamine (VIII), formed from the reaction of two equivalents of I with the nitrile. An investigation is

$$[(C_6H_5)_3Si]_2C(NH_2)CH_3$$

VIII

being made of the mode of reaction leading to this compound which analyzes precisely for two moles of acetonitrile and one mole of triphenylsilane (triphenylsilyllithium).

Brook[4] has obtained benzoyltriphenylsilane from the reaction of triphenylsilylpotassium with benzoyl chloride. The corresponding reaction of triphenylsilyllithium with benzonitrile, however, gave none of the desired ketone. Instead, tetraphenylsilane was isolated in a 50% yield. Also, hydrogen cyanide was evolved on acid hydrolysis of the reaction mixture. The products indicate that the nitrile group in this reaction might have behaved as a pseudo-halogen, giving rise to coupling rather than to addition products.

$$C_6H_5—C\equiv N + (C_5H_5)_3SiLi \longrightarrow (C_6H_5)_4Si + LiCN$$

EXPERIMENTAL[5]

Reaction of triphenylsilyllithium with acetic anhydride. A solution of 0.096 mole of triphenylsilyllithium[6] in tetrahydrofuran was added to 10.8 g. (0.106 mole) of acetic anhydride at −20°. Color Test I[7] was negative after the addition. Hydrolysis was carried out by pouring over crushed ice. The layers were then separated and the organic layer was washed several times with water. The solvent was removed, after drying the mixture over sodium sulfate, leaving an oily residue. Addition of petroleum ether (b.p. 60–70°) to the oil induced crystallization. Filtration gave 5.6 g. (20.8%) of 1,1-bis(triphenylsilyl)ethanol, m.p. 202–208°. Recrystallization from a benzene and petroleum ether mixture raised the melting point to 215–216°. The compound was identified by a mixed melting point determination with an authentic sample,[1] and an infrared spectrum.

The remaining oil was dissolved in petroleum ether (b.p. 60–70°) and chromatographed. Using this solvent as the first eluent, 4.2 g. (16.7%) of triphenylsilane was obtained, m.p. 43–46°. Further elution of the column with benzene, carbon tetrachloride, and ethanol gave traces of oils that were not identified.

Reaction of triphenylsilyllithium with ethyl acetate. A solution of 0.048 mole of triphenylsilyllithium in tetrahydrofuran was slowly added to 4.40 g. (0.05 mole) of ethyl acetate at room temperature. Color Test I was negative 5 min. after the complete addition.

The reaction mixture was hydrolyzed by pouring over crushed ice. The organic layer was separated and dried over sodium sulfate. Removal of the solvent left an oil. Petroleum ether (b.p. 60–70°) was added to the oil and during a 2-hr. interval 1.6 g. (6.1%) of triphenyl(1-triphenylsiloxyethyl)-silane, m.p. 145–148°, crystallized out. Recrystallization from a mixture of petroleum ether (b.p. 60–70°) and benzene

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(2) (a) W. Schlenk and E. Bergmann, *Ann.*, **464**, 1 (1928). (b) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 2680 (1958).

(3) G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957). See also, M. G. Evans, *Angew. Chem.*, **62**, 271 (1950); Y. Landler, *Rec. trav. chim.*, **68**, 992 (1949); F. C. Foster, *J. Am. Chem. Soc.*, **72**, 1370 (1950); R. G. Beaman, *J. Am. Chem. Soc.*, **70**, 3115 (1948).

(4) A. G. Brook, *J. Am. Chem. Soc.*, **79**, 4373 (1957).

(5) All melting points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen.

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

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

raised the m.p. to 157–159°. The product gave no melting point depression when mixed with an authentic sample.

During concentration of the mother liquor, 1.2 g. (4.6%) of 1,1-bis(triphenylsilyl)ethanol crystallized out, m.p. 210–212°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) raised the m.p. to 214–215°. A mixed melting point with an authentic sample gave no depression.

Reaction of propionyl chloride with triphenylsilyllithium. A solution of 0.096 mole of triphenylsilyllithium[7] in tetrahydrofuran was added slowly to 10.6 g. (0.113 mole) of propionyl chloride at −20°. Color Test I[8] was negative immediately after the complete addition. The cold reaction mixture was then poured on ice. After warming to room temperature, 50 ml. of ether was added and the layers were separated. The organic layer was washed several times with water, dried over sodium sulfate, and the solvent removed by distillation. To the viscous oil remaining, 10 ml. of petroleum ether (b.p. 60–70°) was added. Six and four-tenths grams of triphenyl-(1-triphenylsiloxypropyl)silane crystallized out, m.p. 145–150°. Recrystallization from a benzene and petroleum ether (b.p. 60–70°) mixture raised the melting point to 162–164°. The yield of pure product was 6.1 g. (23%). Further recrystallization from the same mixture did not raise the melting point.

Anal. Calcd. for $C_{39}H_{36}OSi_2$: Si, 9.72. Found: Si, 9.79, 9.82.

The mother liquor was chromatographed on alumina. The product eluted with petroleum ether was 3.9 g. (14.7%) of triphenylsilane, m.p. 43–45°. Further elution of the column with benzene yielded an oil. The infrared spectrum of the compound had a strong absorption band at 5.85 μ, indicative of a carbonyl group. Attempts to isolate a crystalline compound failed. Elution with ethanol yielded 1.8 g. (7.2%) of triphenylsilanol, m.p. 152–154°, identified by a mixed melting point with an authentic sample and an infrared spectrum.

Reaction of phenylacetyl chloride with triphenylsilyllithium. A solution of 0.048 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 17 g. (0.112 mole) of phenylacetyl chloride at −60°. Color Test I was positive 5 min. after the complete addition. The reaction mixture was then allowed to warm to room temperature. After 24 hr. of rapid stirring, Color Test I was still slightly positive. Hydrolysis was then carried out by pouring over crushed ice. The layers were separated and the organic layer was washed several times with water. After drying over sodium sulfate, the solvent was removed by distillation. The remaining oil was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Using the same solvent as an eluent, 5.3 g. (43%) of triphenylsilane was obtained, m.p. 46–48°. Elution of the column with benzene produced an oil. The infrared spectrum of the compound had a carbonyl absorption band at 5.85 μ. Attempts to isolate a crystalline ketone (phenylacetyltriphenylsilane) have been unsuccessful. Further elution with carbon tetrachloride, ethanol, and acetone produced only traces of triphenylsilanol.

Reaction of triphenylsilyllithium with acrylonitrile. A solution of 0.054 mole of triphenylsilyllithium was added slowly at −60° to 2.9 g. (0.054 mole) of acrylonitrile in 25 ml. of tetrahydrofuran. Color Test I was negative after the complete addition. The mixture was allowed to warm up to room temperature and to stir for 1 hr. During this time, the reaction mixture turned black.

Hydrolysis was carried out by pouring the reaction mixture over a mixture of crushed ice and dilute hydrochloric acid. A brownish yellow solid precipitated out at this time. Five and six-tenths grams of this resin-like solid was removed by filtration. The product decomposed without melting at 270°.

The organic layer was dried over sodium sulfate. After removal of the solvent by distillation, a yellow resin remained. Attempts to purify this polymer were unsuccessful.

Reaction of triphenylsilyllithium with acetonitrile. A solution of 0.1 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 4.1 g. (0.1 mole) of acetonitrile at −25°. Color Test I was negative when the addition was complete. Subsequent to hydrolysis with dilute sulfuric acid, the organic layer was dried over sodium sulfate, and the solvent was removed by distillation. To the residual oil, 15 ml. of petroleum ether (b.p. 60–70°) was added. A white solid separated out which on treatment with ethanol gave 1.8 g. of triphenylsilanol, m.p. 153–155°, identified by a mixed melting point with an authentic sample. The ethanol insoluble portion was crystallized out from cyclohexane to give 1.2 g. of a white solid, m.p. 187–189°. Further crystallization did not raise the melting point of this substance.

Anal. Calcd. for $C_{22}H_{21}N_2Si$: C, 77.42; H, 6.16; N, 8.21; Si, 8.21. Found: C, 77.55, 77.40; H, 6.14, 6.26; N, 8.11, 8.20; Si, 8.36, 8.40.

Reaction of triphenylsilyllithium with benzonitrile. A solution of 0.048 mole of triphenylsilyllithium was added to 2.5 g. (0.024 mole) of benzonitrile in 15 ml. of tetrahydrofuran at −60°. The reaction mixture was kept at this temperature for 2 hr. and then allowed to warm up to room temperature. Rapid stirring was then continued for 48 hr. During this interval of time Color Test I remained positive.

Hydrolysis was carried out by adding dilute sulfuric acid. The characteristic odor of hydrogen cyanide was noticed. Filtration yielded 4.25 g. (50%) of tetraphenylsilane, m.p. 220–224°. Recrystallization from ethyl acetate raised the melting point to 229–231° (2.3 g. (27%) of pure product). A mixed melting point with an authentic sample gave no depression.

After washing the organic layer of the filtrate with several large portions of water, it was dried over sodium sulfate. Removal of the solvent by distillation left an oil. Addition of petroleum ether (b.p. 60–70°) to the oil produced 4.2 g. of oily crystals. Recrystallization from petroleum ether yielded 2.0 g. (15%) of triphenylsilanol, m.p. 152–155°, identified by a mixed melting point determination.

Reaction of triphenylsilyllithium with propionaldehyde. A solution of 0.048 mole of triphenylsilyllithium in tetrahydrofuran was added slowly to 5.6 g. (0.096 mole) of propionaldehyde. The reaction was exothermic and Color Test I was negative immediately after the complete addition. The reaction mixture was hydrolyzed with dilute acid, the organic layer was dried over sodium sulfate, and the solvent was removed by distillation. The oily residue was chromatographed on alumina. Using petroleum ether (b.p. 60–70°) as an eluent, 5.8 g. (43.6%) of triphenylsilane, m.p. 45–47°, was isolated. Benzene eluted an oil which partially crystallized on standing. Several recrystallizations from petroleum ether gave 0.64 g. (4.3%) of 1-(triphenylsilyl)propan-1-ol, m.p. 80–82°.

Anal. Calcd. for $C_{21}H_{22}OSi$: Si, 8.81. Found: Si, 8.63, 8.73.

Reaction of 1-(triphenylsilyl)propan-1-ol with chlorotriphenylsilane. A mixture of 0.4 g. (0.0011 mole) of 1-(triphenylsilyl)propan-1-ol and 0.32 g. (0.0011 mole) of chlorotriphenylsilane in 3 ml. of pyridine was heated for 3 hr. in a steam bath. After cooling to room temperature, 10 ml. of ether was added and the mixture washed several times with water. Subsequent to drying with sodium sulfate, the solvent was removed. Addition of petroleum ether (b.p. 60–70°) to the residue induced crystallization of 0.55 g. (80%) of triphenyl-(1-triphenylsiloxypropyl)silane, m.p. 152–156°. Recrystallization from the same solvent raised the melting point to 161–162°. A mixed melting point determination with the compound obtained from the reaction of triphenylsilyllithium with propionyl chloride gave no depression. Also the infrared spectra were superimposable.

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AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Cleavage of Diphenyl Sulfone and Diphenyl Sulfide by Triphenylsilyllithium

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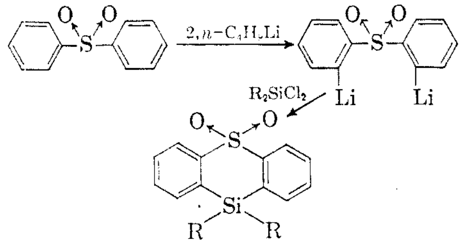
Triphenylsilyllithium (I) has been found to cleave diphenyl sulfone with the formation of phenyllithium and triphenyl(phenylsulfonyl)silane, which in a second step interact to give tetraphenylsilane and lithium benzenesulfinate. In addition, a variety of other products was obtained, when an excess of I was used. The reaction of I with diphenyl sulfide gave, in addition to hexaphenyldisilane, phenyllithium and lithium thiophenolate as the cleavage products.

The metalation of diphenylsulfone with *n*-butyllithium has been reported[1] to give mono- and dimetalated products, depending on the molar ratio of the organolithium reagent. The reaction of the thus formed 2,2′-dilithiodiphenyl sulfone with dichlorodimethylsilane and dichlorodiphenylsilane gave 10,10-dimethyl- and 10,10-diphenylphenothiasilin-5,5-dioxide,[2] respectively.



Triphenylsilylpotassium has been shown to metalate triarylmethanes rapidly and almost quantitatively.[3] Similarly triphenylsilyllithium in tetrahydrofuran was found to metalate fluorene.[4] The present investigation was carried out in order to further test the metalating properties of these highly reactive silylmetallic compounds.

If triphenylsilyllithium (I) or triphenylsilylpotassium (II) metalates diphenyl sulfone (III) in a manner similar to *n*-butyllithium, one might expect a coupling reaction of the initially formed mono- or dimetalated diphenyl sulfone and triphenylsilane[5] to give metal hydride and a silyl-substituted sulfone.

Triphenylsilylpotassium has been allowed to react with III, and tetraphenylsilane was isolated in a 36% yield. Tetraphenylsilane, however, was found to be the main product from the reaction of II with triphenylsilane[3,6] as well as with organic compounds which are metalated by the reagent with the formation of triphenylsilane.[3,6] These results appeared to support the assumption that II metalated III, and that in a secondary step tetraphenylsilane had resulted from the triphenylsilane formed in this manner and excess of triphenylsilylpotassium. In order to exclude the secondary reaction of the silylmetallic compound with the silicon hydride, triphenylsilyllithium (I) was chosen as a reagent in the further study of the reaction. The silyllithium compound I has the advantage over II in that it is fairly stable at room temperature toward triphenylsilane,[7] and furthermore I has been made readily available by lithium cleavage of hexaphenyldisilane in tetrahydrofuran.[8]

When a solution of I in tetrahydrofuran was added at room temperature to diphenyl sulfone (III), a deep red solution resulted. Color Test I[9] was negative after the addition of one equivalent. Subsequent hydrolysis gave tetraphenylsilane in a 50% yield, together with benzenesulfinic acid and 18% of triphenylsilanol. These products suggested as the course of reaction a cleavage of the carbon-sulfur bond of III according to equation A.

$$\text{(A)}\quad \underset{\text{I}}{(C_6H_5)_3SiLi} + \underset{\text{III}}{C_6H_5{-}SO_2{-}C_6H_5} \longrightarrow (C_6H_5)_4Si + C_6H_5SO_2Li$$

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[1] W. E. Truce and M. F. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951); H. Gilman and D. L. Esmay, *J. Am. Chem Soc.*, **75**, 278 (1953).

[2] K. Oita and H. Gilman, *J. Org. Chem.*, **22**, 336 (1957).

[3] A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 2333, 2338 (1954).

[4] D. Wittenberg, unpublished studies.

[5] For general references on the reaction of silicon hydrides with organometallic reagents see, H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, **79**, 4560 (1957).

[6] H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75**, 2509 (1953).

[7] R. D. Gorsich, unpublished studies.

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

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