bomb is amorphous and therefore the value for SiO_2(vitreous) = −202.5 kcal./mole was used. Where the heat of vaporization of the alkylsilane was available, the heat of formation for the gaseous phase also was calculated.

In spite of the large uncertainty attached to the determination of the heats of combustion, it is ininteresting to note the correlation between the thermodynamic stability of these compounds, as measured by their heats of formation (assuming a fairly constant entropy of formation), and the number of Si–H bonds they contain. For example, ethylsilane with three Si–H bonds and a ΔH_f of −20 kcal./mole has a lower heat of formation than its isomer dimethylsilane with two Si–H bonds and a ΔH_f of −41 kcal./mole. Inspection of Table III will confirm this relation for the isomers butyl-, diethyl- and tetramethylsilane; for the homologous series dimethyl-, trimethyl- and tetramethylsilane; and for the homologous series ethyl-, diethyl-, triethyl- and tetraethylsilane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Tetra-substituted Aryl Silanes

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A number of tetra-substituted triphenylsilanes have been prepared by the reaction of triphenylchlorosilane with the appropriate alkyl- or aryllithium compound. Other miscellaneous preparations include the synthesis of trimethyl-(triphenylmethyl)-silane, bis-(*p*-triphenylsilylphenyl)-phenylmethane, 1,3-dimethyl-1,1,3,3-tetrakis-(*p*-chlorophenyl)-disiloxane and triphenyl-*t*-butoxysilane.

We wish to report the synthesis and physical properties of a number of previously unreported tetra-substituted silanes, prepared recently in this Laboratory in connection with studies of the cleavage of silanes by alkaline reagents.

TABLE I

TETRA-SUBSTITUTED TRIPHENYLSILANES $(C_6H_5)_3SiR$

Reagent	Metalating agent	Yield, of RLi, %	Reaction (hr.) with chlorosilane	Product	M.p., °C.	Yield, %	Formula	Si analyses Calcd.	Si analyses Found
n-Propyl bromide	Li	78	24[a]	*n*-Propyltriphenylsilane	84[e]	89	$C_{21}H_{22}Si$	9.29	9.48
n-Amyl bromide	Li	81	24[b]	*n*-Amyltriphenylsilane	47[f]	42	$C_{23}H_{26}Si$	8.49	8.52
n-Hexyl bromide	Li	77	24[a]	*n*-Hexyltriphenylsilane	78[f]	99	$C_{24}H_{28}Si$	8.15	8.00
Fluorene	*n*-PrLi	..	16[b,c]	Triphenyl-9-fluorenylsilane	183[g]–184	70	$C_{31}H_{24}Si$	6.61	6.49
Diphenylmethane	*n*-PrLi	..	24[b,d]	Benzhydryltriphenylsilane	159[g]	66	$C_{31}H_{26}Si$	6.59	6.60
β-Bromoethylbenzene	Li	86	2[b]	Triphenyl-*β*-phenylethylsilane	147[h]	95	$C_{26}H_{24}Si$	7.70	7.69
Phenylacetylene	*n*-BuLi	..	12[a]	Triphenylphenylethynylsilane[k]	100–101	72	$C_{26}H_{20}Si$	7.77	7.55
Indene	*n*-PrLi	..	14[a]	Triphenyl-1-indenylsilane	136[i]	13	$C_{27}H_{22}Si$	7.50	7.55
				(1,1)-Bis-triphenylsilylindene[l]	206[g]	8	$C_{45}H_{36}Si_2$	8.88	8.97
m-Bromobenzotrifluoride	*n*-BuLi	..	17[a]	Triphenyl-*m*-(trifluoromethylphenyl)-silane	101[e]	72	$C_{25}H_{19}F_3Si$	[m]	..

[a] Reaction carried out at room temperature. [b] Reaction carried out at reflux temperature. [c] Solvent was benzene–ether (1.7:1). [d] Solvent was benzene–ether (1:1). [e] Recrystallized from methanol. [f] Recrystallized from ethanol. [g] Recrystallized from ethyl acetate. [h] Recrystallized from ethanol–ethyl acetate (1:1). [i] Recrystallized from ethyl acetate–methanol (5:1). [k] Prepared first by Mary Alys Plunkett in this Laboratory. [l] Cleavage with aqueous alkali yielded 85% triphenylsilanol. The position of the two triphenylsilyl groups has not been definitely established. [m] Silicon analyses were erratically low due to loss of Si possibly as SiF_4. *Anal.* Calcd. for $C_{25}H_{19}F_3Si$: C, 74.3; H, 4.74. Found: C, 75.8; H, 4.62. Cleavage with alkali yielded triphenylsilanol and benzotrifluoride, b.p. 100–101°, $n^{18.6}D$ 1.4155.

The general method of synthesis of the simpler silanes follows that used previously in the preparation of these compounds, namely, treatment of triphenylchlorosilane with the appropriate alkyl- or aryllithium derivative.

$$(C_6H_5)_3SiCl + RLi \longrightarrow (C_6H_5)_3SiR + LiCl$$

The organolithium derivatives were prepared by treatment of the organohalide, where available, with lithium, according to published procedures.[1] In cases where the organohalide was not available, the hydrocarbon was metalated using either *n*-propyl- or *n*-butyllithium, and after metalation was complete, as indicated by the absence of a positive Color Test IIa, the metalated hydrocarbon was treated with triphenylchlorosilane. Using these

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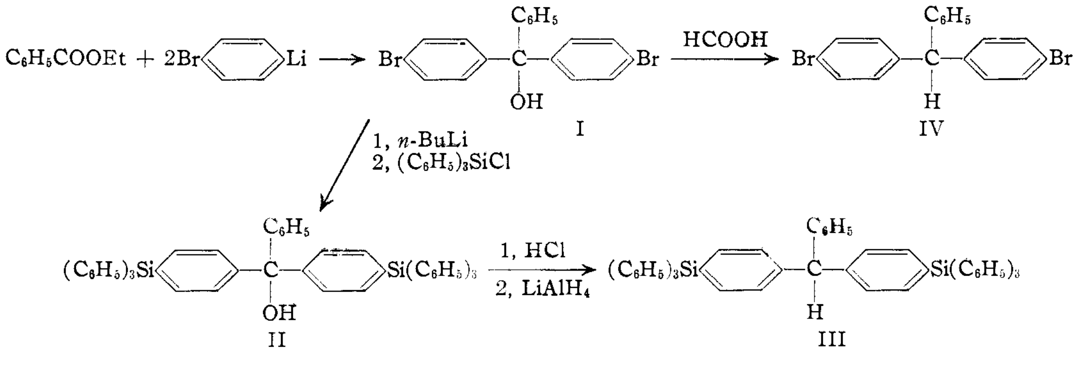
[1] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).

general procedures, the following substituted triphenylsilanes were prepared in yields ranging from 40–95%: *n*-propyl, *n*-amyl, *n*-hexyl, 9-fluorenyl, benzyl, benzhydryl, β-phenylethyl, phenylethynyl, *m*-trifluoromethylphenyl and 1-indenyl. The yields, melting points and analyses are listed in Table I.

Metalation of indene with *n*-propyllithium gave both mono- and dilithium derivatives, since treatment of the product of the metalation with triphenylchlorosilane yielded both mono- and ditrisyl derivatives. Both mono- and dimetalation of indene has recently been employed by Sommer and Marans[2] for the preparation of compounds such as 1-trimethylsilylindene and 1,1-bis-trimethylsilylindene, so that the products isolated in the present study have been assigned the structures 1-triphenylsilylindene and 1,1-bis-triphenylsilylindene.

Analogously to the above preparations, the synthesis of trimethyl-(triphenylmethyl)-silane, reported recently by other workers,[3] using triphenylmethylpotassium, was carried out by treatment of trimethylchlorosilane with either the Grignard, lithium or sodium derivative of triphenylmethane. This compound could be cleaved with alkali to give a high recovery of triphenylmethane, and treatment of the original compound with *n*-propyllithium failed to indicate any active hydrogen, thus eliminating the possibility that the trimethylsilyl group had become attached to one of the rings.

Incidental to another problem, arising from the synthesis of (triphenylmethyl)-triphenylsilane, it became necessary to prepare bis-(*p*-triphenylsilylphenyl)-phenylmethane (III). This was accomplished by the following scheme.



Bis-(*p*-bromophenyl)-phenylcarbinol (I) was prepared from ethyl benzoate and excess *p*-bromophenyllithium. This compound melted at 123–124°, 13° higher than that previously reported.[4] To ensure its identity a portion was converted to the substituted triphenylmethane (IV), which had the melting point reported in the literature.[5] The carbinol I, after treatment with excess *n*-butyllithium, was treated with triphenylchlorosilane to yield the compound II, which was converted to the chloride with dry hydrogen chloride, and then reduced to the hydrocarbon III, a white relatively insoluble compound melting at 315°. This compound was cleaved by treatment with sodium–potassium alloy to yield on carbonation a mixture of acids.

An attempt was made to prepare methyl-bis-(*p*-chlorophenyl)-silanol, by treatment of methyltrichlorosilane with two equivalents of *p*-chlorophenylmagnesium bromide. The oil isolated was probably a mixture of this compound and the corresponding disiloxane, for after standing several months it slowly crystallized to yield 1,3-dimethyl-1,1,3,3-tetrakis-(*p*-chlorophenyl)-disiloxane in about 30% yield.

Triphenyl-*t*-butoxysilane has been prepared by two different methods, one unambiguously, by the reaction of triphenylchlorosilane with *t*-butyl alcohol in the presence of dimethylaniline. The second preparation occurred through reaction of triphenylsilanol with a Karl Fischer type reagent made from pyridine, iodine, sulfur dioxide and *t*-butyl alcohol.

Experimental[6]

General Synthetic Method. A. From a Halide. The Preparation of *n*-Propyltriphenylsilane.—*n*-Propyllithium[1] was prepared by adding 12.3 g. (0.1 mole) of redistilled *n*-propyl bromide in 30 ml. of ether to 2.0 g. (0.286 g. atom) of lithium in 70 ml. of ether at −10°. The yield was 78% as determined by the double titration method.[7] A solution of 0.06 mole of *n*-propyllithium in 81 ml. of ether was added rapidly to 14.8 g. (0.05 mole) of triphenylchlorosilane in 150 ml. of ether, and the mixture was stirred for 20 hours at room temperature, by which time Color Test I[8] was positive. After hydrolyzing the reaction mixture with dilute hydrochloric acid, the ether layer was separated, dried over sodium sulfate, and distilled, leaving 13.4 g. (89%) of product melting at 75–85° after one crystallization from methanol. After two additional recrystallizations from methanol, the melting point was raised to 84°.

Anal. Calcd. for $C_{21}H_{22}Si$: Si, 9.29. Found: Si, 9.48.

B. From a Hydrocarbon. The Preparation of Triphenyl-9-fluorenylsilane.—A solution of 0.127 mole of *n*-propyllithium in 175 ml. of ether was added rapidly to 16.6 g. (0.1 mole) of fluorene. After the mixture had refluxed for 2 hours, Color Test IIa[9] was negative, and 19.5 g. (0.0662 mole) of triphenylchlorosilane in 100 ml. of benzene was added. After refluxing for 16 hours, Color Test I was still faintly positive. The reaction mixture was hydrolyzed with dilute hydrochloric acid, and 13.3 g. of solid, m.p. 181–183°, was filtered from the ether layer. An additional 6.2 g. of material was recovered by removal of the ether from the ether layer and washing the residue with ethanol. The yield of product was 70% based on triphenylchlorosilane, and the product on crystallization from ethyl acetate gave transparent crystals melting at 183–184°.

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[2] L. H. Sommer and N. S. Marans, THIS JOURNAL, **73**, 5135 (1951).

[3] C. R. Hauser and C. R. Hance, *ibid.*, **73**, 5864 (1951). See, L. S. Miller, Doctoral Dissertation, Iowa State College, 1950.

[4] M. Gomberg and L. H. Cone, *Ber.*, **39**, 3274 (1906); B. A. Stagner, THIS JOURNAL, **38**, 2069 (1916).

[5] N. E. Goldthwaite, *Am. Chem. J.*, **30**, 463 (1903).

[6] Melting points are corrected.

[7] H. Gilman and A. H. Haubein, THIS JOURNAL, **66**, 1515 (1944).

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

[9] H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

Anal. Calcd. for $C_{31}H_{24}Si$: Si, 6.61. Found: Si, 6.49.

Trimethyl-(triphenylmethyl)-silane.[3]—A mixture of 31.6 g. (0.114 mole) of triphenylchloromethane, 300 ml. of ether and sodium amalgam made from 187 g. of mercury and 5.8 g. of sodium was shaken for 18 hours.[10] The yield of triphenylmethylsodium as determined by titration of the clear red solution was 63%. To 7.6 g. (0.07 mole) of trimethylchlorosilane in 100 ml. of ether at room temperature was added 0.0695 mole of triphenylmethylsodium in 350 ml. of ether. The blood-red color changed to yellow 10 minutes after addition was complete. After hydrolysis, removal and drying of the ether layer, and the removal of the ether, a residue of 25.2 g. of yellow solid remained, which was extracted with 70 ml. of ethanol, leaving 5.5 g. of white solid, m.p. 161–164°. Two recrystallizations from ethanol–ethyl acetate (1:2) gave 3.0 g. (13.6%) of pure white solid, m.p. 172–173° (reported[3] 169.5–170.5°).

Anal. Calcd. for $C_{22}H_{24}Si$: Si, 8.87. Found: Si, 8.75.

The same compound could be obtained using triphenylmethyllithium, prepared by metalation of triphenylmethane with *n*-propyllithium in 70% yield after 48 hours of refluxing, in 57% yield after refluxing for 20 hours, or from triphenylmethylmagnesium chloride[11] in 13.8% yield after refluxing for 24 hours. Alkaline cleavage of a 0.5-g. sample of this compound in 10 ml. of acetone and 10 ml. of 40% aqueous potassium hydroxide, refluxed 20 hours and then poured into water, yielded triphenylmethane (95%). Treatment of the original compound with excess *n*-propyllithium for 2 days gave no red or yellow color, indicating the absence of aliphatic hydrogen.

Triphenylbenzylsilane.[12]—Benzylmagnesium chloride was prepared from 50.6 g. (0.4 mole) of benzyl chloride and 9.72 g. (0.4 g. atom) of magnesium in 240 ml. of ether. To this was added 59.0 g. (0.2 mole) of triphenylchlorosilane in 200 ml. of benzene. There was no immediate reaction, so the ether and most of the benzene were removed by distillation leaving a viscous paste which was stirred at 180° for 4 hours. The cooled residue was extracted with ether and hydrolyzed in acidified ice-water. The ether layer was separated, dried and distilled giving 56.9 g. of distillate, boiling over the range 197–213° at 0.3 mm. Crystallization from ethyl acetate–methanol (5:1) gave 56.2 g. (80%) of solid, m.p. 97–98°. It failed to depress the mixed melting point with an authentic specimen.

Bis-(*p*-bromophenyl)-phenylcarbinol.—*p*-Bromophenyllithium was prepared from 118 g. (0.5 mole) of *p*-dibromobenzene and 0.5 mole of *n*-butyllithium in 1400 ml. of ether, stirred at 0° until Color Test IIa was negative. To this was added dropwise 67.5 g. (0.45 mole) of ethyl benzoate in 100 ml. of ether. The ether refluxed during the addition, and after the addition was complete, Color Test I was negative. The reaction mixture was hydrolyzed with aqueous acid, the ether layer removed, and all material volatile below 100° at 1 mm. removed. The residual oil, which did not solidify, was taken up in petroleum ether (b.p. 60–70°), from which it slowly crystallized to yield a total of 72.5 g. (39%) of bis-(*p*-bromophenyl)-phenylcarbinol, which melted at 123–124° after recrystallization from benzene–petroleum ether (b.p. 60–70°).

Anal. Calcd. for $C_{19}H_{14}OBr_2$: Br, 38.2; Zerewitinoff H, 1.00. Found: Br, 38.7; Zerewitinoff H, 1.01.

Other authors[4] have reported melting points of 110 and 113.5° for this compound. When 32 g. (0.0765 mole) of the carbinol was refluxed overnight with 550 ml. of 98% formic acid, an oil collected in the bottom of the flask, which was separated, washed with water, taken up in ether and dried, and then distilled at 205–207° (0.6 mm.). It crystallized in 90% yield, to melt sharply at 100°, in agreement with the reported melting point[5] for bis-(*p*-bromophenyl)-phenylmethane prepared in a different way.

Bis-(*p*-triphenylsilylphenyl)-phenylcarbinol.—A solution of 0.086 mole of *n*-butyllithium in 95 ml. of ether was added rapidly at 0° to 12.0 g. (0.0287 mole) of bis-(*p*-bromophenyl)-phenylcarbinol in 150 ml. of ether. After refluxing for 3 hours a heavy white precipitate had formed, and Color Test IIa was barely positive. A solution of 16.9 g. (0.0574 mole) of triphenylchlorosilane in 100 ml. of dry benzene was added rapidly, and the mixture was refluxed overnight, by which time Color Test I was negative. The mixture was hydrolyzed and filtered, leaving 14.6 g. (66%) of white, ether-insoluble material melting at 270–280°. Two recrystallizations from pyridine raised the melting point to 290°.

Anal. Calcd. for $C_{55}H_{44}OSi_2$: Si, 7.22; Zerewitinoff H, 1.00. Found: Si, 6.90; Zerewitinoff H, 0.94.

Bis-(*p*-triphenylsilylphenyl)-phenylmethane.—Dry hydrogen chloride was passed into a solution of 4.7 g. (0.0061 mole) of bis-(*p*-triphenylsilylphenyl)-phenylcarbinol in 80 ml. of dry benzene for 4 hours. The resulting suspension was treated slowly with excess 2 *N* lithium aluminum hydride in ether. After refluxing briefly, the reaction mixture was hydrolyzed, diluted with 100 ml. of ether, and filtered to leave 3.3 g. (71%) of a white compound which melted at 315° after one recrystallization from pyridine.

Anal. Calcd. for $C_{55}H_{44}Si_2$: Si, 7.38; mol. wt., 761. Found: Si, 7.62; mol. wt. (cryoscopic in *p*-dichlorobenzene), 767, 700.

When 1.0 g. of this compound was stirred in 10 ml. of ether with 1 ml. of sodium–potassium alloy (1:5) for 48 hours, an intense red-black color developed. The suspension was carbonated, and then hydrolyzed carefully. Acidification of the alkaline aqueous layer precipitated 0.7 g. of a mixture of acids which could not be obtained pure.

1,3-Dimethyl-1,1,3,3-tetrakis-(*p*-chlorophenyl)-disiloxane.—This material was obtained during an attempted preparation of methyl-bis-(*p*-chlorophenyl)-silanol. *p*-Chlorophenylmagnesium bromide was prepared in 70% yield by the method of Grüttner and Krause[13] by treatment of 6.25 g. (0.257 g. atom) of magnesium in 100 ml. of ether with 47.5 g. (0.25 mole) of *p*-chlorobromobenzene over 90 minutes, followed by refluxing for 20 hours. A solution of 0.175 mole of *p*-chlorophenylmagnesium bromide in 136 ml. of ether was added slowly to 12.4 g. (0.083 mole) of methyltrichlorosilane in 100 ml. of ether. The solution was refluxed for 3 days, the ether was removed, and the residue heated at 60° for 20 hours before a negative Color Test I was obtained. The reaction products were hydrolyzed by stirring with 50 ml. of acetic acid and 100 ml. of 1:20 hydrochloric acid, and the flask contents were evaporated almost to dryness. After extracting the residue for 48 hours in a Soxhlet apparatus with petroleum ether (b.p. 60–70°), the solvent was removed to yield 14.2 g. (31%) of a straw-colored liquid boiling over the range 174–185° (0.1 mm.). It could not be crystallized from methanol or petroleum ether (b.p. 60–70°) but after standing several months formed large crystals melting at 68–69°. The compound gave a negative test for active hydrogen when treated with methylmagnesium iodide.

Anal. Calcd. for $C_{26}H_{22}OCl_2Si_2$: Cl, 25.8; Si, 10.2. Found: Cl, 25.6; Si, 9.96.

Triphenyl-*t*-butoxysilane.—A Karl Fischer type reagent was prepared from 10 ml. of pyridine, 3.15 g. of iodine, 1.67 ml. of liquid sulfur dioxide and 24.8 ml. of *t*-butyl alcohol. The iodine color of this reagent was not destroyed by addition of triphenylsilanol at room temperature[14] although water decolorized the reagent immediately. A 0.26 g. (0.00095 mole) sample of triphenylsilanol was added to 25 ml. of the reagent, and the mixture was heated in a glass-stoppered flask at 90° for 14 hours. After hydrolysis with dilute hydrochloric acid, 0.23 g. (73%) of a solid, m.p. 99–101°, was obtained. Two recrystallizations from methanol gave transparent crystals melting at 104°.

Anal. Calcd. for $C_{22}H_{24}OSi$: Si, 8.45. Found: Si, 8.64.

The material could also be prepared (in 63% yield) by refluxing 2.0 g. (0.0068 mole) of triphenylchlorosilane in 2 ml. of dimethylaniline and 15 ml. of *t*-butyl alcohol for 2 hours.

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(10) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 609.

(11) H. Gilman and E. A. Zoellner, THIS JOURNAL, **51**, 3493 (1929).

(12) This compound was first prepared by H. W. Melvin in this Laboratory.

(13) G. Grüttner and E. Krause, *Ber.*, **50**, 1559 (1917).

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