Hydrolysis of triphenylphosphineacetylmethylene (IV). The phosphine methylene IV (1.1 g.) in 40 ml. of water was heated to reflux for 12 hr. The resulting white solid (0.925 g.) was shown to be triphenylphosphine oxide.

Reaction of triphenylphosphineacetylmethylene (IV) *with benzaldehyde.* A solution of the phosphinemethylene IV (1.1 g.) and benzaldehyde (0.367 g.) in tetrahydrofuran was refluxed for 48 hr. The solvent was removed, the residue was dissolved in 95% ethanol and the solution was treated with an aqueous methanolic solution of 2,4-dinitrophenylhydrazinium sulfate. The precipitate was recrystallized (m.p. 218–221°) and was identified as benzalacetone-2,4-dinitrophenylhydrazone.

The phosphinemethylene IV failed to react with cyclohexanone under similar conditions.

(2-Ethoxypropenyl)-triphenylphosphonium iodide (XIV). A mixture of phosphinemethylene IV (1.0 g.) and freshly distilled ethyl iodide (20 ml.) was refluxed for 7 hr. The solid which precipitated (0.40 g.) had m.p. 163–165° and was recrystallized from methanol–ethyl acetate without change in m.p.: $\lambda_{\text{max.,}}^{\text{EtOH}}$ 220 mμ (ε 44,900), 252 mμ (ε 13,700) and shoulder at 275 mμ (ε 3800). Bands (KBr) at 6.30 (w), 7.02 (m), 7.48 (m) and 9.00 (s).

Anal. Calc'd for $C_{23}H_{24}IOP$: C, 58.2; H, 5.1. Found: C, 58.4; H, 5.2.

Hydrolysis of (2-ethoxypropenyl)-triphenylphosphonium iodide (XIV) *with acid.* The iodide XIV (0.65 g.) and 5% aqueous hydriodic acid (20 ml.) were heated to reflux for 15 hr. The solid formed was collected and had m.p. 206–208° (0.56 g.). It was shown to be acetonyltriphenylphosphonium iodide (XVI) by mixed m.p. and comparison of I.R. spectra.

Hydrolysis of (2-ethoxypropenyl)-triphenylphosphonium iodide (XIV) *with alkali.* A mixture of iodide (7.9 g.) and 5% aqueous methanolic potassium hydroxide was refluxed for 15 hr. Water was added and the precipitated solid was collected; it weighed 4.05 g. (m.p. 146–150°) and was shown to be triphenylphosphine oxide. The filtrate was extracted with ether. Fractionation of the ether solution gave isopropenyl ethyl ether, which (1) decolorized bromine-in-chloroform instantaneously and (2) gave no precipitate with an aqueous-methanolic solution of 2,4-dinitrophenylhydrazinium sulfate. After the solution was warmed and allowed to stand overnight, acetone-2,4-dinitrophenylhydrazone (0.48 g., m.p. 119–124°). was precipitated. Comparison with an authentic sample confirmed the identity.

Ultraviolet absorption spectra. The spectra of the phosphinemethylenes III and IV show variations in hydroxylic and aprotic solvents (*cf.* Figs. 1, 2, and 3). The molecular extinction coefficients (ε) at λ max. in 95% ethanol are recorded above. The corresponding values in dry acetonitrile are, for III: 267 mμ (ε 6000), 275 mμ (ε 5500) and 328 mμ (ε 10,200); for IV: 275 mμ (ε 4700) and 295 mμ (ε 4400).

Acknowledgment. The financial assistance of an Eli Lilly research grant is gratefully acknowledged.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Monomeric Organosilicon Compounds of High Thermal Stability

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Received Aug. 2, 1956

A number of monomeric organosilicon compounds possessing high thermal stability was synthesized. Some organic groups found to impart this property were the *p*-phenoxyphenyl, *m*-tolyl, *m*-trifluoromethylphenyl, and *p*-trimethylsilylphenyl. The molecules containing the 9-fluorenyl group were not promising in this respect. Compounds studied were of the types $(C_6H_5)_3SiR$, $(C_6H_5)_2SiR_2$, $C_6H_5SiR_3$, $C_{12}H_{25}SiR_3$, $HSiR_3$, and SiR_4.

Incidental to studies concerned with the thermal stability of monomeric organosilicon compounds,[1] an examination has been made of the synthesis of a series of R_4Si, $R_3R'Si$, and $R_2R_2'Si$ compounds. In these syntheses both Grignard reagents and organolithium compounds were used. The organolithium compounds were prepared by direct reaction with lithium metal, by halogen-metal interconversion reactions using *n*-butyllithium, and by the direct replacement of hydrogen in a metalation reaction.

Preliminary or orienting screening for thermal stabilities indicates that the following groups tend to increase thermal stability: *p*-phenoxyphenyl, *m*-tolyl, *m*-trifluoromethylphenyl, and *p*-trimethylsilylphenyl.

EXPERIMENTAL

Diphenyl-bis-(p-phenoxyphenyl)-silane. To 105 ml. of an ethereal solution containing 0.090 mole of *n*-butyllithium[2] was slowly added 75 ml. of an ethereal solution containing 22.4 g. (0.090 mole) of *p*-bromophenyl phenyl ether.[3] The temperature of the reaction was maintained at −15°. Color Test II[4] was negative after 2 hr. Then there was slowly added 50 ml. of an ethereal solution containing 9.60 g. (0.038 mole) of diphenyldichlorosilane. The reaction mixture was allowed to come to room temperature and stirred overnight. Color Test I[5] was negative at that time and a white solid was suspended in the reaction mixture. Hydrolysis with 200 ml. of water resulted in two clear liquid layers. The ether layer was separated and a solid began to precipitate from it. There was filtered 8.4 g. of a white solid melting

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[1] Burkhard, Rochow, Booth, and Hart, *Chem. Revs.*, **41**, 97 (1947); Post, *Silicones and Other Organosilicon Compounds*, Reinhold Publishing Corp., New York, N. Y., 1949; Rochow, *An Introduction to the Chemistry of the Silicones*, 2nd ed., John Wiley & Sons, New York, N. Y., 1951; Gilman and Dunn, *Chem. Revs.*, **52**, 77 (1953).

[2] Gilman, Beel, Brannen, Bullock, Dunn, and Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

[3] Gilman, Langham, and Moore, *J. Am. Chem. Soc.*, **62**, 3277 (1940).

[4] Gilman and Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

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

over the range 156–159°.[6] The ether layer was dried over anhydrous sodium sulfate and distilled. There was recovered 4.5 g. of *p*-bromophenyl phenyl ether. In addition, the residue contained 1.1 g. of a white solid melting over the range 154–158°. The combined product was recrystallized from a mixture of dioxane and ethanol. There was obtained 7.20 g. (36.8%) of the desired product melting at 162–163°.

Anal.[7] Calc'd for $C_{36}H_{28}O_2Si$: Si, 5.39. Found: Si, 5.34, 5.40.

This procedure outlines the general method used in the work-up of the following reaction mixtures.

Phenyl-tris-(p-phenoxyphenyl)-silane. In analogous fashion there was added 22.4 g. (0.090 mole) of *p*-bromophenyl phenyl ether to 0.0895 mole of *n*-butyllithium. Following this addition, 5.30 g. (0.025 mole) of phenyltrichlorosilane was slowly added. Hydrolysis of the resulting mixture gave 10.1 g. of a white solid melting at 160–169°. Distillation of the dried ether fraction afforded 3.3 g. of a solid melting at 155–160°. Recrystallization of the combined solids from a mixture of dioxane and ethanol yielded 10.2 g. (67.1%) of the desired compound melting at 149–150°.

Anal. Calc'd for $C_{42}H_{32}O_3Si$: Si, 4.57. Found: Si, 4.51, 4.61.

Tetrakis-(p-phenoxyphenyl)-silane. In like manner, to 115 ml. of an ethereal solution containing 0.09 mole of *n*-butyllithium was added 23.7 g. (0.095 mole) of *p*-bromophenyl phenyl ether. There was then added 3.4 g. (0.020 mole) of silicon tetrachloride. Hydrolysis caused the suspension of a white solid between the two layers. This material weighed 10.7 g. and melted at 200–204°. No solid was isolated from the ether fraction. The 10.7 g. was recrystallized from ethyl acetate and there was finally obtained 8.21 g. (58.3%) of the desired product melting at 204°.

Anal. Calc'd for $C_{48}H_{36}O_4Si$: Si, 3.99. Found: Si, 3.95, 3.90.

The compounds, in order of the foregoing listing of preparations, had the following volatilization temperatures at atmospheric pressure: 505–510°, 530–533°, and 550–560°.[8] With the exception of the tetrakis-substituted molecule, b.p. 550–560° which was deep amber, all were pale amber at their boiling points. The melting point of phenyl-tris-(*p*-phenoxyphenyl)-silane was found unchanged when taken on a cooled sample previously tested for thermal stability.

Tris-(p-phenoxyphenyl)-n-dodecylsilane. Following the same procedure, there was added 47.5 g. (0.190 mole) of *p*-bromophenyl phenyl ether to an ethereal solution containing 0.187 mole of *n*-butyllithium. After 2 hr., 17.6 g. (0.057 mole) of *n*-dodecyltrichlorosilane was added. A white precipitate slowly formed during 18 hr. of reflux. Hydrolysis caused the solid to dissolve, and a highly viscous oil was isolated from the ether fraction. This material distilled at 315–320°/0.004 mm. in a Hickman molecular still. The total weight of the pale yellow liquid was 10.3 g. (25.2%).

Anal. Calc'd for $C_{48}H_{32}O_3Si$: Si, 3.99. Found: Si, 4.03, 4.09.

The compound volatilized at 423–425° without any color change.

Diphenyl-bis-(9-fluorenyl)-silane. To 250 ml. of an ethereal solution containing 21.2 g. (0.127 mole) of fluorene[9] were slowly added 150 ml. of an ethereal solution containing 0.127 mole of phenyllithium.[10] The solution became yellow, then orange during the addition. Then 75 ml. of an ethereal solution containing 12.7 g. (0.050 mole) of diphenyldichlorosilane was slowly added. The reaction mixture became a mustard color during this addition. Color Test I was negative after refluxing overnight.

The reaction mixture was hydrolyzed with 250 ml. of water. The ether layer was separated, dried, and distilled. The residual solid was recrystallized from a mixture of dioxane and ethanol, and 2.4 g. of a white solid melting over the range 225–240° was isolated. Several recrystallizations did not narrow the melting point range. Concentration of the original recrystallizing solvent gave 2.7 g. (10.6%) of the pure product melting at 270°.

Anal. Calc'd for $C_{38}H_{28}Si$: Si, 5.47. Found: Si, 5.55, 5.50.

Phenyl-tris-(9-fluorenyl)-silane. In similar fashion, there was added an ethereal solution containing 0.075 mole of phenyllithium to 12.3 g. (0.075 mole) of fluorene. After 4 hr. of reflux, there was slowly added an ethereal solution containing 4.88 g. (0.023 mole) of phenyltrichlorosilane. Hydrolysis of the reaction mixture resulted in the suspension of a white solid between the water and ether layers. This material was filtered and air-dried. It weighed 10.0 g. and had an m.p. of 290–318°. Recrystallization from a mixture of ethyl acetate and ethanol afforded 6.6 g. (46.6%) of the desired compound melting at 333–334°.

The ether layer gave only 2.1 g. of a solid having the odor and melting range of fluorene.

Anal. Calc'd for $C_{45}H_{32}Si$: Si, 4.66. Found: Si, 4.62, 4.50.

Two attempts were made to prepare tetrakis-(9-fluorenyl)-silane. In both cases there were isolated dark brown glass-like solids which have not been further purified. The failure to synthesize the compound may be due in part to steric factors.

Both compounds prepared were wine-red by 330–335°. The remaining material vaporized with considerable decomposition at 455–465° and 410–420° for the bis- and tris-9-fluorenyl molecules, respectively.

Diphenyl-bis(m-trifluoromethylphenyl)-silane. To a solution of 0.087 mole of *n*-butyllithium in 112 ml. of ether at −15° was slowly added an ethereal solution of 19.5 g. of *m*-trifluoromethylbromobenzene in 50 ml. of ether.[11] The solution turned brown during the addition. Color Test II was negative after 2 hr. There was then added 50 ml. of an ethereal solution containing 8.85 g. (0.035 mole) of diphenyldichlorosilane. The temperature was allowed to rise slowly, and then heat was applied to bring the solution to reflux. After 24 hr., Color Test I was doubtful. Hydrolysis with 150 ml. of water resulted in a brown, ether layer and colorless, aqueous layer. The ether fraction was separated, dried, and distilled. There remained an oil which became a semisolid on cooling in an ice bath. Stirring with methanol gave a white solid melting over the range 93–96°. Recrystallization from the same solvent yielded 9.1 g. (56%) of the pure product melting at 97–98°.

Anal. Calc'd for $C_{26}H_{18}F_6Si$: C, 66.0; H, 3.82. Found: C, 65.60, 65.55; H, 3.86, 3.92.

Phenyl-tris-(m-trifluoromethylphenyl)-silane. Similarly, to an ethereal solution containing 0.094 mole of *n*-butyllithium was added 21.2 g. (0.094 mole) of *m*-trifluoromethylbromobenzene. This was followed by an ethereal solution of 5.71 g. (0.027 mole) of phenyltrichlorosilane. The mixture was hydrolyzed and the organic fraction separated and dried. On distillation of the solvent there was obtained an oily residue, which crystallized on standing overnight. This material, recrystallized from methanol, weighed 6.3 g. (43.4%) and melted at 81°.

Anal. Calc'd for $C_{27}H_{17}F_9Si$: C, 60.0; H, 3.15. Found: C, 60.09, 60.24; H, 3.23, 3.20.

Tetrakis-(m-trifluoromethylphenyl)-silane. In analogous manner there was added to 0.190 mole of *n*-butyllithium, an ethereal solution containing 42.7 g. (0.190 mole) of *m*-trifluoromethylbromobenzene. An ethereal solution containing 7.48 g. (0.044 mole) of silicon tetrachloride was then

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(6) All melting points are uncorrected. All reactions were carried out under dry oxygen-free nitrogen.

(7) Gilman, Hofferth, Melvin and Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

(8) The volatilization temperatures were determined in accordance with the procedure of Gilman and Oita, *J. Org. Chem.*, **20**, 862 (1955).

(9) Ziegler and Wenz, *Ber.*, **83**, 354 (1950).

(10) Jones and Gilman, *Org. Reactions*, **6**, 354 (1951).

(11) Gilman and Woods, *J. Am. Chem. Soc.*, **66**, 198 (1944); Gilman, Brook and Miller, *J. Am. Chem. Soc.*, **75**, 3757 (1953).

added. A gelatinous solid was formed during the hydrolysis of the reaction mixture. The organic layer was separated, dried, and distilled. The residual "wet" solid was washed with methanol and recrystallized from petroleum ether (b.p. 60–70°). There was finally isolated 11.1 g. (41.7%) of tetrakis-(*m*-trifluoromethylphenyl)-silane melting at 102–103°.

Anal. Calc'd for $C_{28}H_{16}F_{12}Si$: C, 55.4; H, 2.63. Found: C, 55.47, 55.43; H, 2.67, 2.66.

The volatilization temperatures of the fluorine-containing compounds, in order of increasing molecular weight, are 375–380°, 370–374°, and 362°. All become pale amber at or near the boiling points. The melting point of diphenyl-bis-(*m*-trifluoromethylphenyl)-silane was found unchanged when taken on a cooled sample previously tested for thermal stability.

Triphenyl-m-tolylsilane. To 0.052 mole of *m*-tolyllithium[12] in 75 ml. of ether was slowly added 100 ml. of an ethereal solution containing 13.5 g. (0.046 mole) of triphenylchlorosilane. The mixture became a rust color on completion of the addition. The temperature of the solution was raised to reflux and maintained there for 6 hr. Color Test I was then negative. Hydrolysis with 150 ml. of water turned the ether solvent a pale amber color. The organic layer was separated, dried and distilled. There remained 14.8 g. of a white solid melting over the range 143–148°. After recrystallization from petroleum ether (b.p. 60–70°), 12.3 g. (77%) of the desired product melting at 150–151° was obtained.

Anal. Calc'd for $C_{25}H_{22}Si$: Si, 8.00. Found: Si, 8.02, 8.08.

Diphenyl-bis-(m-tolyl)-silane. Following the same procedure, 8.85 g. (0.035 mole) of diphenyldichlorosilane was added to 0.075 mole of *m*-tolyllithium. After 6 hr. reflux, the reaction mixture was hydrolyzed. The ether layer was separated, dried, and distilled. The residual white solid weighed 11.6 g. and melted over the range 112–116°. Several recrystallizations from a mixture of ethanol and benzene yielded 9.7 g. (76.5%) of the pure product melting at 119–120°.

Anal. Calc'd for $C_{26}H_{24}Si$: Si, 7.69. Found: Si, 7.71, 7.74.

Phenyl-tris-(m-tolyl)-silane. This compound, m.p. 128–129°, was prepared in 76% yield (8.6 g.) by the reaction between 0.096 mole of *m*-tolylithium and 6.38 g. (0.030 mole) of phenyltrichlorosilane by the described procedure.

Anal. Calc'd for $C_{27}H_{26}Si$: Si, 7.40. Found: Si, 7.41, 7.48.

Tetrakis-(m-tolyl)-silane. Following the above procedure, 5.45 g. (0.035 mole) of silicon tetrachloride and 0.154 mole of *m*-tolyllithium gave 8.9 g. (65%) of tetrakis-(*m*-tolyl)-silane melting at 155–156°.

Anal. Calc'd for $C_{28}H_{28}Si$: Si, 7.15. Found: Si, 7.24, 7.19.

The compounds, in order of increasing number of *m*-tolyl groups, had volatilization temperatures of 430°, 435°, 420–425°, and 435–438°. All members of this series turned deep amber before vaporization.

Tris-(m-trifluoromethylphenyl)-silane. Thirty drops of an ethereal solution of 56.4 g. (0.250 mole) of *m*-trifluoromethylbromobenzene were added to a suspension of 6.1 g. (0.25 g. atom) of magnesium turnings and a small crystal of iodine. The solution became turbid after several minutes and the remaining 100 ml. were added at a rate sufficient to maintain gentle reflux. After 2 hr. of stirring, a simple acid titration gave an 81% yield. The Grignard reagent was cooled to 0° and 50 ml. of an ethereal solution containing 8.10 g. (0.060 mole) of trichlorosilane[13] was slowly added. Then the temperature was allowed to rise slowly and heat applied to bring the reaction mixture to reflux. Color Test I was negative at that time. Hydrolysis with 100 ml. of 3 *N* hydrochloric acid resulted in two colorless layers. The ether fraction was separated, dried, and distilled. A deep brown viscous oil remained. Vacuum distillation first gave 4.3 g. of colorless liquid (b.p. 32–50°/0.45 mm.) followed by 25.4 g. (92.2%) of product boiling at 147–150°/0.05 mm., n_D^{20} 1.4948, d_{20}^{20} 1.3500. The product on treatment with aqueous alcoholic potassium hydroxide[14] evolved a gas (H_2) indicating the presence of the silicon–hydrogen bond.

Anal. Calc'd for $C_{21}H_{13}F_4Si$: C, 54.4; H, 2.81; MR_D,[15] 101.48. Found: C, 54.12, 54.25; H, 2.88, 2.91; MR_D, 101.3.

Tris-(p-trimethylsilylphenyl)-silane. Employing the same technique, *p*-trimethylsilylphenylmagnesium bromide was prepared in 93.5% yield by the reaction between 18.7 g. (0.770 g. atom) of magnesium turnings, a small crystal of iodine, and 171 g. (0.750 mole) of trimethyl-*p*-bromophenylsilane.[16] There was then added an ethereal solution containing 27.0 g. (0.20 mole) trichlorosilane. A large quantity of gelatinous solid remained after hydrolysis. This material was filtered and air-dried. The product (54.6 g.) melted over the range 154–158°. From the ether layer there was isolated 10.2 g. melting over the range 156–159°. Recrystallization of the combined solids from a mixture of ethanol and ethyl acetate gave 61.3 g. (64.8%) of the desired compound, m.p. 159–160°.

Anal.[17] Calc'd for $C_{27}H_{40}Si_4$: Si, 23.5. Found: Si, 24.1, 23.8.

This compound volatilized at 452–456° with very little discoloration. The analogous *m*-trifluoromethylphenyl compound boiled at 322–325° with no signs of decomposition.

Attempts to react both tris-(*m*-trifluoromethylphenyl)- and tris-(*p*-trimethylsilylphenyl)-silane with various organolithium compounds, such as *p*-phenoxyphenyllithium, 2-biphenylyllithium, and *m*-tolyllithium were unsuccessful. The lack of reactivity may be due in part to steric factors.

Tris-(p-trimethylsilylphenyl)-n-dodecylsilane. *n*-Dodecyllithium was prepared in 85% yield by the reaction between 0.38 g. (0.055 g. atom) of lithium wire and 6.25 g. (0.025 mole) of *n*-dodecyl bromide in 75 ml. of ether according to the procedure described for the preparation of *n*-butyllithium.

To the organometallic reagent, at 0°, was slowly added 75 ml. of a benzene solution containing 11.4 g. (0.024 mole) of tris-(*p*-trimethylsilylphenyl)-silane. The reaction mixture was heated to the reflux temperature and maintained there for 24 hr. Color Test I was negative at that time. Hydrolysis with 150 ml. of water caused the evolution of a gas. The resultant ether fraction was separated, dried, and distilled. There remained a light brown oil. This material became a "wet" solid on cooling in an ice bath. By fractional crystallization from a mixture of ethanol and ethyl acetate 6.1 g. (53.5%) of starting silane and 5.2 g. of a highly viscous oil were separated. The latter product finally crystallized to a "wet" solid melting over the range 68–75°.

All attempts to recrystallize the product resulted in an oil which has not solidified.

Anal. Calc'd for $C_{39}H_{64}Si_4$: Si, 17.4. Found: Si, 16.7, 16.9.

The pale yellow solid volatilized at 390–392° without further color change.

Acknowledgments. The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, for financial assistance. Infrared spectra were obtained through the courtesy of Dr. V. A. Fassel, R. D. Kross, and R. McCord of the Institute for Atomic Research.

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[12] Unpublished studies of Dr. K. Oita. The compound was prepared by the reaction between *m*-chlorotoluene and lithium wire in anhydrous ethyl ether.

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[16] Gilman and Melvin, *J. Am. Chem. Soc.*, **72**, 995 (1950).

[17] Tseng and Chao, *Science Repts. Natl. Univ. Peking*, **1**, No. 4, 21 (1936); *Chem. Abstr.*, **31**, 655 (1937).