Preparation of Compound IX, Dimethylethoxysilylmethyltributyltin.—Compound IX was prepared by refluxing 100 g. (0.275 mole) of compound VIII, $Bu_3SnCH_2SiMe_2H$, in 86.4 g. (1.875 moles) of absolute ethanol to which 0.4 g. of metallic sodium had been added. After the evolution of a theoretical volume of hydrogen, the reaction mixture was neutralized with glacial acetic acid and distilled. Excess ethanol was removed at atmospheric pressure and fractional distillation at reduced pressure yielded 108.5 g. of IX, a yield of 97%. Properties are summarized in Table I.

Preparation of Compound X, *sym*-Bis-tributyltinmethyltetramethyldisiloxane.—Compound X was prepared from compound VIII, $Bu_3SnCH_2SiMe_2H$, by refluxing 40 g. (0.11 mole) of VIII in 100 ml. of absolute alcohol and 5.7 g. of water to which 0.2 g. of potassium hydroxide had been added. After a 3-hour refluxing period, a quantitative volume of hydrogen was evolved. Benzene was then added to the reaction mixture and the ethanol and excess water were removed as the ternary azeotrope. Following removal of solvents, fractional distillation at reduced pressure yielded 16.5 g. of X, a yield of 40.5%. The 23.4-g. precut of this distillation, average $n^{25}D$ 1.4740, was assumed to be largely the ethoxy and hydroxy compounds. This precut was allowed to stand for 16 hours with 3.9 g. of water, 0.12 g. of concentrated HCl and 50 ml. of dioxane. The system was homogeneous at the beginning of this period, but after 16 hours two phases were observed. After neutralization with dilute KOH and removal of solvents, distillation yielded 11.9 g. of X giving a total yield of 69.7%.

Addition of Dimethylhydrogensilylmethyltributyltin to Vinyldimethylchlorosilane.—In a flask equipped with condenser and thermometer, 50 g. (0.1375 mole) of $Bu_3SnCH_2SiHMe_2$ was added dropwise to 16.6 g. (0.1375 mole) of $CH_2 = CHSiMe_2Cl$ to which had been added 2 drops of 0.1 *M* chloroplatinic acid catalyst in isopropyl alcohol. During this addition, the mixture was maintained at reflux temperature which rose from 90 to 150° over a 2-hour period. Fractional distillation of the reaction products gave 21 g. (42%) of recovered starting material, $Bu_3SnCH_2SiMe_2H$, and 21.3 g. (32.1%) of compound XI, $Bu_3SnCH_2SiMe_2CH_2CH_2SiMe_2Cl$, the properties of which are listed in Table I.

Hydrolysis of $Bu_3SnCH_2SiMe_2CH_2CH_2SiMe_2Cl$.—Compound XII, $(Bu_3SnCH_2SiMe_2CH_2CH_2SiMe_2)_2O$, was easily prepared in the conventional way by shaking the chlorosilane with water, neutralizing the resulting mixture with 5% NaOH, and drying over anhydrous sodium sulfate. Without further purification, analysis revealed $d^{25}{}_4$ 1.045, $n^{25}D$ 1.4850, *R*D found 0.2742, *R*D calcd. 0.2727.

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PITTSBURGH, PENNA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reactions of Some Metallic Halides and of Some Organomercury Compounds with Triphenylsilyllithium

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The reactions of mercury(II) halides and organomercury compounds with triphenylsilyllithium have been investigated. Whereas the reactions of mercury(II) chloride or bromide with triphenylsilyllithium give hexaphenyldisilane, the interaction of triphenylsilyllithium with either phenylmercuric bromide or diphenylmercury gives tetraphenylsilane. Similarly, the reaction of triphenylsilyllithium with di-*p*-tolylmercury gives triphenyl-*p*-tolylsilane. Unstable compounds containing silicon–mercury bonds are postulated as intermediates in these reactions. In a few related experiments, the reactions of copper(II), silver, zinc, cadmium, mercury(I), aluminum(III), tin(II), tin(IV), lead(II) and iron(III) chlorides with triphenylsilyllithium were studied, and a few tentative observations concerning these reactions are described.

During the course of an investigation in this Laboratory concerned with the chemistry of organosilylmetallic compounds, we have studied the reactions of triphenylsilyllithium with some metal halides and organo-mercury compounds. It seemed possible that reactions of this nature might lead to the formation of silicon–metal bonds in a manner analogous to the well-known reactions of organosodium, -lithium and -magnesium compounds with other metallic halides to give new organometallic compounds.[1]

From the reaction of mercury(II) chloride with triphenylsilyllithium (1:1 molar ratio) the products isolated were chlorotriphenylsilane (18%), hexaphenyldisilane (45%) and a mixture of mercury(I) chloride and metallic mercury. One possible explanation for these products is based on a halogen – metal interconversion reaction[2] which would give chlorotriphenylsilane and an unstable intermediate, Cl–Hg–Li. Decomposition of this intermediate would give lithium chloride and free mercury. The formation of hexaphenyldisilane would be attributed to a simple coupling reaction between chlorotriphenylsilane and triphenylsilyllithium which we have shown to occur readily. The higher yield of hexaphenyldisilane (63%) when two equivalents of triphenylsilyllithium were allowed to react with mercury(II) bromide is in agreement with the above reaction scheme.

$$HgCl_2 + LiSi(C_6H_5)_3 \longrightarrow [Cl\text{-}Hg\text{-}Li] + (C_6H_5)_3SiCl$$

$$[Cl\text{-}Hg\text{-}Li] \longrightarrow LiCl + Hg$$

$$(C_6H_5)_3SiCl + (C_6H_5)_3SiLi \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3 + LiCl$$

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(1) For the preparation of organometallic compounds using a variety of organometallic reagents, see the following references, some of which contain extensive citations: P. Pfeiffer and P. Truskier, *Ber.*, **37**, 1125 (1904); R. G. Jones and H. Gilman, *Chem. Revs.*, **54**, 835 (1954); H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1943; E. Krause and A. von Grosse, "Die Chemie der Metall-Organischen Verbindungen," Gebruder Borntraeger, Berlin, 1937.

(2) For halogen–metal interconversion in silicon chemistry see, A. G. Brook, H. Gilman and S. Miller, THIS JOURNAL, **75**, 4759 (1953); A. G. Brook and S. Wolfe, *ibid.*, **79**, 1431 (1957); D. Wittenberg and H. Gilman, *ibid.*, **80**, 2677 (1958); for a general reference on the halogen-metal interconversion reactions see R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339.

The formation of tetraphenylsilane from the reactions of either phenylmercuric bromide or diphenylmercury with triphenylsilyllithium cannot be explained adequately on the basis of an exchange reaction similar to the halogen–metal interconversion reaction outlined in the preceding discussion. A more plausible explanation centers about the formation of an unstable silicon–mercury intermediate. The reaction of phenylmercuric

$$C_6H_5HgBr + (C_6H_5)_3SiLi \longrightarrow [C_6H_5HgSi(C_6H_5)_3] + LiBr$$

$$[C_6H_5HgSi(C_6H_5)_3] \longrightarrow (C_6H_5)_4Si + Hg$$

bromide with triphenylsilyllithium (1:1 molar ratio) gave tetraphenylsilane (73%), hexaphenyldisilane (6%) and metallic mercury. The formation of chlorotriphenylsilane from the reaction of triphenylsilyllithium with mercury(II) chloride may be explained on a similar basis. From the reaction

$$HgCl_2 + (C_6H_5)_3SiLi \longrightarrow [ClHgSi(C_6H_5)_3] + LiBr$$

$$[ClHgSi(C_6H_5)_3] \longrightarrow ClSi(C_6H_5)_3 + Hg$$

of diphenylmercury with triphenylsilyllithium (1:1 ratio) were obtained tetraphenylsilane (69%) and phenyllithium (74% as benzoic acid after carbonation). Here again the formation of an unstable silicon–mercury intermediate may be postulated. Similarly, the reaction of di-*p*-tolylmercury with triphenylsilyllithium gave, after carbonation

$$(C_6H_5)_2Hg + (C_6H_5)_3SiLi \longrightarrow [C_6H_5HgSi(C_6H_5)_3] + C_6H_5Li$$

$$[C_6H_5HgSi(C_6H_5)_3] \longrightarrow (C_6H_5)_4Si + Hg$$

and hydrolysis, *p*-toluic acid (71%) and triphenyl-*p*-tolylsilane (88%). When the reaction was carried out using two equivalents of triphenylsilyllithium, the products isolated were *p*-toluic acid (51% based on the cleavage of both *p*-tolyl groups), triphenyl-*p*-tolylsilane (46%) and triphenylsilanol (46%).

The reactions of triphenylsilyllithium with a series of related anhydrous metal chlorides were carried out. One group, mercury(I) chloride, lead(II) chloride and tin(IV) chloride, reacted with triphenylsilyllithium to give chlorotriphenylsilane (18, 17 and 25%), thus resembling mercury(II) chloride in their mode of reaction.

A second group of anhydrous metal chlorides: namely, silver(I) chloride, copper(II) chloride, iron(III) chloride and tin(II) chloride, reacted with triphenylsilyllithium to give triphenylsilane (3, 29, 30% and trace amounts, respectively); and hexaphenyldisilane (41, 26, 20 and 16%, respectively). Chlorotriphenylsilane was not isolated in these reactions. The mode of formation of triphenylsilane in these reactions is currently under further investigation. For the present it may be stated that water was excluded as far as possible during the reaction and subsequent work-up, suggesting a possible role of tetrahydrofuran as a hydrogen donor.

It was recognized that the formation of chlorotriphenylsilane from the reactions of mercury(II), mercury(I), tin(IV) and lead(II) chlorides with triphenylsilyllithium could arise through the initial formation of triphenylsilane, which by reduction with the metal chloride could yield chlorotriphenylsilane. However, of the four metal chlorides mentioned, only mercury(II) chloride was capable of converting triphenylsilane to chlorotriphenylsilane. This is in line with the observation that mercury(II) ion is the strongest oxidizing agent.

$$(C_6H_5)_3SiH + 2HgCl_2 \longrightarrow (C_6H_5)_3SiCl(66\%) + Hg_2Cl_2(91\%) + HCl$$

Triphenylsilyllithium reacts instantly with aluminum chloride or fused zinc chloride to give almost clear, colorless solutions. The nature of the reactions are as yet unknown.

Experimental

All melting points are uncorrected. In general, reactions were carried out under an atmosphere of dry, oxygen-free[3] nitrogen. Tetrahydrofuran, boiling at 65–66°, was freed from peroxides and moisture before use by refluxing over sodium followed by distillation from lithium aluminum hydride. The metal halides employed were anhydrous samples. Silicon analyses were carried out by a reported procedure,[4] Triphenylsilyllithium solutions in tetrahydrofuran were prepared by cleavage of hexaphenyldisilane with lithium.[5]

Triphenylsilyllithium and Mercury(II) Chloride.—To a solution of 15.7 g. (0.058 mole) of mercury(II) chloride in 75 ml. of tetrahydrofuran was added a solution of triphenylsilyllithium (150 ml., 0.058 mole) during a period of 20 min. Color Test I[6] was negative after the addition was complete. The solvent was distilled, and the residue was treated with anhydrous petroleum ether (b.p. 60–70°). The portion soluble in petroleum ether was filtered under nitrogen, and the solvent was removed by distillation to give an oil. This was distilled under reduced pressure to give 7.7 g. (45%) of chlorotriphenylsilane, b.p. 240–243° (35 mm.), which solidified immediately to give a white, crystalline solid, m.p. 95–97°. A mixed melting point with an authentic specimen of chlorotriphenylsilane was not depressed. The identity was further confirmed by a comparison of the infrared spectra, which were identical.

The portion insoluble in petroleum ether was washed thoroughly with water to remove unchanged mercury(II) chloride and extracted repeatedly with hot benzene to give 2.7 g. (18.1%) of hexaphenyldisilane, m.p. 368–370° (mixed m.p.). The benzene-insoluble residue was identified by qualitative tests as a mixture of mercury(I) chloride and metallic mercury.

Triphenylsilyllithium and Mercury(II) Bromide.—A solution of 0.05 mole of triphenylsilyllithium in 66 ml. of tetrahydrofuran was added, over a period of 30 min., to 9.0 g. (0.025 mole) of mercury(II) bromide in 50 ml. of tetrahydrofuran. The reaction was exothermic, and, after the addition was complete, Color Test I[6] was negative. The reaction mixture was hydrolyzed with 100 ml. of water, and the insoluble material was removed by filtration. Extraction of the solid with hot tetralin gave 8.2 g. (63.3%) of hexaphenyldisilane, m.p. 365–366°(mixed m.p.). The tetralin-insoluble portion weighing 3.8 g. was identified as metallic mercury.

The ether extract was dried over sodium sulfate. Removal of the solvent under reduced pressure gave a solid which dissolved partially in 50 ml. of methanol. The methanol extract was evaporated, and the residue was recrystallized from cyclohexane to give 2.5 g. (18.1%) of triphenylsilanol, m.p. 154–155° (mixed m.p.). The methanol-insoluble portion was recrystallized from benzene to give 0.6 g. of white, crystalline solid, m.p. 227–228°, identified as hexaphenyldisiloxane by the method of mixed melting points.

In a second run, using a 1:2 molar ratio of mercury(II) bromide and triphenylsilyllithium, the addition was carried out at −70°. After a 30-min. reaction period, the mixture was worked up in the same manner. The products were hexaphenyldisilane (50.3%), triphenylsilanol (33.3%), hexaphenyldisiloxane (11.2%) and metallic mercury (77.5%).

Triphenylsilane and Mercury(II) Chloride.—To a solution of 21.3 g. (0.0708 mole) of mercury(II) chloride in 100 ml. of tetrahydrofuran was added 50 ml. of a tetrahydrofuran solution containing 10.0 g. (0.0384 mole) of triphenylsilane. A white precipitate formed during the 30-min. addition

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[3] L. J. Brady, *Ind. Eng. Chem., Anal. Ed.*, **20**, 1034 (1948).

[4] H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950).

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

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

period, and the solution was distinctly acidic to litmus. Solvent from the reaction mixture was removed by distillation, and the residue was extracted with petroleum ether (b.p. 60–70°). The petroleum ether was removed by distillation, and the residual liquid was distilled under reduced pressure to give 7.5 g. (66%) of chlorotriphenylsilane, b.p. 224–226° (20 mm.). The distillate solidified promptly and melted at 94–96°. A mixed melting point with an authentic sample of chlorotriphenylsilane was not depressed. The identity of the product was further confirmed by a comparison of the infrared spectra, which were identical. The petroleum ether-insoluble portion was washed thoroughly with water to remove any unchanged mercury(II) chloride. The remaining white solid was identified as mercury(I) chloride, 16.9 g. (91%).

Fritz[7] has treated mercury(II) chloride with Si-H compounds in aqueous solution to give mercury(I) chloride and the corresponding silanols. It is interesting to note that in some splendid studies, Anderson, under anhydrous conditions, treated triethylstannane[8] and triethylgermane[9] with transition metal halides to give the corresponding triethyltin halides and triethylgermyl halides, respectively.[10] Quite recently he has also reported some of the reactions of triethyl- and diethylsilane with inorganic halides and acids.[10]

Reactions of Triphenylsilyllithium with Several Other Anhydrous Metal Chlorides.—Several experiments were carried out in which triphenylsilyllithium was allowed to react with anhydrous metal chlorides in a 1:1 mole ratio. Work-up was carried out without hydrolysis in the manner described for the reaction of mercury(II) chloride with triphenylsilyllithium.

From lead(II) chloride, tin(IV) chloride or mercury(I) chloride were obtained hexaphenyldisilane in 17, 30, and 33% yields, respectively; and chlorotriphenylsilane in yields of 17, 25, and 18%, respectively.

From the reactions of silver chloride, copper(II) chloride, iron(III) chloride and tin(II) chloride with triphenylsilyllithium were obtained hexaphenyldisilane in yields of 41, 26, 20 and 16%, respectively; and triphenylsilane in yields of 3, 29, 30% and trace amounts, respectively. No chlorotriphenylsilane was isolated in these cases.

Triphenylsilyllithium reacted instantly with aluminum chloride or fused zinc chloride to give clear, colorless solutions which did not give a positive Color Test I[6]. No products have as yet been identified.

Triphenylsilyllithium reacted with cadmium chloride at −60° to give a yellow suspension which on warming to room temperature steadily deposited metallic cadmium. Neither hexaphenyldisilane nor chlorotriphenylsilane have been isolated, however.

Triphenylsilyllithium and Diphenylmercury.—A triphenylsilyllithium solution in tetrahydrofuran (66 ml., 0.05 mole) was added during a period of 30 min. to a solution of 17.7 g. (0.05 mole) of diphenylmercury in 50 ml. of tetrahydrofuran. A gray precipitate formed, and the suspension gave a positive Color Test I[6]. The reaction mixture was carbonated by pouring jet-wise into a mixture of Dry Ice and ether and subsequently hydrolyzed. The insoluble portion was removed by filtration and extracted with hot benzene. On cooling, 10.1 g. of tetraphenylsilane was deposited, which after recrystallization from benzene melted at 232–233°. A mixed melting point with an authentic sample of tetraphenylsilane was not depressed.

The aqueous layer was extracted with ether and evaporated to give a viscous solid. This was dissolved in carbon tetrachloride and chromatographed on an alumina column to give 2.1 g. of unchanged diphenylmercury, m.p. 122–124° (mixed m.p.). Elution of the column with benzene gave 1.2 g. of tetraphenylsilane, m.p. 232–233°, identified by a mixed melting point with an authentic specimen. The combined yield of tetraphenylsilane was 12.3 g. (69.4%).

The aqueous layer was acidified with dilute hydrochloric acid to give 4.5 g. of benzoic acid, m.p. 122–124° (mixed m.p.).

Triphenylsilyllithium and Phenylmercuric Bromide.—To a solution of 17.9 g. (0.05 mole) of phenylmercuric bromide in 50 ml. of tetrahydrofuran was added, during a period of 30 min., a solution of 0.05 mole of triphenylsilyllithium in 66 ml. of tetrahydrofuran. The reaction was exothermic, and the solution gave a negative Color Test I after the addition was complete. Hydrolysis, followed by work-up in the usual way, gave 13.0 g. (73.3%) of tetraphenylsilane, 0.8 g. (5.8%) of hexaphenyldisilane, 0.3 g. (2.2%) of triphenylsilanol and 8.1 g. (78.8%) of metallic mercury.

In a second experiment, using a 1:2 molar ratio of phenylmercuric bromide and triphenylsilyllithium, the addition was carried out at −70°. Work-up in the usual manner gave 15.6% tetraphenylsilane, 2.4% hexaphenyldisilane, 55.2% triphenylsilanol and 50% metallic mercury.

Triphenylsilyllithium and Di-*p*-Tolylmercury.—A solution of 0.05 mole of triphenylsilyllithium in 60 ml. of tetrahydrofuran was added slowly to a mixture of 19.2 g. (0.05 mole) of di-*p*-tolylmercury in 75 ml. of tetrahydrofuran. The reaction mixture became dark red-brown in color and gave a positive Color Test I[6] after the addition was complete. The reaction mixture was hydrolyzed and extracted with ether. Evaporation of the ether left 19.1 g. of a solid material, m.p. 110–120°, which was treated with cold methanol. From the methanol-soluble portion was obtained 0.9 g. (6.5%) of triphenylsilanol, m.p. 155–156° (mixed m.p.). The methanol-insoluble portion was recrystallized from ethanol to give 15.4 g. (88%) of triphenyl-*p*-tolylsilane, m.p. 141–142°, identified by a mixed melting point with an authentic specimen.

The aqueous layer was acidified with dilute hydrochloric acid to give 4.9 g. (71.3%) of *p*-toluic acid, m.p. 178.5–179.5° (mixed m.p.).

In a second experiment, using a 1:2 mole ratio of the reagents, the reaction was carried out at 0°. Work-up by the procedure described above gave 45.7% triphenyl-*p*-tolylsilane, 51% *p*-toluic acid (calculated on the basis of the cleavage of two *p*-tolyl groups), 45.9% triphenylsilanol and 4% hexaphenyldisiloxane.

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